Supporting Information

Iron-Catalyzed Urea Synthesis: Dehydrogenative Coupling of Methanol and Amines

Elizabeth M. Lane,a Nilay Hazari,b and Wesley H. Bernskoetter*c

aDepartment of Chemistry, Brown University, Providence, Rhode Island 02912, United States
bDepartment of Chemistry, Yale University, New Haven, Connecticut 06511, United States
cDepartment of Chemistry, The University of Missouri, Columbia, Missouri 65201, United States

Experimental Details S1-S2
Optimization Tables for Symmetric Urea Synthesis S3-S4
Optimization Tables for Unsymmetric Urea Synthesis S5-S6
Mechanistic NMR Experiments S7-S16
NMR Spectra for Synthesized Symmetric Ureas S17-S29
Postulated Mechanism for Coupling of Methanol and Amines to Urea S30
Supporting Information References S31
Experimental Details

General Considerations:

All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk, vacuum, cannula, or glovebox techniques. Catalyst 1 was prepared as previously described. Formamides that were not commercially available were prepared using previously reported procedures. All other chemicals were purchased from Aldrich, Fisher, Strem, Oakwood Chemicals, VWR, or Cambridge Isotope Laboratories. Liquid amine and alcohol substrates were dried over calcium hydride or sodium hydride, purified by vacuum transfer or distillation, and stored over 3 Å molecular sieves. Solid substrates were purified by sublimation, followed by recrystallization (if necessary). Bulk solvents were dried and deoxygenated using literature procedures. NMR solvents were dried over 3 Å molecular sieves and then used without further manipulation, or sodium and then vacuum transferred prior to use. Hydrogen was purchased from Airgas and was used as received. 1H, 13C and 31P NMR spectra were recorded on Bruker 300 MHz Avance II+, 300 MHz DRX, 500 MHz DRX or 600 MHz spectrometers at ambient temperature, unless otherwise noted. Chemical shifts are reported in ppm; J values are given in Hz. 1H and 13C chemical shifts are referenced to residual solvent signals; 31P chemical shifts are referenced to an external standard of H3PO4. Probe temperatures were calibrated using ethylene glycol and methanol as previously described. Gas chromatography was performed on a Thermofisher Scientific Trace 1300 Series gas chromatograph with FID using helium as a carrier gas.

General Methods for Symmetric Urea Formation from Catalytic Methanol Dehydrogenation in the Presence of Amines

In a glovebox, a 100-mL Schlenk tube was loaded with 5 mL of tetrahydrofuran (THF), 12 mmol of amine, 15 µmol of catalyst, and 3 mmol of alcohol, then sealed. It was immediately placed in an oil bath preheated to 120 °C and stirred for 8 hours. It was then cooled in an ice bath for 30 minutes. If the starting amine was benzylamine or its derivatives, all of the following sample preparations and reaction workups were performed in a glovebox due to the air sensitivity of the remaining starting material.

Analysis of formamide yield:

If analyzed by NMR, 100 µl of reaction solution were added to an NMR tube with 395 µl CDCl3 and 5 µl of mesitylene standard and an NMR delay time of 60 seconds was used. If analyzed by GC, 100 µl of reaction solution were diluted to 1 mL with THF and mesitylene standard (0.024 M or 0.0024M after final dilution) was added.

Urea isolation:

The solvent was then removed from the reaction mixture using glovebox vacuum or rotary evaporation. The resulting oily solid was transferred to a filtration frit and washed with room temperature pentane in a glovebox for benzylamine-type starting materials and cold pentane in air for alkylamine starting materials. The filtrate for alkylamine starting materials was collected, dried, and re-washed until no more solid was recovered. In the case of diaminocyclohexane, the product
was an oil that was purified with silica gel column chromatography using 20:1 CH$_2$Cl$_2$:methanol as the eluent according to previously established procedures. Ureas were identified by comparison to previously reported literature data.$^5$ $^6$ $^7$ $^8$ $^9$ $^{10}$ $^{11}$ $^{12}$

**General Methods for Unsymmetric Urea Formation from Catalytic Dehydrogenative Coupling of Formamides and Amines**

In a glovebox, a 100-mL Schlenk tube was loaded with 5 mL of tetrahydrofuran (THF), 3 mmol of amine, 15 µmol of catalyst, and 3 mmol of formamide, then sealed. It was immediately placed in an oil bath preheated to 120 °C and stirred for 16 hours. It was then cooled in an ice bath for 30 minutes. If the starting amine was benzylamine or its derivatives, all of the following sample preparations and reaction workups were performed in a glovebox due to the air sensitivity of the remaining starting material.

**Analysis of formamide yield:**

If analyzed by NMR, 100 µl of reaction solution were added to an NMR tube with 395 µl CDCl$_3$ and 5 µl of mesitylene standard and an NMR delay time of 60 seconds was used. If analyzed by GC, 100 µl of reaction solution were diluted to 1 mL with THF and mesitylene standard (0.024 M or 0.0024M after final dilution) was added.

**Urea isolation:**

The solvent was then removed from the reaction mixture using glovebox vacuum or rotary evaporation. The resulting oily solid was transferred to a filtration frit and washed with room temperature pentane in a glovebox for benzylamine-type starting materials and cold pentane in air for alkylamine starting materials. The filtrate for alkylamine starting materials was collected, dried, and re-washed until no more solid was recovered. In the case of isobutylformamide as the substrate, the product was an oil that was dried under vacuum and then analyzed by NMR spectroscopy.
Optimization Tables for Symmetric Urea Synthesis

\[
\text{CH}_3\text{OH} + \text{RNH}_2 \xrightarrow{\text{Catalyst 1, X mol\%}} \text{O} \xrightarrow{\text{Solvent, Y \text{ \textdegree}C, Z hrs}} \text{RHN} \xrightarrow{3\text{H}_2} \text{NHR}
\]

Table S1: Catalyst Loading

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>Catalyst Loading (mol%)</th>
<th>TON (Urea)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cyclohexylamine</td>
<td>0.1</td>
<td>33</td>
<td>3%</td>
</tr>
<tr>
<td>2</td>
<td>Cyclohexylamine</td>
<td>0.25</td>
<td>34</td>
<td>9%</td>
</tr>
<tr>
<td>3</td>
<td>Cyclohexylamine</td>
<td>0.5</td>
<td>23</td>
<td>12%</td>
</tr>
</tbody>
</table>

* Reaction conditions: X mol\% catalyst 1, 3 mmol alcohol, and 12 mmol amine in 5 mL THF at 80°C for 8 hrs. Each entry is an average of two trials unless otherwise indicated. TON determined from isolated yield of urea.

Table S2: Alcohol:Amine Ratio

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>Alcohol:Amine</th>
<th>TON (Urea)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cyclohexylamine</td>
<td>1:1</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Cyclohexylamine</td>
<td>1:4</td>
<td>23</td>
</tr>
<tr>
<td>3</td>
<td>Cyclohexylamine</td>
<td>1:6</td>
<td>29</td>
</tr>
<tr>
<td>4</td>
<td>Cyclohexylamine</td>
<td>1:10</td>
<td>34</td>
</tr>
</tbody>
</table>

* Reaction conditions: 0.5 mol\% catalyst 1, 3 mmol alcohol, and X mmol amine in 5 mL THF at 80°C for 8 hrs. Each entry is an average of two trials unless otherwise indicated. TON determined from isolated yield of urea. TON error is ±13.

Table S3: Solvent

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>Solvent</th>
<th>TON (Urea)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cyclohexylamine</td>
<td>Ethyl acetate</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>Cyclohexylamine</td>
<td>1,4-Dioxane</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>Cyclohexylamine</td>
<td>Tetrahydrofuran</td>
<td>23</td>
</tr>
<tr>
<td>4</td>
<td>Cyclohexylamine</td>
<td>Toluene</td>
<td>28</td>
</tr>
</tbody>
</table>

* Reaction conditions: 0.5 mol\% catalyst 1, 3 mmol alcohol, and 12 mmol amine in 5 mL solvent at 80°C for 8 hrs. Each entry is an average of two trials unless otherwise indicated. TON determined from isolated yield of urea.
### Table S4: Temperature

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>Temperature (°C)</th>
<th>TON (Urea)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cyclohexylamine</td>
<td>60&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Cyclohexylamine</td>
<td>80</td>
<td>23</td>
</tr>
<tr>
<td>3</td>
<td>Cyclohexylamine</td>
<td>80&lt;sup&gt;c&lt;/sup&gt;</td>
<td>28</td>
</tr>
<tr>
<td>4</td>
<td>Cyclohexylamine</td>
<td>100</td>
<td>55</td>
</tr>
<tr>
<td>5&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Cyclohexylamine</td>
<td>120</td>
<td>66</td>
</tr>
<tr>
<td>6</td>
<td>Cyclohexylamine</td>
<td>120&lt;sup&gt;c&lt;/sup&gt;</td>
<td>66</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 0.5 mol% catalyst 1, 3 mmol alcohol, and 12 mmol amine in 5 mL THF at X°C for 8 hrs. Each entry is an average of two trials unless otherwise indicated. TON determined from isolated yield of urea. <sup>b</sup>16 hrs. <sup>c</sup>Toluene solvent. <sup>d</sup>Average of three trials.

### Table S5: Time

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>Time (hrs)</th>
<th>TON (Urea)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cyclohexylamine</td>
<td>1</td>
<td>11</td>
</tr>
<tr>
<td>2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Cyclohexylamine</td>
<td>4</td>
<td>44</td>
</tr>
<tr>
<td>3&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Cyclohexylamine</td>
<td>8</td>
<td>66</td>
</tr>
<tr>
<td>4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Cyclohexylamine</td>
<td>16</td>
<td>56</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 0.5 mol% catalyst 1, 3 mmol alcohol, and 12 mmol amine in 5 mL THF at 120°C for X hrs. Each entry is an average of two trials unless otherwise indicated. TON determined from isolated yield of urea. <sup>b</sup>Average of three trials.

### Table S6: Addition of Base

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>DBU Additive (mol%)</th>
<th>TON (Urea)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-(trifluoromethyl)benzylamine</td>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4-(trifluoromethyl)benzylamine</td>
<td>5</td>
<td>108</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 0.5 mol% catalyst 1, 3 mmol alcohol, and 12 mmol amine in 5 mL THF at 120°C for 8 hrs, with X mol% 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU). Each entry is an average of three trials unless otherwise indicated. TON determined from isolated yield of urea. <sup>b</sup>Only one trial.
Optimization Tables for Unsymmetric Urea Synthesis

\[
\text{H} - \text{NHR} \xrightarrow{\text{Catalyst 1, X mol\%}} \text{THF, Y \(^\circ\)C, Z hrs} \rightarrow \text{R'NH} + \text{RHN} + \text{R'HN} \text{NHR'}
\]

Table S7: Time\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>R'</th>
<th>Time (hrs)</th>
<th>TON (Urea)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzyl</td>
<td>Cyclohexyl</td>
<td>4(^b)</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Benzyl</td>
<td>Cyclohexyl</td>
<td>4</td>
<td>68</td>
</tr>
<tr>
<td>3</td>
<td>Benzyl</td>
<td>Cyclohexyl</td>
<td>8</td>
<td>156</td>
</tr>
<tr>
<td>4</td>
<td>Benzyl</td>
<td>Cyclohexyl</td>
<td>16</td>
<td>170</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: 0.5 mol\% catalyst 1, 3 mmol formamide, and 3 mmol amine in 5 mL THF at 120\(^\circ\)C for X hrs. Each entry is an average of two trials unless otherwise indicated. TON determined from isolated yield of unsymmetric urea. \(^b\)No catalyst.

Table S8: Temperature\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>R'</th>
<th>Temperature ((^\circ)C)</th>
<th>TON (Urea)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzyl</td>
<td>Cyclohexyl</td>
<td>100</td>
<td>162</td>
</tr>
<tr>
<td>2</td>
<td>Benzyl</td>
<td>Cyclohexyl</td>
<td>120</td>
<td>170</td>
</tr>
<tr>
<td>3</td>
<td>Benzyl</td>
<td>Cyclohexyl</td>
<td>140</td>
<td>138</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: 0.5 mol\% catalyst 1, 3 mmol formamide, and 3 mmol amine in 5 mL THF at X\(^\circ\)C for 16 hrs. Each entry is an average of two trials unless otherwise indicated. TON determined from isolated yield of unsymmetric urea.

Table S9: Catalyst Loading\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>R'</th>
<th>Catalyst Loading (mol%)</th>
<th>TON (Urea)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzyl</td>
<td>Cyclohexyl</td>
<td>0.5</td>
<td>170</td>
<td>85%</td>
</tr>
<tr>
<td>2</td>
<td>Benzyl</td>
<td>Cyclohexyl</td>
<td>1</td>
<td>83</td>
<td>83%</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: X mol\% catalyst 1, 3 mmol formamide, and 3 mmol amine in 5 mL THF at 120\(^\circ\)C for 16 hrs. Each entry is an average of two trials unless otherwise indicated. TON determined from isolated yield of unsymmetric urea.
**Table S10: Formamide Scrambling**

Reaction conditions: 0.5 mol% catalyst I or no catalyst, 3 mmol formamide, and 3 mmol amine in 5 mL THF at 120°C for 4 hrs. Each entry represents only one trial. NA = not applicable. *b* Determined by amount of unsymmetric urea as compared to the amounts of the two symmetric ureas.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>R’</th>
<th>Starting Formamide Left (mmol)</th>
<th>Scrambled Formamide (mmol)</th>
<th>Catalyst</th>
<th>Yield, Unsymmetric Urea (%)</th>
<th>Selectivity<em>b</em> (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cyclohexyl</td>
<td>Benzyl</td>
<td>1.53</td>
<td>0.02</td>
<td>1, 0.5 mol%</td>
<td>34%</td>
<td>72%</td>
</tr>
<tr>
<td>2</td>
<td>Cyclohexyl</td>
<td>Benzyl</td>
<td>2.70</td>
<td>0.04</td>
<td>None</td>
<td>0</td>
<td>NA</td>
</tr>
</tbody>
</table>
Mechanistic NMR Experiments

Figure S1: Hydrogenation of Ureas

Room temperature $^1$C/$^1$H NMR spectra in THF-$d_8$, 600 MHz, carbonyl region; blue spectrum is straight after mixing at room temperature, red spectrum is after 16 hrs. at 120 °C. GC-FID showed only ~1.5% conversion to formamide.
Figure S2: Reaction of Urea with Amine under H$_2$

\[
\text{BnHN} - \text{NH}_{\text{Bn}} + \text{CyNH}_2 \xrightarrow{10 \text{ mol}\% \text{ 1}} \text{CyHN} - \text{NH}_{\text{Bn}}
\]

THF-d$_8$, 120 °C, 16 hrs + 0.5 atm H$_2$

Bn = \includegraphics[width=1cm]{benzyl}
Cy = \includegraphics[width=1cm]{cyclohexyl}

Room temperature $^{13}$C [$^{1}$H] NMR spectrum in THF-d$_8$, 600 MHz, carbonyl region; after 16 hrs. at 120 °C. The unsymmetric urea product is marked by a box.
Figure S3: Reaction of Urea with Formamide under H₂

\[ \text{BnHN} \text{NH} \text{Bn} + \text{CyHN} \text{H} \rightarrow \text{CyHN} \text{NH} \text{Bn} \]

\[ \text{THF-d}_8, \text{120 °C, 16 hrs} + 0.5 \text{ atm H}_2 \]

Bn = ![Benzylic group]
Cy = ![Cyclohexyl group]

Room temperature $^1$C ($^1$H) NMR spectrum in THF-d$_8$, 600 MHz, carbonyl region; after 16 hrs. at 120 °C. The unsymmetric urea product is marked by a box. The peak at 160.6 ppm is a second rotamer of the cyclohexylformamide reactant.
Figure S4: Reaction of Urea with Formamide, No H₂

\[
\text{BnHN} - \text{NH} - \text{Bn} + \text{CyHN} - \text{H} \rightleftharpoons 10 \text{ mol\% } 1 \\
\text{THF-d}_8, 120 ^\circ \text{C}, 16 \text{ hrs} \\
\text{CyHN} - \text{NH} - \text{Bn} \quad \text{Bn} = \begin{array}{c}
\text{Cy} = \begin{array}{c}
\text{Cy}
\end{array}
\end{array}
\]

Room temperature $^{13}$C NMR spectrum in THF-d$_8$, 600 MHz, carbonyl region; after 16 hrs. at 120 °C. The unsymmetric urea product is marked by a box. The peak at 160.6 ppm is a second rotamer of the cyclohexylformamide reactant.
Figure S5: Reaction of Formamides and Amines

\[

cyNH_2 + \text{CyNH}_2 \xrightarrow{10 \text{ mol}\% \ 1} \text{CyHN}_2\text{NNHBn}
\]

\[
\text{THF-d}_8, 120^\circ C, 16 \text{ hrs} + 0.5 \text{ atm H}_2
\]

\[
\text{Bn} = \text{Cy} = + 0.5 \text{ atm H}_2
\]

Room temperature $^1$C/$^1$H NMR spectra in THF-d$_8$, 600 MHz, carbonyl region; blue spectrum is straight after mixing at room temperature, red spectrum is after 2 hrs. at 120 °C, green spectrum is after 5 hrs.
Figure S6: Attempt to Make a Tetrasubstituted Urea: NMR-Scale

\[
\text{H} \quad \text{NBn}_2 \quad 10 \text{ mol\% } 1 \quad \text{MorphNH} \quad +0.5 \text{ atm } \text{H}_2 \quad \text{THF-}d_8 \\
\text{No reaction}
\]

Room temperature $^{13}$C/$^1$H NMR spectra in THF-$d_8$, 600 MHz carbonyl region; blue spectrum is straight after mixing at room temperature, red spectrum is after 16 hrs. at 120 °C.

Table S11: Attempt to Make a Tetrasubstituted Urea: Standard Catalytic Conditions$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Formamide Left</th>
<th>Urea Produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3 mmol</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: 0.5 mol% catalyst 1, 3 mmol formamide, and 12 mmol amine in 5 mL THF at 80°C for 8 hrs. Each entry represents only one trial.
Figure S7: Reaction of Pentylformamide with Dipentylamine

\[
\text{H} - \text{NH}_{\text{pentine}} + \text{pentyl}_2\text{NH} \rightarrow 10 \text{ mol}\% 1 \rightarrow \text{pentylHN} - \text{N}_{\text{pentyl}_2}
\]

THF-d\textsubscript{8}, 120 °C, 24 hrs

Room temperature \textsuperscript{13}C{\textsuperscript{1}H} NMR spectra in THF-d\textsubscript{8}, 600 MHz, carbonyl region; blue spectrum is straight after mixing at room temperature, red spectrum is after 1 hr. at 120 °C, green spectrum is after 2 hrs., and purple spectrum is after 24 hrs. Carbonyl carbon for the trisubstituted urea is shown by the blue box. The other carbonyl carbon is from the starting formamide. GC-FID showed presence of the trisubstituted urea and no dipentylformamide or pentylamine from scrambling.
Figure S8: Reaction of Dipentylformamide with Pentylamine

\[
\text{H} \quad \text{N\textsubscript{pentyl}}_2 \quad + \quad \text{pentylNH}_2 \quad \xrightarrow{10 \text{ mol}\% \ 1} \quad \text{pentylHN} \quad \text{N\textsubscript{pentyl}}_2
\]

THF-\text{d}_8, 120 \ 0^\circ\text{C, 24 hrs}

No reaction

24 hrs. @ 120 °C

2 hrs. @ 120 °C

1 hr. @ 120 °C

Immediate

Room temperature $^1\text{C}/^1\text{H} \text{ NMR spectra in THF-}d_8, 600 \text{ MHz, carbonyl region; blue spectrum is straight after mixing at room temperature, red spectrum is after 1 hr. at 120 °C, green spectrum is after 2 hrs., and purple spectrum is after 24 hrs. The carbonyl carbon shown is from the starting formamide. GC-FID showed no trisubstituted urea and no pentylformamide or dipentylamine from scrambling.}$
Figure S9: Dehydrogenation of a Formamide to an Isocyanate

H\_NHCy \xrightarrow{1} O\_C\_N\_Cy

THF-d\textsubscript{8}, 120 °C,
24 hrs

A.
A. Room temperature $^1$H NMR spectrum in THF-$d_8$, hydride region, after 1 hr. at 120 °C. Presence of the iron-dihydride (trans isomer) is marked by a box. B. $^{31}$P($^1$H) NMR spectrum in THF-$d_8$ after 1 hr. at 120 °C. Presence of 5 and some free ligand due to catalyst decomposition. Arrows indicate phosphorous resonances for both the cis (red) and trans (green) dihydride isomers. 300 MHz. GC-FID showed presence of cyclohexyl isocyanate.
NMR Spectra for Synthesized Symmetric Ureas
All $^1$H NMRs are taken on a 300$^+$ MHz spectrometer and all $^{13}$C{$^1$H} NMRs are taken on a 600 MHz spectrometer unless otherwise indicated. * = small amount of formamide impurity

1,3-di-$n$-pentylurea (Table 1, Entry 1)

$^1$H NMR, CDCl$_3$

$^{13}$C{$^1$H} NMR, CDCl$_3$
1,3-bis(2-methylpropyl)urea (Table 1, Entry 2)

$^1$H NMR, CDCl$_3$

$^{13}$C{$^1$H} NMR, CDCl$_3$
1,3-di-\textit{n}-heptylurea (Table 1, Entry 3)

$^1$H NMR, CDCl$_3$

$^{13}$C\{\textit{H}\} NMR, CDCl$_3$
1,3-bis(2-methoxyethyl)urea (Table 1, Entry 4)

$^1$H NMR, CDCl$_3$

$^{13}$C($^1$H) NMR, CDCl$_3$
1,3-bis(1-methylhexyl)urea (Table 1, Entry 5)

$^1$H NMR, CDCl$_3$

$^{13}$C$_{^1}$H NMR, CDCl$_3$
1,3-bis(4-methoxybenzyl)urea (Table 1, Entry 6)

$^1$H NMR, CDCl$_3$

$^{13}$C{$^1$H} NMR, CDCl$_3$
1,3-bis(4-methylbenzyl)urea (Table 1, Entry 7)

$^1$H NMR, CDCl$_3$

$^{13}$C($^1$H) NMR, CDCl$_3$
1,3-dibenzylurea (Table 1, Entry 8)

$^1$H NMR, CDCl$_3$

$^{13}$C($^1$H) NMR, CDCl$_3$
1,3-bis(4-trifluoromethylbenzyl)urea (Table 1, Entry 9)

$^1$H NMR, CDCl$_3$

$^{13}$C$\{$$^1$$H$\}$ NMR, CDCl$_3$
1,3-bis(2-phenylethyl)urea (Table 1, Entry 10)

$^1$H NMR, CDCl$_3$

$^{13}$C{$^1$H} NMR, CDCl$_3$
1,3-dicyclopentylurea (Table 1, Entry 11)

$^1$H NMR, CDCl$_3$

$^{13}$C($^1$H) NMR, CDCl$_3$
1,3-dicyclohexylurea (Table 1, Entry 12)

$^1$H NMR, CDCl$_3$

$^{13}$C{$^{1}$H} NMR, CDCl$_3$
Octahydro-benzoimidazol-2-one (Table 1, Entry 13)

Note: observe both cis and trans isomers of the product urea

$^1$H NMR, CDCl$_3$

$^{13}$C{$^1$H} NMR, CDCl$_3$
Figure S10. Postulated Mechanism for Dehydrogenative Coupling of Methanol and Amines to Urea.

\[ 2 \text{H}_2\text{NR} + \text{CH}_3\text{OH} \xrightarrow{1} (\text{HNR})_3\text{CO} + 3 \text{H}_2 \]

Dehydrogenation could occur via a concerted pathway (as shown) or sequential OH & CH bond cleavage.

Methanol dehydrogenation as previously described in *ACS Catal.* 2015, 5, 2404-2415.

Dehydrogenative amidation as previously described in *Organometallics* 2017, 36, 2020-2025.
References