An Efficient and Eco-friendly Process for the Conversion of Carbon Dioxide into Oxazolones and Oxazolidinones under Supercritical Conditions

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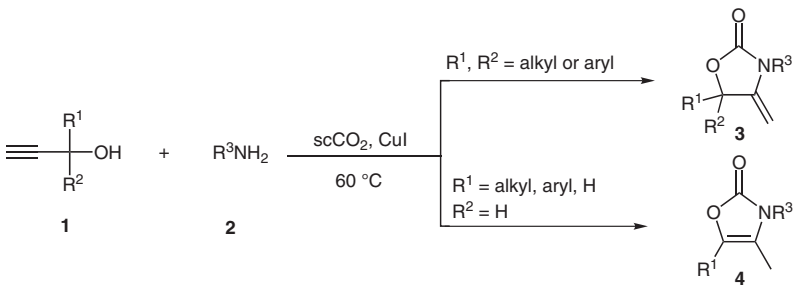
Abstract: The cycloaddition reactions of carbon dioxide with propargylic alcohols and amines under supercritical conditions produce 4-methyleneoxazolidin-2-ones or 4-methyloxazol-2-ones. The optimized conditions consist of the use of an alcohol (2 mmol), an amine (2 mmol), copper(I) iodide (0.1 mmol), carbon dioxide (8 MPa), and a temperature of 60 °C. The regiochemical control is dependent on the substituents of the propargylic alcohols. Tertiary propargylic alcohols give 4-methyleneoxazolidin-2-ones, while primary and secondary ones generate 4-methyloxazol-2-ones. The effects of various parameters such as temperature, pressure, and time have also been investigated.

Key words: propargylic alcohols, cycloadditions, heterocycles, oxazolones and oxazolidinones, supercritical carbon dioxide

Chemical fixation of carbon dioxide into valuable organic molecules has been an essential subject in synthetic organic chemistry during the last two decades, owing to its economic and environmental benefits and the growing concern about the greenhouse effect.[1] Carbon dioxide is an abundant, cheap, and nontoxic biorenewable C1 building block in organic synthesis; however, due to its inert nature, efficient and eco-friendly processes for chemical fixation remain a significant challenge. Recently, we have developed highly efficient carbon dioxide–epoxide cycloadditions catalyzed by natural α-amino acids or polymer-supported phenol/4-(*N*,*N*-dimethylamino)pyridine or zinc maleate/1,8-diazabicyclo[5.4.0]undec-7-ene.[2] The thus obtained five-membered cyclic carbonates have been proved to be valuable as aprotic polar solvents, pharmaceutical and fine chemical intermediates, and sources for polymer and engineering plastic syntheses.[3] Besides epoxides, aziridines, amino alcohols, propargylic alcohols, and amines have also appeared to be useful substrates for cycloaddition reactions with carbon dioxide, and they afford oxazolidinones, another group of valuable heterocyclic compounds.[4,5]

Oxazolidinones have been used not only as multipurpose chiral synthons in asymmetric syntheses of biologically active compounds or their synthetic intermediates,[6] but also as chiral auxiliaries in many asymmetric transformations such as alkylation, acylation and Diels–Alder reactions, and aldolic condensations.[7] Furthermore, some suitably substituted oxazolidinones are also being used as antibacterial drugs in pharmaceutical chemistry.[6a,8] However, various approaches to oxazolidinones by cycloaddition reactions of carbon dioxide with the above substrates have suffered from drawbacks such as the need for toxic and noble-metal catalysts,[4a,5c] the involvement of volatile organic chemicals (VOCs),[4a,5c] and harsh reaction conditions.[4b,c,5a,b]

Supercritical carbon dioxide ($scCO_2$, T_c = 31.0 °C, P_c = 73.75 bar) has been established as an environmentally benign alternative to organic solvents because of its advantages in terms of nonflammability, easy separation from reaction mixtures, as well as eco-compatibility, low cost, and availability.[9] More importantly, it is quite significant that carbon dioxide could be used both as an attractive raw material and as a green reaction medium.[10] Herein, we wish to report an efficient and eco-friendly process for conversion of carbon dioxide into 4-methyleneoxazolidin-2-ones **3** and 4-methyloxazol-2-ones **4** (Scheme 1), in which carbon dioxide is employed not only as solvent but also as starting material.



Scheme 1 Cycloaddition reaction of propargylic alcohols with amines in $scCO_2$

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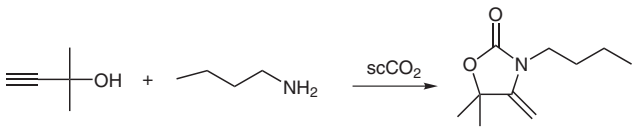
Table 1 Optimizing the Reaction Conditions for the Cycloaddition of Propargylic Alcohols with Amines in $scCO_2$[a]



1a 2a 3a

Entry	Temp (°C)	Pressure (MPa)	Time (h)	Catalyst	Yield[b] (%)
1	80	12	24	CuI	89
2	60	12	24	CuI	89
3	40	12	24	CuI	68
4	60	10	24	CuI	89
5	60	8	24	CuI	89
6	60	6	24	CuI	32
7	60	8	12	CuI	55
8	60	8	24	CuBr	84
9	60	8	24	CuCl	73

[a] Reagents and conditions: **1a** (2 mmol), **2a** (2 mmol), cat. (0.1 mmol).
[b] Determined by GC analysis.

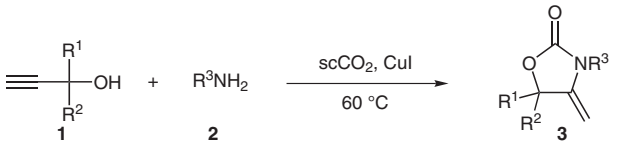
2-Methylbut-3-yn-2-ol (**1a**) and *n*-butylamine (**2a**) were chosen as model substrates for the cycloaddition reaction with supercritical carbon dioxide, and to optimize reaction conditions (Table 1). Our investigation showed that the optimal temperature is 60 °C: when the total pressure was kept at 12 MPa, the yields were 89%, 89%, and 68%, respectively, as the temperature was decreased from 80 °C, to 60 °C, and then to 40 °C (Table 1, entries 1–3). Preliminary results indicated that a higher carbon dioxide pressure could shift the reaction favorably to the desired product, but 8 MPa of carbon dioxide pressure is enough for the cycloaddition reaction at the optimal temperature (Table 1, entries 2, 4–6). When the reaction time was shortened to 12 hours, the alcohol could not be converted completely and the yield was only 55% (Table 1, entry 7). The catalytic activity of several copper(I) halides in the reaction was evaluated, and copper(I) iodide was found to be better than copper(I) bromide and copper(I) chloride (Table 1, entries 5, 8, 9). Therefore, the optimum reaction conditions consisted of the following: 2-methylbut-3-yn-2-ol (**1a**; 2 mmol), *n*-butylamine (**2a**; 2 mmol), copper(I) iodide (0.1 mmol) as catalyst, a temperature of 60 °C, a pressure of 8 MPa, and a reaction time of 24 hours.

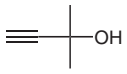
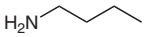
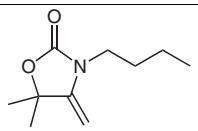
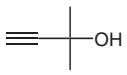
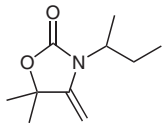
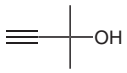
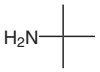
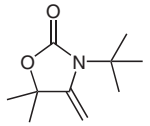
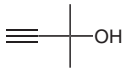
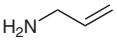
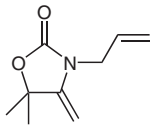
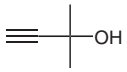
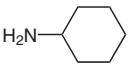
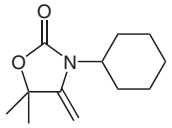
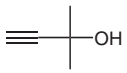
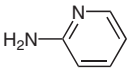
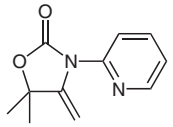
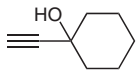
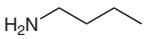
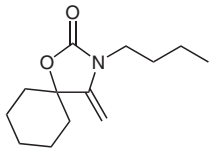
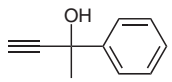
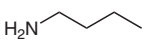
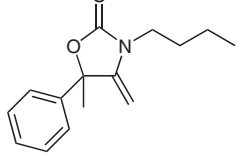
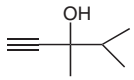
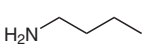
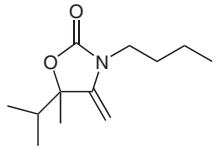
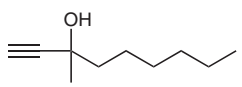
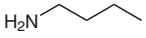
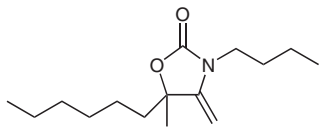
With the optimum conditions determined, we extended the process to a variety of propargylic alcohols and primary amines in $scCO_2$. We were pleased to find that $scCO_2$ could successfully substitute for VOCs or room-temperature ionic liquids (RTILs) in the cycloaddition. The results are summarized in Table 2. Under the given reaction conditions, the reaction between 2-methylbut-3-yn-2-ol (**1a**) and various primary amines **2a–f** took place in $scCO_2$, and satisfactory isolated yields were generally obtained (Table 2, entries 1–6). As the results showed, the steric hindrance of the substituents on the primary amines could affect the cycloaddition significantly (Table 2, entries 1–3). Thus, when *n*-, *sec*-, and *tert*-butylamine (**2a–c**) were employed, *n*-butylamine (**2a**) yielded the best result (85% isolated yield; Table 2, entry 1), but no desired product was detected when *tert*-butylamine (**2b**) was used (entry 3). It is not difficult to understand that allylamine (**2d**) and cyclohexylamine (**2e**) undergo cycloaddition efficiently, giving products **3d** and **3e**, respectively, in excellent yields (Table 2, entries 4 and 5). We also found that electronic effects could affect the reaction remarkably. Aromatic primary amines, such as 2-pyridylamine (**2f**), did not react at all under the given conditions (Table 2, entry 6). Presumably, aromatic amines possess poor nucleophilicity because of weaker basicity. A variety of other propargylic alcohols were then screened with *n*-butylamine (**2a**) for the fixation of carbon dioxide (Table 2, entries 7–10). The reactions with 1-ethynylcyclohexanol (**1b**) and 2-phenylbut-3-yn-2-ol (**1c**) proceeded effectively, with **3g** and **3h** obtained in yields of 91% and 95%, respectively (Table 2, entries 7 and 8). 3,4-Dimethylpent-1-yn-3-ol (**1d**) and 3-methylnon-1-yn-3-ol (**1e**) gave the corresponding products **3i** and **3j** in yields of 77% and 70%, respectively (Table 2, entries 9 and 10).

Unexpectedly and interestingly, propargylic alcohols **1f–j** with α-hydrogens could react with primary amines **2** and carbon dioxide smoothly under the given reaction conditions (Table 3). This was quite different from the reported processes in which only tertiary propargylic alcohols could react with primary amines and carbon dioxide.[4] It is noteworthy that the obtained products are 4-methyloxazol-2-ones, the isomers of 4-methyleneoxazolidin-2-ones, which could be used in natural product synthesis and pharmaceutical chemistry.[11] Secondary propargylic alcohols **1f–j** reacted with *n*-butylamine (**2a**) and carbon dioxide to give the corresponding 4-methyloxazol-2-ones **4a–e** in satisfactory isolated yields (88–96%, Table 3, entries 1–4). Propargyl alcohol (**1j**) also underwent the reaction, giving **4e** in excellent yield (Table 3, entry 5). We suggest that $scCO_2$ as reaction medium might play an important role in the cycloaddition reaction of propargylic alcohols with α-hydrogens, primary amines, and carbon dioxide.

Based on the above experimental results and the literature,[12] a proposed mechanism is illustrated in Scheme 2. Several investigations have shown that propargyl alcohols can react with carbon dioxide to form α-alkylidene cyclic carbonates in the presence of base.[13] On the other hand, the reaction of α-alkylidene cyclic carbonates with amines to form oxazolidones has also been reported.[14] The reaction reported herein is a tandem process of the two reactions. The metal along with the base, the free amine, formed by the equilibrium between the amine and carbamic acid in $scCO_2$,[15] catalyze the conversion of propargyl alcohols and carbon dioxide into α-alkylidene cyclic carbonates **III** (Scheme 2). Immediate subsequent reac-

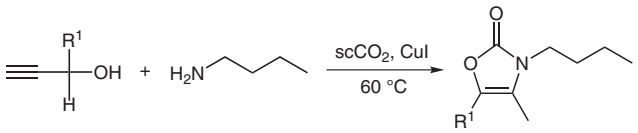
Table 2 Synthesis of 4-Methyleneoxazolidin-2-ones **3** from the Corresponding Propargylic Alcohols **1** and Primary Amines **2** in $scCO_2$[a]



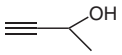
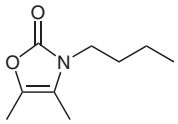
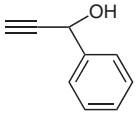
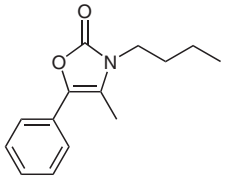
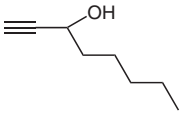
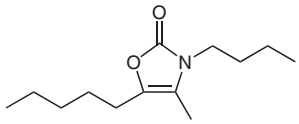
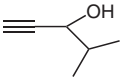
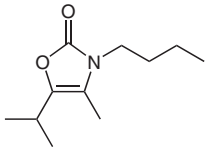
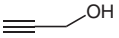
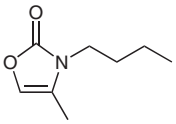
Entry	Alcohol	Amine	Product	Yield[b] (%)
1	**1a** 	**2a** 	**3a** 	85
2	**1a** 	**2b** 	**3b** 	75
3	**1a** 	**2c** 	**3c** 	0[c]
4	**1a** 	**2d** 	**3d** 	81
5	**1a** 	**2e** 	**3e** 	93
6	**1a** 	**2f** 	**3f** 	0[d]
7	**1b** 	**2a** 	**3g** 	91
8	**1c** 	**2a** 	**3h** 	95
9	**1d** 	**2a** 	**3i** 	77
10	**1e** 	**2a** 	**3j** 	70

[a] Reagents and conditions: alcohol **1** (2 mmol), amine **2** (2 mmol), CuI (0.1 mmol), Pco_2 = 8 MPa, 60 °C.
[b] Isolated yield.
[c] No desired product detected.
[d] 2-Methylbut-3-yn-2-ol (**1a**) remained unchanged.

Table 3 Synthesis of 5-Substituted 4-Methyloxazol-2-ones **4** from α-Hydrogen-Containing Propargylic Alcohols **1** and *n*-Butylamine (**2a**) in $scCO_2$[a]



1 **2a** **4**

Entry	Alcohol		Product		Yield[b] (%)
1	**1f**		**4a**		96
2	**1g**		**4b**		94
3	**1h**		**4c**		88
4	**1i**		**4d**		90
5	**1j**		**4e**		91

[a] Reagents and conditions: alcohol **1** (2 mmol), amine **2** (2 mmol), CuI (0.1 mmol), Pco_2 = 8 MPa, 60 °C.
[b] Isolated yield.

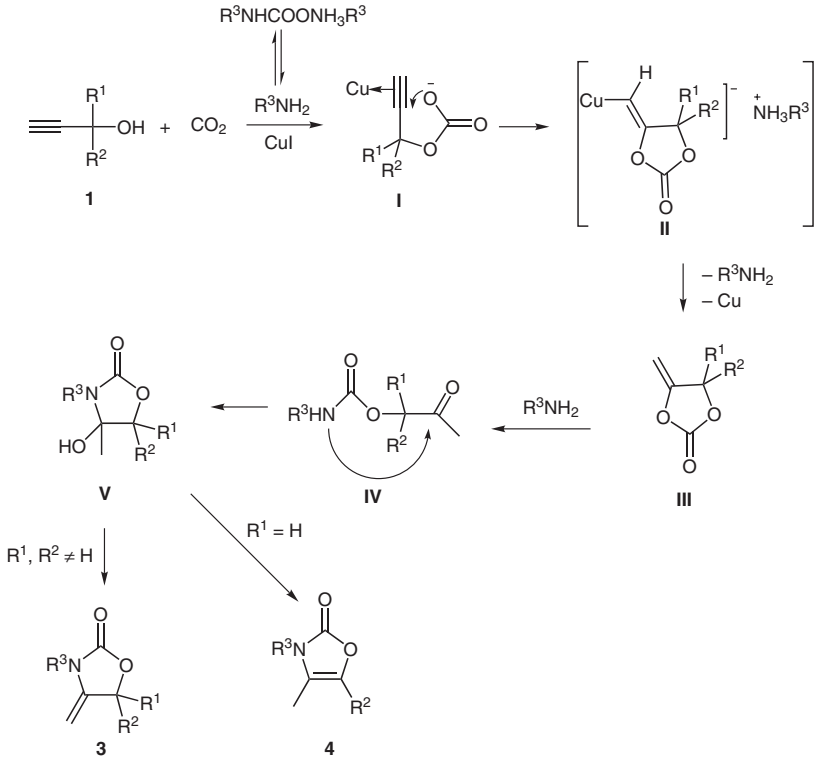
tion of **III** with the free amine affords the 2-oxoalkyl carbamate **IV** (Scheme 2). 4-Hydroxy cyclic carbamate **V** is the key intermediate formed by intramolecular cyclization (Scheme 2). The regioselectivity derives from alternative elimination via **V**: the 4-hydroxy group is eliminated together with 5-H to form conjugated oxazolones **4** if there is a hydrogen atom in the 5-position; if not, 4-hydroxy is eliminated with the hydrogen atom of 4-methyl to afford the oxazolidinones **3** (Scheme 2). When tertiary and secondary amines, instead of primary amines, react with propargyl alcohols in $scCO_2$, **III** and **IV** are obtained, respectively.

We have developed an efficient and eco-friendly process to synthesize 4-methyleneoxazolidin-2-ones and 4-methyloxazol-2-ones from propargylic alcohols and primary amines in supercritical carbon dioxide. In this method for chemical carbon dioxide fixation, carbon dioxide was employed not only as reaction medium, but also as starting material. Especially primary and secondary propargylic alcohols react smoothly with primary amines to form 4-methyloxazol-2-ones. Further efficient chemical transformations of carbon dioxide into valuable fine chemicals are investigated in our laboratory.

^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer; $CDCl_3$ was used as solvent and TMS as an internal standard. GC analyses were performed on a GC-930 chromatograph (Shanghai Haixian Chromatograph Instrument Ltd. Co.) with an FID and equipped with an OV-101 capillary column (internal diameter = 0.25 mm, length = 30 m). Mass spectra were recorded on a Shimadzu GCMS–QP5050A mass spectrometer at an ionization voltage of 70 eV and equipped with a DB-WAX capillary column (internal diameter = 0.25 mm, length = 30 m). IR spectra were recorded on an Analect RFX–65A spectrometer. All starting materials and catalysts were commercially purchased and used without further purification.

Oxazolidinones 3 and Oxazolones 4; General Procedure

A 15 mL polytetrafluoroethylene (PTFE) reaction vessel was charged with catalyst (0.1 mmol), propargylic alcohol **1** (2 mmol) and amine **2** (2 mmol). The vessel was fixed into a stainless steel autoclave with a pressure-regulating system. The autoclave was sealed. Liquid CO_2 was introduced from a cylinder and the reaction was carried out at the selected temperature under magnetic stirring for the required reaction time. When the reaction was complete, the



Scheme 2 Proposed mechanism for the cycloaddition of propargylic alcohols with amines in $scCO_2$

vessel was cooled with an ice bath and the pressure was released slowly to atmospheric pressure. The residual material was flushed with Et_2O (3 × 10 mL). The products were purified by column chromatography (silica gel, PE–EtOAc, 6:1) and identified by ^1H and ^{13}C NMR and MS.

3-Butyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (3a)[4c]
Orange oil.

IR (KBr): 2981, 2874, 1731, 1680 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.4 Hz, 3 H), 1.29–1.40 (m, 2 H), 1.40–1.64 (m, 8 H), 3.42 (t, *J* = 7.4 Hz, 2 H), 3.95 (d, *J* = 2.8 Hz, 1 H), 4.05 (d, *J* = 2.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 19.9, 27.9, 28.3, 41.1, 79.0, 81.9, 151.0, 155.7.

MS (EI, 70 eV): *m*/*z* (%) = 183 [M^+] (34), 141 (27), 128 (43), 96 (31), 84 (18), 43 (10), 32 (24), 28 (100).

3-*sec*-Butyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (3b)
Orange oil.

IR (KBr): 2977, 2878, 1765, 1673 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.84–0.88 (m, 3 H), 1.33–1.39 (m, 3 H), 1.45 (s, 6 H), 1.60–1.64 (m, 2 H), 3.78–3.84 (m, 1 H), 3.94 (d, *J* = 2.8 Hz, 1 H), 4.15 (d, *J* = 2.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.1, 16.9, 25.6, 28.1, 51.5, 79.9, 81.2, 150.6, 155.2.

MS (EI, 70 eV): *m*/*z* (%) = 183 [M^+] (18), 128 (100), 110 (22), 84 (48), 41 (13).

Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.45; H, 9.39; N, 7.57.

3-Allyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (3d)[4a,b]
Orange oil.

IR (KBr): 2985, 2938, 1732, 1647 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.50 (s, 6 H), 3.97 (d, *J* = 2.8 Hz, 1 H), 4.04–4.06 (m, 3 H), 5.10–5.22 (m, 2 H), 5.68–5.89 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 43.7, 80.1, 90.5, 117.5, 134.4, 150.4, 157.3.

MS (EI, 70 eV): *m*/*z* (%) = 167 [M^+] (90), 122 (100), 108 (96), 82 (50), 55 (57), 41 (48), 28 (68).

3-Cyclohexyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (3e)[4b]
White solid; mp 54–56 °C.

IR (KBr): 2929, 2855, 1731, 1681 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.08–1.17 (m, 1 H), 1.26–1.35 (m, 2 H), 1.43 (s, 6 H), 1.65 (d, *J* = 9.4 Hz, 3 H), 1.80 (d, *J* = 10.4 Hz, 2 H), 2.02–2.05 (m, 2 H), 3.52 (m, 1 H), 3.94 (d, *J* = 2.8 Hz, 1 H), 4.16 (d, *J* = 2.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.2, 25.9, 28.0, 28.3, 53.7, 79.8, 81.2, 150.7, 155.0.

MS (EI, 70 eV): *m*/*z* (%) = 209 [M^+] (23), 128 (100), 112 (15), 84 (45), 55 (17), 41 (15).

3-*n*-Butyl-5,5-pentamethylene-4-methyleneoxazolidin-2-one (3g)
White solid; mp 60–62 °C.

IR (KBr): 2935, 2864, 1729, 1671 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.4 Hz, 3 H), 1.23–1.84 (m, 14 H), 3.41 (t, *J* = 7.2 Hz, 2 H), 3.92 (d, *J* = 2.4 Hz, 1 H), 4.00 (d, *J* = 2.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ =13.7, 19.9, 21.7, 29.6, 36.9, 79.3, 83.6, 150.9, 155.9.

MS (EI, 70 eV): *m*/*z* (%) = 223 [M^+] (38), 181 (58), 168 (100), 122 (25), 112 (38), 55 (11), 41 (13).

3-Butyl-5-methyl-4-methylene-5-phenyloxazolidin-2-one (3h)
Orange-red oil.

IR (KBr): 2933, 2867, 1760 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.88–0.93 (m, 3 H), 1.29–1.34 (m, 2 H), 1.55–1.60 (m, 2 H), 1.85 (s, 3 H), 3.42–3.51 (m, 2 H), 4.08 (d, *J* = 2.8 Hz, 1 H), 4.21 (d, *J* = 3.2 Hz, 1 H), 7.31–7.45 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 20.1, 27.5, 28.3, 41.3, 82.0, 91.4, 124.8, 127.8, 128.6, 141.2, 149.7, 155.6.

MS (EI, 70 eV): *m*/*z* (%) = 245 [M^+] (20), 190 (22), 158 (100), 144 (100), 129 (32), 97 (65), 77 (23), 41 (8).

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.19; H, 8.01; N, 5.46.

3-Butyl-5-isopropyl-5-methyl-4-methyleneoxazolidin-2-one (3i)
Orange-red oil.

IR (KBr): 2968, 2876, 1775, 1673 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.87–0.99 (m, 9 H), 1.30–1.36 (m, 2 H), 1.43 (s, 3 H), 1.53–1.57 (m, 2 H), 1.80–1.82 (m, 1 H), 3.31–3.38 (m, 1 H), 3.43–3.57 (m, 1 H), 3.91 (d, *J* = 2.8 Hz, 1 H), 4.08 (d, *J* = 2.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 16.1, 20.0, 24.9, 28.3, 41.1, 79.5, 86.6, 149.4, 156.2.

MS (EI, 70 eV): *m*/*z* (%) = 211 [M^+] (32), 169 (90), 126 (29), 112 (100), 84 (10), 55 (14), 41 (22).

Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63. Found: C, 67.89; H, 10.09; N, 6.30.

3-Butyl-5-hexyl-5-methyl-4-methyleneoxazolidin-2-one (3j)
Dark-red oil.

IR (KBr): 2929, 2863, 1675 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 6.8 Hz, 3 H), 0.92 (t, *J* = 7.2 Hz, 3 H), 1.23–1.34 (m, 10 H), 1.44–1.64 (m, 5 H), 3.41 (m, 2 H), 3.90 (d, *J* = 2.8 Hz, 1 H), 4.07 (d, *J* = 2.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 14.0, 20.0, 22.5, 22.8, 26.9, 28.3, 29.1, 31.6, 40.8, 79.1, 84.4, 149.8, 156.0.

MS (EI, 70 eV): *m*/*z* (%) = 253 [M^+] (5), 169 (100), 126 (25), 113 (30), 98 (38), 55 (10), 41 (12).

Anal. Calcd for $C_{15}H_{27}NO_2$: C, 71.10; H, 10.74; N, 5.53. Found: C, 70.83; H, 10.62; N, 5.37.

3-Butyl-4,5-dimethyloxazol-2 (3*H*)-one (4a)
Orange oil.

IR (KBr): 2954, 2872, 1756, 1706 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.4 Hz, 3 H), 1.28–1.35 (m, 2 H), 1.53–1.59 (m, 2 H), 1.91 (s, 3 H), 1.99 (s, 3 H), 3.46 (t, *J* = 3.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.8, 9.7, 13.5, 19.7, 31.2, 41.4, 117.0, 131.1, 155.6.

MS (EI, 70 eV): *m*/*z* (%) = 169 [M^+] (90), 126 (29), 113 (100), 98 (42), 57 (12), 42 (36).

Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.93; N, 8.28. Found: C, 63.49; H, 9.06; N, 8.05.

3-Butyl-4-methyl-5-phenyloxazol-2 (3*H*)-one (4b)
Orange-red oil.

IR (KBr): 2957, 2870, 1760, 1667 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.93–0.97 (m, 3 H), 1.36–1.41 (m, 2 H), 1.61–1.67 (m, 2 H), 2.27 (s, 3 H), 3.59 (t, *J* = 7.4 Hz, 2 H), 7.35–7.47 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.4, 13.6, 19.9, 31.3, 41.6, 118.7, 124.9, 127.4, 128.7, 134.1, 155.0.

MS (EI, 70 eV): *m*/*z* (%) = 231 [M^+] (100), 175 (88), 105 (25), 77 (13), 42 (11), 28 (28).

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.57; H, 7.34; N, 6.04.

3-Butyl-4-methyl-5-pentyloxazol-2 (3*H*)-one (4c)
Orange-red oil.

IR (KBr): 2955, 2866, 1756, 1685 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.84–0.93 (m, 6 H), 1.22–1.33 (m, 6 H), 1.49–1.58 (m, 4 H), 1.92 (s, 3 H), 2.30 (t, *J* = 7.2 Hz, 2 H), 3.45 (t, *J* = 7.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.9, 13.6, 13.9, 19.8, 22.3, 24.3, 27.2, 31.0, 31.3, 41.5, 117.0, 135.3, 155.8.

MS (EI, 70 eV): *m*/*z* (%) = 225 [M^+] (40), 168 (100), 112 (90), 41 (11).

Anal. Calcd for $C_{13}H_{23}NO_2$: C, 69.29; H, 10.29; N, 6.22. Found: C, 69.09; H, 10.14; N, 6.22.

3-Butyl-5-isopropyl-4-methyloxazol-2 (3*H*)-one (4d)
Orange-red oil.

IR (KBr): 2966, 2873, 1754, 1698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.4 Hz, 3 H), 1.12 (t, *J* = 9.4 Hz, 6 H), 1.30–1.35 (m, 2 H), 1.54–1.66 (m, 2 H), 2.71–2.75 (m, 1 H), 3.45 (t, *J* = 7.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.8, 13.6, 19.9, 20.8, 24.9, 31.3, 41.4, 115.1, 139.5, 155.7.

MS (EI, 70 eV): *m*/*z* (%) = 197 [M^+] (41), 182 (89), 141 (11), 126 (100), 44 (6), 42 (13).

Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 66.71; H, 9.74; N, 7.15.

3-Butyl-4-methyloxazol-2 (3*H*)-one (4e)
Orange oil.

IR (KBr): 2958, 2971, 1749, 1662 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.91 (q, *J* = 4.9 Hz, 3 H), 1.30–1.36 (m, 2 H), 1.55–1.72 (m, 2 H), 1.99 (s, 3 H), 3.49 (t, *J* = 7.4 Hz, 2 H), 6.52 (q, *J* = 1.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.7, 13.6, 19.8, 31.2, 41.4, 123.1, 123.9, 156.2.

MS (EI, 70 eV): *m*/*z* (%) = 155 [M^+] (76), 126 (25), 99 (100), 85 (20), 42 (39).

Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.88; H, 8.53; N, 8.98.

Acknowledgments

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