Catalyst-Free Process for the Synthesis of 5-Aryl-2-Oxazolidinones via Cycloaddition Reaction of Aziridines and Carbon Dioxide

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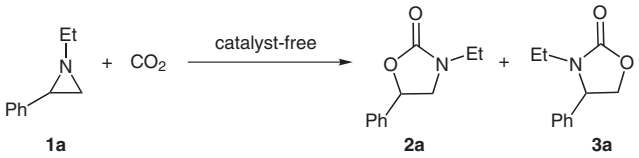
Abstract: A simple approach for facile synthesis of 5-aryl-2-oxazolidinones in excellent regioselectivity from aziridines under compressed CO_2 conditions was developed in the absence of any catalyst and organic solvent. The reaction outcome was found to be tuned by subtly adjusting CO_2 pressure. The adduct formed in situ of aziridine and CO_2 is assumed to act as a catalyst in this reaction, which was also studied by means of in situ FT-IR technique.

Key words: carbon dioxide, aziridine, catalyst-free, 5-aryl-2-oxazolidinones

Oxazolidinones are important five-membered heterocyclic compounds in organic chemistry and medicinal chemistry, which have been widely used as chiral auxiliaries, intermediates in organic synthesis, and building blocks for biologically active pharmaceutical agents.[1] With the awareness of environment pollution and sustainable development, great efforts have been devoted to synthesizing 2-oxazolidinones using CO_2 as a raw material in recent years, as a alternative to toxic, corrosive phosgene and carbon monoxide route.[2] Currently, there are mainly four accesses to 2-oxazolidinones starting from CO_2: (1) cycloaddition of aziridines with CO_2;[3] (2) carboxylative cyclization of propargylamines with CO_2;[4] (3) reaction of propargylic alcohols, primary amines, and CO_2;[5] and (4) cyclocondensation of 1,2-amino alcohols with CO_2.[6] Recently, Li and co-workers demonstrated that oxazolidinones can be synthesized through the copper-catalyzed coupling of aldehydes, amines, terminal alkynes, and CO_2.[7] As a nitrogen analogue of epoxides, aziridines have high ring strain and could readily react with CO_2 to afford 2-oxazolidinones. A variety of homogeneous catalysts including (salen)-Cr(III)/DMAP,[3a] phenol/DMAP,[3b] alkali metal halide,[3c–f] tetraalkylammonium halide system,[3f] iodine,[3g,h] have been developed for the carboxylation of aziridines. And electrochemical procedure is an alternative for this transformation.[3i] However, hazardous organic solvents, catalysts, and/or co-catalysts are generally required to achieve high catalytic efficiency.

In this context, Kayaki's group made a significant advance and found copolymerization of secondary aliphatic aziridines and CO_2 under supercritical conditions to give poly(urethane amine)s as main products.[8] We also developed a quaternary ammonium salt functionalized PEG[3j] and zirconyl chloride[3k] as effective, recyclable catalysts for this reaction to selectively synthesize 5-aryl-2-oxazolidinones without any organic solvent and additional additive. Furthermore, product separation from catalyst and catalyst recycling is also an important issue to be addressed. Thanks to unique features such as low cost, availability, tunable solvent properties, and easy separation, supercritical carbon dioxide has been widely used as environmentally benign reaction medium and clean extractant. Moreover, it is worthy to be pointed out that properties of CO_2 could be easily tunable by means of pressure or temperature.[9] Herein, we would like to introduce a simple and straightforward approach for selective synthesis of 5-aryl-2-oxazolidinones **2** via carboxylation of aziridines **1** with CO_2 by elaborately tuning pressure of CO_2 or reaction temperature in the absence of any catalyst (Scheme 1).



Scheme 1 Carboxylation of aziridine with CO_2 without any catalyst

We firstly examined the reaction of 1-ethyl-2-phenylaziridine (**1a**) and CO_2 at 100 °C and 8.0 MPa. As shown in Table 1, a low yield (29%) of 3-ethyl-5-phenyl-2-oxoazolidinone (**2a**) was obtained after 10 hours (Table 1, entry 1). When the temperature rose up to 120 °C, the yield of **2a** was increased to 63% (entry 2), but further rising temperature did not give markedly improvement in **2a** yield (entry 3). On the other hand, CO_2 pressure would be another important factor for this reaction. Indeed, **2a** yield increased as CO_2 pressure rising from 3.5 to 9 MPa (entries 4, 7–9), and reached the maximum value of 68% at 9 MPa. A further increase in CO_2 pressure resulted in a drop in the yield (entry 9). This is reasonable because near-critical CO_2 conditions may facilitate the formation of the zwitterionic adduct of **1** with CO_2,[4f] thereby leading to improvement of the reaction, whereas higher pressure may suppress the interaction between the aziridine and CO_2 because of CO_2 diluting effect, thus resulting in a lower activity.[10] A prolonged reaction time gave full conversion with excellent **2a** yield as high as 89% (entry 10). The only byproducts were found to be slightly amounts of 1,4-diethyl-2,5-diphenylpiperazine and 1,4-diethyl-2,3-diphenylpiperazine, that is, dimers of **2a**. In addition,

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Table 1 Carboxylation of 1-Ethyl-2-phenylaziridine (**1a**) with CO_2 in the Absence of Catalyst[a]

Entry	Temp (°C)	Time (h)	Pressure (Mpa)	Conv. (%)[b]	Yield of **2a** (%)[b]	Regioselectivity **2a/3a** (%)[b]
1	100	10	8.0	48	29	96:4
2	120	10	8.0	73	63	95:5
3	140	10	8.0	77	67	95:5
4	120	10	3.5	37	27	95:5
5[c]	120	10	3.5	75	69	98:2
6[d]	120	10	3.5	70	53	97:3
7	120	10	5.5	70	52	97:3
8	120	10	9.0	76	68	95:5
9	120	10	10.0	68	54	95:5
10	120	24	9.0	>99	89	95:5

[a] All the reactions were run with **1a** (147 mg, 1 mmol).
[b] Determined by GC using biphenyl as an internal standard.
[c] Triethylamine (14 mol%) was added.
[d] Diethylamine (14 mol%) was added.

diethylamine and triethylamine can promote the reaction (entries 5, 6 vs. 4).

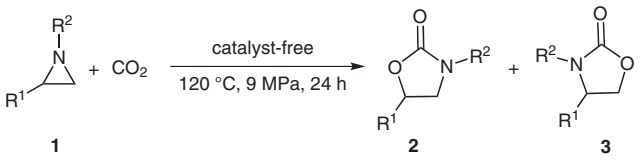
To examine the generality of this approach, we conducted the reaction under the identical reaction conditions, and the results are summarized in Table 2.[11,12]

It is found that the aziridines bearing different alkyl groups at the nitrogen atom (Table 2, entries 1–7) showed good performance, while **1b** and **1c** displayed a relatively low activity being ascribed to formation of oligomers[3j,8a,b,13] which were detected by ESI-MS. Owing to steric hindrance, the substrates with branched alkyl groups at the nitrogen atom exhibited lower performance (entry 8). The aziridines with electron-withdrawing or electron-donating groups on the aryl ring gave excellent results (entries 9, 10). It is worth mentioning that all of the examples showed high chemo- and regioselectivity (from 84:16 to 97:3) towards 5-substituted product. When altering R^1 to an alkyl-like group, 4-substituted oxazolidinone could be obtained as a main product with high regioselectivity (**2k/3k** = 3:97), being in agreement with the previous results (entry 10).[3a,j–k] Whereas only the starting material was recovered and no product was detected in the case of R^2 being aryl or electron-withdrawing group (entries 12, 13).

To gain a deep insight into this reaction, in situ FT-IR spectroscopy was employed to identify the possible intermediates during the reaction. As previously reported,[14] amines can react with CO_2 to form the carbamate salts, being considered as an analogue of the adduct formed by aziridine and CO_2. As shown in Figure 1 (A), the absorption intensity of asymmetric ν(C=O) vibrations (1658 cm^{-1}) gradually increased with proceeding the reaction of CO_2 with diethyl amine, indicating the formation of the ammonium carbamate.[15] That could account for tertiary or secondary amine's positive effect on the reaction (entries 5 and 6, Table 1). When diethyl amine was added to the reaction of **1a** with CO_2, the characteristic absorption peaks of the carbamate salt at 1669 cm^{-1} and the oxalidinone **2a** at 1766 cm^{-1}, were changing (Figure 1, B) as the reaction running. Notably, absorption of the carbonyl group was migrated from 1688 cm^{-1} (the carbamate salt) to 1762 cm^{-1} (the product **2b**) when **1b** was used as the substrate (Figure 1, C), presumably implying the adduct in situ formed from aziridine with CO_2 could act as a catalyst. As a result, the reaction worked well without additional catalyst.

Based on the experimental results and previous reports, a hypothetic reaction mechanism for this catalyst-free process was proposed as depicted in Scheme 2, which is analogous to the LiI-catalyzed version.[3c,d] It mainly comprises three steps: firstly, coordinating of CO_2 with aziridine to generate the zwitterionic adduct in situ which was detected by in situ FT-IR under CO_2 pressure (step I); then ring opening through a nucleophilic attack by the partially anionic oxygen of the other adduct, assisted by the pseudo carbocations scattered on the three-membered ring (step II); and final cyclization via an intramolecular nucleophilic attack leading to the product as well as regeneration of the adduct (step III). The coordination of CO_2 to aziridine is the rate-dominating step, which can explain the R^1 and R^2 group effect on the activity and selectivity. The branched substituted group at N atom makes the formation of the adduct (step I) more difficult and thus shows lower activity. Furthermore, the aryl or electron-withdrawing group would cause the coordination between aziridine and CO_2 impossible presumably due to the low electron density at the N atom, being inconsistent with the experimental results (entries 11, 12, Table 2). There exist two possible cycles (A or B) in this catalytic cycle de-

Table 2 Substrate Scope[a]



1 2 3

1a R^1 = Ph, R^2 = Et
1b R^1 = Ph, R^2 = H
1c R^1 = Ph, R^2 = Me
1d R^1 = Ph, R^2 = *n*-Pr
1e R^1 = Ph, R^2 = *n*-Bu
1f R^1 = Ph, R^2 = *i*-Amyl
1g R^1 = Ph, R^2 = Bn
1h R^1 = Ph, R^2 = Cy
1i R^1 = 4-ClC_6H_4, R^2 = Et
1j R^1 = 4-MeC_6H_4, R^2 = Et
1k R^1 = CH_2Cl, R^2 = Bn
1l R^1 = Ph, R^2 = Ph
1m R^1 = Ph, R^2 = Ts

Entry	Substrate	Conv. (%)[b]	Isolated yield (%)[c]	Regioselectivity **2/3** (%)[d]
1	**1a**	>99	89	95:5
2	**1b**	>99	69	91:9
3	**1c**	100	79	88:12
4	**1d**	100	86	95:5
5	**1e**	>99	91	94:6
6	**1f**	100	93	96:4
7	**1g**	100	97	94:6
8	**1h**	79	66	86:14
9	**1i**	100	88	97:3
10	**1j**	100	87	97:3
11	**1k**	100	94	3:97
12	**1l**	0	0	–
13	**1m**	0	0	–

[a] Reaction conditions: substrate (1 mmol), 120 °C, 9 MPa, 24 h.
[b] Determined by GC.
[c] The total yield of **2** and **3**.
[d] Molar ratio of **2** to **3**, determined by GC.

pending on the nature of R^1. When R^1 is aryl group, cycle A would be favorable, leading to preferential formation of **2a**; while if R^1 is alkyl, cycle B could be predominant, thus resulting in dominantly generating **3a**. On the other hand, CO_2 pressure effect also supports our hypothesis (Table 1).

In order to gain further insight into the above mechanism, we also examined the reaction of (*S*)-1-butyl-2-phenylaziridine [(*S*)-**1e**] with CO_2, as shown in Scheme 3, that there is a double inversion of stereochemistry at the chiral carbon center, which is attacked, to form (*S*)-**2e**. The reaction afforded (*S*)-**2e** in 85% yield and (*S*)-**3e** in 5% yield with retention of stereochemistry, implying the reaction does not involve the chiral center to generate (*S*)-**3e**.

In summary, we developed an efficient, simple, and self-catalytic process for selective synthesis of 5-aryl-2-oxazolidinones from aziridine and CO_2, which requires neither organic solvent nor catalyst. A variety of 5-aryl-2-oxazolidinones were obtained in high chemo- and regioselectivity. Notably, the chemoselectivity can be controlled by tuning CO_2 pressure. The detailed reaction mechanism and further extension of this protocol are under investigation in our laboratory.

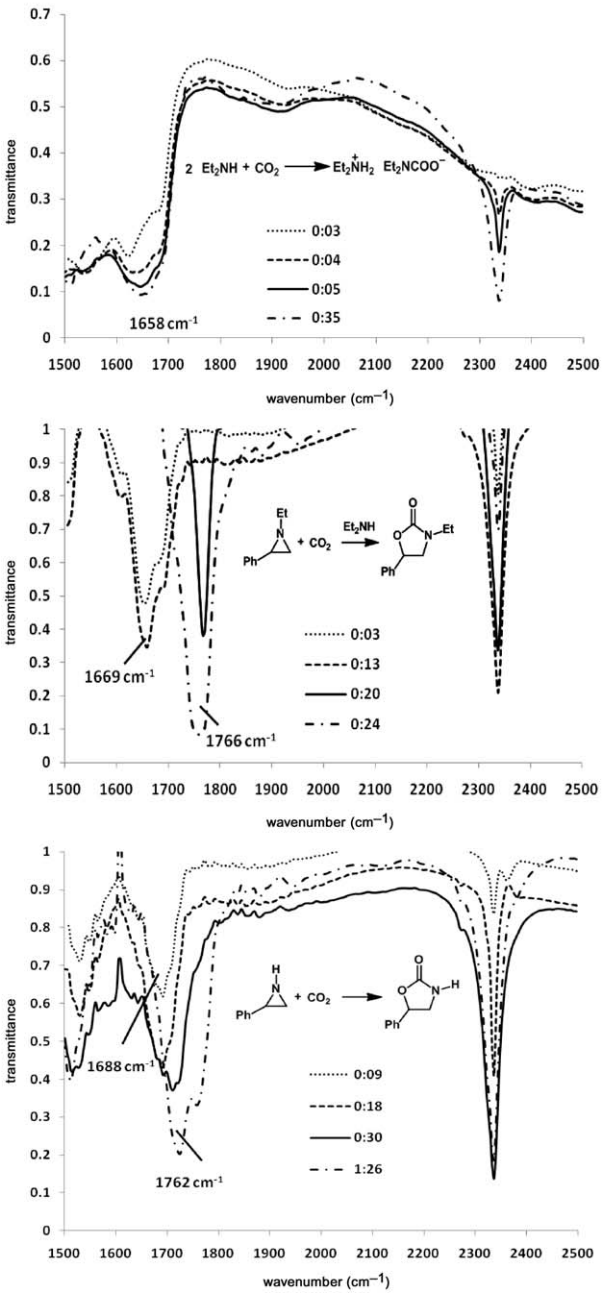
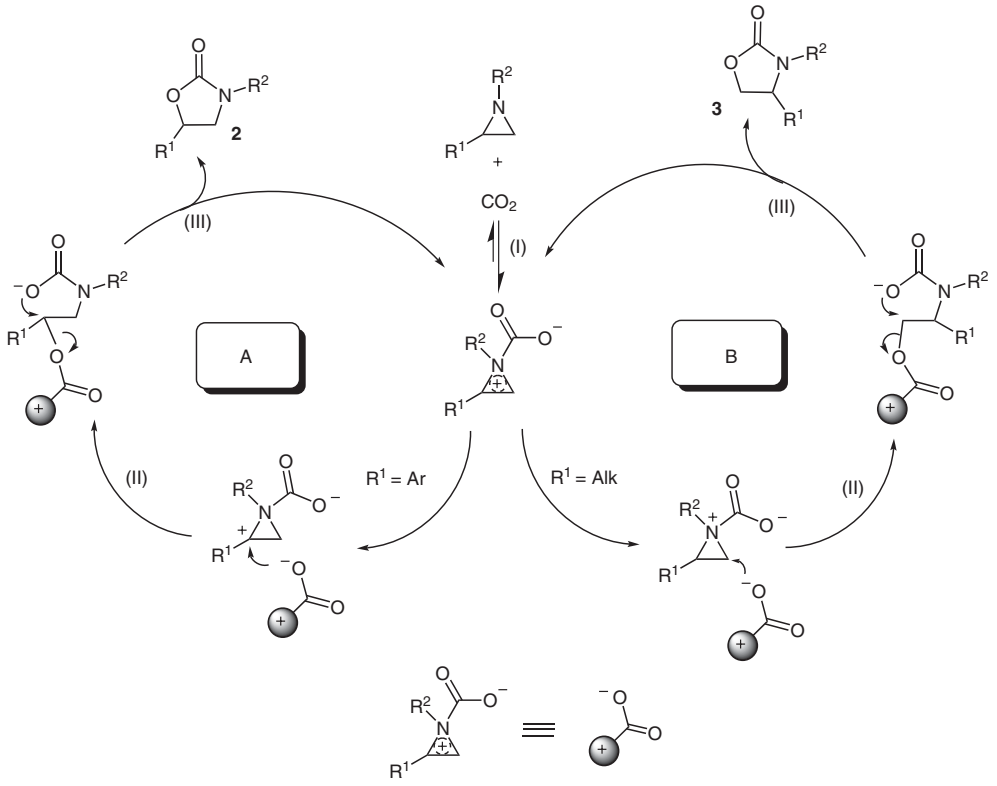
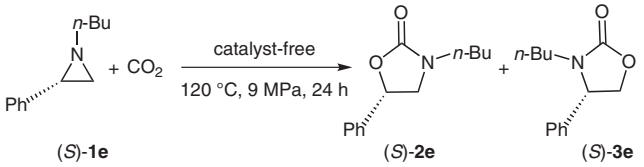


Figure 1 Results of in situ IR spectroscopy monitoring at various reaction time (min). *Reagents and conditions*: A. Et_2NH (5 mmol), 25 °C, 4 MPa; B. **1a** (5 mmol), Et_2NH (45 mol%), 120 °C, 4 MPa; C. **1b** (5 mmol), 120 °C, 9 MPa. IR data: 1658, 1669, and 1688 cm^{-1} correspond to absorption of carbonyl group in the carbamate salt; 1766 and 1762 cm^{-1} can be the absorption of carbonyl group in oxazolidines; 2340 cm^{-1} is the absorption of free CO_2.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.



Scheme 2 The proposed mechanism



Scheme 3 Carboxylation of (*S*)-1-butyl-2-phenylaziridine

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Reference and Notes

(1) (a) Gawley, R. E.; Campagna, S. A.; Santiago, M.; Ren, T. *Tetrahedron: Asymmetry* **2002**, *13*, 29. (b) Aurelio, L.; Brownlee, R. T. C.; Hughus, A. B. *Chem. Rev.* **2004**, *104*, 5823. (c) Makhtar, T. M.; Wright, G. D. *Chem. Rev.* **2005**, *105*, 529. (d) Barbachyn, M. R.; Ford, C. W. *Angew. Chem. Int. Ed.* **2003**, *42*, 2010. (e) Hoellman, D. B.; Lin, G.; Rattan, L. M. A.; Jacobs, M. R.; Appelbaum, P. C. *Antimicrob. Agents Chemother.* **2003**, *47*, 1148.

(2) (a) Ben-Ishai, D. *J. Am. Chem. Soc.* **1956**, *78*, 4962. (b) Vo, L.; Ciula, J.; Gooding, O. W. *Org. Process Res. Dev.* **2003**, *7*, 514. (c) Close, W. J. *J. Am. Chem. Soc.* **1951**, *73*, 95. (d) Lynn, J. W. US 2975187, **1961;** *Chem. Abstr.* **1961**, *55,* 87561. (e) Steele, A. B. US 2868801, **1959**; *Chem. Abstr.* **1959**, *53*, 56549. (f) Yoshida, T.; Kambe, N.; Ogawa, A.; Sonoda, N. *Phosphorus, Sulfur Relat. Elem.* **1988**, *38*, 137.

(3) (a) Miller, A. W.; Nguyen, S. T. *Org. Lett.* **2004**, *6*, 2301. (b) Shen, Y. M.; Duan, W. L.; Shi, M. *Eur. J. Org. Chem.* **2004**, 3080. (c) Hancock, M. T.; Pinhas, A. R. *Tetrahedron Lett.* **2003**, *44*, 5457. (d) Mu, W. H.; Chasse, G. A.; Fang, D. C. *J. Phys. Chem. A.* **2008**, *112*, 6708. (e) Sudo, A.; Morioka, Y.; Sanda, F.; Endo, T. *Tetrahedron Lett.* **2004**, *45*, 1363. (f) Sudo, A.; Morioka, Y.; Koizumi, E.; Sanda, F.; Endo, T. *Tetrahedron Lett.* **2003**, *44*, 7889. (g) Kawanami, H.; Ikushima, Y. *Tetrahedron Lett.* **2002**, *43*, 3841. (h) Kawanami, H.; Matsumoto, H.; Ikushima, Y. *Chem. Lett.* **2005**, *34*, 60. (i) Tascedda, P.; Dunach, E. *Chem. Commun.* **2000**, 449. (j) Du, Y.; Wu, Y.; Liu, A. H.; He, L. N. *J. Org. Chem.* **2008**, *73*, 4709. (k) Wu, Y.; He, L. N.; Du, Y.; Wang, J. Q.; Miao, C. X.; Li, W. *Tetrahedron* **2009**, *65*, 6204.

(4) (a) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *Tetrahedron Lett.* **1987**, *28*, 4417. (b) Shi, M.; Shen, Y. M. *J. Org. Chem.* **2002**, *67*, 16. (c) Costa, M.; Chiusoli, G. P.; Rizzardi, M. *Chem. Commun.* **1996**, 1699. (d) Costa, M.; Chiusoli, G. P.; Taffurelli, D.; Dalmonego, G. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1541. (e) Maggi, R.; Bertolotti, C.; Orlandini, E.; Oro, C.; Sartoria, G.; Selvab, M. *Tetrahedron Lett.* **2007**, *48*, 2131. (f) Kayaki, Y.; Yamamoto, M.; Suzuki, T.; Ikariya, T. *Green Chem.* **2006**, *8*, 1019.

(5) (a) Gu, Y. L.; Zhang, Q. H.; Duan, Z. Y.; Zhang, J.; Zhang, S. G.; Deng, Y. Q. *J. Org. Chem.* **2005**, *70*, 7376. (b) Jiang, H. F.; Zhao, J. W. *Tetrahedron Lett.* **2009**, *50*, 60. (c) Fournier, J.; Brunean, C.; Dixneuf, P. H. *Tetrahedron Lett.* **1990**, *31*, 1721. (d) Zhang, Q. H.; Shi, F.; Gu, Y. L.; Yang, J.; Deng, Y. Q. *Tetrahedron Lett.* **2005**, *46*, 5907. (e) Jiang, H. F.; Zhao, J. W.; Wang, A. Z. *Synthesis* **2008**, 763.

(6) (a) Matsuda, H.; Baba, A.; Nomufa, R.; Korl, M.; Ogawa, S. *Ind. Eng. Chem. Prod. Res. Dev.* **1985**, *24*, 239. (b) Tominaga, K.; Sasaki, Y. *Synlett* **2002**, 307. (c) Kubota, Y.; Kodaka, M.; Tomohiro, T.; Okuno, H. *J. Chem. Soc., Perkin Trans. 1* **1993**, 5. (d) Kodaka, M.; Tomihiro, T.; Lee,

A. L.; Okuno, H. *J. Chem. Soc., Chem. Commun.* **1989**, 1479. (e) Paz, J.; Perez-Balado, C.; Iglesias, B.; Munoz, L. *Synlett* **2009**, 395. (f) Dinsmore, C. J.; Mercer, S. P. *Org. Lett.* **2004**, *6*, 2885. (g) Patil, Y. P.; Tambade, P. J.; Jagtap, S. R.; Bhanage, B. M. *J. Mol. Catal. A: Chem.* **2008**, *289*, 14. (h) Du, Y.; Wang, J. Q.; Chen, J. Y.; Cai, F.; Tian, J. S.; Kong, D. L.; He, L. N. *Tetrahedron Lett.* **2006**, *47*, 1271. (i) Bhanage, B. M.; Fujita, S.; Ikushima, Y.; Arai, M. *Green Chem.* **2003**, *5*, 340. (j) Bhanage, B. M.; Fujita, S.; Ikushima, Y.; Arai, M. *Green Chem.* **2004**, *6*, 78. (k) Fujita, S.; Kanamaru, H.; Senboku, H.; Arai, M. *Int. J. Mol. Sci.* **2006**, *7*, 438.

(7) Yoo, W. J.; Li, C. J. *Adv. Synth. Catal.* **2008**, *350*, 1503.

(8) (a) Ihata, O.; Kayaki, Y.; Ikariya, T. *Angew. Chem. Int. Ed.* **2004**, *43*, 717. (b) Ihata, O.; Kayaki, Y. *Macromolecules* **2005**, *38*, 6429. (c) Soga, K.; Chiang, W. Y.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 121. (d) Lundberg, R. D.; Albans, S.; Montgomery, D. R. US 3523924, **1970**; *Chem. Abstr.* **1970**, *73*, 111037.

(9) (a) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1999**, *99*, 475. (b) *Green Chemistry Using Liquid and Supercritical Carbon Dioxide*; DeSimone, J. M.; Tumas, W., Eds.; Oxford University: New York, **2003**. (c) *Chemical Synthesis Using Supercritical Fluids*; Jessop, P. G.; Leitner, W., Eds.; Wiley-VCH: Weinheim, **1999**. (d) Leitner, W. *Acc. Chem. Res.* **2002**, *35*, 746. (e) Beckman, E. J. *J. Supercrit. Fluids* **2004**, *28*, 121. (f) Prajapati, D.; Gohain, M. *Tetrahedron* **2004**, *60*, 815.

(10) Lu, X. B.; Xiu, J. H.; He, R.; Jin, K.; Luo, L. M.; Feng, X. *J. Appl. Catal. A* **2004**, *275*, 73.

(11) **Typical Procedure for the Carboxylation of Aziridine with CO_2**
In a typical reaction, the carboxylation of aziridine with CO_2 was carried out in a 25 mL stainless steel autoclave. Aziridine (1 mmol) was charged into the reactor at r.t. CO_2 was introduced into the autoclave, and then the mixture was stirred at predetermined temperature for 20 min to reach the equilibration. The pressure was then adjusted to the desired pressure, and the mixture was stirred continuously. When the reaction finished, the reactor was cooled in ice-water and CO_2 was ejected slowly. An aliquot of sample was taken from the resultant mixture and dissolved in dry CH_2Cl_2 for GC analysis. GC analyses were performed on Shimadzu GC-2014, equipped with a capillary column (RTX-5, 30 m × 0.25 mm × 0.25 μm) using a flame-ionization detector. The residue was purified by column chromatography on silica gel (eluting with 8:1 to 1:1 PE–EtOAc) to furnish the product. The products were further identified by ^{1}H NMR, ^{13}C NMR, and MS which are consistent with those reported in the literature[3a–j] and in good agreement with the assigned structures.

(12) Spectral characteristics for representative examples of the products were provided.
3-Ethyl-5-phenyl-2-oxazolidinone (2a)
Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17 (t, 3 H, *J* = 7.2 Hz), 3.29–3.45 (m, 3 H), 3.92 (t, 1 H, *J* = 8.7 Hz), 5.48 (t, 1 H, *J* = 7.8 Hz), 7.34–7.42 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.4, 38.8, 51.5, 74.2, 125.4, 128.6, 128.8, 138.8, 157.5. ESI-MS: *m/z* calcd for $C_{11}H_{13}NO_2$: 191.09; found: 192.29 $[M + H]^+$, 214.38 $[M + Na]^+$, 405.01 $[2 M + Na]^+$.
3-Ethyl-4-phenyl-2-oxazolidinone (3a)
Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, 3 H, *J* = 5.4 Hz), 2.79–2.88 (m, 1 H), 3.48–3.57 (m, 1 H), 4.10 (t, 1 H, *J* = 6.0 Hz), 4.62 (t, 1 H, *J* = 6.6 Hz), 4.81 (t, 1 H, *J* = 5.4 Hz),7.30–7.44 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.1, 36.9, 59.4, 69.8, 127.0, 129.0, 129.2, 137.9, 158.1. ESI-MS: *m/z* calcd for $C_{11}H_{13}NO_2$: 191.09; found: 192.29 $[M + H]^+$, 214.38 $[M + Na]^+$.

(13) Kong, D. L.; He, L. N.; Wang, J. Q. *Catal. Commun.* **2010**, *11*, 992.

(14) CO_2 activation by tertiary amines: (a) Pérez, E. R.; Franco, D. W. *Tetrahedron Lett.* **2002**, *43*, 4091. (b) Endo, T.; Nagai, D. *Macromolecules* **2004**, *37*, 2007. (c) Phan, L.; Andreatta, J. R.; Horvey, L. K.; Edie, C. F.; Luco, A. L.; Mirchandani, A.; Darensbourg, D. J.; Jessop, P. G. *J. Org. Chem.* **2008**, *73*, 127. (d) Pereira, F. S.; deAzevedo, E. R. *Tetrahedron* **2008**, *64*, 10097. (e) North, M.; Pasquale, R. *Angew. Chem. Int. Ed.* **2009**, *48*, 2946. (f) Wykes, A.; MacNeil, S. L. *Synlett* **2007**, 107. (g) Masahiro, Y. F.; MacFarlane, D. R. *Electrochem. Commun.* **2006**, *8*, 445. (h) Masahiro, Y. F.; Johansson, K. *Tetrahedron Lett.* **2006**, *47*, 2755. (i) Ying, A. G.; Chen, X. Z.; Ye, W. D. *Tetrahedron Lett.* **2009**, *50*, 1653.

(15) Formation of Et_2NH with CO_2 identified by ^{1}H NMR: Kong, D. L.; He, L. N.; Wang, J. Q. *Synlett* **2010**, 1276.