Ionic Liquid as an Efficient Promoting Medium for Fixation of Carbon Dioxide: A Clean Method for the Synthesis of 5-Methylene-1,3-oxazolidin-2-ones from Propargylic Alcohols, Amines, and Carbon Dioxide Catalyzed by Cu(I) under Mild Conditions

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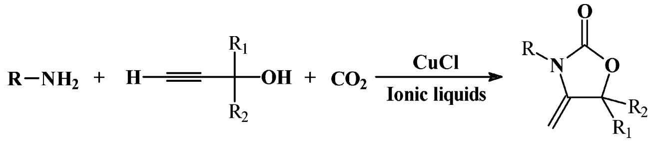

The reactions of propargylic alcohols, aliphatic primary amines, and CO_2 were conducted in CuCl/[BMIm]BF_4 system to produce the corresponding 5-methylene-1,3-oxazolidin-2-ones under relatively mild conditions. The products could be conveniently isolated by means of liquid−liquid extraction. The solvent ionic liquid as well as CuCl catalyst can be recovered and reused three times without appreciable loss of activity. By this green approach, several new 5-methylene-1,3-oxazolidin-2-ones were prepared in excellent yields and purity and were well-characterized.

Introduction

Cyclic carbamates 1,3-oxazolidin-2-ones are useful substrates in organic synthesis.[1] In their optically active form, they are frequently used as chiral auxiliaries in a wide range of asymmetric synthesis such as alkylation, acylation and Diels−Alder reactions, and aldolic condensations.[2] Moreover, the cyclic carbamate nucleus constitutes the core unit of many therapeutic agents, including antibacterial drugs.[3] Thus, synthesis of this heterocyclic system is of much interest, and a number of procedures have been developed.[4] 1,3-Oxazolidin-2-ones with an exocyclic double bond (5-methylene-1,3-oxazolidin-2-ones or α-methylene oxazolidinones) allow the further transformation of the 1,3-oxazolin-2-one and the preparation of synthetically useful derivatives. 5-Methylene-1,3-oxazolidin-2-ones could be prepared from propynyl carbamates through an intramolecular nucleophilic cyclization in the presence of a base.[5] Alternatively, propargylic amines can react with carbon dioxide, leading to the formation of 5-methylene-1,3-oxazolidin-2-ones in the presence of catalysts, such as copper salts,[6] ruthenium or palladium complexes,[7] and strong organic bases.[8] Analogous synthetic reactions could also be conducted in an aprotic solvent using tetraethylammonium carbonate or tetraethylammonium hydrogen carbonate instead of carbon dioxide as the carbonyl contributor.[9] Moreover, α-methylene cyclic carbonates have also been used as substrates to react with amines to give 5-methylene-1,3-

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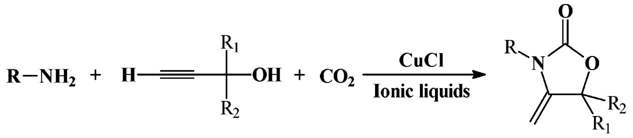
oxazolidin-2-ones under mild conditions.[10] However, propynyl carbamates, propargylic amines, and α-methylene cyclic carbonates are not easily available and are expensive; their preparations are also hard tasks. Regarding the availability and the economic viability, the most attractive method for the synthesis of 5-methylene-1,3-oxazolidin-2-ones should be the three-component reactions of propargylic alcohols, primary amines, and carbon dioxide, which are usually catalyzed by copper salts or tributylphosphine.[11,12] However, most of the synthetic protocols for 5-methylene-1,3-oxazolidin-2-ones reported thus far suffer from harsh conditions (5.0 MPa of CO_2 pressure and 110−140 °C), poor yields (38−72%), prolonged time period (20 h), and use of hazardous and often expensive catalysts.[12] Moreover, the synthesis of these heterocycles has been usually carried out in polar solvents such as acetonitrile, DMF, and DMSO, leading to complex isolation and recovery procedures. These processes also generate waste-containing solvent and catalyst, which have to be recovered, treated, and disposed of. With increasing environmental concerns, it is imperative that new "environment friendly" approaches for the synthesis of 5-methylene-1,3-oxazolidin-2-ones be developed and used.

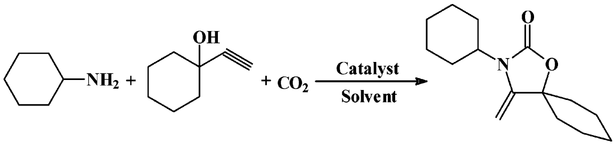
In recent years, studies of low waste routes and reusable reaction media for enhanced selectivity and energy minimization have been the key interests of synthetic organic chemists the world over.[13] In this context, the use of room-temperature ionic liquids as "green" solvents in organic synthetic processes has gained considerable importance due to their solvating ability, negligible vapor pressure, and easy recyclability.[14] They have the potential to be highly polar yet noncoordinating. In addition to the above-mentioned salient features of ionic liquids as reaction media, we have also recently shown that they can act as promoting media for the chemical fixation of carbon dioxide. The reactions investigated by us are cyclic addition of epoxide to CO_2,[15] electrochemical synthesis of cyclic carbonates,[16] and direct synthesis of symmetrical dialkylurea from CO_2 and aliphatic amines,[17] which proceed in significantly enhanced reaction rates, high selectivity, and excellent isolated yields. In particular, we have recently reported the atom-economic reactions of propargylic alcohols with CO_2 in the CuCl/[BMIm][$PhSO_3$] system to afford α-methylene cyclic carbonates in excellent isolated yields under mild conditions.[18]

SCHEME 1. General Reaction



1 2 3

TABLE 1. Three-Component Reaction of 1a, 2a, and Carbon Dioxide in [BMIm]BF_4[a]



3*a*

entry	catalyst	amount of catalyst (mol %)	solvent	yield (%)
1	CuCl	2	[BMIm]BF_4	92
2	CuBr	2	[BMIm]BF_4	84
3	CuI	2	[BMIm]BF_4	85
4	$CuCl_2$	2	[BMIm]BF_4	66
5[b]	−	0	[BMIm]BF_4	9
6	CuCl	2	[BPy]BF_4	59
7	CuCl	2	[BMIm]PF_6	67
8	CuCl	2	DMF	42
9[b]	CuCl	2	$ClCH_2CH_2Cl$	4
10[b]	CuCl	2	toluene	3
11[c]	CuCl	2	DMF	50

[a] Reaction conditions: ionic liquid, 3.0 mL, **2a**, 10 mmol; **1a**, 10 mmol; carbon dioxide, 2.5 MPa, temperature, 100 °C, reaction time, 10 h. [b] Reaction time is 20 h, and the result was recorded as GC yield. [c] 5.0 MPa CO_2 and 20 h, and the result was recorded as GC yield.

Proceeding along the same lines, we chose to evolve an efficient and ecofriendly process for the preparation of 5-methylene-1,3-oxazolidin-2-ones based on the propargylic alcohols/amines/CO_2 protocol using the "green" ionic liquids as reaction media as well as promoters. Herein we disclose the successful outcome of this endeavor in which propargylic alcohols, primary aliphatic amines, and CO_2 afforded excellent yields of the products in CuCl/[BMIm]BF_4 system. Scheme 1 shows the general reaction.

Results and Discussion

Initial experimentation was undertaken in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF_4) using 1-ethynyl-1-cyclohexanol (**1a**) and cyclohexylamine (**2a**) as substrates under 2.5 MPa of CO_2, the mixture being heated at 100 °C for 10 h (Table 1, entry 1). After a simple treatment as described in the Experimental Section, a white solid was obtained. The structure was confirmed as 4,4-pentamethylene-*N*-cyclohexyl-5-methylene-1,3-oxazolidin-2-one (**3a**) from the spectroscopic data and elemental analysis. The GC−MS analysis revealed that the peak at *m/z* 249 is the best choice for the molecular ion. This implies that the nitrogen number contained in this molecule should be odd. The base peak in the spectrum occurs at *m/z* = 168. It represents loss of *m/z*

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= 81 from the molecular ion, suggesting the presence of cyclohexyl group. The IR spectra exhibited a sharp band at 1711 cm^{-1} (C=O). The ^{1}H NMR spectra showed the absence of $-NH_2$ and $-OH$ proton and the presence of two protons at 3.95 and 4.21 (s, 1H, and s, 1H), indicating the presence of the methylene group. UV−vis spectra exhibited a sharp band at 223 nm. This observation implies that a conjugate action between C=O and the methylene group may occur in this molecule. The elemental analysis was also in conformity with the structure **3a**.

A preliminary screening of commercially available cuprous salts as promoters for the three-component reaction of **1a**, **2a**, and carbon dioxide in [BMIm]BF$_4$ is summarized in Table 1. As depicted, **3a** was formed in ca. 92% yield over CuCl/[BMIm]BF$_4$ after 10 h. In this reaction, the only identified byproduct is *N*-cyclohexylformamide (<1%, tested by GC−MS analysis). α-Methylene cyclic carbonate, which could be formed by addition reaction of carbon dioxide to propargylic alcohol,[18] was not detected in the present condition. CuBr and CuI also efficiently promoted the reaction as did CuCl (entries 1−3). CuCl$_2$ is also capable of catalyzing the synthesis of α-methylene oxazolidinone, but the efficiency seems to be slightly inferior as compared with that of CuCl (entry 4). In the absence of CuCl catalyst, the reaction seems to be sluggish, and only 9% yield of **3a** was obtained even after prolonged time (entry 5).

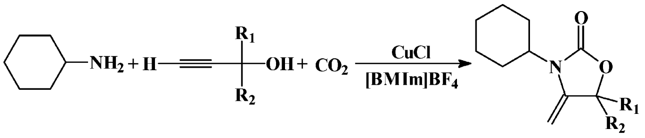
To determine whether [BMIm]BF$_4$ was an essential factor to realize the high yield of the present three-component reaction, the same reaction was carried out in other ionic or molecular solvents, and the results are presented in Table 1. [BMIm]BF$_4$ has proved to be an excellent medium for the synthesis of **3a**. Some other ionic liquids, such as 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm]PF$_6$) and *N*-butylpyridinium tetrafluoroborate ([BPy]BF$_4$), also worked well, but the yields of **3a** were slightly inferior (entries 6 and 7). It is quite noteworthy that the produced **3a** could be obtained as a white solid in the [BMIm]BF$_4$ system because all nongaseous substrates were completely consumed after 10 h reaction. In the case of DMF, a mixture of product, unreacted starting substrates, and solvent was obtained after reaction; therefore the separation of product has to be performed using column chromatography (entry 8). In toluene and 1,2-dichloroethane, the three-component reaction afforded no **3a** and the unreacted amine **1a** and propargylic alcohol **2a** were recovered, although the reaction time was prolonged to 20 h (entries 9 and 10). In contrast to organic solvents, enhanced reaction rates, improved yields, and mild conditions are the features obtained in ionic liquids. For example, the treatment of **1a** and **2a** with 2.5 MPa carbon dioxide in [BMIm]BF$_4$ ionic liquid for 10 h afforded the corresponding **3a** in 92% yield, whereas the same reaction in DMF after 20 h under 5.0 MPa of carbon dioxide gave the product in 50% GC yield (entry 11). It should be pointed out here that the yield obtained over CuCl/[BMIm]BF$_4$ system is much higher than those hitherto reported for **3a**.[12] The use of ionic liquids as reaction media for this transformation avoids the use of toxic reagents or high CO$_2$ pressure reaction conditions to affect the reaction. This clearly indicates the efficiency of ionic liquids for this transformation.

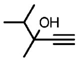
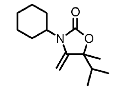
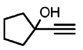
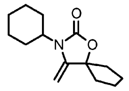
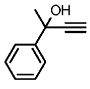
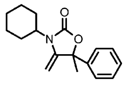
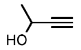
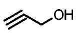
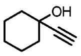
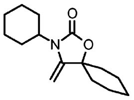
TABLE 2. Three-Component Reaction of 1a, 2a, and Carbon Dioxide in CuCl/[BMIm]BF$_4$ System[a]

entry	time (h)	temp (°C)	pressure(MPa)	yield (%)
1	10	100	2.5	92
2	10	80	2.5	24
3	6	100	2.5	26
4	10	100	1.5	9[b]

[a] Reaction conditions: ionic liquid, 3 mL, **1a**, 10 mmol; **2a**, 10 mmol; CuCl, 0.2 mmol. [b] Conversion of **2a**.

TABLE 3. Three-Component Reactions of Propargylic Alcohols, 1a, and Carbon Dioxide in CuCl/[BMIm]BF$_4$ System[a]



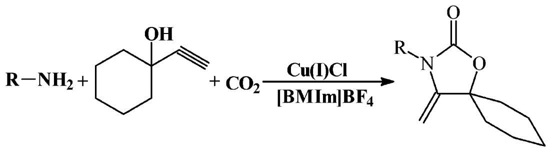
Entry	Alcohol	Time (h)	Product (*number*)		Yield (%)
1		15		**3*b***	84
2		12		**3*c***	87
3		15		**3*d***	95
4		15	No	—	0
5		15	No	—	0
6[b]		10		**3*a***	81

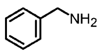
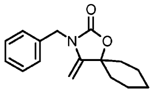
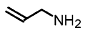
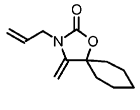
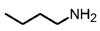
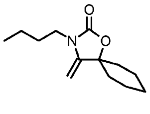
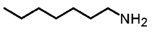
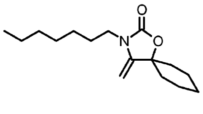
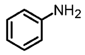
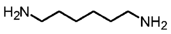
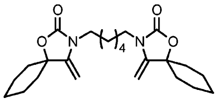
[a] Reaction conditions: ionic liquid, 3.0 mL; CuCl, 0.2 mmol; propargylic alcohol, 10 mmol; **1a**, 10 mmol; carbon dioxide, 2.5 MPa, temperature, 100 °C. [b] Reused in the fourth time.

We then focused our attention on investigating the optimization of reaction conditions in CuCl/[BMIm]BF$_4$ system, and the results are listed in Table 2. It was found that 2.5 MPa of carbon dioxide, 100 °C, and 10 h should be an optimum condition for the synthesis of **3a** (entry 1). Under lower temperature (80 °C) and shortened time (6 h), the substrate cannot be completely consumed, and thus the yields were decreased (entries 2 and 3). It should be noted that CO$_2$ pressure appeared to considerably affect the reaction. Low pressure (1.5 MPa) led to poor conversion level (entry 4). By contrast, the desired product **3a** could be obtained with good yield at 2.5 MPa. In addition to the high yield of product, our optimized conditions are milder and more attractive compared with that of literature,[12] in which 5.0 MPa, 110 °C, and 20 h were required to affect reaction.

To prove the general utility of the above protocol, a variety of propargylic alcohols were used to react with

TABLE 4. Three-Component Reactions of 2a, Amines, and Carbon Dioxide in CuCl/[BMIm]BF$_4$ System[a]



Entry	Amines	Products (*number*)		Yield (%)
1			*3e*	88
2			*3f*	78
3			*3g*	80
4			*3h*	89
5		——		0
6			*3i*	82

[a] Reaction conditions: ionic liquid, 3.0 mL; CuCl, 0.2 mmol; **2a**, 10 mmol; amine, 10 mmol; carbon dioxide, 2.5 MPa; temperature, 100 °C, reaction time, 10 h.

1a and CO_2 under conditions identical to those of **3a** over 10−15 h. As indicated in Table 3, various commercially available propargylic alcohols, including 3,4-dimethyl-1-pentyn-3-ol (**2b**), 1-ethynyl-1-cyclopentanol (**2c**), and 2-phenyl-3-butyn-2-ol (**2d**), have been successfully used. The corresponding 5-methylene-1,3-oxazolidin-2-one **3b**, **3c**, and **3d** could be obtained in 84−95% yields (entries 1−3). As to secondary and primary propargylic alcohols, even no desired products were detected which showed that such a reaction seems to be specific for tertiary alcohols (entries 4 and 5).

Variation of amines was also examined, and the results are listed in Table 4. In the presence of **2a**, the reactions of benzylamine (**1e**), allylamine (**1f**), *n*-butylamine (**1g**), and *n*-heptylamine (**1h**) were found to proceed smoothly with yields in the range of 78−89% (entries 1−4). As to aniline, only unreacted amine and **2a** were recovered (entry 5). An aliphatic diamine, hexamethylenediamine (**1i**), also underwent the three-component reaction to give the double nucleus compound **3i** in 82% isolated yield (entry 6).

In these synthetic reactions of 5-methylene-1,3-oxazolidin-2-ones, the products could be conveniently isolated by means of liquid−liquid extraction, thus allowing the recycling of both catalyst and ionic liquid. For the subsequent reaction, [BMIm]BF$_4$ as well as CuCl catalyst were reused intact simply after evacuation under reduced pressure to remove the resulting water in the previous run. In the reaction of **1a**, **2a**, and carbon dioxide, the [BMIm]BF$_4$/CuCl system can be reused up to four times, although with some loss of activity (Table 3, entry 6).

Conclusion

In summary, we have demonstrated that the three-component reactions between propargylic alcohols, aliphatic amines, and CO_2 can be successfully conducted in [BMIm]BF$_4$/CuCl system under relatively mild conditions. By this green approach, several new 5-methylene-1,3-oxazolidin-2-ones were prepared in excellent yields and purity and were well-characterized. The solvent ionic liquid as well as CuCl catalyst can be recovered and reused three times without appreciable loss of activity. Moreover, this methodology offers significant improvements with regard to yield of products, simplicity in operation, cost efficiency, and green aspects avoiding toxic or expensive reagents.

Experimental Section

Synthesis of 5-Methylene-1,3-oxazolidin-2-ones and Analysis. All reactions were conducted in a 100-mL autoclave with glass tube inside equipped with magnetic stirring. In each reaction, ionic liquid, 3 mL, propargylic alcohol (10 mmol), amine (10 mmol), catalyst (0.2 mmol), and CO_2 (1.5−2.5 MPa) were successively introduced and reacted at 100 °C for the desired period. After reaction, the reaction vessel was cooled to room temperature, and the resulting mixture was extracted with diethyl ether (4 mL × 3). To determine the substrate conversion, the combined organic phase was then analyzed with GC−MS (qualitative analysis) and GC equipped with a FID detector (quantitative analysis). Then, the combined organic phase was evaporated and dried in a vacuum to afford the primary product. A pure product was obtained by further recrystallization of the primary product with a solution containing water and ethanol.

Spectroscopic Data for Products. 4,4-Pentamethylene-*N*-cyclohexyl-5-methylene-1,3-oxazolidin-2-one (3a): White solid (yield: 92%, 2.29 g) mp 120−123 °C; δ_H (400; CCl_3D) 1.00−1.92 (20 H, m), 3.48 (1H, m), 3.93 (1H, d, J = 2.8 Hz), and 4.21 (1H, d, J = 2.8 Hz) ν/cm^{-1} 1711 (C=O); λ_{max}/nm 223, GC−MS: m/z = 249 (M$^+$), 168, 124, 112, 91, 79, 67, 55, 41; $C_{15}H_{23}NO_2$ (249.352) Calcd: C, 72.25; H, 9.30; N, 5.62. Found: C, 71.98; H, 9.55; N, 5.77.

4-Methyl-4-isopropyl-*N*-cyclohexyl-5-methylene-1,3-oxazolidin-2-one (3b): White solid (yield: 84%, 1.99 g) mp 99−101 °C; δ_H (400; CCl_3D) 0.89 (1H, d, J = 6.4), 0.96−1.17 (7H, m), 1.20−1.36 (4H, m), 1.44 (3H, s), 1.63−1.78 (3H, m), 1.79−1.86 (2H, m), 3.59 (1H, t, J = 12.0 Hz), 3.94 (1H, d, J = 2.8 Hz), and 4.25 (1H, d, J = 2.4 Hz) ν/cm^{-1} 1762 (C=O); λ_{max}/nm 224, GC−MS: m/z = 237 (M$^+$), 195, 194, 178, 156, 113, 112, 83, 67, 55, 41; $C_{14}H_{23}NO_2$ (237.341) Calcd: C, 70.85; H, 9.77; N, 5.90. Found: C, 70.64; H, 9.91; N, 5.99.

4,4-Tetramethylene-*N*-cyclohexyl-5-methylene-1,3-oxazolidin-2-one (3c): White solid (yield: 87%, 2.05 g) mp 73−75 °C; δ_H (400; CCl_3D) 1.00−2.07 (18 H, m), 3.59 (1H, m), 4.01 (1H, d, J = 2.8 Hz), and 4.22 (1H, d, J = 2.8 Hz) ν/cm^{-1} 1711 (C=O); λ_{max}/nm 224, GC−MS: m/z = 235 (M$^+$), 154, 112, 93, 77, 67, 55, 41; $C_{14}H_{21}NO_2$ (235.325) Calcd: C, 71.46; H, 8.99; N, 5.95. Found: C, 71.74; H, 9.23; N, 6.11.

4-Methyl-4-phenyl-*N*-cyclohexyl-5-methylene-1,3-oxazolidin-2-one (3d): White solid (yield: 95%, 2.57 g) mp 109−110 °C; δ_H (400; CCl_3D) 0.95−1.88 (13 H, m), 3.35 (1H, m), 4.11 (1H, s), 4.36 (1H, s), and 7.27−7.48 (4 H, m), ν/cm^{-1} 1709 (C=O); λ_{max}/nm 221 and 263, GC−MS: m/z = 271 (M$^+$), 190, 146, 130, 118, 103, 91, 77, 67, 55, 41; $C_{17}H_{21}NO_2$ (271.358) Calcd: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.39; H, 7.62; N, 5.27.

4,4-Pentamethylene-*N*-benzyl-5-methylene-1,3-oxazolidin-2-one (3e): White solid (yield: 88%, 2.26 g) mp 174−177 °C; δ_H (400; CCl_3D) 1.19−1.76 (9 H, m), 1.88 (1H, s), 3.93 (1H, d, $J = 2.4$, Hz), 4.11 (1H, d, $J = 2.8$, Hz), 4.65 (2 H, s), and 7.24−7.35 (5 H, m) ν/cm^{-1} 1708 (C═O); λ_{max}/nm 219 and 252, GC−MS: $m/z = 257$ (M^+), 215, 202, 170, 122, 91, 77, 65, 55, 41; $C_{16}H_{19}NO_2$ (257.332) Calcd: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.82; H, 7.25; N, 5.57.

4,4-Pentamethylene-*N*-allyl-5-methylene-1,3-oxazolidin-2-one (3f): White solid (yield: 78%, 1.61 g) mp 46−47 °C; δ_H (400; CCl_3D) 1.22−1.77 (10 H, m), 3.98 (1H, d, $J = 2.4$ Hz), 4.04 (2H, s), 4.07 (1H, d, $J = 1.6$ Hz), 5.13−5.27 (2 H, m), and 5.70−5.79 (1 H, m) ν/cm^{-1} 1768 (C═O); λ_{max}/nm 221, GC−MS: $m/z = 207$ (M^+), 162, 152, 134, 120, 106, 94, 81, 67, 55, 41; $C_{12}H_{17}NO_2$ (207.272) Calcd: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.81; H, 8.25; N, 6.69.

4,4-Pentamethylene-*N*-butyl-5-methylene-1,3-oxazolidin-2-one (3g): White solid (yield: 80%, 1.78 g) mp 61−63 °C; δ_H (400; CCl_3D) 0.944 (3H, m), 1.23−1.68 (14 H, m), 3.44 (2H, t, $J = 5.6$ Hz), 3.96 (1H, d, $J = 2.8$ Hz), and 4.00 (1H, d, $J = 3.2$ Hz) ν/cm^{-1} 1768 (C═O); λ_{max}/nm 221, GC−MS: $m/z = 223$ (M^+), 208, 181, 168, 137, 122, 112, 106, 94, 79, 67, 55, 41; $C_{13}H_{21}NO_2$ (223.314) Calcd: C, 69.92; H, 9.48; N, 6.27. Found: C, 69.80; H, 9.59; N, 6.50.

4,4-Pentamethylene-*N*-heptyl-5-methylene-1,3-oxazolidin-2-one (3h): White solid (yield: 89%, 2.36 g) mp 41−43 °C; δ_H (400; CCl_3D) 0.88 (3H, t, $J = 6.8$ Hz), 1.27−1.87 (20 H, m), 3.43 (2H, t, $J = 7.4$ Hz), 3.96 (1H, d, $J = 2.4$ Hz), and 4.07 (1H, d, $J = 2.8$ Hz) ν/cm^{-1} 1766 (C═O); λ_{max}/nm 225, GC−MS: $m/z = 265$ (M^+), 210, 192, 181, 168, 151, 136, 122, 79, 67, 55, 41; $C_{16}H_{27}NO_2$ (265.395) Calcd: C, 72.41; H, 10.25; N, 5.28. Found: C, 72.59; H, 10.01; N, 5.14.

***N,N′*-Hexamethylene-bis(4,4-pentamethylene-5-methylene-1,3-oxazolidin-2-one) (3i):** White solid (yield: 82%, 3.41 g) mp 139−140 °C; δ_H (400; CCl_3D) 1.25−1.87 (28 H, m), 3.43 (4H, t, $J = 7.2$ Hz), 3.96 (2H, d, $J = 2.8$ Hz), and 4.06 (2H, d, $J = 2.8$ Hz) ν/cm^{-1} 1755 (C═O); λ_{max}/nm 227, MS: $m/z = 416$ (M^+), 375, 331, 250, 236, 206, 192, 181, 159, 150, 136, 122, 108, 94, 79, 67, 55, 41; $C_{24}H_{36}N_2O_4$ (416.560) Calcd: C, 69.20; H, 8.71; N, 6.72. Found: C, 69.47; H, 8.62; N, 6.53.

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Supporting Information Available: General experimental methods, ^{1}H NMR, UV−vis, MS, and IR spectra of compounds **a**−**i** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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