Synthesis of N-Methylated Amines from Acyl Azides using Methanol

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1. General Procedure and Materials

All the reactions were carried out under argon atmosphere either inside the argon filled glove box or by using standard schlenk line technique. Glasswares were oven dried prior to use. Solvents were dried according to literature methods. All solvents were distilled under argon atmosphere and deoxygenated prior to use. All the commercial reagents and metal precursors were purchased from Sigma-aldrich, Alfa-acear, Spectrochem, Avra, SD-fine chemical and Arora matthey India. The metal complexes were synthesized according to our previous work. $^1$H, $^{13}$C, $^{31}$P NMR spectra were recorded with CDCl$_3$, D$_2$O or DMSO-d$_6$ in JEOL 500 MHz and 400MHz Spectrometers. ESI-MS were recorded on a Waters Micromass Quattro Micro triple-quadrupole mass spectrometer. FT-IR were recorded on a Perkin Elmer IR spectrometer. All the GC analysis were performed using Perkin Elmer Clarus 600 and Agilent 7890 B Gas Chromatograph, where as GC-MS were measured using Agilent 7890 A Gas Chromatograph equipped with Agilent 5890 triple-quadrupole mass system. (Caution: Azides are known for their explosive nature. Thus, all the catalytic reactions were carried out inside the fume hood and after the reactions screw cap pressure tubes were carefully opened under proper ventilation.)

2. Synthesis of Acyl Azide Derivatives

In a 25 mL round-bottom flask, carboxylic acid derivatives (0.500 g) and thionyl chloride (3 mL) were taken under argon atmosphere and heated at the 70 °C for 4 hours. After that, the mixture was allowed to cool to room temperature under inert atmosphere. Then, NaN$_3$ (9.65 mmol) and acetone (12 mL) were added to it under ice-cold condition and stirred for 12 h at room temperature. Next, the reaction mixture was neutralized with triethylamine and extracted with dichloromethane. The dichloromethane layer was washed with saturated brine solution and finally dried over anhydrous sodium sulphate. The solvent was removed in reduced pressure and the final product was purified by column chromatography using hexane and ethyl acetate as eluent.

3. General Procedure for Experiments using Methanol-d$_4$

A) Experiments with methanol-d$_4$

In a screw cap tube, 4-methylbenzoazide (0.19 mmol) and methanol-d$_4$ (0.4 mL) were taken under argon atmosphere and heated at 70 °C in oil bath for 3 h. Then, it was cooled to room temperature and catalyst 3 (2 mol%), K$_2$CO$_3$ (1 mmol), methanol-
d₄ (0.2 mL) were added and heated for specified time at 140 °C (oil bath temperature). After that, the reaction mixture was allowed to cool down at room temperature and subjected to ¹H NMR analysis for the calculation of the yield. The products were further confirmed by ESI-MS analysis. In case of other intermediates such as (4-methylphenylisocyanate, methyl-p-tolylcarbamate, 4-methylaniline and 4-methyl-N-methyleneaniline), the reactions were carried with catalyst 3 (2 mol%), K₂CO₃ (1 mmol), methanol-d₄ (0.6 mL) and heated for specified time at 140 °C (oil bath temperature).

B) KIE in N-methylation of 4-methylaniline catalysed by complex 3 (figure 4B)

Two parallel set of experiments were conducted one with methanol and another with methanol-d₄. In a screw cap tube, 4-methylaniline (0.19 mmol), Cat. 3 (2 mol%), base (0.19 mmol) and methanol/methanol-d₄ (0.6 mL) were taken under argon atmosphere and heated at 140 °C (oil bath temperature) for specified time. After that, the reaction mixture was allowed to cool down at room temperature. The solvent was evaporated and was subjected to ¹H NMR analysis to check the conversion (1,3,5-trimethoxybenzene was used as internal standard).

4. Control Experiments

Several experiments for the N-methylation of acyl azide and other intermediates were conducted following the outlined procedure (3A) with varying time. The progress of the reaction was monitored by ¹H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. All the reactions were repeated for three times and the average data were plotted as conversion (%) vs time (h).

Time dependent product distribution studies

In a screw cap tube, carbamate ester (0.19 mmol), Cat. 3 (2 mol%), K₂CO₃ (0.19 mmol) and methanol (0.6 mL) were taken under argon atmosphere and heated at 140 °C (oil bath temperature) for specified time. After that, the reaction mixture was allowed to cool down at room temperature. The solvent was evaporated and was subjected to ¹H NMR analysis to check the conversion of carbamate ester (1,3,5-trimethoxybenzene was used as internal standard).

Effect of counter cation of bases in N-methylation of 4-methylaniline (figure 4A)

In a screw cap tube, 4-methylaniline (0.19 mmol), Cat. 3 (2 mol%), base (0.19 mmol) and methanol (0.6 mL) were taken under argon atmosphere and heated at 140 °C (oil bath temperature) for 4 h. After that, the reaction mixture was allowed to cool
down at room temperature. The solvent was evaporated and was subjected to $^1$H NMR analysis to check the conversion of carbamate ester (1,3,5-trimethoxybenzene was used as internal standard).

5. Transformation of Carbamate Ester to Amine

In presence of Cat. 3 (figure 3A)

In a screw cap tube, carbamate ester (0.19 mmol), Cat. 3 (2 mol%), $K_2CO_3$ (0.19 mmol) and methanol (0.6 mL) were taken under argon atmosphere and heated at 140 °C (oil bath temperature) for specified time. After that, the reaction mixture was allowed to cool down at room temperature. The solvent was evaporated and was subjected to $^1$H NMR analysis to check the conversion of carbamate ester (1,3,5-trimethoxybenzene was used as internal standard).

In absence of Cat. 3 (figure 3B)

In a screw cap tube, carbamate ester (0.19 mmol), base (0.19 mmol) and methanol (0.6 mL) were taken under argon atmosphere and heated at 140 °C (oil bath temperature) for 12 h. After that, the reaction mixture was allowed to cool down at room temperature. The solvent was evaporated and was subjected to $^1$H NMR analysis to check the conversion of carbamate ester (1,3,5-trimethoxybenzene was used as internal standard).

6. Computational Studies

All the calculations were performed using the Gaussian 09 package. Full geometry optimization followed by frequency calculations on the stationary points were carried out to ascertain the nature of the stationary points as minima or first order saddle point. Hybrid functional, M06-2X was used with the LANL2DZ basis set$^6$ for Ru and 6-31G** basis set$^7-^9$ for non-metal elements. The transition states (TS) were further confirmed by performing intrinsic reaction coordinate (IRC) calculation using same method. Solvent effect was incorporated using the conductor-like polarizable continuum model (CPCM) with methanol as solvent.$^{10}$

7. Cartesian Coordinates and Statistical Thermodynamic Analysis

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Thermal correction to Gibbs free energy 0.005613

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*Triphenylphosphine*

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Zero-point correction

Thermal correction to Gibbs free energy

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SCF done for solvent

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SCF done for solvent

Zero-point correction

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8. Characterization of the Products

4, N-Dimethylaniline (a1)\(^1\)
80% (97 mg) Isolated yield; pale yellow liquid. Purified by column chromatography using silica gel and ethyl acetate-hexane as eluent. \(^1\)H NMR (400 MHz, CDCl\(_3\)):\( \delta = 7.04 (d, J = 8.2 \text{ Hz}, 2\text{H}), 6.58 (d, J = 8.4 \text{ Hz}, 2\text{H}), 3.45(\text{brs}, 1\text{H}), 2.84 (s, 3\text{H}), 2.29 (s, 3\text{H}). \)
\(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 147.27, 129.81, 126.56, 112.34, 31.20, 20.50. \) GC-MS (M\(^+\)) = 121.0.

N-Methylaniline (a2)\(^2\)
83% (89 mg) Isolated yield; pale yellow liquid. Purified by column chromatography using silica gel and ethyl acetate-hexane as eluent. \(^1\)H NMR (400 MHz, CDCl\(_3\)):\( \delta = 7.23-7.19 (m, 2\text{H}), 6.73 (t, J = 7.4 \text{ Hz}, 1\text{H}), 6.63 (d, J = 8.36 \text{ Hz}, 1\text{H}), 3.44 (\text{brs}, 1\text{H}), 2.84 (s, 3\text{H}). \) \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 149.45, 129.31, 117.34, 112.52, 30.83. \) GC-MS (M\(^+\)) = 107.1.

4-Methoxy-N-methylaniline (a3)\(^3\)
78% (107 mg) Isolated yield; pale yellow liquid. Purified by column chromatography using silica gel and ethyl acetate-hexane as eluent. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 6.81 (d, J = 9 \text{ Hz}, 2\text{H}), 6.59 (d, J = 9 \text{ Hz}, 2\text{H}), 3.76 (s, 3\text{H}), 3.40 (\text{brs}, 1\text{H}), 2.80 (s, 3\text{H}). \) \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 152.16, 143.79, 114.99, 113.74, 55.92, 31.71. \) GC-MS (M\(^+\)) = 137.0.

4-Chloro-N-methylaniline (a4)\(^4\)
93% (131 mg) Isolated yield; pale yellow liquid. Purified by column chromatography using silica gel and ethyl acetate-hexane as eluent. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = \)
7.13 (d, $J = 8.92$ Hz, 2H), 6.51 (d, $J = 8.88$ Hz, 2H), 3.62 (broad s, 1H), 2.80 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 147.96, 129.08, 121.83, 113.51, 30.87$. GC-MS (M$^+$) = 141.2.

4-Fluoro-N-methylaniline (a5)$^{15}$

92% (115 mg) Isolated yield; pale yellow liquid. Purified by column chromatography using silica gel and ethyl acetate-hexane as eluent. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 6.93$-$6.86$ (m, 2H), 6.53 (m, 2H), 3.36 (broad s, 1H), 2.80 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 157.10$, 154.74, 145.71, 115.57 (d, $J = 92$ Hz, C-F), 113.26 (d, $J = 28$ Hz, C-F), 31.44. GC-MS (M$^+$) = 125.0.

3-Methyl-N-methylaniline (a6)$^{16}$

77% (93 mg) Isolated yield; pale yellow liquid. Purified by column chromatography using silica gel and ethyl acetate-hexane as eluent. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.14$-$7.09$ (m, 1H), 6.56 (d, $J = 7.44$ Hz, 1H), 6.47-$6.45$ (m, 2H), 3.27 (broad s, 1H), 2.84 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 149.52$, 139.07, 129.19, 118.34, 113.34, 113.32, 109.78, 30.89, 21.75. GC-MS (M$^+$) = 121.1.

3-Chloro-N-methylaniline (a7)$^{17}$

84% (119 mg) Isolated yield; pale yellow liquid. Purified by column chromatography using silica gel and ethyl acetate-hexane as eluent. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.07$ (t, $J = 8.12$ Hz, 1H), 6.66 (d, $J = 7.8$ Hz, 1H), 6.57 (t, $J = 1.92$ Hz, 1H), 6.46 (dd, $J = 8.24$ Hz, 1.96 Hz, 1H), 3.67 (broad s, 1H), 2.80 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 150.50$, 135.11, 130.20, 117.07, 111.96, 110.91, 30.60. GC-MS (M$^+$) = 141.2.
2-Methoxy-N-methylaniline (a8)\textsuperscript{18}

47\% (65 mg) Isolated yield; pale yellow liquid. Purified by column chromatography using silica gel and ethyl acetate-hexane as eluent. \textbf{\(^1\)H NMR} (500 MHz, CDCl\(_3\)): \(\delta = 6.92\) (t, \(J = 7.6\) Hz, 1H), 6.78 (d, \(J = 7.85\) Hz, 1H), 6.69 (t, \(J = 7.65\) Hz, 1H), 6.62 (d, \(J = 7.75\) Hz, 1H), 3.86 (s, 3H), 2.88 (s, 3H). \textbf{\(^{13}\)C NMR} (125 MHz, CDCl\(_3\)): \(\delta = 147.01, 139.50, 121.46, 116.40, 109.44, 55.49, 30.46\). \textbf{GC-MS} (M\(^+\)) = 137.1.

\begin{center}
\includegraphics[width=0.2\textwidth]{2-methoxy-n-methylaniline.png}
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3,4-Dimethoxy-N-methylaniline (a9)\textsuperscript{19}

76\% (127 mg) Isolated yield; pale yellow oil. Purified by column chromatography using silica gel and ethyl acetate-hexane as eluent. \textbf{\(^1\)H NMR} (400 MHz, CDCl\(_3\)): \(\delta = 6.75\) (d, \(J = 8.6\) Hz, 1H), 6.23 (d, \(J = 2.6\) Hz, 1H), 6.13 (dd, \(J = 8.6, 2.6\), 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.44 (brs, 1H), 2.78 (s, 3H). \textbf{\(^{13}\)C NMR} (100 MHz, CDCl\(_3\)): \(\delta = 150.11, 144.45, 141.52, 113.50, 103.08, 98.62, 56.84, 55.74, 31.74\). \textbf{GC-MS} (M\(^+\)) = 167.1.

\begin{center}
\includegraphics[width=0.2\textwidth]{3,4-dimethoxy-n-methylaniline.png}
\end{center}

N-Methylnaphthalen-1-amine (a10)\textsuperscript{12}

79\% (124 mg) Isolated yield; pale yellow liquid. Purified by column chromatography using silica gel and ethyl acetate-hexane as eluent. \textbf{\(^1\)H NMR} (400 MHz, CDCl\(_3\)): \(\delta = 7.83\) (d, \(J = 7.92\) Hz, 1H), 7.79 (d, \(J = 8.2\) Hz, 1H), 7.50-7.39 (m 3H), 7.29 (d, \(J =8.32\) Hz, 1H), 6.64 (d, \(J = 7.6\) Hz, 1H), 4.37 (brs, 1H), 3.02 (s, 3H). \textbf{\(^{13}\)C NMR} (100 MHz, CDCl\(_3\)): \(\delta = 144.51, 134.34, 128.78, 126.79, 125.85, 124.84, 123.59, 119.95, 117.57, 104.10, 31.21\). \textbf{GC-MS} (M\(^+\)) = 157.1.

\begin{center}
\includegraphics[width=0.2\textwidth]{n-methylnaphthalen-1-amine.png}
\end{center}

N-Methylbenzo[\(d\)][1,3]dioxol-5-amine (a11)\textsuperscript{20}

84\% (127 mg) Isolated yield; pale yellow liquid. Purified by column chromatography using silica gel and ethyl acetate-hexane as eluent. \textbf{\(^1\)H NMR} (400 MHz, CDCl\(_3\)): \(\delta = 6.66\) (d, \(J = 8.3\) Hz, 1H), 6.23 (d, \(J = 2.4\) Hz, 1H), 6.03 (dd, \(J = 8.3\) Hz, 2.4 Hz, 1H),
5.83 (s, 2H), 3.41 (br s, 1H), 2.77 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 148.44$, 145.32, 139.62, 108.67, 103.87, 100.62, 95.66, 31.70. GC-MS (M$^+$) = 151.1.

N-Methylpyridin-2-amine hydrochloride (a12)

55% (79 mg) Isolated yield; isolated as HCl salt, white solid. Purified by column chromatography using silica gel and ethyl acetate-methanol as eluent. $^1$H NMR (500 MHz, D$_2$O): $\delta = 7.66$ (t, $J = 7.65$ Hz, 1H), 7.58 (d, $J = 6.35$ Hz, 1H), 6.79 (d, $J = 9.1$ Hz, 1H), 6.67 (t, $J = 6.7$ Hz, 1H), 2.80 (s, 3H). $^{13}$C NMR (125 MHz, D$_2$O): $\delta = 153.21$, 143.13, 134.54, 113.18, 112.21, 28.00. ESI-MS calculated for C$_6$H$_9$N$_2$; 109.0766 (M+H)$^+$, found: 109.0764.

N-Methylpyridin-3-amine hydrochloride (a13)

63% (91 mg) Isolated yield; isolated as HCl salt, white solid. Purified by column chromatography using silica gel and ethyl acetate-methanol as eluent. $^1$H NMR (500 MHz, D$_2$O): $\delta = 7.80$ (s, 2H), 7.55 (s, 2H), 2.72 (s, 3H). $^{13}$C NMR (125 MHz, D$_2$O): $\delta = 148.45$, 127.89, 127.81, 126.92, 123.35, 28.93. ESI-MS calculated for C$_6$H$_9$N$_2$; 109.0766 (M+H)$^+$, found: 109.0764.

N, N-Dimethyl-1-phenylethanamine (a14)

75% (112 mg) Isolated yield; pale yellow liquid. Purified by column chromatography using neutral alumina and ethyl acetate-hexane as eluent. $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.35$-7.30 (m, 2H), 7.28-7.20 (m, 3H), 3.22 (q, $J = 6.7$ Hz, 1H), 2.17 (s, 6H), 1.35 (d, $J = 6.7$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 144.03$, 128.28, 127.62, 126.99, 66.06, 43.27, 20.25. GC-MS (M$^+$) = 149.1.
N, N-Dimethyl-1,1-diphenylmethanamine (a15)²²

66% (139 mg) Isolated yield; dense oil. Purified by column chromatography using neutral alumina and ethyl acetate-hexane as eluent. $^1$H NMR (400 MHz, CDCl₃): $\delta =$ 7.51-7.40 (m, 6H), 7.31-7.27 (m, 3H), 7.21-7.17 (m, 1H), 4.09 (s, 1H), 2.25 (s, 6H). $^{13}$C NMR (100 MHz, CDCl₃): $\delta =$ 143.45, 128.59, 127.84, 127.03, 78.21, 44.86. GC-MS (M⁺) = 211.1.

N, N-Dimethyladamantyl-1-amine (a16)²³

77% (138 mg) Isolated yield; pale yellow liquid. Purified by column chromatography using neutral alumina and ethyl acetate-hexane as eluent. $^1$H NMR (400 MHz, CDCl₃): $\delta =$ 2.23 (s, 6H), 2.05 (s, 3H), 1.68-1.65 (m, 6H), 1.61-1.54 (m, 6H). $^{13}$C NMR (100 MHz, CDCl₃): $\delta =$ 53.65, 38.05, 37.17, 36.95, 29.63. ESI-MS calculated for C₁₂H₂₁N; 180.1752 (M+H)⁺, found: 180.1750. GC-MS (M⁺) = 179.1.

N, N, 2-Trimethylpropan-2-amine hydrochloride (a17)

46% (63 mg) Isolated yield; isolated as HCl salt, white solid. Purified by column chromatography using neutral alumina and ethyl acetate-methanol as eluent. $^1$H NMR (400 MHz, D₂O): $\delta =$ 2.82 (s, 6H), 1.40 (d, $J =$ 8.08 Hz, 9H). $^{13}$C NMR (100 MHz, D₂O): $\delta =$ 62.67, 37.61, 23.53. ESI-MS calculated for C₆H₁₅N; 102.1283 (M+H)⁺, found: 102.1279.
86% (116 mg) Isolated yield; yellow liquid. Purified by column chromatography using neutral alumina and ethyl acetate-hexane as eluent. \textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}): $\delta = 7.33$-$7.24$ (m, 5H), 3.41 (s, 2H), 2.23 (s, 6H). \textbf{\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}): $\delta = 138.95, 129.20, 128.33, 127.13, 64.51, 45.47$. \textbf{GC-MS (M$^+$)} = 135.1.

\[ \text{N, N-Dimethyl-1-(naphthalen-1-yl)methanamine (a19)} \]

82% (152 mg) Isolated yield; yellow liquid. Purified by column chromatography using neutral alumina and ethyl acetate-hexane as eluent. \textbf{\textsuperscript{1}H NMR} (500 MHz, CDCl\textsubscript{3}): $\delta = 8.31$ (d, $J = 8.4$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.81 (t, $J = 5.5$ Hz, 1H), 7.56 (t, $J = 7.3$ Hz, 1H), 7.51 (t, $J = 7.2$ Hz, 1H), 7.41-$7.43$ (m, 2H), 3.85 (s, 2H), 2.33 (s, 6H). \textbf{\textsuperscript{13}C NMR} (125 MHz, CDCl\textsubscript{3}): $\delta = 133.96, 133.01, 131.68, 127.53, 127.09, 126.49, 125.07, 124.68, 124.19, 123.65, 61.68, 44.77$. \textbf{GC-MS (M$^+$)} = 185.1.

\[ \text{N, N-Dimethyl-2-phenylethanamine hydrochloride (a20)} \]

57% (106 mg) Isolated yield; isolated as HCl salt, white solid. Purified by column chromatography using neutral alumina and ethyl acetate-methanol as eluent. \textbf{\textsuperscript{1}H NMR} (500 MHz, D\textsubscript{2}O): $\delta = 7.39$-$7.36$ (m, 2H), 7.31-$7.27$ (m, 3H), 3.23-$3.19$ (m, 2H), 2.95-$2.91$ (m, 2H), 2.84 (s, 6H). \textbf{\textsuperscript{13}C NMR} (125 MHz, D\textsubscript{2}O): $\delta = 136.10, 129.25, 129.07, 127.52, 58.35, 42.89, 30.26$. \textbf{ESI-MS} calculated for C\textsubscript{10}H\textsubscript{15}N; 150.1283 (M+H)$^+$, found: 150.1281.
9. Copies of $^1$H and $^{13}$C NMR spectra of the products
10. References