JOC*Note*

Quaternary Ammonium Bromide Functionalized Polyethylene Glycol: A Highly Efficient and Recyclable Catalyst for Selective Synthesis of 5-Aryl-2-oxazolidinones from Carbon Dioxide and Aziridines Under Solvent-Free Conditions

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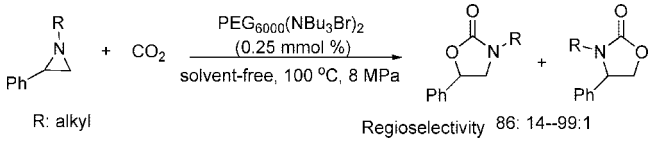

A quaternary ammonium bromide covalently bound to polyethylene glycol (PEG, MW = 6000), i.e., PEG_{6000}-$(NBu_3Br)_2$, was found to be an efficient and recyclable catalyst for the cycloaddition reaction of aziridines to CO_2 under mild conditions without utilization of additional organic solvents or cocatalysts. As a result, 5-aryl-2-oxazolidinone was obtained in high yield with excellent regioselectivity. The catalyst worked well for a wide variety of 1-alkyl-2-arylaziridines. Besides, the catalyst could be recovered by centrifugation and reused without significant loss of catalytic activity and selectivity.

Oxazolidinones are important heterocyclic compounds showing a large application as intermediates[1] and chiral auxiliaries[2] in organic synthesis. Cyclic carbamates like 5-substituted oxazolidinones are often employed as fragments in biologically active materials for pharmaceutical and agricultural uses.[3] There are three main synthetic strategies starting from C1 resources: (i) carbonylation of amino alcohols with phosgene, CO, etc.;[4] (ii) reaction of propargylamines or propargylic alcohols with CO_2;[5] and (iii) insertion of CO_2 into the aziridines moiety.[6] Methods ii and iii utilizing CO_2 as a feedstock, which is an abundant, nontoxic, and cheap C1 building block, are promising from a green chemistry perspective.[7] In this respect, numerous homogeneous catalysts have currently been developed for the cycloaddition reaction of aziridines to CO_2, such as a dual-component system, viz., SalenCr(III)/DMAP[6f] or Phenol/DMAP,[6g] alkali metal halide,[6c–e] or the tetraalkylammonium halide system.[6d] Particularly, iodine was extremely active for this reaction under supercritical CO_2 ($scCO_2$) conditions.[6b,h] In addition, the cycloaddition of aziridines to CO_2 also proceeded smoothly under electrochemical reaction conditions.[6a] Nonetheless, toxic organic solvents and cocatalysts are generally required to achieve high yields, along with a limited substrate scope in those above-mentioned cases. Therefore, the recyclability of the catalysts and product separation and developing highly effective catalysts for regioselective synthesis of 5-substituted-2-oxazolinones are still important issues to be addressed.

As catalyst recycling is often a vital problem in homogeneous catalysis efficient recycling concepts have to be developed. To preserve the benefits of a homogeneous catalyst while co-opting the primary benefits of a heterogeneous catalyst, one strategy is to graft the active species onto an insoluble support, whereby the catalyst can be readily separated from the reaction mixture by filtration. Notably, An appealing methodology would employ a CO_2-philic support for the reaction such that the supported catalyst dissolves during the reaction and can precipitate quantitatively at the separation stage. The most commonly used parameters to induce the precipitation are temperature, solvent, polarity, and pH of the solution. In this context, PEG should be an excellent candidate, being regarded as an environmentally benign medium for chemical reactions.[8] We envisioned that a functionalized PEG, with a quaternary ammonium salt as a catalytically active species being covalently grafted onto PEG, could be utilized as an active and recyclable homogeneous catalyst for oxazolidinone synthesis from aziridine and CO_2. In

(1) For selected examples with oxazolidinones as intermediates, see: (a) Watson, R. J.; Batty, D.; Baxter, A. D.; Hannah, D. R.; Owen, D. A.; Montana, J. G. *Tetrahedron Lett.* **2002**, *43*, 683. (b) Aurelio, L.; Brownlee, R. T. C.; Hughus, A. B. *Chem. Rev.* **2004**, *104*, 5823. (c) Shi, Z. D.; Liu, H. P.; Zhang, M. C.; Yang, D. J.; Burke, T. R., Jr *Synth. Commun.* **2004**, *34*, 3883. (d) Makhtar, T. M.; Wright, G. D. *Chem. Rev.* **2005**, *105*, 529. (e) Andreou, T.; Costa, A. M.; Esteban, L.; Gonzalez, L.; Mas, G.; Vilarrasa, J. *Org. Lett.* **2005**, *7*, 4083.

(2) For selected examples using oxazolidinones as chiral auxiliaries, see: (a) Phoon, C. W.; Abell, C. *Tetrahedron Lett.* **1998**, *39*, 2655. (b) Prashad, M.; Liu, Y. G.; Kim, H. Y.; Repic, O.; Blacklock, T. J. *Tetrahedron: Asymmetry* **1999**, *10*, 3479. (c) Gawley, R. E.; Campagna, S. A.; Santiago, M.; Ren, T. *Tetrahedron: Asymmetry* **2002**, *13*, 29.

(3) (a) Brickner, S. J. *Curr. Pharm. Des.* **1996**, *2*, 175. (b) Barbachyn, M. R.; Ford, C. W. *Angew. Chem, Int. Ed.* **2003**, *42*, 2010. (c) Nilus, A. M. *Curr. Opin. Invest. Drugs.* **2003**, *4*, 149.

(4) Selected examples for condensation of amino alcohols with carbonyl derivatives to afford oxazolidinones, see: (a) Crowther, H. L.; McCombie, H. *J. Chem. Soc.* **1913**, *103*, 27. (b) Close, W. J. *J. Am. Chem. Soc.* **1951**, *73*, 95. (c) Ben-Ishai, D. *J. Am. Chem. Soc.* **1956**, *78*, 4962. (d) Vo, L.; Ciula, J.; Gooding, O. W. *Org. Process Res. Dev.* **2003**, *7*, 514. Oxazolidinones synthesis by direct addition of carbon dioxide or carbon monoxide to β-amino alcohols, see: (e) Steele, A. B. U.S. Patent 2 868 801, 1959. (f) Lynn, J. W. U.S. Patent 2 975 187, 1961. (g) Yoshida, T; Kambe, N.; Ogawa, A; Sonoda, N. *Phosphorus Sulfur* **1988**, *38*, 137.

(5) Selected examples concerning the reaction of propargylamines with carbon dioxide to afford oxazolidinones, see: (a) Costa, M.; Chiusoli, G. P.; Rizzardi, M. *Chem. Commun.* **1996**, 1699. (b) Shi, M.; Shen, Y. M. *J. Org. Chem.* **2002**, *67*, 16. (c) Feroci, M.; Orsini, M.; Sotgiu, G.; Rossi, L.; Inesi, A. *J. Org. Chem.* **2005**, *70*, 7795. (d) Kayaki, Y.; Yamamoto, M.; Suzuki, T.; Ikariya, T. *Green Chem.* **2006**, *8*, 1019. Reaction of propargylic alcohols and amines to give oxazolidinones, see: (e) Gu, Y. L.; Zhang, Q. H.; Duan, Z. Y.; Zhang, J.; Zhang, S. G.; Deng, Y. Q. *J. Org. Chem.* **2005**, *70*, 7376.

(6) The insertion of CO_2 into the aziridines moiety to give oxazolidinones, see: (a) Tascedda, P.; Dunach, E. *Chem. Commun.* **2000**, 449. (b) Kawanami, H.; Ikushima, Y. *Tetrahedron Lett.* **2002**, *43*, 3841. (c) Hancock, M. T.; Pinhas, A. R. *Tetrahedron Lett.* **2003**, *44*, 5457. (d) Sudo, A.; Morioka, Y.; Koizumi, E.; Sanda, F.; Endo, T. *Tetrahedron Lett.* **2003**, *44*, 7889. (e) Sudo, T.; Morioka, Y.; Sanda, F.; Endo, T. *Tetrahedron Lett.* **2004**, *45*, 1363. (f) Miller, A. W.; Nguyen, S. T. *Org. Lett.* **2004**, *6*, 2301. (g) Shen, Y. M.; Duan, W. L.; Shi, M. *Eur. J. Org. Chem.* **2004**, 3080. (h) Kawanami, H.; Matsumoto, H.; Ikushima, Y. *Chem. Lett.* **2005**, *34*, 60. (i) Ihata, O.; Kayaki, Y.; Ikariya, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 717.

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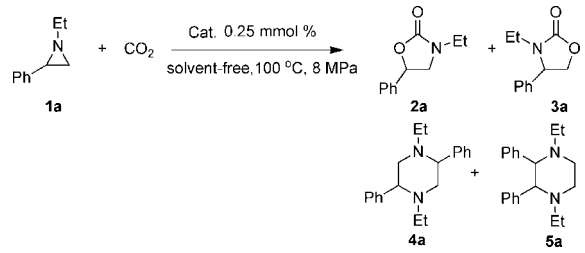
TABLE 1. Carboxylation of Aziridine into Oxazolidinone[a]



entry	catalyst	*t* (min)	yield (%)[b]	regio-sel (%)[c]	TOF (h^{-1})[d]
1		5	trace		
2[e]	PEG_{6000}	5	trace		
3	Bu_4NBr	5	6	94:6	274
4	Bu_4NBr/PEG_{6000}	5	38	91:9	1805
5	$PEG_{6000}(NBu_3Br)_2$	5	71	93:7	3394
6[f]	I_2	5	88	96:4	2575
7[g]	LiBr	5	94	94:6	1416
8	$PEG_{6000}(NBu_3Br)_2$	10	89	92:8	2126
9	$PEG_{6000}(NBu_3Br)_2$	15	93	93:7	1490
10	$PEG_{6000}(NBu_3Br)_2$	20	98	92:8	1162
11[h]	$PEG_{6000}(NBu_3Br)_2$	20	97	92:8	1170
12[i]	$PEG_{6000}(NBu_3Br)_2$	20	96	96:4	1157

[a] Reaction conditions: catalyst (0.005 mmol, 0.25 mol % with respect to **1a**), **1a** (294 mg, 2 mmol), CO_2 8 MPa, 100 °C. [b] The total yield of **2a** and **3a**, determined by GC with biphenyl as an internal standard. [c] Molar ratio of **2a** to **3a**. [d] Turnover frequency (TOF): sum of moles of **2a** and **3a** produced per mole of catalyst per hour. [e] PEG (30 mg) alone. [f] Catalyst: I_2, 2.1 mg, 0.008 mmol, 0.4 mol % relative to **1a**. [g] Catalyst: LiBr, 1.4 mg, 0.016 mmol, 0.8 mol % with regard to **1a**. [h] The second run of the catalyst recovered from entry 10 (fresh catalyst). [i] The third run of the reused catalyst.

the present work, we would like to report the use of $PEG_{6000}(NBu_3Br)_2$ gave rise to a high yield and regioselectivity for 5-substituted-2-oxazolidinone synthesis under mild conditions, without the need of any additives. Furthermore, the catalyst is quite efficacious for a wide scope of substrates under organic solvent-free conditions.

The cycloaddition reaction of aziridines with CO_2 was conducted in a batch-wise operation in the presence of 0.25 mol % of the catalyst relative to the initial amount of substrate. 1-Ethyl-2-phenylaziridine (**1a**) was chosen as the standard substrate to investigate suitable reaction conditions for the desired reaction. The results are summarized in Table 1. Without any catalyst or in the presence of 30 mg of PEG_{6000} alone, the coupling reaction of **1a**/CO_2 did not occur at all (entries 1 and 2). Bu_4NBr itself showed low catalytic activity in the carboxylation of **1a** with CO_2 (entry 3). A mixture of Bu_4NBr with PEG_{6000} has higher catalytic activity than the unsupported ammonium salt, i.e., Bu_4NBr (entry 4 vs 3). Interestingly, $PEG_{6000}(NBu_3Br)_2$ actually has higher catalytic activity than the unsupported quaternary ammonium (Bu_4NBr), even more effective than the simple physical mixture of Bu_4NBr with PEG_{6000} under the identical conditions (Table 1, entry 5 vs entries 3 and 4). The enhancement of catalytic performance for the PEG-supported ammonium salt is presumably attributed to the benefits

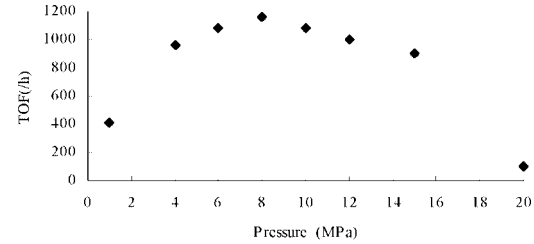


FIGURE 1. Plot of TOF as a function of CO_2 pressure for the reaction of CO_2 and **1a**. Reaction conditions: $PEG_{6000}(NBu_3Br)_2$ (32.4 mg, 0.005 mmol), **1a** (294 mg, 2 mmol), 100 °C, 20 min.

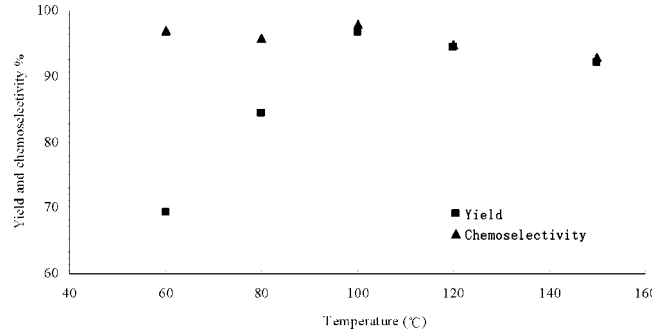


FIGURE 2. Reaction temperature dependence of yield and chemoselectivity with $PEG_{6000}(NBu_3Br)_2$ as a catalyst. Reaction conditions: $PEG_{6000}(NBu_3Br)_2$ (32.4 mg, 0.005 mmol), **1a** (294 mg, 2 mmol), 8 MPa, 20 min.

from changes in the physical properties[8] of the reaction mixture, such as low viscosity and increased solubility for the reactants. Consequently, the ammonium salt can be considered as the active species for the reaction and supporting Bu_4NBr on the CO_2-expandable polymer[8d,9] improves the catalytic activity. Note that 5-aryl-2-oxazolidinone (**2a**) was preferentially formed with high regioselectivities in all cases listed in Table 1. The major isomer, i.e., **2a**, corresponds to the incorporation of CO_2 at the more sterically hindered side of the monosubstituted aziridine; in other words, the more substituted carbon−nitrogen is predominately carboxylated.

It is worth mentioning that the turnover frequency (TOF, 3394 h^{-1}) of $PEG_{6000}(NBu_3Br)_2$ was attained under reaction conditions much higher than those of the most active catalysts like I_2[6h] and LiBr[6e] for the aziridine/CO_2 reaction (entry 5 vs entries 6 and 7). The only byproducts of this reaction were trace amounts of 1,4-diethyl-2,5-diphenylpiperazine (**4a**) and 1,4-diethyl-2,3-diphenylpiperazine (**5a**) being detected by MS and ^1H NMR (see the Supporting Information). In other words, excellent chemoselectivity was attained in this catalytic process.

Shown in Figure 1 is the activity of $PEG_{6000}(NBu_3Br)_2$ as a function of CO_2 pressure in the reaction of CO_2 and **1a**. As is easily seen, pressure has a great influence on the reaction rate with variation of CO_2 pressure from 1 to 8 MPa. On the other hand, the reaction rate slightly changes from 8 to 15 MPa. However, the reaction rate dramatically decreases with further increase in CO_2 pressure. Excessive CO_2 pressure may cause a low concentration of aziridine in the vicinity of the catalyst, thus resulting in a low reaction rate.[10]

Figure 2 shows the temperature dependence on the yield of oxazolidinones. The yield of **2a** increases sharply with a

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SCHEME 1. A Putative Mechanism

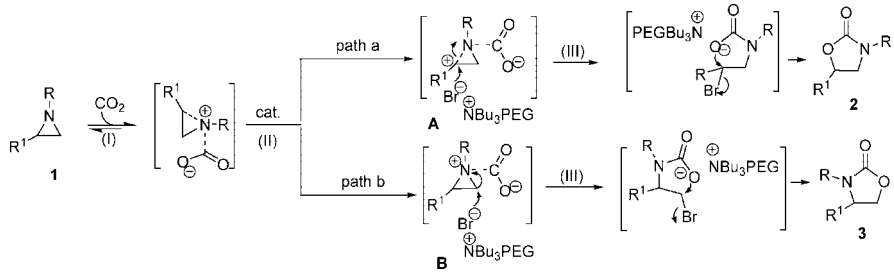
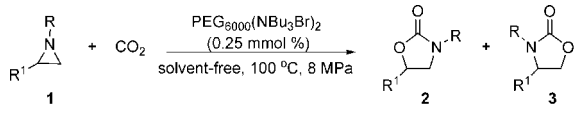


TABLE 2. Substrate Scope[a]



1a: R=Et, R[1]=Ph
1b: R=CH_3, R[1]=Ph
1c: R=H, R[1]=Ph
1d: R=*n*-Pr, R[1]=Ph
1e: R=*n*-Bu, R[1]=Ph
1f: R=Bn, R[1]=Ph
1g: R=*t*-Bu, R[1]=Ph
1h: R=*i*-Pr, R[1]=Ph
1i: R=*i*-Bu, R[1]=Ph
1j: R=*i*-Amyl, R[1]=Ph
1k: R=cyclopropyl, R[1]=Ph
1l: R=*c*-Hex, R[1]=Ph
1m: R=*c*-Hex, R[1]=4-CH_3Ph
1n: R=*c*-Hex, R[1]=4-ClPh
1o: R=Bn R[1]=CH_2OPh
1p: R=Ph, R[1]=Ph

entry	substrate	time	conv (%)[b]	isolated yield (%)[c]	regioselectivity (%)[d]
1	**1a**	20 min	>99	95	92:8
2	**1b**	15 min	>99	83	93:7
3	**1c**	15 min	>99	59	86:14
4	**1d**	20 min	99	89	93:7
5	**1e**	25 min	>99	94	91:9
6	**1f**	45 min	>99	>99	96:4
7	**1g**	72 h	50	49	100
8	**1h**	24 h	>99	96	99:1
9	**1i**	14h	>99	93	96:4
10	**1j**	12 h	>99	91	91:9
11	**1k**	11 h	>99	88	94:6
12	**1l**	10 h	97	94	99:1
13	**1m**	10 h	>99	94	99:1
14	**1n**	15 h	>99	95	100
15	**1o**	1 h	99	88	20:80
16[e]	**1p**	24 h	100		

[a] Reaction conditions: $PEG_{6000}(NBu_3Br)_2$ (32.4 mg, 0.005 mmol), substrate (2 mmol), CO_2 8 MPa, 100 °C. [b] Determined by GC. [c] The total yield of **2** and **3**. [d] Molar ratio of **2** to **3**. [e] 1,2,4,5-Tetraphenylpiperazine and 1,2,3,4-tetraphenylpiperazine were detected by LC-MS.

temperature increase from 60 to 100 °C, with no significant change in yield observed from 100 to 120 °C. A further increase in temperature causes a slight decrease in the chemoselectivity, due to facile formation of piperazines **4a** and **5a** at a higher temperature. Accordingly, 100 °C is suitable for conducting the reaction at a reasonable rate.

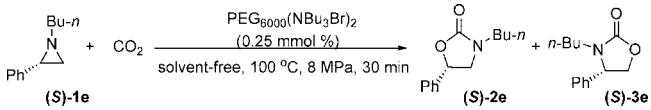
It is worth mentioning that variation of temperature and pressure had no influence on the regioselectivity of **2a** ,which remained over 92% in all cases. Furthermore, the catalyst $PEG_{6000}(NBu_3Br)_2$ can be recovered by centrifugation[11]and reused for the next run with excellent activity (entries 11 and 12, Table 1).

To demonstrate the utility and generality of this approach, we examined the cycloaddition reactions of various aziridines (**1a**−**p**) with CO_2 by performing the reaction under the given conditions. The results are listed in Table 2. It is found that the reactions of aziridines (**1a**, **1b**, **1d**, and **1e**) bearing alkyl groups at the nitrogen atom proceeded smoothly and good yields were achieved within about 20 min (entries 1, 2, 4, and 5, Table 2). However, 2-phenylaziridine (**1c**) displayed a relatively low selectivity probably due to the formation of self-oligomers as detected by GC-MS (entry 3). The substrates **1g**−**n** bearing a branched alkyl group at the nitrogen atom showed in slower reaction rate, presumably due to the steric interactions in terms of reaction mechanistic consideration (Scheme 1). Nonetheless, excellent results except for **1g** were also obtained at a prolonged reaction time (entries 7−14). With regard to regioselectivity, the nature of the R^1 group is a crucial factor in dominating the selectivity of the reaction, as has been previously reported.[6b] If R^1 is an aryl group, product **2** is favored, whereas if R^1 is an alkyl group, product **3** is favored. It seems to be shown that the regioselectivity can be significantly enhanced from 86:14 (**2**:**3**) to an exclusive generation of **2** (entries 3 and 7−10) as the alkyl substituent at the nitrogen atom is augmented. On the other hand, an electron-donating group on the C1-aryl group gave a faster reaction rate than the presence of an electron-withdrawing group (entry 13 vs 14) to accelerating this reaction. Interestingly, the 4-substituted oxazolidinone **3o** was preferentially produced in a molar ratio of 80:20 (**3o** to **2o**) when R^1 at the carbon atom is an alkyl group, which would be explained by the proposed mechanism as outlined in Scheme 1 (entry 15). It is also noted that 1,2,4,5-tetraphenylpiperazine and 1,2,3,4-tetraphenylpiperazine were formed, as detected by LC-MS, when both R and R^1 in the substrate **1** are phenyl groups (entry 16).

On the basis of the experiment results, a possible mechanism for the $PEG_{6000}(NBu_3Br)_2$-catalyzed cycloaddition of CO_2 with aziridine was proposed as shown in Scheme 1. This proposal is analogous to that of the LiI-catalyzed version for the same reaction.[6c] The mechanism involves three steps: coordination of CO_2 to aziridine (step I), then ring opening of the aziridine through two different pathways as represented by paths a and b mainly depending on the nature of the R^1 group with alkyl substitution at the N-position (step II), and subsequent cyclization via an intramolecular nucleophilic attack leading to oxazolidinones and regeneration of the catalyst (step III). In this respect, the following observation supports our hypothesis. The rate dependence on the steric effect of the R group on the nitrogen atom shown in Table 2 implies that the coordination of CO_2 to the aziridine(I) is a reversible step in the catalytic cycle and the substrates with less sterically hindered R would be favorable for the coordination with CO_2, thus resulting in higher reaction rate compared with those substrates with more sterically hindered R. This proposed mechanism could also account for the effect of the R^1 substituent on the selective formation of **2** or **3**. As deduced from Scheme 1, if R^1 is an aryl group, the intermediate **A** would be more stable than **B** and thus **2** would be predominantly formed; in contrast, if R^1 is an alkyl group, **B** would be favored, which in turn results in dominantly producing **3**. Furthermore, the reaction of (*S*)-1-

(11) After the reaction, Et_2O (2 × 4 mL) was added to the reaction mixture; the catalyst was then precipitated and separated by centrifugation.

SCHEME 2. Carboxylation of (*S*)-1-Butyl-2-phenylaziridine into Oxazolidinone



butyl-2-phenylaziridine (*S*-**1e**)[12] with CO_2 in the presence of 0.25 mol % $PEG_{6000}(NBu_3Br)_2$ (Scheme 2) affords *S*-**2e** in 91.4% yield and *S*-*3e* in 8.6% yield with retention of stereochemistry,[13,14] further supporting the above mechanism where there is a double inversion of stereochemistry at the chiral carbon center, which is attacked. In addition, Scheme 1 can also be used to rationalize the dependence of the reaction on CO_2 pressure in the range of 1 to 8 MPa (Figure 1). As Scheme 1 suggests, the coordination of CO_2 with aziridine would be a reversible step in the catalytic cycle. Therefore, a higher CO_2 pressure could be favorable for the CO_2 coordination leading to the desired product and suppressing the formation of **4a** and **5a**.

In conclusion, we developed an efficient and recyclable catalyst for high selective synthesis of 5-substituted-2-oxazolidinones from CO_2 and various aziridines without any added organic solvents or cocatalysts. It is also found that selective formation 5-substituted-2-oxazolidinone **2** or 4-substituted isomer **3** relies on R^1 at the carbon of the substrate when R is a fixed alkyl group. To our knowledge, the PEG-supported ammonium catalyst system is one of the most efficient catalyst systems to date for this carboxylation reaction under mild conditions. One of the salient features of this protocol would be that the catalyst can be readily recovered by centrifugation and reused with retention of high catalytic activity and regioselectivities. This process represents a pathway for the environmentally benign chemical fixation of CO_2 to afford 5-substituted-2-oxazolidinones.

(12) (*S*)-1-Butyl-2-phenylaziridine (*S*-**1e**) was synthesized according to a literature procedure: Calet, S.; Urso, F.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 931.

(13) The reaction of (*S*)-1-butyl-2-phenylaziridine (*S*-**1e**) with CO_2 in the presence of 0.25 mol % catalyst affords (S)-3-butyl-5-phenyloxazolidione (*S*-**2e**) in 96.7% ee with 91.4% yield and (*S*)-3-butyl-4-phenyloxazolidione (*S*-**3e**) in 97.5% ee with 8.6% yield. The enantiomeric excess of *S*-**2e** and *S*-**3e** was determined by HPLC, using Agilent 1100 series with a chiralcel AD-H (hexane/isopropyl alcohol 95:5, 220 nm) at room temperature. The retention times of *S*-**2e** and *R*-**2e** are 14.87 and 16.39 min, and the retention times of *S*-**3e** and *R*-**3e** are 21.24 and 23.51 min, respectively.

(14) The absolute configuration is *S*, as compared the optical rotation value with the literature data.[14a,b] The optical rotation values were recorded with Perkin-Elmer Instruments (model 341) $[\alpha]^{20}_D$ +13.6 (*c* 1.5, $CHCl_3$) and $[\alpha]^{20}_D$ +31.1 (*c* 0.8, $CHCl_3$) for the (+)-**2e** and (+)-**3e**, respectively. (a) Claude, A.; Francois, C.; Louis, H.; Olivier, V. *Tetrahedron Lett.* **1993**, *34*, 4509–4512. (b) Tanis, S. P.; Evans, B. R.; Nieman, J. A.; Parker, T. T.; Taylor, W. D.; Heasley, S. E.; Herrinton, P. M.; Perrault, W. R.; Hohler, R. A.; Dolak, L. A.; Hester, M. R.; Seest, E. P. *Tetrahedron: Asymmetry,* **2006**, *17*, 2154–2182.

Experimental Section

General Procedure for Carboxylation of Aziridine with CO_2. A 25 mL autoclave reactor was charged with catalyst $PEG_{6000}(NBu_3Br)_2$ (32.4 mg, 0.005 mmol) and aziridine (2 mmol). CO_2 was introduced into the autoclave and then the mixture was stirred at 100 °C for 5 min to allow equilibration. Finally, the pressure was adjusted to 8 MPa and the mixture was stirred continuously. When the reaction was 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 CH_2Cl_2 for GC analysis. The residue was purified by column chromatography on silica gel (200−300 mesh, eluting with 8:1 to 1:1 petroleum ether/ethyl acetate) to afford the desired product. The products were further identified by NMR and MS (see the Supporting Information), which are consistent with those reported in the literature[6f,15] and in good agreement with the assigned structures.

3-Ethyl-5-phenyloxazolidin-2-one (2a). Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (t, ^3J = 7.2 Hz, 3H), 3.29−3.45 (m, 3H), 3.92 (t, ^3J = 8.7 Hz, 1H), 5.48 (t, ^3J = 7.8 Hz, 1H), 7.34−7.42 (m, 5H); ^{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; MS (ESI) calcd for $C_{11}H_{13}NO_2$ 191.09, found 192.29 $(M + H)^+$, 214.38 $(M + Na)^+$, 405.01 $(2\ M + Na)^+$; HRMS calcd for $C_{11}H_{13}NO_2$ $(M + H)^+$ 192.1019, found 192.1015.

3-Ethyl-4-phenyloxazolidin-2-one (3a). Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, ^3J = 7.2 Hz, 3H), 2.79−2.88 (m, 1H), 3.48−3.57 (m, 1H), 4.10 (t, ^3J = 8.0 Hz, 1H), 4.62 (t, ^3J = 8.8 Hz, 1H), 4.81 (t, ^3J = 7.2 Hz, 1H), 7.30−7.44 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.1, 36.8, 59.3, 69.7, 126.9, 129.0, 129.2, 137.8, 158.1; MS (ESI) calcd for $C_{11}H_{13}NO_2$ 191.09, found 192.29 $(M + H)^+$, 214.38 $(M + Na)^+$, 405.01 $(2\ M + Na)^+$; HRMS calcd for $C_{11}H_{13}NO_2$ $(M + H)^+$ 192.1019, found 192.1015.

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Supporting Information Available: General experimental methods, experimental procedures, and characterization for aziridines, oxazolidinones, and piperazines and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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