Supplementary Information

One-pot catalytic synthesis of urea derivatives from alkyl ammonium carbamates using low concentrations of CO₂

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General Information
All commercial amines and catalysts except Cp₂Ti(OTf)₂ were purchased from TCI, FUJIFILM Wako Pure Chemical or Sigma-Aldrich and used without any purification. Cp₂Ti(OTf)₂ were synthesized according to the literature method¹ and stored in a glove box. EtOH and n-hexane for ammonium carbamate salts synthesis were purchased from FUJIFILM Wako Pure Chemical as a special grade and used without any purifications. Simulated exhaust gas was purchased from TAKACHIHO CHEMICAL INDUSTRIAL CO., LTD. and contains 300 ppm of CO, 500 ppm of NO₂, 500 ppm of SO₂, 15 vol% of CO₂ and 85 vol% of N₂. ¹H and ¹³C {¹H} NMR spectra were recorded in DMSO-d₆, methanol-d₄, or D₂O by Bruker AVANCE-III high-resolution spectrometer with 400 MHz magnetic field. Chemical shifts of compounds in NMR spectra were corrected by using reported residual solvent signals as reference². Elemental analyses were carried out by PerkinElmer 2400II.

Synthesis of ammonium carbamate salts using a high purity CO₂ gas
All ammonium carbamate salts were synthesized according to a similar method. Thus, a synthetic procedure of 2-ammonioethylcarbamate is shown as a typical example herein. Different aspects such as substrate amount are described in sections for each compound. 3.00 g (50.0 mmol) of ethylenediamine was dissolved in 50 mL of EtOH at a 100 mL eggplant flask. This solution was bubbled by pure CO₂ gas for 10 min. A white precipitate was filtered and washed with EtOH. After drying under reduced pressure at room temperature for 15 h, 2-ammonioethylcarbamate (1a) was obtained as white powder.

2-Ammonioethylcarbamate (1a)

\[
\text{H}_2\text{N}\begin{array}{c}
\text{O} \\
\end{array}\begin{array}{c}
\text{O} \\
\end{array}\begin{array}{c}
\text{H} \\
\end{array}
\]

Yield: 4.82 g (4.63 mmol), 93%. Anal. Calcd. for C₃H₈N₂O₂: C, 34.61; H, 7.75; N, 26.91. Found: C, 34.65; H, 7.95; N, 26.73.
Mixture of 2-ammoniopropylcarbamate and 2-ammonio-1-methylethylecarbamate (1b)

\[
\begin{align*}
\text{H}_3\text{N} & \quad \text{O} \\
\quad & \quad \text{H} \\
\end{align*}
\]

This mixture was treated in a glove box due to hygroscopicity except for CO₂ bubbling. After CO₂ bubbling for 50 mL of dehydrated n-hexane containing 2.96 g (40.0 mmol) of 1,2-diaminopropane, the vessel was tightly closed and transferred to a glove box. Filtrating to separate a precipitate, washing with n-hexane and drying under reduced pressure, the mixture of target compounds was obtained as impure white powder.

Yield: 3.74 g (79%; This yield was tentative isolated yield if 1b was pure). Anal. Calcd. for C₄H₁₀N₂O₂: C, 40.67; H, 8.53; N, 23.71. Found: C, 37.64; H, 8.57; N, 23.08.

Cis-(2-ammoniocyclohexyl)carbamate (1c)

\[
\begin{align*}
\text{H}_3\text{N} & \quad \text{HN} \\
\quad & \quad \text{O} \\
\end{align*}
\]

This compound was synthesized from 2.28 g (20.0 mmol) of cis-1,2-diaminocyclohexane in 50 mL of EtOH. After filtration, washing with EtOH and drying under reduced pressure, this compound was obtained as white powder.

Yield: 2.77 g (17.5 mmol), 88%. Anal. Calcd. for C₇H₁₄N₂O₂: C, 53.15; H, 8.92; N, 17.71. Found: C, 52.91; H, 8.85; N, 17.55.

Trans-(2-ammoniocyclohexyl)carbamate (1d)

\[
\begin{align*}
\text{H}_3\text{N} & \quad \text{HN} \\
\quad & \quad \text{O} \\
\end{align*}
\]

This compound was synthesized from 2.28 g (20.0 mmol) of trans-1,2-diaminocyclohexane in 50 mL of EtOH. After filtration, washing with EtOH and drying under reduced pressure, this compound was obtained as pale yellow powder.

Yield: 2.28 g (14.4 mmol), 72%. Anal. Calcd. for C₇H₁₄N₂O₂: C, 53.15; H, 8.92; N, 17.71. Found: C, 53.01; H, 8.83; N, 17.50.
3-Ammoniopropylcarbamate (1e)

\[
\text{H}_3\text{N} \quad \text{O} \\
\text{N} \quad \text{O} \\
\text{N} \quad \text{O}
\]

This compound was synthesized from 2.96 g (40.0 mmol) of 1,3-diaminopropane in 50 mL of EtOH. After filtration, washing with EtOH and drying under reduced pressure, this compound was obtained as white powder.
Yield: 4.47 g (37.8 mmol), 95%. Anal. Calcd. for C\textsubscript{14}H\textsubscript{10}N\textsubscript{2}O\textsubscript{2}: C, 40.67; H, 8.53; N, 23.71. Found: C, 40.66; H, 9.02; N, 23.58.

\[\text{N},\text{N}'-\text{dimethyl-2-ammonioethylecarbamate (1f)}\]

\[
\text{H}_2 \quad \text{N} \quad \text{O} \\
\text{N} \quad \text{O} \\
\text{N} \quad \text{O}
\]

This compound was synthesized from 3.52 g (40.0 mmol) of \textit{N},\textit{N}'-dimethylethylenediamine in 50 mL of \textit{n}-hexane. After filtration, washing with \textit{n}-hexane and drying under reduced pressure for 4 h, this compound was obtained as white powder.
Yield: 4.70 g (35.5 mmol), 89%. Anal. Calcd. for C\textsubscript{15}H\textsubscript{12}N\textsubscript{2}O\textsubscript{2}: C, 45.44; H, 9.15; N, 21.20. Found: C, 45.37; H, 9.15; N, 21.07.

\[\text{N},\text{N}'-\text{dibenzyl-2-ammonioethylecarbamate (1g)}\]

\[
\text{Ph} \quad \text{H} \quad \text{N} \quad \text{O} \\
\text{N} \quad \text{O} \\
\text{Ph} \quad \text{Ph}
\]

This compound was synthesized from 4.81 g (20.0 mmol) of \textit{N},\textit{N}'-dibenzylethylenediamine in 50 mL of \textit{n}-hexane. After filtration, washing with \textit{n}-hexane and drying under reduced pressure for 4 h, this compound was obtained as white powder.
Yield: 5.49 g (19.3 mmol), 97%. Anal. Calcd. for C\textsubscript{22}H\textsubscript{18}N\textsubscript{2}O\textsubscript{2}: C, 71.81; H, 7.09; N, 9.85. Found: C, 71.80; H, 7.20; N, 9.87.
Benzylammonio benzylcarbamate (2a)

\[
\begin{array}{c}
\text{Ph}^+ \\
\text{NH}_3 \\
\end{array}
\begin{array}{c}
\text{Ph} \\
\text{N} \\
\text{O} \\
\end{array}
\begin{array}{c}
\text{O}^- \\
\end{array}
\]

This compound was synthesized from 44.5 g (415 mmol) of benzylamine in 300 mL of n-hexane at an 500 mL eggplant flask for 10 min CO₂ bubbling. After filtration to afford a precipitate, CO₂ was bubbled to the filtrate again. These operations were conducted three times. Then, washing the obtained solid with n-hexane and drying under reduced pressure, this compound was obtained as white powder. Yield: 49.6 g (19.2 mmol), 93%. Anal. Calcd. for C₁₅H₁₈N₂O₂: C, 69.74; H, 7.02; N, 10.84. Found: C, 69.38; H, 7.14; N, 10.82.

n-Hexylammonio n-hexylcarbamate (2b)

\[
\begin{array}{c}
n-\text{hex}^- \\
\text{NH}_3 \\
\end{array}
\begin{array}{c}
n-\text{hex}^- \\
\text{N} \\
\text{O} \\
\end{array}
\begin{array}{c}
\text{O}^- \\
\end{array}
\]

This compound was synthesized from 3.03 g (30.0 mmol) of n-hexylamine in 50 mL of n-hexane. After filtration, washing with n-hexane and drying under reduced pressure, this compound was obtained as white powder. Yield: 3.40 g (13.8 mmol), 92%. Anal. Calcd. for C₁₃H₃₅N₂O₂: C, 63.37; H, 12.27; N, 11.37. Found: C,63.33; H, 12.39; N, 11.28.

Cyclohexylammonio cyclohexylcarbamate (2c)

\[
\begin{array}{c}
\text{Cy}^- \\
\text{NH}_3 \\
\end{array}
\begin{array}{c}
\text{Cy}^- \\
\text{N} \\
\text{O} \\
\end{array}
\begin{array}{c}
\text{O}^- \\
\end{array}
\]

This compound was synthesized from 2.99 g (30.0 mmol) of n-hexylamine in 50 mL of n-hexane. After filtration, washing with n-hexane and drying under reduced pressure for 4 h, this compound was obtained as white powder. Yield: 3.10 g (12.6 mmol), 84%. Anal. Calcd. C₁₃H₂₆N₂O₂: C, 64.43; H, 10.81; N, 11.56. Found: C,64.34; H, 11.18; N, 11.49.

2-Aminobenzylammonio 2-aminobenzylcarbamate (2d)

\[
\begin{array}{c}
\text{Ph}^- \\
\text{NH}_3 \\
\end{array}
\begin{array}{c}
\text{Ph} \\
\text{N} \\
\text{O} \\
\end{array}
\begin{array}{c}
\text{O}^- \\
\end{array}
\]

This compound was synthesized from 3.66 g (30.0 mmol) of 2-aminobenzylamine in 50 mL of EtOH. After filtration, washing with Et₂O and drying under reduced pressure, this compound was obtained as white powder. Yield: 4.24 g (14.7 mmol), 98%. Anal. Calcd. for C₁₅H₂₀N₄O₂: C, 62.51; H, 6.98; N, 19.28. Found: C,62.48; H, 6.99; N, 19.43.
Synthesis of 2-ammonioethylcarbamate from CO$_2$/N$_2$ mixed gas (v:v = 15:85) or ambient air

Synthesis of 2-ammonioethylcarbamate (1a) from CO$_2$/N$_2$ mixed gas (v:v = 15:85) or simulated exhaust gas (CO$_2$: 15 vol%, N$_2$: 85 vol%, CO: 300 ppm, NO$_2$: 500 ppm, SO$_2$: 500 ppm) were conducted according to the similar method mentioned above except for bubbling time. Yield of 1a were 96% (5.09 g, 48.9 mmol) or 92% (4.88 g, 46.8 mmol) using CO$_2$/N$_2$ mixed gas (v:v = 15:85) or simulated exhaust gas respectively, when 50 mL of EtOH containing 3.00 g (50.0 mmol) of ethylenediamine was bubbled for 30 min.

Synthesis of 1a from ambient air were conducted in absence of solvent. 1.01 g (17 mmol) of ethylenediamine was in a 50 mL screw vial. Three of same ones were prepared and kept static in a draft chamber for about 1 week. Precipitated solids were filtered, washed with EtOH and dried under reduced pressure at room temperature for 15 h. 2-Ammonioethylcarbamate 1a was afforded as a white solid at 45% (2.39 g, 23.0 mmol) yield.

| Condition                        | C     | H     | N     |
|----------------------------------|-------|-------|-------|
| Pure CO$_2$                      | 34.65 | 7.62  | 26.68 |
| CO$_2$/N$_2$ mixed gas (v:v = 15:85) | 34.65 | 7.95  | 26.73 |
| Simulated exhaust gas            | 34.44 | 8.04  | 26.73 |
| Ambient air                      | 34.68 | 7.97  | 26.44 |

a: Calcd. for C$_3$H$_8$N$_2$O$_2$: C, 34.61; H, 7.75; N, 26.91.
Supplementary Fig. 1 | $^1$H NMR spectra of 1a synthesized from various CO$_2$ concentration gas and ethylenediamine measured in D$_2$O. These signals were assigned by $^1$H-$^{13}$C HMQC spectrum (Supplementary Fig. 3).
Supplementary Fig. 2 | $^{13}$C{$^1$H} NMR spectra of 1a synthesized from various CO$_2$ concentration gas and ethylenediamine measured in D$_2$O. † at 49.5 ppm is MeOH signal as an internal standard. These signals were assigned by $^1$H-$^{13}$C HMQC spectrum (Supplementary Fig. 3)
Supplementary Fig. 3 | $^1$H-$^{13}$C HMQC spectrum of 1a measured in D$_2$O.
**Determination of conversion rate for ethylenediamine during CO$_2$ bubbling**

All reactions were conducted in 50 mL of EtOH containing 1.20 g (20.0 mmol) of ethylenediamine and 1,3,5-trimethylbenzene as an internal standard for $^1$H NMR measurement. Various CO$_2$ concentration gases were bubbled to this EtOH solution at 50 mL/min of flow rate controlled by a mass-flow controller MC100SCCM-D/5M (ALICAT SCIENTIFIC). A small amount of this solution was extracted at fixed intervals and then diluted by DMSO-$d_6$ to measure $^1$H NMR. Conversion rate of ethylenediamine was determined by correction and comparing ratio between signals of ethylenediamine and 1,3,5-trimethylbenzene.

**Supplementary Fig. 4** | Intensity changes of ethylenediamine signal in NMR spectra measured during CO$_2$/N$_2$ mixed gas (v:v = 15:85) bubbling. All spectra were normalized at mesitylene signal and corrected for the horizontal axis to easily compare.
Catalyst performance for ethylene urea synthesis.

Catalytic activities of various catalysts for ethylene urea (3a) synthesis were investigated in 4.5 mL of DMI containing 208 mg (2.00 mmol) of 1a at 170 °C for 3 h by using 10 mol% of a catalyst. Yield of 3a was determined by $^1$H NMR in DMSO-$d_6$ with 1,3,5-trimethylebenzene as an internal standard.

**Supplementary Table 2** | Catalyst performance for ethylene urea synthesis

| Entry | Catalyst | Yield of 3a |
|-------|----------|-------------|
| 1     | Bu$_2$SnO | 46          |
| 2     | Bu$_2$Sn(C$_{12}$H$_{23}$O$_2$)$_2$ | 24          |
| 3     | InCl$_3$ | 3           |
| 4     | Cp$_2$TiCl$_2$ | 42          |
| 5     | Cp$_2$Ti(OTf)$_2$ | 52          |
| 6     | TiCl$_4$(THF)$_2$ | 36          |
| 7     | TiCl$_4$(THF)$_2$ + AgOTf (4 eq.) | 46          |
| 8     | Ti(OEt)$_4$ | 22          |
| 9     | Ti(O’Bu)$_4$ | 22          |
| 10    | Cp$_2$ZrCl$_2$ | 41          |
| 11    | Zr(OEt)$_4$ | 30          |
| 12    | Hf(OTf)$_4$ | 28          |
| 13    | Y(OTf)$_3$ | 2           |
| 14    | Sc(OTf)$_3$ | 2           |
| 15    | Fe(OTf)$_3$ | 6           |
| 16    | Zn(OTf)$_3$ | 1           |
| 17    | Ce(OTf)$_3$ | 3           |
| 18    | Yb(OTf)$_3$ | 2           |
| 19    | Ln(OTf)$_3$ | 1           |
| 20    | Nd(OTf)$_3$ | 1>          |
| 21    | Tm(OTf)$_3$ | 2           |
| 22    | K$_2$CO$_3$ | 27          |
| 23    | Cs$_2$CO$_3$ | 34          |
| 24    | CsOH | 28          |
| 25    | DBU | 43          |
| 26    | $N,N$-diisopropylethylamine | 7           |
| 27    | CeO$_2$ (25> nm, Sigma-Aldrich) | 29          |
Investigation of activation energy for ethylene urea synthesis

Activation energy $E_a$ for ethylene urea synthesis were calculated from Arrhenius plot (Supplementary Fig. 3 and Eq. 1), which was based on reaction results using 95.8 mg (200 μmol, 10mol%) of Cp₂Ti(OTf)₂ as a catalyst, 208 mg (2.00 mmol) of 1a and 4.5 mL of DMI as a solvent for 1 h at each temperature. Rate constants $k$ were obtained by using the first order rate equation (Eq. 2) depending on the concentration of 1a ($[M_{1a}]$), which was calculated by subtraction the concentration of 3a from the initial concentration of 1a ($[M_{1a0}]$). $R = 8.314$ J K⁻¹mol⁻¹, $[M_{1a0}] = 0.44$ M.

\[
\ln k = -\frac{E_a}{RT} + \ln A \quad \text{Eq. 1}
\]

\[
\ln [M_{1a}] = -kt + \ln [M_{1a0}] \quad \text{Eq. 2}
\]

Supplementary Fig. 5| Arrhenius plot for ethylene urea synthesis.
**Synthesis of urea derivatives**

All urea derivatives were synthesized by a similar method. Therefore, a procedure of 2-imidazolidinone is shown as an example for typical urea derivative synthesis herein. The different aspects such as substrate amount are described in sections for each compound. 1.04 g (10.0 mmol) of 1a, 95.2 mg (200 μmol, 2 mol%) of Cp₂Ti(OTf)₂ and 4.5 mL of DMI were added to an 5 mL autoclave reactor vessel and completely shielded with a stainless plate gasket. The vessel was dunked in a heated oil bath, and the reaction solution was stirred at 170 °C for 24 h. After reaction, the vessel was removed from the oil bath and cooled to room temperature. The reaction mixture was extracted with MeOH (ca. 20 mL) and 1,3,5-trimethylebenzene (~100 mg) was added as an internal standard for ¹H NMR to determine NMR yield. After measuring the ¹H NMR spectrum, MeOH was removed under reduced pressure by an evaporator apparatus. Then, components other than the target compound were roughly eliminated using a Kugelrohr apparatus. The obtained solid was washed with Et₂O/n-hexane and dried under reduced pressure at 50 °C to afford 2-imidazolidinone (3a) as a white solid.

### 2-Imidazolidinone (3a)

![2-Imidazolidinone](image)

Yield: 703 mg (8.17 mmol), 82%. ¹H NMR (DMSO-d₆, 400 MHz): δ (ppm) 6.10 (br, s, 2H), 3.26 (s, 4H). ¹³C {¹H} NMR (MeOH-d₆, 101 MHz): δ (ppm) 163.7, 48.0, 47.9, 21.7.

### 4-Methyle-2-imidazolidinone (3b)

![4-Methyle-2-imidazolidinone](image)

This compound was synthesized, using 1.18 g of crude 1b, 95.8 mg (200 μmol, 2 mol%) of Cp₂Ti(OTf)₂ and 4.5 mL of DMI and obtained as a white solid according to the typical method.

Yield: 803 mg, 80% (This yield was tentative isolated yield if pure 1b was used). ¹H NMR (DMSO-d₆, 400 MHz): δ (ppm) 6.26 (br, s, 1H), 6.06 (br, s, 1H), 3.71-3.63 (m, 1H), 3.38 (ddd, J = 8.5, 8.5, 0.8Hz, 1H), 2.82 (ddd, J = 8.5, 6.9, 1.2 Hz, 1H), 1.09 (d, J = 6.2 Hz, 3H). ¹³C {¹H} NMR (DMSO-d₆, 101 MHz): δ (ppm) 163.7, 48.0, 47.9, 21.7.

### (3aR*,7aS*)-Octahydro-2-benzimidazolinone (3c)

![Octahydro-2-benzimidazolinone](image)

This compound was synthesized, using 1.27 g (8.00 mmol) of 1c, 76.7 mg (160 μmol, 2 mol%) of Cp₂Ti(OTf)₂ and 4.0 mL of DMI and obtained as a white solid according to the typical method.

Yield: 921 mg (6.57 mmol), 82%. ¹H NMR (DMSO-d₆, 400 MHz): δ (ppm) 6.12 (br, s, 2H), 3.48-3.38 (m, 2H), 1.65-
1.51 (m, 2H), 1.50-1.35 (m, 4H), 1.30-1.15 (m, 2H). $^{13}$C $^1$H NMR (DMSO-d$_6$, 101 MHz): $\delta$ (ppm) 163.9, 51.0, 28.2, 20.3.

**3a$^R$,7a$^R$)-Octahydro-2-benzimidazolinone (3d)$^5$**

This compound was synthesized, using 316 mg (2.00 mmol) of 1d, 95.8 mg (200 $\mu$mol, 10 mol%) of Cp$_2$Ti(OTf)$_2$ and 4.5 mL of DMI and obtained as a white solid according to the typical method.

Yield: 173 mg (1.24 mmol), 62%.

$^1$H NMR (DMSO-d$_6$, 400 MHz): $\delta$ (ppm) 6.31 (br, s, 2H), 2.93-2.78 (m, 2H), 1.95-1.75 (m, 2H), 1.75-1.58 (m, 2H) 1.40-1.20 (m, 4H). $^{13}$C $^1$H NMR (DMSO-d$_6$, 101 MHz): $\delta$ (ppm) 164.8, 60.2, 29.4, 23.7.

**3,4,5,6-Tetrahydro-2-pyrimidone (3e)$^3$**

This compound was synthesized, using 1.18 g (10.0 mmol) of 1e, 95.8 mg (200 $\mu$mol, 2 mol%) of Cp$_2$Ti(OTf)$_2$ and 4.5 mL of DMI and obtained as a pale brown solid. Purification of this compound was carried out by reprecipitation, which was conducted by adding 20 mL of DMSO and 50 mL of Et$_2$O to the reaction solution, due to low solubility for various solvents.

Yield: 787 mg (7.86 mmol), 79%.

$^1$H NMR (DMSO-d$_6$, 400 MHz): $\delta$ (ppm) 6.04 (br, s, 2H), 3.07 (dt, $J$ = 2.4 Hz, $J$ = 5.8 Hz, 4H), 1.67 (q, $J$ = 5.8 Hz, 2H). $^{13}$C $^1$H NMR (DMSO-d$_6$, 101 MHz): $\delta$ (ppm) 163.3, 47.5, 47.4, 21.2.

**1,3-Dimethyle-2-imidazolidinone (3f)$^6$**

This compound was synthesized at 170 °C for 40 h, using 1.32 g (10.0 mmol) of 1f, 95.8 mg (200 $\mu$mol, 2 mol%) of Cp$_2$Ti(OTf)$_2$ and 4.5 mL of 1,4-dioxane. After separation by Kugelrohr, this compound was obtained as pale yellow liquid.

Yield: 734 mg (6.43 mmol), 64%.

$^1$H NMR (DMSO-d$_6$, 400 MHz): $\delta$ (ppm) 3.20 (s, 4H), 2.63 (s, 6H) ppm. $^{13}$C $^1$H NMR (DMSO-d$_6$, 101 MHz): $\delta$ (ppm) 161.3, 44.5, 31.1 ppm.

**1,3-Dibenzyle-2-imidazolidinone (3g)$^7$**
Synthesis of this compound was conducted at 170 °C for 15 h, using 569 mg (2.00 mmol) of 1g, 95.8mg (200 μmol, 10 mol%) of Cp₂Ti(OTf)₂ and 4.5 mL of DMI. After removing the solvent under reduced pressure, this compound was obtained as a colorless oil by column chromatography using diol modified silica with CH₂Cl₂ as an eluent.

Yield: 347 mg (1.30 mmol), 65%. ¹H NMR (DMSO-d₆, 400 MHz): δ (ppm) 7.39-7.22 (m, 10H), 4.32 (s, 4H), 3.13 (s, 4H). ¹³C{¹H} NMR (DMSO-d₆, 101 MHz): δ (ppm) 160.4, 137.5, 128.5, 127.7, 127.1, 127.0, 47.4, 41.7.

3,4-Dihidro-2-quinazolinone (3h)⁵

This compound was synthesized, using 1.32 g (4.61 mmol) of 2d, 76.7 mg (160 μmol, 3.5 mol%) of Cp₂Ti(OTf)₂ and 4.0 mL of DMI and obtained as a white solid according to the typical method.

Yield: 587g (3.96 mmol), 85%. ¹H NMR (DMSO-d₆, 400 MHz): δ (ppm) 8.99 (br, s, 1H), 7.13-7.03 (m, 2H), 6.87-6.73 (m, 3H), 4.29 (s, 2H).

¹³C{¹H} NMR (DMSO-d₆, 101 MHz): δ (ppm) 154.6, 138.1, 127.6, 125.7, 120.9, 118.1, 113.5, 42.5.

1,3-Dibenzyurea (4a)⁵

Synthesis of this compound was conducted at 170 °C for 48 h, using 516 mg (2.00 mmol) of 2a, 95.8 mg (200 μmol, 10 mol%) of Cp₂Ti(OTf)₂ and 4.5 mL of DMI and obtained as a white solid according to the typical method.

Yield: 233 mg (0.97 mmol), 48%. ¹H NMR (DMSO-d₆, 400 MHz): δ (ppm) 7.35-7.19 (m, 10H), 6.44 (t, J = 6.0 Hz, 2H), 3.13 (d, J = 6.0 Hz, 4H) ppm. ¹³C{¹H} NMR (DMSO-d₆, 101 MHz): δ(ppm) 158.0, 140.8, 128.1, 126.9, 126.4, 42.9.

1,3-Di-n-hexylurea (4b)⁵

This compound was synthesized at 170 °C for 48 h, using 493 mg (2.00 mmol) of 2b, 95.8 mg (200 μmol, 10 mol%) of Cp₂Ti(OTf)₂ and 4.5 mL of DMI and obtained as a white solid according to the typical method.

Yield: 236 mg (1.03 mmol) 52%. ¹H NMR (DMSO-d₆, 400 MHz): δ (ppm) 5.70 (t, J = 5.6 Hz, 2H), 2.94 (dt, J = 6.7, 5.6 Hz, 4H), 1.40-1.18 (m, 16H), 0.86 (t, J = 6.8 Hz, 6H). ¹³C{¹H} NMR (DMSO-d₆, 101 MHz): δ (ppm) 157.9, 39.1, 30.9, 29.9,25.9, 22.0, 13.8.
1,3-Dicyclohexylurea (4c)

This compound was synthesized at 170 °C for 15 h, using 484 mg (2.00 mmol) of 2c, 95.8 mg (200 μmol, 10 mol%) of Cp₂Ti(OTf)₂ and 4.5 mL of DMI. Yield of this compound was obtained as NMR yield in DMSO-d₆ containing 1,3,5-trimethylebenzene as an internal standard.

Yield: 13%.
Copies of NMR spectra for the synthesized urea derivatives

**Supplementary Fig. 6** $^1$H NMR spectrum of 3a.

**Supplementary Fig. 7** $^{13}$C{$^1$H} NMR spectrum of 3a.
Supplementary Fig. 8 | $^1$H NMR spectrum of 3b.

Supplementary Fig. 9 | $^{13}$C{$^1$H} NMR spectrum of 3b.
Supplementary Fig. 10 | $^1$H NMR spectrum of 3c.

Supplementary Fig. 11 | $^{13}$C{$^1$H} NMR spectrum of 3c.
Supplementary Fig. 12 | $^1$H NMR spectrum of 3d.

Supplementary Fig. 13 | $^{13}$C{${^1}$H} NMR spectrum of 3d.
Supplementary Fig. 14 $^1$H NMR spectrum of 3e.

Supplementary Fig. 15 $^{13}$C ($^1$H) NMR spectrum of 3e.
Supplementary Fig. 16 | $^1$H NMR spectrum of 3f.

Supplementary Fig. 17 | $^{13}$C{$^1$H} NMR spectrum of 3f.
Supplementary Fig. 18 | $^1$H NMR spectrum of 3g.

Supplementary Fig. 19 | $^{13}$C{$^1$H} NMR spectrum of 3g.
Supplementary Fig. 20 | $^1$H NMR spectrum of 3h

Supplementary Fig. 21 | $^{13}$C NMR spectrum of 3h
Supplementary Fig. 22 | $^1$H NMR spectrum of 4a.

Supplementary Fig. 23 | $^{13}$C($^1$H) NMR spectrum of 4a.
Supplementary Fig. 24 | $^1$H NMR spectrum of 4b.

Supplementary Fig. 25 | $^{13}$C($^1$H) NMR spectrum of 4b.
One-pot synthesis of urea derivatives

2 mmol of diamine was mixed into 2 mL of DMI in a 5 mL autoclave reactor vessel and shielded with a ring gasket and a lid with two-way cock. CO₂/N₂ mixed gas (v:v = 15:85) was vented into only gas phase through the branch using syringe needles and a septum at constant flow rate (20 mL/min) controlled by a mass flow controller for 60 min to prevent clogging of a needle tip by precipitated ammonium carbamate derivatives. Then, this gas was bubbled for the reaction mixture for 30 min with the same flow rate. After that, the lid and the ring gasket were removed from the vessel and 95.2 mg of Cp₂Ti(OTf)₂ (0.2 mmol, 10 mol%) solved in 2.5 mL of DMI was added to the vessel in a N₂ filled glove box. This vessel was completely shielded with a stainless plate gasket and dunked in a heated oil bath. The reaction solution was stirred at 170 °C for 24 h. After reaction, the vessel was removed from the oil bath and cooled to room temperature. The reaction mixture was extracted with MeOH (ca. 20 mL) and 1,3,5-trimethylbenzene (~100 mg) was added as an internal standard for the ¹H NMR. The ¹H NMR spectra were measure in DMSO-d₆.

Pressure change during reaction of 3a synthesis

A reaction of 3a synthesis to measure inner pressure change was conducted in 5 mL autoclave reactor vessel with a ring type gasket and a lid with pressure gage at 170 °C for 24 h, using 95.2 mg of Cp₂Ti(OTf)₂ (0.2 mmol, 2 mol%), 1041 mg of 1a (10 mmol) and 4.5 mL of DMI. The preparation was conducted in a N₂ filled glove box.

Supplementary Fig 26 | Time course of inner pressure during 3a synthesis.
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