Supporting Information

Transition Metal-free 1,3-Dimethylimidazolium Hydrogen Carbonate Catalyzed Hydration of Organonitriles to Amides

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Table of Contents:

General information .................................................................S2
General experimental procedure hydration of nitriles into amides ......................S2
General experimental procedure for synthesis of metal phthalocyanines ............S3
Table S1 for hydration of nitriles ..................................................S3
Figure S1, pictures of reaction solution (a) before and (b) after hydration............S4
Characterization data of compounds ................................................S5-S9
NMR and mass spectra of compounds ................................................S10-S21
UV-Vis spectra of compounds .......................................................S22-S23
References ....................................................................................S24
General Information:

Metal salts used were purchased from Merck, Germany. Silica gel (60-120 mesh) used for column chromatography was purchased from Sisco Research Laboratories Pvt. Ltd. India and all other chemicals were purchased from Spectrochem, India, Merck, Germany, and Sigma-Aldrich, USA and were used without further purification. NMR spectra were recorded on a Bruker Avance-300 spectrometer. Mass spectra were recorded on QTOF-Micro of Waters Micromass and Maxis-Bruker. The GC-MS analysis was carried out on a Shimadzu (QP 2010) series Gas Chromatogram-Mass Spectrometer (Tokyo, Japan), AOC-20i auto-sampler coupled, and a DB-5MS capillary column, (30 m x 0.25 mm i.d., 0.25µm). The initial temperature of column was 70 °C held for 4 min. and was programmed to 230 °C at 4°C/min., then held for 15 min. at 230 °C; the sample injection volume was 2 µl in GC grade dichloromethane. Helium was used as carrier gas at a flow rate of 1.1 ml min⁻¹ on split mode (1:50). Melting points were determined on a Barnstead Electrothermal 9100.

General experimental procedure for hydration of nitriles into amides:

To a mixture of nitrile (1 mmol) and EtOH: H₂O (1:1, 5mL), NHC precursor (5 mol%) was added. The reaction solution was stirred at 80 °C and the progress of the reaction was monitored by TLC (silica gel; hexane/ethyl acetate) and GC-MS. After completion, the entire mixture was transferred into a 50 mL round-bottom flask, evaporated in vacuo, and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate) to give amide. Some of the amides were crystallized on cooling the reaction mixture and filtered directly from the reaction mixture to give pure amides.
General experimental procedure for synthesis of metal phthalocyanines:

To a mixture of dinitriles (1 mmol), metal salt (0.25 equiv.) and EtOH: H$_2$O (1:1, 5mL), NHC precursor (5 mol %) was added. The reaction solution was stirred at 160 °C for 8 h. After completion, the reaction mixture turns to blue semisolid (crude metal phthalocyanine). The blue semisolid was then successively washed with 5% (w/v) NaOH, distilled water, 2% (v/v) HCl and then again with distilled water. The blue semisolid then dissolved in minimum amount of H$_2$SO$_4$ and poured in excess of water to precipitate out the purified metal phthalocyanines. The synthesized metal phthalocyanines were then analyzed by UV-Vis and NMR spectroscopy.

### Table S1 Hydration of nitriles using A$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Time (h)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="CN" /></td>
<td>12</td>
<td><img src="image" alt="CONH2" /></td>
<td>0 &gt;99$^b$</td>
</tr>
<tr>
<td>2</td>
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<td>12</td>
<td><img src="image" alt="CONH2" /> <img src="image" alt="HOOC" /></td>
<td>0 &gt;99$^b$</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="CN" /> <img src="image" alt="H" /></td>
<td>12</td>
<td><img src="image" alt="CONH2" /> <img src="image" alt="H" /></td>
<td>0 &gt;99$^b$</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: nitrile (1 mmol), A (5 mol %), EtOH: H$_2$O (1:1, 5 mL), 80 °C temperature.

$^b$ Nitriles remains unreacted, calculated by GC-MS.
Fig. S1 Pictures of reaction solution (a) before and (b) after hydration of 4-chlorobenzonitrile (Table 2, entry 3) catalyzed by A. Reaction conditions are shown in Table 2.
Characterization data of compounds:

Benzamide (Table 2, entry 1):\(^1\,^2,^3\):

Following the general experimental procedure with benzonitrile (1 mmol or 10 mmol) and catalyst A (5 mol%). After 2.5 h at 80 °C, extraction with ethyl acetate afforded benzamide (97%) as a white solid. Mp = 125-127 °C (Lit\(^2\) mp = 127-128 °C). \(^1\)H NMR (300 MHz, CD\(_3\)OD): \(\delta\) 7.88 (d, \(J = 7.5\), Hz, 2H), 7.55 (t, \(J = 7.3\), Hz, 1H), 7.44-7.49 (m, 2H). \(^13\)C NMR (75 MHz, CD\(_3\)OD): \(\delta\) (ppm) = 171.4, 133.9, 131.9, 128.5, 127.6; HRESIMS calcd for C\(_7\)H\(_8\)NO [M+H]\(^+\) 122.0606, found 122.0621.

4-Fluorobenzamide (Table 2, entry 2):

Following the general experimental procedure with 4-fluorobenzonitrile (1 mmol) and catalyst A (5 mol%). After 6 h at 80 °C, on cooling the reaction mixture 4-fluorobenzamide (90%) was obtained as white crystals after filtration and washing with distilled water. Mp = 150-153 °C (Lit\(^4\) mp = 149-150 °C). \(^1\)H NMR (300 MHz, CD\(_3\)OD): \(\delta\) 7.97-7.92 (m, 2H), 7.22-7.16 (m, 2H). \(^13\)C NMR (75 MHz, CD\(_3\)OD): \(\delta\) 170.1, 167.0, 163.7, 130.4, 130.3, 115.5, 115.2. HRESIMS calcd for C\(_7\)H\(_7\)NOCl [M+H]\(^+\) 140.0512, found 140.0529.

4-Chlorobenzamide (Table 2, entry 3):\(^1\):

Following the general experimental procedure with 4-chlorobenzonitrile (1 mmol or 10 mmol) and catalyst A (5 mol%). After 6 h at 80 °C, on cooling the reaction mixture 4-chlorobenzamide (91%) was obtained as white crystals after filtration and washing with distilled water. Mp = 171-174 °C (Lit\(^2\) mp = 172-174 °C). \(^1\)H NMR (300 MHz, CD\(_3\)OD): \(\delta\) 7.87 (d, \(J = 8.7\), Hz, 2H), 7.46 (d, \(J = 8.7\), Hz, 2H). \(^13\)C NMR (75 MHz, CD\(_3\)OD): \(\delta\) 171.3, 139.2, 133.8, 130.5, 129.9. HRESIMS calcd for C\(_7\)H\(_7\)NOCl [M+H]\(^+\) 156.0216, found 156.0216.
4-Bromobenzamide (Table 2, entry 4)\textsuperscript{1,3}:

![4-Bromobenzamide structure](image)

Following the general experimental procedure with 4-bromobenzonitrile (1 mmol) and catalyst A (5 mol\%). After 6 h at 80 °C, extraction with ethyl acetate afforded 4-bromobenzamide (84\%) as a white solid. Mp = 190-193 °C (Lit mp\textsuperscript{6} = 190-192 °C). \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{3}OD): δ 7.79 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H). \textsuperscript{13}C NMR (75 MHz, CD\textsubscript{3}OD): δ 171.7, 134.6, 133.2, 131.0, 127.8. HRESIMS calcd for C\textsubscript{7}H\textsubscript{7}NOBr [M+H]\textsuperscript{+} 199.9711, found 199.9702.

4-Nitrobenzamide (Table 2, entry 8)\textsuperscript{1,3}:

![4-Nitrobenzamide structure](image)

Following the general experimental procedure with 4-nitrobenzonitrile (1 mmol or 10 mmol) and catalyst A (5 mol\%). After 4 h at 80 °C, extraction with ethyl acetate afforded 4-nitrobenzamide (96\%) as a white solid. Mp = 198-202 °C (Lit\textsuperscript{4} mp = 198-200 °C). \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{3}OD): δ 7.79 (d, J = 8.6, Hz, 2H), 7.63 (d, J = 8.6, Hz, 2H). \textsuperscript{13}C NMR (75 MHz, CD\textsubscript{3}OD): δ 169.1, 150.2, 139.9, 129.0, 123.6. HRESIMS calcd for C\textsubscript{7}H\textsubscript{7}N\textsubscript{2}O\textsubscript{3} [M+H]\textsuperscript{+} 167.0457, found 167.0442.

Isonicotinamide (Table 2, entry 11)\textsuperscript{1,3}:

![Isonicotinamide structure](image)

Following the general experimental procedure with 4-cyanopyridine (1 mmol or 10 mmol) and catalyst A (5 mol\%). After 3 h at 80 °C, on cooling the reaction mixture isonicotinamide (96\%) was obtained as white crystals after filtration and washing with distilled water. Mp = 152-155 °C. \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{3}OD): δ 7.79 (dd, J = 4.5 Hz, J = 1.6 Hz, 2H), 7.63 (dd, J = 4.5 Hz, J = 1.6 Hz, 2H). \textsuperscript{13}C NMR (75 MHz, CD\textsubscript{3}OD): δ (ppm) = 170.2, 151.5, 143.9, 123.6. HRESIMS calcd for C\textsubscript{6}H\textsubscript{7}N\textsubscript{2}O [M+H]\textsuperscript{+} 123.0558, found 123.0526.
Thiophene-2-carboxamide (Table 2, entry 12)\textsuperscript{4}:

\[
\begin{array}{c}
\text{S} \\
\text{CONH}_2
\end{array}
\]

Following the general experimental procedure with thiophene-2-carbonitrile (1 mmol) and catalyst A (5 mol\%). After 4 h at 80 °C, extraction with ethyl acetate afforded thiophene-2-carboxamide (97%) as a white solid. Mp = 175-176 °C (Lit\textsuperscript{4} mp = 177-178 °C). \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{3}OD): \(\delta\) 7.74-7.66 (m, 2H), 7.15-7.12 (m, 1H). \textsuperscript{13}C NMR (75 MHz, CD\textsubscript{3}OD): \(\delta\) 167.1, 140.3, 132.6, 131.1, 129.3. HRESIMS calcd for C\textsubscript{5}H\textsubscript{6}NOS [M+H]\textsuperscript{+} 128.0170, found 128.0186.

Phthalimide (Table 3, entry 1):

\[
\begin{array}{c}
\text{O} \\
\text{NH}
\end{array}
\]

Following the general experimental procedure with 1,2-benzenedinitrile (1 mmol) and catalyst A (5 mol\%). After 4 h at 80 °C, extraction with ethyl acetate afforded phthalimide (90%) as a white solid. Mp = 230-232 °C (Lit\textsuperscript{5} mp = 228-230 °C). \textsuperscript{1}H NMR (300 MHz, DMSO-\textsubscript{d}\textsubscript{6}): \(\delta\) 6.19 (s, 4H), 9.78 (brs, NH). \textsuperscript{13}C NMR (75 MHz, DMSO-\textsubscript{d}\textsubscript{6}): \(\delta\) 170.1, 135.1, 133.3, 123.7.

Isophthalimide (Table 3, entry 2)\textsuperscript{1}:

\[
\begin{array}{c}
\text{CONH}_2 \\
\text{CONH}_2
\end{array}
\]

Following the general experimental procedure with isophthalonitrile (1 mmol) and catalyst A (5 mol\%). After 6.5 h at 80 °C, extraction with ethyl acetate afforded isophthalimide (91%) as a white solid. Mp = 290-292 °C. \textsuperscript{1}H NMR (300 MHz, DMSO-\textsubscript{d}\textsubscript{6}): \(\delta\) 8.37 (s, 1H), 8.04 (brs, 2xNH), 7.99 (d, \(J\) = 7.7 Hz, 2H), 7.53 (t, 7.7 Hz, 1H), 7.46 (brs, 2xNH); \textsuperscript{13}C NMR (75 MHz, DMSO-\textsubscript{d}\textsubscript{6}): \(\delta\) 167.5, 134.4, 130.0, 128.2, 126.7; HRESIMS calcd for C\textsubscript{8}H\textsubscript{9}N\textsubscript{2}O\textsubscript{2} [M+H]\textsuperscript{+} 165.0664, found 165.0639.
**Terephthalimide (Table 3, entry 3):**

Following the general experimental procedure with terephthalonitrile (1 mmol) and catalyst A (5 mol%). After 6.5 h at 80 °C, extraction with ethyl acetate afforded terephthalimide (95%) as a white solid. Mp = 318-320 °C. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 8.07 (brs, 2xNH), 7.93 (s, 4H), 7.48 (brs, 2xNH); $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 166.7, 136.0, 126.8; HRESIMS calcd for C$_8$H$_9$N$_2$O$_2$ [M+H]$^+$ 165.0664, found 165.0648.

**3-Nitrophthalimide (Table 3, entry 6):**

Following the general experimental procedure with 3-nitrophthalonitrile (1 mmol) and catalyst A (5 mol%). After 6 h at 80 °C, extraction with ethyl acetate afforded 3-nitrophthalimide (92%) as a white solid. Mp = 210-213 °C. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 7.99-8.05 (m, 1H), 8.08-8.11 (m, 1H), 8.22-8.24 (m, 1H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 167.5, 164.9, 144.6, 136.4, 134.9, 128.4, 127.1, 124.2.

**Cobalt (II) phthalocyanine (Table 4, entry 1):**

Following the general experimental procedure with 1,2-dicyanobenzene (1 mmol), CoCl$_2$.6H$_2$O (0.25 equiv) and EtOH: H$_2$O (1:1, 5mL), NHC precursor (5 mol%) was added. The reaction solution was stirred at 160 °C for 8 h. After completion, the reaction mixture turns to blue semisolid (crude cobalt (II) phthalocyanine). The blue semisolid was then successively washed with 5 % (w/v) NaOH, distilled water, 2 % (v/v) HCl and then again with distilled water. The blue semisolid then dissolved in minimum amount of H$_2$SO$_4$ and poured in excess of water to precipitate out the purified cobalt (II) phthalocyanines (59%). UV/Vis (THF): $\lambda_{max}$ (nm) 660, 596, 335.
Iron (II) phthalocyanine (Table 4, entry 2):

Following the general experimental procedure with 1,2-dicyanobenzene (1 mmol), FeSO$_4$.7H$_2$O (0.25 equiv.) and EtOH: H$_2$O (1:1, 5mL), NHC precursor (5 mol %) was added. The reaction solution was stirred at 160 °C for 8 h. After completion, the reaction mixture turns to blue semisolid (crude iron (II) phthalocyanine). The blue semisolid was then successively washed with 5% (w/v) NaOH, distilled water, 2% (v/v) HCl and then again with distilled water. The blue semisolid then dissolved in minimum amount of H$_2$SO$_4$ and poured in excess of water to precipitate out the purified iron (II) phthalocyanines (54%). UV/Vis (MeOH): $\lambda_{\text{max}}$ (nm) 659, 602, 332; UV/Vis (THF): $\lambda_{\text{max}}$ (nm) 705, 667.

4-tert-Butyl cobalt (II) phthalocyanine (Table 4, entry 3):

Following the general experimental procedure with 4-tert-Butyl-1,2-dicyanobenzene (1 mmol), CoCl$_2$.6H$_2$O (0.25 equiv.) and EtOH: H$_2$O (1: 1, 5mL), NHC precursor (5 mol%) was added. The reaction solution was stirred at 160 °C for 8 h. After completion, the reaction mixture turns to blue semisolid (crude 4-tert-Butyl cobalt (II) phthalocyanine). The blue semisolid was then successively washed with 5% (w/v) NaOH, distilled water, 2% (v/v) HCl and then again with distilled water. The blue semisolid then dissolved in minimum amount of H$_2$SO$_4$ and poured in excess of water to precipitate out the purified 4-tert-butyl cobalt (II) phthalocyanines (66%). UV/Vis (THF): $\lambda_{\text{max}}$ (nm) 666, 601, 333. $^1$H NMR (300 MHz, CD$_3$OD): $\delta$ 7.75-8.03 (m, 12H), 1.41 (s, 36H); $^{13}$C NMR (75 MHz, CD$_3$OD): $\delta$ 162.3, 160.1, 132.7, 124.1, 121.3, 36.8, 31.7.
NMR and mass spectra of compounds:
CONH$_2$
UV-Vis spectra of metal phthalocyanines:

**Figure S2**: UV spectrum of cobalt (II) phthalocyanine in THF.

**Figure S3**: UV spectrum of iron (II) phthalocyanine in THF.
**Figure S4:** UV spectrum of iron (II) phthalocyanine in methanol.

**Figure S5:** UV spectrum of tetra tert-butyl cobalt (II) phthalocyanine in THF.
References:


