Efficient Solvent-Free Synthesis of Urea Derivatives Using Selenium-Catalyzed Carbonylation of Amines with Carbon Monoxide and Oxygen

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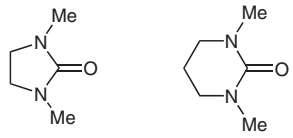
Abstract: In the presence of a catalytic amount of selenium under ambient pressure of carbon monoxide with oxygen, solvent-free facile synthesis of urea derivatives was developed; the aim is for green and sustainable chemistry. For example, *N*,*N*′-dimethylethylenediamine (20 mmol) successfully afforded 1,3-dimethylimidazolidin-2-one (DMI) in 74% yield (1487% based on Se) using selenium catalyst (5 mol%) under mixed gas (CO/O_2, 2:1) at 0.1 MPa, 20 °C without any additive or solvent.

Key words: solvent-free, DMI, urea derivatives, carbon monoxide, selenium

1,3-Dimethylimidazolidin-2-one (DMI, **1a**) is a non-corrosive, colorless, highly polar solvent with high thermal and chemical stability. DMI (**1a**) has a high boiling point (225 °C), a high flash point (120 °C) and a low melting point (8.2 °C). It can be used in a variety of applications (detergents, dyestuffs, and electronic materials) and in the manufacture of polymers. Its versatility can be attributed to its chemical properties; its excellent solubility for inorganic and organic compounds, high dielectric constant, and solvation effect.[1] 1,3-Dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (DMPU, **1d**) is used as a polar, aprotic organic solvent.[2] In particular, DMI (**1a**) and DMPU (**1d**) are suitable replacements for the carcinogenic solvent, hexamethylphosphoramide (HMPA) (Figure 1).[3,4]



DMI (**1a**) DMPU (**1d**)

Figure 1 1,3-Dimethylimidazolidin-2-one (DMI, **1a**) and 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (DMPU, **1d**)

A variety of synthetic methods for *N*,*N*′-dialkyl cyclic ureas containing **1a** and **1d** have been developed using the carbonylation of secondary α,ω-diamines. Among them, a general synthetic method for cyclic ureas was based upon the carbonylation of α,ω-diamines with phosgene as a carbonyl source.[5,6] However, the use of this preparative method is limited because of the high toxicity of phosgene. Urea and carbon dioxide in the presence of transition-metal catalysts were recognized as a carbonyl source for the synthesis of cyclic ureas.[7–11] Also, cyclic ureas were obtained from α,ω-diamines with carbon dioxide and phosphorylating agents.[12] Cyclic ureas were obtained by displacement from the corresponding cyclic thioureas.[13,14] Furthermore, carbon monoxide was a useful raw material for the preparation of cyclic ureas. Transition-metal-catalyzed reaction of secondary diamines and carbon monoxide gave *N*,*N*′-dialkyl cyclic ureas.[15]

Recently, we reported the synthesis of cyclic ureas from secondary amines using sulfur-assisted carbonylation and oxidation.[16] By the combined sulfur-assisted carbonylation of secondary α,ω-diamines under an ambient pressure of carbon monoxide at 20 °C with oxidation by molecular oxygen (0.1 MPa, 20 °C) in *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide (DMAc), or dimethyl sulfoxide, *N*,*N*′-dialkyl cyclic ureas including DMI (**1a**) were obtained in good yields. However, in this reaction procedure the separation of *N*,*N*′-dialkyl cyclic ureas from the solvent (DMF, DMAc, or DMSO) was sometimes difficult, because the *N*,*N*′-dialkyl cyclic ureas and the solvents have similar properties (highly polar, water-soluble, and high boiling points).

We also developed a synthetic process for acyclic urea derivatives from primary amines, carbon monoxide, sulfur, and oxygen under solvent-free conditions (0.1 MPa).[17] However, this urea synthesis using sulfur-assisted carbonylation and oxidation has a serious limitation; it is only applicable to primary amines as reactants.

About 40-years ago, Sonoda and co-workers found that selenium-catalyzed carbonylation of amines **2** with carbon monoxide and oxygen under mild reaction conditions (0.1 MPa, 20 °C) mainly using tetrahydrofuran solvent gave the corresponding urea derivatives **1** in excellent yields.[18,19] However, solvent-free selenium-catalyzed carbonylation is very rare. To the best of our knowledge, solvent-free selenium-catalyzed thiocarbamate synthesis from nitroarenes, carbon monoxide, and thiols has only been reported.[20]

Therefore, in our practical and environmentally friendly strategy, our objective has been to develop a selenium-catalyzed solvent-free synthesis for urea derivatives **1**, e.g. DMI (**1a**) and DMPU (**1d**), by the carbonylation of amines **2** with carbon monoxide and oxygen under mild conditions (0.1 MPa, 20 °C).

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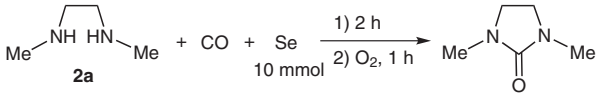
The model preparation of 1,3-dimethylimidazolidin-2-one, DMI (**1a**) was used to examine the influence the quantity of *N*,*N*′-dimethylethylenediamine (**2a**), the base, and the solvent (Table 1).

Initially, the synthesis of DMI (**1a**) was carried out under 0.1 MPa at 20 °C by carbonylation of **2a** (12 mmol) using elemental selenium (10 mmol) with carbon monoxide for two hours and oxidation with molecular oxygen for one hour. The reactions proceeded smoothly and **1a** was obtained in moderate yield (55%) (entry 1). Then, the effect of additives and solvent on the synthesis of **1a** was checked. The addition of 1-methylpyrrolidine improved the yield of **1a** to 74% (entry 3). However, using tetrahydrofuran as the solvent, which is easily separated from **1a**, was unsuitable for the preparation of DMI (**1a**) (entry 4).

Next, the influence of the quantity of **2a** on the synthesis of **1a** was examined (entries 5–7). Using 3.0 equivalents of **2a** gave DMI (**1a**) in excellent yield under solvent-free condition (entry 7). Additionally, the use of sulfur (10 mmol) in place of selenium gave a poor result (entry 8).

Table 1 Influence of Quantity of **2a**, Base, and Solvent on the Synthesis of **1a**



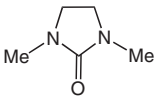
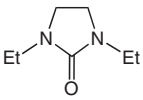
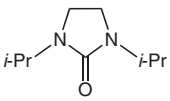
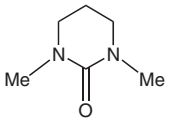
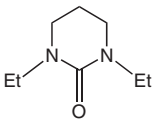
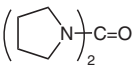
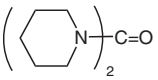
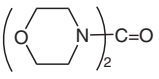
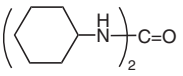
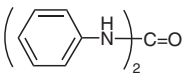
Entry	**2a** (mmol)	Additive or solvent	Yield[a] (%)
1	12	–	55
2	12	Et_3N (20 mmol)	48
3	12	1-methylpyrrolidine (20 mmol)	74
4	12	THF (20 mL)	n.r.
5	15	–	64
6	20	–	77
7	30	–	90
8	30	–	6[b]

[a] Isolated yields, based on Se; n.r. = no reaction.
[b] Sulfur (10 mmol) was used in place of selenium.

The effective formation of **1a** under solvent-free conditions led us to consider whether this reaction could provide general access to urea derivatives **1**. To demonstrate the efficiency and scope of the present solvent-free synthetic method on urea derivatives **1**, various ureas **1a–k** were prepared under the optimized conditions [**2a–k** (3.0 equiv), solvent-free, 0.1 MPa, 20 °C], by carbonylation with carbon monoxide for two hours and oxidation with oxygen for one hour (Table 2).

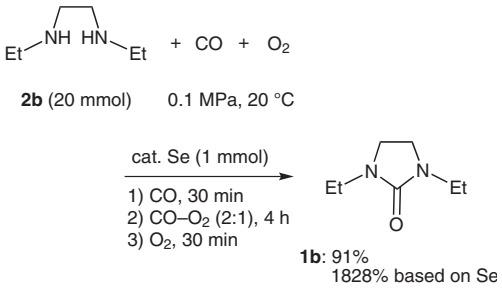
Generally, *N*,*N*′-dialkyl cyclic ureas **1a–e**, including DMI (**1a**) and DMPU (**1d**), were obtained in good to excellent yields from diamines **2a–e** at ambient pressure and room temperature by stoichiometric reaction. However, 1,3-diisopropylimidazolidin-2-one (**1c**) was obtained in moderate yield, because of the bulkiness of *N*,*N*′-diisopropylethylenediamine (**2c**). Symmetrical ureas **1f–j** from secondary amines **2f–h** and primary amines **2i,j** were also af-

Table 2 Synthesis of Urea Derivatives **1a–k**[a]

Product	Yield[b] (%)
 **1a**	90
 **1b**	96
 **1c**	59
 **1d**	94
 **1e**	80
 **1f**	100[c]
 **1g**	100
 **1h**	85
$(n\text{-}C_5H_{11}NH)_2C{=}O$ **1i**	100
 **1j**	99
 **1k**	n.r., 51[d]

[a] Reaction conditions: amine (60 mmol) or diamine (30 mmol), Se (790 mg, 10 mmol), CO (0.1 MPa), 20 °C, 2 h for carbonylation and O_2 (0.1 MPa), 20 °C, 1 h for oxidation.
[b] Isolated yields, based on Se; n.r. = no reaction.
[c] Pyrrolidine (40 mmol) was used.
[d] Aniline (24 mmol) and 1-methylpyrrolidine (20 mmol) were used.

forded in excellent yields. Furthermore, the use of aniline (**2k**) gave no reaction, the addition of 1-methylpyrrolidine with **2k** afforded *N*,*N*′-diphenylurea (**1k**) in moderate yield.



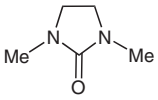
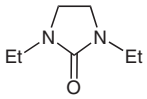
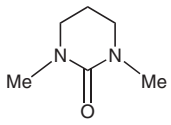
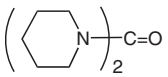
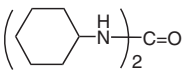
Scheme 1 Selenium-catalyzed synthesis of **1b**

Although selenium is an essential trace element, it is toxic. Therefore, it is unsuitable for industrial large-scale production of urea derivatives **1** using a stoichiometric amount of selenium. Hence, the synthesis of **1** was also examined in the presence of a catalytic amount of selenium. Under carbon monoxide (0.1 MPa) for 30 minutes, the mixed gas of carbon monoxide and oxygen atmosphere (CO/O_2, 2:1, 0.1 MPa) for four hours and oxygen (0.1 MPa) for 30 minutes, the solvent-free synthesis of 1,3-diethylimidazolidin-2-one (**1b**) by the carbonylation of *N*,*N*′-diethylethylenediamine (**2b**) with 5 mol% of selenium at 20 °C was attempted (Scheme 1). 1,3-Diethylimidazolidin-2-one (**1b**) was obtained in excellent yield; the yield based on selenium of **1b** was 1828%. Under similar catalytic reaction conditions using the mixed gas (CO/O_2, 2:1), a variety of ureas **1a**,**b**,**d**,**g**,**i**,**j** were synthesized. DMI (**1a**) and **1b** were obtained in good to excellent yields (1487% and 1828% respectively, based on Se used). However, yields of DMPU (**1d**) and **1g** were lower. Surprisingly, primary amines **2i**,**j** gave corresponding urea **1i**,**j** in moderate yields, in spite of the solidification of the reaction mixture.

Scheme 2 shows possible paths for the synthesis of 1,3-dimethylimidazolidin-2-one, DMI (**1a**) by the carbonylation of *N*,*N*′-dimethylethylenediamine (**2a**) followed by oxidation of the selenocarbamate salt **5a**. First, elemental selenium undergoes Se–Se bond fission by reaction with **2a** to form selenolate anion **3a**. The reaction of **3a** with carbon monoxide gives selenocarbamate salt **5a** from carbonylated species **4a**. The thus formed **5a** is oxidized by molecular oxygen giving **1a** and hydrogen selenide (**7a**) via biscarbamoyl diselenide **6a**. Then, **7a** was oxidized to recover elemental selenium. In the selenium-catalyzed carbonylation of secondary amines with carbon monoxide, biscarbamoyl diselenide was formed by oxidation of selenocarbamate salt with oxygen, and isolated.[21]

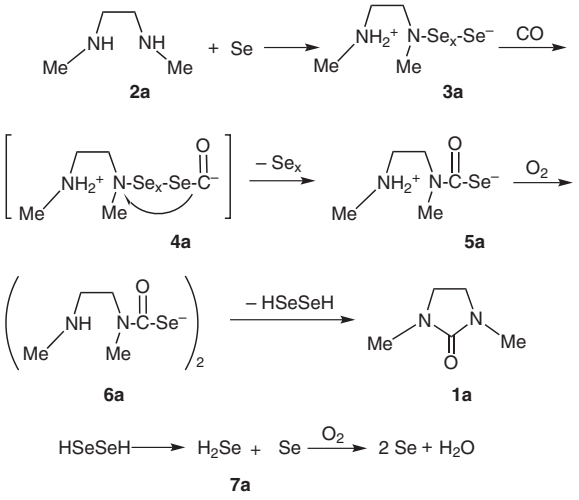
In summary, a useful and environmentally benign solvent-free synthesis for urea derivatives **1** including DMI (**1a**) and DMPU (**1d**) in excellent yields was developed under mild conditions (0.1 MPa, 20 °C), using selenium-catalyzed carbonylation with carbon monoxide and oxidation

Table 3 Synthesis of **1a**,**b**,**d**,**g**,**i**,**j** Using a Catalytic Amount of Selenium[a]

Product	Yield[b] (%)	
	Based on **2**	Based on Se
 **1a**	74	1487
 **1b**	91	1828
 **1d**	21	429
 **1g**	8	163
(n-$C_5H_{11}NH)_2C$=O **1i**	50	1008
 **1j**	48	965

[a] Reaction conditions: amine (40 mmol) or diamine (20 mmol), selenium (79 mg, 1.0 mmol), CO (0.1 MPa), 20 °C, 30 min, CO/O_2, 2:1 (0.1 MPa), 20 °C, 4 h and O_2 (0.1 MPa), 20 °C, 30 min.
[b] Isolated yields based on amine or diamine and in parentheses based on selenium.

of with molecular oxygen. Also, in the presence of a catalytic amount of selenium, the solvent-free synthesis of urea derivatives **1** in good yields under the a mixed carbon monoxide and oxygen atmosphere (CO/O_2, 2:1, 0.1 MPa, 20 °C) was established.



Scheme 2 Reaction path for the formation of **1a**

From the viewpoint of practical and solvent-free production of DMI (**1a**) and DMPU (**1d**), the present method is very significant in terms of the use of easily available and inexpensive carbon monoxide and oxygen and mild reaction conditions (0.1 MPa, 20 °C).

Melting points were determined on a Mettler FP 5 instrument and were uncorrected. FT-IR spectra were recorded on a Jasco FT/IR-4100 instrument. ^{1}H and ^{13}C NMR spectra were obtained on a Jeol JNM-AL300 (300 MHz, 75 MHz) instrument relative to TMS. Both LR-MS and HRMS were measured on a Jeol JMS-600 spectrometer. Amines **2a**–**k**, base (Et_3N, 1-methylpyrrolidine), Se (99.9%), and THF were used as purchased. CO (99.9%) and O_2 (99.9%) were also used.

1,3-Dimethylimidazolidin-2-one (DMI, 1a) by Stoichiometric Reaction; Typical Procedure

To a 100-mL flask, *N*,*N*′-dimethylethylenediamine (**2a**, 3.2 mL, 30 mmol) and metallic Se (790 mg, 10 mmol) were added under argon. Ambient pressure of CO was charged and vigorously stirred under CO from a balloon (0.1 MPa) at 20 °C for 2 h. Then, the soln changed from black to transparent and colorless. CO was purged and O_2 (0.1 MPa) was charged at 20 °C. The mixture was stirred under O_2 from a balloon (0.1 MPa) at 20 °C for an additional 1 h. The resulting soln was diluted with MTBE (100 mL) and metallic Se was recovered by filtration. After evaporation of the solvent and purification by short-column chromatography (silica gel, EtOAc–MeOH, 1:1), 1,3-dimethylimidazolidin-2-one, DMI (**1a**) was obtained as an oil;[16] yield: 1.03 g (90%). For the identification of **1a**, IR, NMR and MS spectra of **1a** were compared with those of commercially available DMI (**1a**).

IR (neat): 2940, 2865, 1698, 1507, 1444, 1397, 1291, 1249 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.79 (s, 6 H, 2 CH_3), 3.27 (s, 4 H, 2 CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.3, 44.9, 161.9.

MS (EI, 70 eV): *m*/*z* (%) = 114 (100) [M$^+$], 113 (70), 85 (20), 72 (16), 58 (22), 56 (34).

1,3-Diethylimidazolidin-2-one (1b)

Compound **1b** was purified by short-column chromatography (silica gel, EtOAc–MeOH, 1:1) to give an oil; yield: 1.37 g (96%).[16]

IR (neat): 2975, 2934, 2873, 1689, 1496, 1452, 1265 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (t, *J* = 7.2 Hz, 6 H, 2 CH_3), 3.24 (q, *J* = 7.2 Hz, 4 H, 2 CH_2), 3.28 (s, 4 H, 2 CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.7, 38.7, 42.1, 161.0.

MS (EI, 70 eV): *m*/*z* (%) = 142 (54) [M$^+$], 127 (100), 99 (19), 56 (39).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_7H_{14}ON_2$: 142.1106; found: 142.1067.

1,3-Diisopropylimidazolidin-2-one (1c)

Compound **1c** was purified by short-column chromatography (silica gel, EtOAc–MeOH, 1:1) to give an oil; yield: 1.00 g (59%).[16]

IR (neat): 2971, 1677, 1489, 1434, 1271, 1224 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 6.8 Hz, 12 H, 4 CH_3), 3.22 (s, 4 H, 2 CH_2), 4.14 (septet, *J* = 6.8 Hz, 2 H, 2 CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.4, 37.2, 43.3, 160.1.

MS (EI, 70 eV): *m*/*z* (%) = 170 (20) [M$^+$], 155 (100), 113 (38).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_9H_{18}ON_2$: 170.1419; found: 170.1392.

1,3-Dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (DMPU, 1d)

Compound **1d** was purified by short-column chromatography (silica gel, EtOAc–MeOH, 1:1) to give an oil; yield: 1.20 g (94%).[16] For the identification of **1d**, IR, NMR and MS spectra of **1d** were compared with those of commercially available DMPU (**1d**).

IR (neat): 2933, 2860, 1635, 1523, 1446, 1402, 1317, 1252, 1216 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.97 (quintet, *J* = 6.0 Hz, 2 H, CH_2), 2.92 (s, 6 H, 2 CH_3), 3.24 (t, *J* = 6.0 Hz, 4 H, 2 CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.1, 35.5, 47.8, 156.7.

MS (EI, 70 eV): *m*/*z* (%) = 128 (100) [M$^+$], 127 (29), 99 (37), 70 (31), 57 (28).

1,3-Diethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (1e)

Compound **1c** was purified by short-column chromatography (silica gel, EtOAc–MeOH, 1:1) to give an oil; yield: 1.24 g (80%).[22]

IR (neat): 2970, 2932, 2870, 1631, 1509, 1451, 1292, 1213 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09 (t, *J* = 7.0 Hz, 6 H, 2 CH_3), 1.94 (quintet, *J* = 5.9 Hz, 2 H, CH_2), 3.23 (t, *J* = 5.9 Hz, 4 H, 2 CH_2), 3.37 (q, *J* = 7.0 Hz, 4 H, 2 CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.8, 22.4, 42.5, 44.9, 155.4.

MS (EI, 70 eV): *m*/*z* (%) = 156 (59) [M$^+$], 141 (100), 113 (36), 70 (41).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_8H_{16}ON_2$: 156.1263; found: 156.1222.

1,1′-Carbonyldipyrrolidine (1f)

Compound **1f** was purified by short-column chromatography (silica gel, EtOAc–MeOH, 1:1) to give an oil; yield: 1.69 g (100%).[19]

IR (neat): 2966, 2871, 1631, 1412, 1339 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.80–1.85 (m, 8 H, 4 CH_2), 3.35–3.39 (m, 8 H, 4 CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.5, 47.9, 161.4.

MS (EI, 70 eV): *m*/*z* (%) = 168 (68) [M$^+$], 98 (70), 70 (100), 55 (63).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_9H_{16}ON_2$: 168.1263; found: 168.1236.

1,1′-Carbonyldipiperidine (1g)

Compound **1g** was purified by short-column chromatography (silica gel, EtOAc) to give an oil; yield: 1.96 g (100%).[19]

IR (neat): 2932, 2851, 1645, 1415, 1370, 1250, 1212 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.53–1.56 (m, 12 H, 6 CH_2), 3.16–3.18 (m, 8 H, 4 CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.7, 25.7, 47.9, 164.8.

MS (EI, 70 eV): *m*/*z* (%) = 196 (30) [M$^+$], 112 (19), 84 (100), 69 (21).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{11}H_{20}ON_2$: 196.1576; found: 196.1537.

4,4′-Carbonyldimorpholine (1h)

Compound **1h** was purified by short-column chromatography (silica gel, EtOAc–MeOH, 1:1); yield: 1.70 g (85%); mp 142.2 °C (Lit.[23] 141–142 °C).

IR (KBr): 2974, 2857, 1647, 1414, 1263, 1236 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.12 (t, *J* = 4.6 Hz, 8 H, 4 CH_2), 3.54 (t, *J* = 4.6 Hz, 8 H, 4 CH_2).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 46.8, 65.8, 163.0.

MS (EI, 70 eV): *m*/*z* (%) = 200 (44) [M$^+$], 169 (75), 114 (100), 86 (46), 70 (95).

***N*,*N*′-Dipentylurea (1i)**
Compound **1i** was purified by short-column chromatography (silica gel, EtOAc); yield: 2.01 g (100%); mp 87.2 °C (Lit.[17] 85.6 °C).

IR (KBr): 3336, 2955, 2932, 1625, 1578 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.8 Hz, 6 H, 2 CH_3), 1.26–1.37 (m, 8 H, 4 CH_2), 1.50 (quintet, *J* = 6.8 Hz, 4 H, 2 CH_2), 3.15 (t, *J* = 6.8 Hz, 4 H, 2 CH_2), 4.26 (br s, 2 H, 2 NH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 22.4, 29.1, 30.0, 40.4, 158.8.

MS (EI, 70 eV): *m*/*z* (%) = 200 (100) [M$^+$], 171 (60), 144 (34), 101 (33).

***N*,*N*′-Dicyclohexylurea (1j)**
Compound **1j** was purified by washing with toluene and MTBE; yield: 2.22 g (99%); mp 233.9 °C (Lit.[17] 231.7 °C).

IR (KBr): 3327, 2927, 2850, 1626, 1575, 1536, 1311, 1244 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.08–1.34 (m, 10 H, 5 CH_2), 1.50–1.78 (m, 10 H, 5 CH_2), 3.36–3.40 (m, 2 H, 2 CH), 5.38 (d, *J* = 7.0 Hz, 2 H, 2 NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 23.8, 24.9, 32.8, 47.2, 156.3.

MS (EI, 70 eV): *m*/*z* (%) = 224 (58) [M$^+$], 143 (38), 99 (58), 56 (100).

***N*,*N*′-Diphenylurea (1k)**
Compound **1k** was purified by washing with toluene and MTBE; yield: 1.09 g (51%); mp 242.4 °C (Lit.[17] 241.0 °C).

IR (KBr): 3329, 1649, 1594, 1552, 1232, 753, 697 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.95 (t, *J* = 7.8 Hz, 2 H, 2 CH), 7.27 (t, *J* = 7.8 Hz, 4 H, 4 CH), 7.44 (d, *J* = 7.8 Hz, 4 H, 4 CH), 8.63 (s, 2 H, 2 NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 118.1, 121.7, 128.7, 139.7, 152.5.

MS (EI, 70 eV): *m*/*z* (%) = 212 (43) [M$^+$], 119 (6), 93 (100), 66 (6).

1,3-Diethylimidazolidin-2-one (1b) Using Catalytic Amount of Selenium; Typical Procedure
A soln containing *N*,*N*′-diethylethylenediamine (**2b**, 2.9 mL, 20 mmol) and metallic Se (79 mg, 1.0 mmol) was vigorously stirred under CO (0.1 MPa) at 20 °C for 30 min. Into the obtained black soln, mixed gas of CO and O_2 (CO/O_2, 2:1, 0.1 MPa) was flowed continuously with stirring at 20 °C for 4 h. After the carbonylation, the soln was also stirred under O_2 (0.1 MPa) for an additional 30 min at 20 °C. The resulting soln was diluted with MTBE (100 mL) and the generated Se was filtered out. After evaporation of the solvent, 1,3-diethylimidazolidin-2-one (**1b**) was purified by short-column chromatography (silica gel, EtOAc–MeOH, 1:1); yield: 2.60 g (91%), 1828% based on selenium.

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