Tetrahedron 65 (2009) 6204–6210

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Zirconyl chloride: an efficient recyclable catalyst for synthesis of 5-aryl-2-oxazolidinones from aziridines and CO_2 under solvent-free conditions

Ying Wu, Liang-Nian He *, Ya Du, Jin-Quan Wang, Cheng-Xia Miao, Wei Li *

Institute of Elemento-Organic Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, PR China

ARTICLE INFO

Article history:
Received 2 April 2009
Received in revised form 9 May 2009
Accepted 15 May 2009
Available online 21 May 2009

Keywords:
Zirconyl chloride
5-Aryl-2-oxazolidinone
Aziridine
Carbon dioxide

ABSTRACT

Zirconyl chloride was found to be an efficient catalyst for the cycloaddition reaction of aziridines with CO_2, thus leading to the preferential formation of 5-aryl-2-oxazolidinones under solvent-free conditions. The methodology could be extended to various substituted aziridines with high conversion and chemo-, regio-, and stereoselectivity. Furthermore, the catalyst could be reused over five times without significant loss in activity. Interestingly, the recovered catalyst showed higher activity in comparison with the fresh catalyst, presumably due to its morphological variation. The use of this cheap and moisture stable catalyst make this protocol practical, environmentally benign, and economically attractive.

1. Introduction

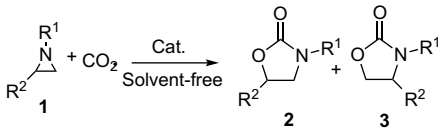
Given the importance of oxazolidinones in medicinal chemistry[1] and synthetic chemistry,[2,3] a growing effort has been devoted to developing new efficient methodology for synthesis of oxazolidinones. Currently, there are mainly three synthetic strategies from C1 resource: (i) carbonylation of amino alcohols using 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] The methods (ii) and (iii) utilizing abundant, renewable and nontoxic CO_2 as a feedstock[7] are promising from a green chemistry perspective. In this respect, numerous homogeneous catalysts have been developed for the cycloaddition reaction of aziridines and CO_2, such as dual-component system viz. SalenCr(III)/DMAP[6a] or Phenol/DMAP,[6b] alkali metal halide[6c–e] or tetraalkyl-ammonium halide system.[6e] Particularly, iodine was extremely active for this reaction even under supercritical CO_2 conditions.[6f,g] Nonetheless, toxic organic solvents and co-catalysts are generally required to achieve high yields, along with toilsome purification of product and a limited substrate scope in the most of above-mentioned cases. In this context, developing more environmentally benign heterogeneous catalysts for regio-selective synthesis of 5-substituted-2-oxazolidinones will be more desirable.

$ZrOCl_2 \cdot 8H_2O$ has drawn much attention because of its water-stability, low toxicity, and commercial availablity,[8] especially wide utilization as a catalyst in organic reactions, such as oxidation of alcohols,[9] nitration of phenolic compounds,[10] acylation of alcohols, phenols, amines and thiols,[11] esterification of carboxylic acids and alcohols,[12] Michael addition of amines and indoles to α,β-unsaturated ketones,[13] Biginelli reaction,[14] Mannich-type reactions,[15] synthesis of 2-aliphatic aryloxazolines, benzimidazole, benzothiazoles, and bis-oxazolines.[16] Recently, zirconyl chloride was also proven to be highly effective for the synthesis of β-acetamido ketones,[17] enaminones and enamino esters,[18] α-aminophosphonates,[19] homoallylic alcohols or amines.[20] Furthermore, $ZrOCl_2 \cdot 8H_2O$ is regarded to be an ionic cluster of $[Zr_4(OH)_8(H_2O)_{16}]Cl_8 \cdot 12H_2O$; and whereby the zirconium cation cluster $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ is usually thought to be active species for the Lewis acid-catalyzed reactions.[12–20]

We recently reported a quaternary ammonium bromide covalently bound to polyethylene glycol was an efficient and recyclable homogeneous catalyst for the synthesis of 5-substituted oxazolidinones from carbon dioxide.[6k] However, organic solvents are required for the separation of products and catalysts. As our continuing effort on developing efficient approaches for fixing CO_2 into oxazolidinones, we herein would like to report the use of zirconyl chloride as an effective and recyclable catalyst for the cycloaddition of CO_2 to aziridines to afford 5-aryl-2-oxazolidinones under mild conditions without the need of any additive as depicted in Scheme 1. Moreover, this methodology was successfully applied to the synthesis of a variety of 5-substituted oxazolidinones with excellent yields and regio- and stereoselectivities.

* Corresponding authors. Tel./fax: +86 22 2350 4216 (L.-N.H.); tel./fax: +86 22 2350 8662 (W.Li).
E-mail addresses: heln@nankai.edu.cn (L.-N. He), weili@nankai.edu.cn (W. Li).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.05.034

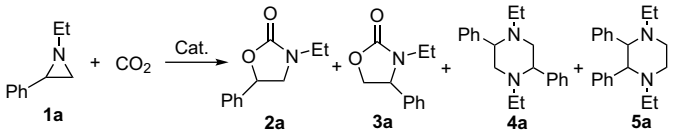


Scheme 1. Synthesis of 2-oxazolidinones from aziridines and CO_2.

2. Results and discussion

In the preliminary study, we first screened those commercially available Lewis acids and organic bases (Table 1, entries 3–13) for cycloaddition of 1-ethyl-2-phenylaziridine **1a** and CO_2, and carried out reactions at 313 K for 4 h in the presence of 8 MPa CO_2. The desired product (**2a**) was scarcely obtained without the use of any catalyst (entry 1); and CH_2Cl_2 gave rise to a trace amounts of **2a** and **4a**+**5a**. Either Lewis acids (entries 5, 6) or bases (entries 8–13) displayed poor catalytic activity, or inactive toward the reaction. Fortuitously, $ZrOCl_2\cdot 8H_2O$ under solvent-free conditions (entry 7) was found to show comparable catalytic activity with one of the most active catalysts like I_2[6f] (entry 4), even higher than LiBr[6d] by employing CH_2Cl_2 as a solvent (entry 3).

Table 1
Cycloaddition reaction of CO_2 to aziridine into oxazolidinones[a]



Entry	Catalyst (mol %)	Solvent	T (K)	P (MPa)	t (h)	Conv. (%)	Yield[b] (%)		
							2a	**3a**	**4a**+**5a**
1	—	—	313	8	4	5	—	—	1
2	—	CH_2Cl_2	313	8	4	10	1	—	2
3	LiBr (20)	CH_2Cl_2	313	8	4	35	31	1	11
4	I_2 (20)	CH_2Cl_2	313	8	4	98	30	1	9
5	$AlCl_3$ (20)	CH_2Cl_2	313	8	4	58	22	1	11
6	$ZnCl_2$ (20)	CH_2Cl_2	313	8	4	1	1	—	—
7	$ZrOCl_2\cdot 8H_2O$ (20)	—	313	8	4	96	41	2	4
8	Morpholine (20)	—	313	8	4	6	3	1	1
9	DMAP[c] (20)	—	313	8	4	8	1	—	—
10	DBN[d] (20)	—	313	8	4	36	0.4	—	—
11	DBU[e] (20)	—	313	8	4	11	—	—	1
12	DABCO[f] (20)	CH_2Cl_2	313	8	4	—	—	—	—
13	HMTA[g] (20)	CH_2Cl_2	313	8	4	—	—	—	—
14	$ZrOCl_2\cdot 8H_2O$ (0.1)	—	373	6	2	97	58	3	6
15	$ZrOCl_2\cdot 8H_2O$ (1)	—	373	6	2	100	70	6	6
16	$ZrOCl_2\cdot 8H_2O$ (5)	—	373	6	2	100	80	6	5
17	$Zr(SO_4)_2\cdot 4H_2O$ (5)	—	373	6	2	70	30	1	16
18	$ZrOSO_4\cdot 4H_2O$ (5)	—	373	6	2	97	53	1	3
19	$ZrO(NO_3)_2\cdot 2H_2O$ (5)	—	373	6	2	99	30	1	11

[a] All the reactions were carried out using **1a** (0.147 g, 1 mmol).
[b] Determined by GC using an internal standard technique.
[c] DMAP: 4-dimethylamino-pyridine.
[d] DBN: 1,5-diazabicyclo(4,3,0)non-5-ene.
[e] DBU: 1,8-diazabicyclo[5,4,0]-undec-7-ene.
[f] DABCO: 1,4-diazabicyclo[2,2,2]octane.
[g] HMTA: hexamethyl phosphoric triamide.

Subsequently, the influence of the catalyst amount was evaluated by performing the reactions at 373 K and 6 MPa of CO_2 for 2 h. As shown in Table 1, **2a** yield was 58% when 0.1 mol % catalyst was used; and hereby increased to 70% as catalyst loading went to 1 mol % (entries 14, 15). Notably, further increasing the catalyst quantity to 5 mol %, the reaction gave quantitative conversion with 80% yield of **2a**, and 6% of **3a**, alongside with small amounts of 1,4-diethyl-2,5-diphenyl-piperazine **4a** and 1,4-diethyl-2,3-diphenyl-piperazine **5a** (entry 16). In other words, 2-oxazolidinone **2a** was formed in high chemo- and regio-selectivity by employing 5 mol % of $ZrOCl_2\cdot 8H_2O$ as a catalyst. It is worth mentioning that the by-products could be detected as oligomers of homopolymerization of aziridines and copolymerization aziridines/CO_2 as reported in the literature.[6i,j]

The commonly used zirconium (IV) compounds were also examined for this purpose. It was found that $Zr(SO_4)_2\cdot 4H_2O$, $ZrOSO_4\cdot 4H_2O$, and $ZrO(NO_3)_2\cdot 2H_2O$ displayed relatively low catalytic activity in comparison with $ZrOCl_2\cdot 8H_2O$ under the otherwise identical reaction conditions (entries 17–19). Those findings presumably imply that the coexistence of Lewis acidic sites, i.e., zirconium(IV) cation and Lewis basic species viz. chloride anion in zirconyl chloride would be crucial for promoting this reaction.[12a]

The influence of temperature was studied as shown in Figure 1. It was obvious that the catalytic activity and yield of **2a** were both sensitive to reaction temperature. The catalytic activity of $ZrOCl_2\cdot 8H_2O$ showed slight alteration from 293 K to 313 K, then increased sharply with the temperature increasing from 313 K to 373 K. However, a slight decrease of **2a** yield and increase of **3a** yield was found from 373 K to 413 K, probably due to that higher temperature could presumably accelerate the nucleophilic ring-opening reaction at the methylene position, as shown in the proposed mechanism (Scheme 3), thus leading to increasing in the amount of **3a**. Accordingly, the appropriate reaction temperature would be 373 K.

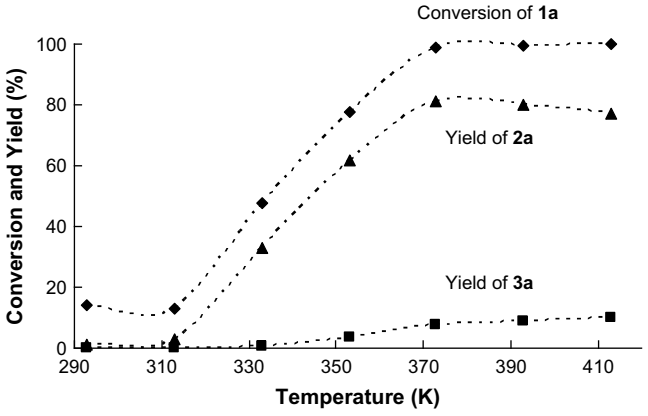


Figure 1. Influence of temperature on the reaction outcome. Reaction conditions: **1a** (1 mmol, 0.147 g), catalyst ($ZrOCl_2\cdot 8H_2O$, 0.0161 g, 5 mol %), 8 MPa, 4 h.

As well-known, a significant drawback associated with using CO_2 as a reagent or reaction medium in organic synthesis is the potential dangers associated with operating at high temperatures and pressures. As easily seen from Figure 2, pressure has great

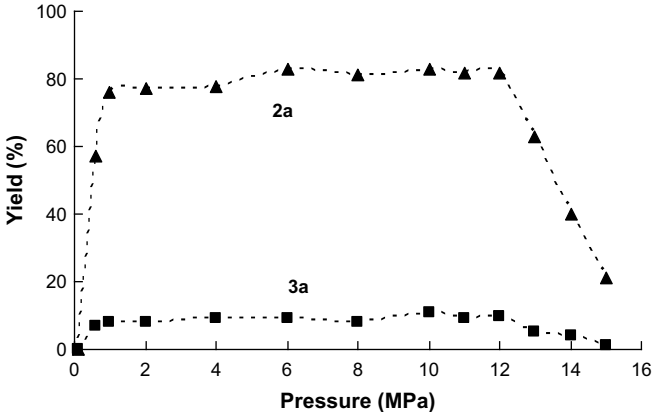


Figure 2. Yield versus CO_2 pressure. Reaction conditions: **1a** (1 mmol, 0.147 g), catalyst ($ZrOCl_2\cdot 8H_2O$, 0.0161 g, 5 mol %), 373 K, 4 h.

influence on the reaction outcome with variation of CO_2 pressure from 0.1 to 1 MPa. We are glad to find that the reaction performed smoothly at low pressures (1 MPa). Specifically, 57% yield of **2a** was obtained even at 0.6 MPa of CO_2. The **2a** yield was slightly changed from 1 to 12 MPa, but sharply decreased by further increasing in CO_2 pressure up to 15 MPa. Excessive CO_2 pressure may cause a low concentration of aziridine in the vicinity of the catalyst, thus resulting in a low reaction rate. On the other hand, too high CO_2 pressure may retard the interaction between the aziridine and the catalyst, whereby also cause a low yield of **2a**. Moreover, the phase behavior[6k,21] of the reaction visually inspected through a sapphire window attached to the autoclave revealed that the catalyst existed as a solid during the reaction.

Furthermore, the influence of reaction time on the reaction was also examined, and the results were shown in Figure 3. The reaction of **1a** was almost finished in 10 min. Indeed, 2 h is needed for the reaction to give the best yield of **2a**.

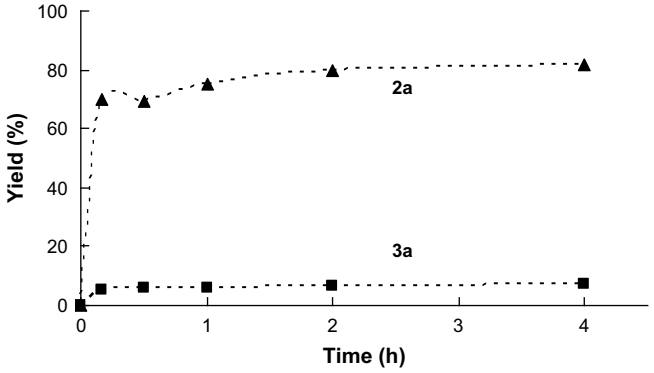


Figure 3. Dependence of the yield on reaction time. Reaction conditions: **1a** (1 mmol, 0.147 g), catalyst ($ZrOCl_2 \cdot 8H_2O$, 0.0161 g, 5 mol %), 373 K, 6 MPa.

Another advantage of this approach could be related to the heterogeneous catalytic process under solvent-free conditions. The catalyst can be easily recovered from the reaction mixture simply by filtration and reused for the next run after washing with CH_2Cl_2 and drying at 333 K. As shown in Table 2, the catalyst can be reused at least five times without significant loss in catalytic activity. Therefore, the recyclability of catalyst makes the process economically and potentially viable for commercial applications. Interestingly, the yield of **2a** for the fresh catalyst was much lower than that in the subsequent run (run 1 vs 2–5) under otherwise identical conditions.

Table 2
Recyclability of the catalyst[a]

Run	Conv. (%)	Yield (%)		
		2a	**3a**	**4a+5a**
1	>99	80	6	5
2	>99	94	1	4
3	>99	91	3	5
4	>99	89	4	5
5	>99	90	4	4

[a] Reaction conditions: **1a** (5 mmol, 0.735 g), $ZrOCl_2 \cdot 8H_2O$ (5 mol %, 0.0805 g), the recovered zirconyl chloride (5 mol %, 0.0445 g), 373 K, 6 MPa, 2 h.

In order to well understanding the present catalysis, both fresh catalyst and recovered catalyst were characterized using XRD, IR, and pyridine adsorption IR. The XRD patterns of the samples are shown in the 2θ of 3°–80° region (Fig. 4). The fresh catalyst was found to be a mixture of $ZrOCl_2 \cdot 8H_2O$ and $ZrOCl_2 \cdot 4H_2O$, being in good agreement with standard spectra, revealing slight loss of water content of $ZrOCl_2 \cdot 8H_2O$. The XRD pattern also shows the recovered zirconyl chloride could be a typical amorphous material.

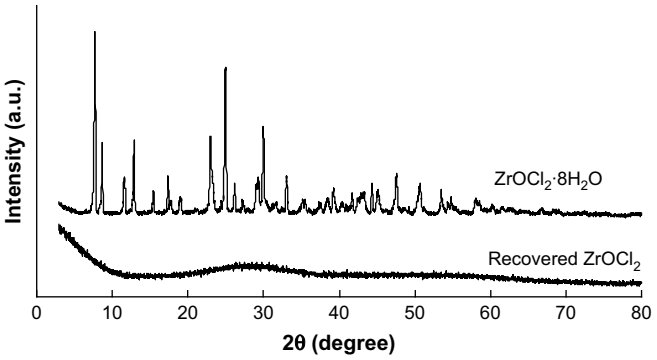


Figure 4. XRD patterns of the catalysts (fresh catalyst and the recovered zirconyl chloride).

The FTIR spectra were recorded between 400 cm^{-1} and 4000 cm^{-1} (Fig. 5). The peaks at 1640 and 574 cm^{-1} are ascribed to typical absorption of $ZrOCl_2 \cdot 8H_2O$. However, the peak shifts (from 1640 to 1510 cm^{-1}, from 574 to 492 cm^{-1}) and the new peaks (1084 and 700 cm^{-1}) were found in the IR of the recovered zirconyl chloride as an indication of Zr coordinating with aziridine. In the region of 3000–3500 cm^{-1}, the broad adsorption was observed at ca. 3400 cm^{-1} for both fresh catalyst and the recovered zirconyl chloride.

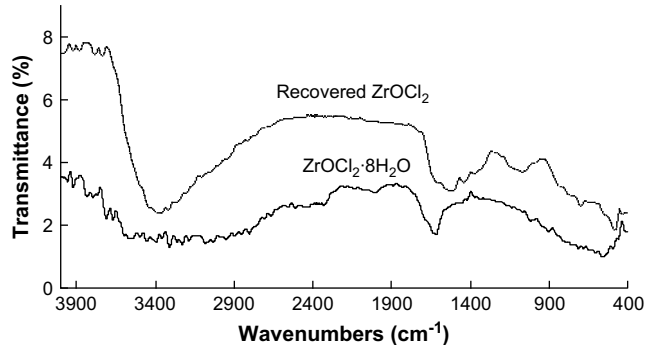


Figure 5. FTIR spectrum of fresh catalyst and the recovered zirconyl chloride.

Pyridine is a useful basic probe molecule to distinguish the acidic nature and the number of acidic sites. Figure 6 shows the IR spectra of fresh catalyst and the recovered zirconyl chloride after Py adsorption. Upon adding pyridine to the fresh catalyst, the band of 1403–1484 cm^{-1} was observed, which generally is regarded as an indication[22] of Lewis acidic sites.

However, there is scarcely any peak near 1535–1550 cm^{-1}, showing the absence of Brønsted acid sites. By contrast, the amount[23] of Lewis acidic sites (1411–1484 cm^{-1}) for the recovered

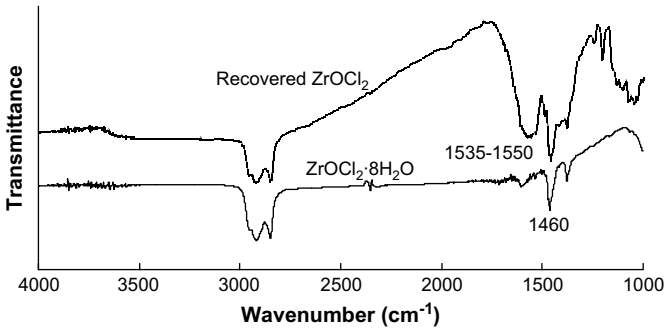
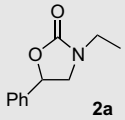
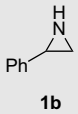
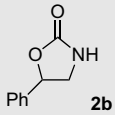
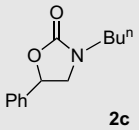
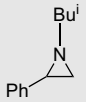
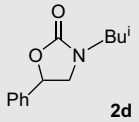
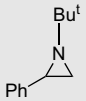
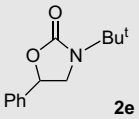
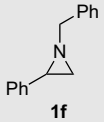
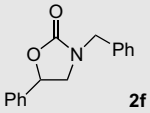
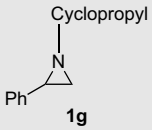
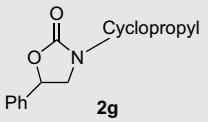
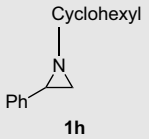
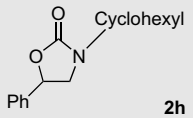
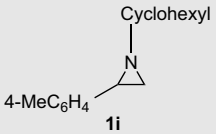
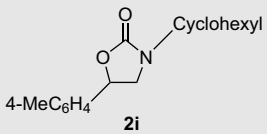
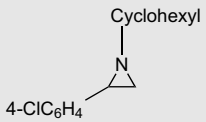
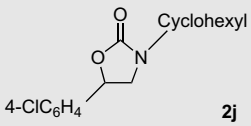
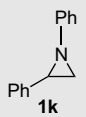
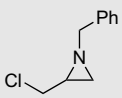
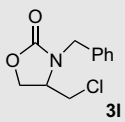


Figure 6. FTIR spectra of fresh catalyst and the recovered zirconyl chloride after pyridine adsorption.

Table 3
Cycloaddition reaction of CO_2 to aziridines[a]

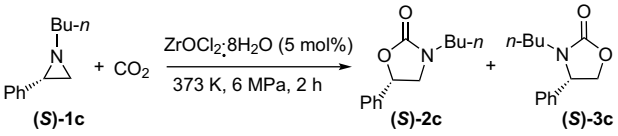
Entry	Substrate	Major product	Time (h)	Conv. (%)[a]	Yield[b] (%)	Regioselectivity[c] (%)
1	 **1a**	 **2a**	2	99	86	93:7
2	 **1b**	 **2b**	1	100	59	92:8
3	 **1c**	 **2c**	2	99	93	92:8
4[d]	 **1d**	 **2d**	2.5	97	92	93:7
5	 **1e**	 **2e**	19	91	71	99:1
6	 **1f**	 **2f**	2	98	97	93:7
7[e]	 **1g**	 **2g**	3	100	89	87:13
8	 **1h**	 **2h**	3	98	97	99:1
9	 **1i**	 **2i**	2	98	97	98:2
10	 **1j**	 **2j**	2	53	52	96:4
11	 **1k**	—[f]	24	100	—	—
12	 **1l**	 **3l**	2	99	97	3:97

[a] Reaction conditions: **1** (2 mmol), catalyst ($ZrOCl_2 \cdot 8H_2O$, 5 mol%), 6 MPa, 373 K. The conversions were determined by GC.
[b] The total yield of (**2**+**3**).
[c] Molar ratio of **2** to **3**.
[d] The isolated yield of (**2d**+**3d**) is 89%.
[e] The isolated yield of (**2g**+**3g**) is 85%.
[f] 1,2,4,5-Tetraphenylpiperazine and 1,2,3,4-tetraphenylpiperazine were detected by LC–MS.

zirconyl chloride could be 2.8 times of fresh catalyst. On the other hand, the amount of Brønsted acid sites (1535–1550 cm^{-1})[22] also increases for the recovered zirconyl chloride compared with fresh catalyst. A possible explanation may be that amorphous state enlarges the surface area[24] in the case of the recovered zirconyl chloride. Indeed, the recovered catalyst showed higher activity in comparison with the fresh catalyst (Table 2, run 1 vs 2–5).

The generality and utility of this approach with a variety of aziridines (**1a**–**l**) were evaluated under the identical reaction conditions. As shown in Table 3, a wide set of oxazolidinones were selectively formed in good yields. Especially, aziridines (**1a**, **1c**) bearing alkyl groups at the nitrogen atom proceeded smoothly (entries 1, 3). The 2-phenylaziridine **1b** (R^1=H) displayed a relatively low chemoselectivity probably due to the formation of self-oligomers detected by GC–MS (entry 2). Increasing steric hindrance of *N*-substituted group R^1 led to a lower activity (entries 3–5), and a longer time is required to obtain the satisfactory result (entry 5). In this study, the regioselectivity can be also enhanced from 87:13 (**2**/**3**) to 99:1 (entries 1–8) with variation of alkyl substituent at the nitrogen atom. On the other hand, an electron-donating group on benzene ring showed higher activity than an electron-withdrawing group (entry 9 vs 10). However, 1,2,4,5-tetraphenylpiperazine and 1,2,3,4-tetraphenylpiperazine were obtained when both R^1 and R^2 are phenyl group (entry 11). Concerning regioselectivity, R^2 group is a crucial factor in dominating the selectivity of the reaction.[6f] If R^2 is an aryl group, producing **2** is favored (entries 1–10); whereas if R^2 is an alkyl group, the main product is **3**. Indeed, the 4-substituted oxazolidinone **3l** was preferentially produced in a molar ratio of 3:97 (**2l** to **3l**) when R^2 at the carbon atom is an alkyl group (entry 12), which would be explained by the proposed reaction mechanism as outlined in Scheme 3.

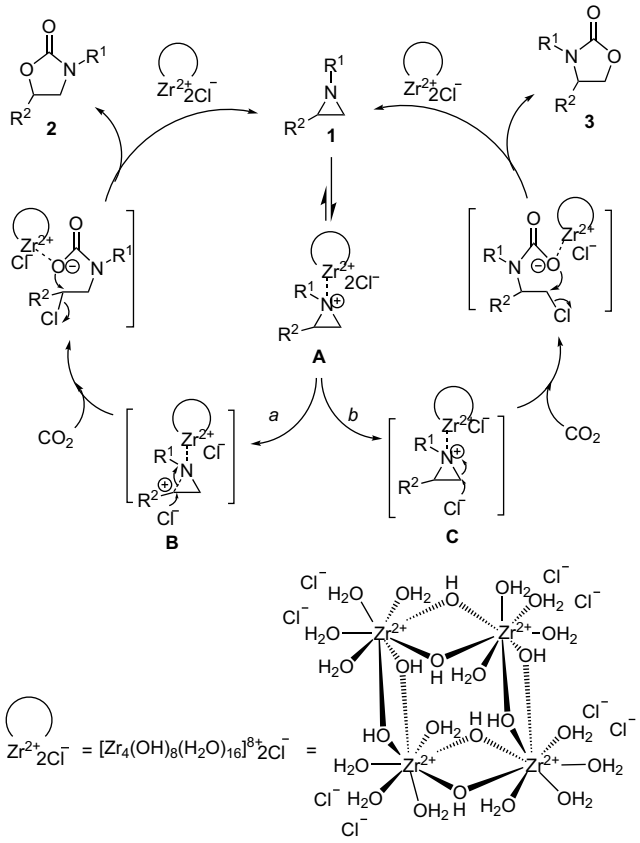
Moreover, the reaction of a chiral aziridine (*S*)-**1c** with CO_2 catalyzed by 5 mol % of $ZrOCl_2 \cdot 8H_2O$ (Scheme 2) gave the desired products, i.e., (*S*)-**2c** and (*S*)-**3c** with retention of stereochemistry.[25]



Scheme 2. Carboxylation of (*S*)-**1c** into oxazolidinones.

Based on the above results, a plausible mechanism is proposed to go through a Lewis acid-base bifunctional pathway, as depicted in Scheme 3.

Cationic cluster $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ in the crystal[26] of zirconyl chloride has a strong coordinating ability toward aziridines, and whereby generates an intermediate **A** through a ligand exchange process.[12b] Accordingly, the present catalytic cycle includes a Zr-promoted ring-opening of the aziridine through two different pathways (a and b) mainly depending on the nature of R^2 group when alkyl substitution at the N-position, following by CO_2 insertion, and subsequent cyclization via an intramolecular nucleophilic attack leading to oxazolidinones and regeneration of the catalyst. This proposed mechanism could also account for effect of the R^2 substituent on the selective formation of **2** or **3**. As deduced from Scheme 3, if R^2 is an aryl group, the intermediate **B** would be more stable than **C**, and thus **2** would be predominantly formed; in contrast, if R^2 is an alkyl group, **C** would be favored, which in turn results in dominantly producing **3**. Notably, the stereochemistry for this reaction (Scheme 2) could also support the above mechanism (Scheme 3); where there is a double inversion of stereochemistry at the chiral carbon center, which is attacked, to produce (*S*)-**2c** or the reaction does not involve the chiral carbon center to generate (*S*)-**3c**.



Scheme 3. A plausible reaction mechanism.

3. Conclusions

We developed an efficient, simple, and environmentally friendly process for the synthesis of 5-aryl-2-oxazolidinones by using zirconyl chloride as a solid catalyst from aziridines and CO_2 without any solvent and additive. Furthermore, the catalyst could be easily separated by filtration and reused for at least five times. The protocol presented herein offers salient advantages and features: (1) it requires no organic solvent; (2) the catalyst is very effective under mild conditions; (3) the catalyst is moisture stable, cheap and low toxic, easily handling, and readily available reagent; (4) excellent yields, regio-, and stereoselectivities toward the target products were attained; (5) simple workup procedure; (6) the utility of this method was proven as evidenced from synthesizing various 5-aryl-2-oxazolidinones.

4. Experimental

4.1. Caution

Experiments using compressed gases CO_2 are potentially hazardous and must only be carried out by using the appropriate equipment and under rigorous safety precautions.

4.2. Materials

Aziridines were synthesized according to the published procedures.[27] Carbon dioxide with a purity of 99.99% was commercially available. The other organic and inorganic compounds from Tianjin Guangfu Fine Chemical Research Institute were used without further purification except for the solvents, which were distilled by the known method prior to use.

4.3. Characterization

The X-ray diffraction was measured at room temperature using a Rigaku D/max-2500 powder diffractometer, with Cu Kα radiation (40 kV, 100 mA). The powder samples were mounted on a silicon plate for X-ray measurement. Pore size distributions, BET surface areas, and pore volumes were measured by nitrogen adsorption/desorption using a BELSORP-mini gas sorption analyzer (BEL Japan, INC). FTIR measurements were performed on a Bruker EQUINOX 55 FTIR instrument. Potassium bromide pellets containing 0.5% of the catalyst were used in FTIR experiments and 32 scans were accumulated for each spectrum in transmission, at a spectral resolution of 4 cm^{-1}. The spectrum of dry KBr was taken for background subtraction. Pyridine adsorption–desorption was monitored by infrared spectroscopy. Self-supported wafers of 20 mg and 16 mm diameter were evacuated in situ in an infrared glass vacuum cell equipped with calcium fluoride windows. The samples were degassed under high vacuum steady state at 200 °C for 1.5 h. Pyridine adsorption IR spectra were recorded after pyridine adsorption at room temperature. Pyridine was then desorbed at 200 °C in dynamic vacuum and spectra were recorded on a Bruker Vector 22 (IR-FT) spectrometer.

The products were analyzed by a gas chromatograph (Shimadzu 2014 chromatographer) equipped with a capillary column (RTX-5, 30 m×0.25 μm) using a flame ionization detector, and were further identified by NMR (Bruker 300 or Varian Mercury-Plus 400 spectrometer) and ESI-MS (spray voltage 4.8 KV). High-resolution mass spectrometry was conducted using an Ionspec 7.0T spectrometer by ESI-FTICR technique. Melting points were measured on an X4 apparatus and uncorrected. The characterization data (^{1}H NMR, ^{13}C NMR, and ESI-MS) and physical properties are reported below.

4.4. General procedure for the $ZrOCl_2\cdot 8H_2O$-catalyzed cycloaddition reaction of CO_2 with aziridines

In a 25 mL autoclave reactor equipped with a magnetic stirrer, aziridine (1 mmol), catalyst ($ZrOCl_2\cdot 8H_2O$, 16.1 mg, 0.05 mmol), and biphenyl (50 mg, an internal standard for GC analysis) were charged. Then CO_2 was introduced into the autoclave. The pressure was adjusted to 6 MPa at 373 K, and the mixture was stirred for 2 h. After the reaction was completed, the reactor was cooled in ice-water and CO_2 was ejected slowly. An aliquot of sample was taken from the resultant mixture 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 provide the desired products. The products were further identified by NMR and MS as below, being in good agreement with the assigned structures and consistent with those reported in the literature[6a,28] for known compounds. The NMR charts for the products and the XRD patterns for fresh $ZrOCl_2\cdot 8H_2O$ and the recovered zirconyl chloride were given in Supplementary data.

4.5. Characterization data

*4.5.1. 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; ESI-MS calcd for $C_{11}H_{13}NO_2$ 191.09, found 192.29 $(M+H)^+$, 214.38 $(M+Na)^+$, 405.01 $(2M+Na)^+$. HRMS calcd for $C_{11}H_{13}NO_2$ $(M+H)^+$ 192.1019, found 192.1015.

*4.5.2. 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; ESI-MS calcd for $C_{11}H_{13}NO_2$ 191.09, found 192.29 $(M+H)^+$, 214.38 $(M+Na)^+$, 405.01 $(2M+Na)^+$. HRMS calcd for $C_{11}H_{13}NO_2$ $(M+H)^+$ 192.1019, found 192.1015.

*4.5.3. 5-Phenyloxazolidin-2-one (**2b**)*

White crystals, mp 85–86 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.55 (t, ^3J=8.4 Hz, 1H), 3.99 (t, ^3J=8.4 Hz, 1H), 5.62 (t, ^3J=8.4 Hz, 1H), 6.08 (br s, 1H), 7.35–7.43 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 48.2, 77.8, 125.6, 128.9, 138.4, 160.1; ESI-MS calcd for $C_9H_9NO_2$ 163.06, found 164.18 $(M+H)^+$, 186.28 $(M+Na)^+$, 349.03 $(2M+Na)^+$.

*4.5.4. 3-Butyl-5-phenyloxazolidin-2-one (**2c**)*

Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, ^3J=7.2 Hz, 3H), 1.31–1.40 (m, 2H), 1.51–1.58 (m, 2H), 3.23–3.38 (m, 2H), 3.43 (t, ^3J=8.0 Hz, 1H), 3.92 (t, ^3J=8.8 Hz, 1H), 5.49 (t, ^3J=8.0 Hz, 1H), 7.28–7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 19.5, 29.1, 43.6, 51.8, 74.1, 125.2, 128.4, 128.5, 138.7, 157.7; ESI-MS calcd for $C_{13}H_{17}NO_2$ 219.13, found 220.34 $(M+H)^+$, 259.48 $(M+K)^+$, 461.05 $(2M+Na)^+$.

*4.5.5. 3-Isobutyl-5-phenyloxazolidin-2-one (**2d**)*

White crystals, mp 38–42 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (d, ^3J=4.8 Hz, 3H), 0.93 (d, ^3J=4.8 Hz, 3H), 1.81–1.95 (m, 1H), 3.02–3.16 (m, 2H), 3.42 (dd, ^2J=8.7 Hz, ^3J=7.5 Hz, 1H), 3.91 (t, ^3J=8.7 Hz, 1H), 5.48 (t, ^3J=8.4 Hz, 1H), 7.32–7.41 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.7, 19.8, 26.7, 51.6, 52.6, 74.1, 125.3, 128.5, 128.7, 138.8, 158.0; ESI-MS calcd for $C_{13}H_{17}NO_2$ 219.13, found 461.22 $(2M+Na)^+$, 679.70 $(3M+Na)^+$. HRMS calcd for $C_{13}H_{17}NO_2$ $(M+H)^+$ 220.1332, found 220.1339.

*4.5.6. 3-tert-Butyl-5-phenyloxazolidin-2-one (**2e**)*

Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (s, 9H), 3.45 (t, ^3J=8.4 Hz, 1H), 3.95 (t, ^3J=8.7 Hz, 1H), 5.36 (t, ^3J=8.1 Hz, 1H), 7.32–7.41 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.3, 50.9, 53.5, 73.4, 125.4, 128.5, 128.7, 138.9, 156.6; ESI-MS calcd for $C_{13}H_{17}NO_2$ 219.13, found 242.46 $(M+Na)^+$, 259.30 $(M+K)^+$.

*4.5.7. 3-Benzyl-5-phenyloxazolidin-2-one (**2f**)*

White crystals, mp 60–64 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.28 (t, ^3J=8.4 Hz, 1H), 3.75 (t, ^3J=8.7 Hz, 1H), 4.45 (ABq, J_{AB}=15.0 Hz, $\Delta\nu_{AB}$=36.0 Hz, 2H), 5.43 (t, ^3J=8.1 Hz, 1H), 7.27–7.35 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 48.1, 51.3, 74.3, 125.3, 127.8, 127.9, 128.6, 128.7, 135.5, 138.5, 157.8; ESI-MS calcd for $C_{16}H_{15}NO_2$ 253.11, found 276.44 $(M+Na)^+$, 781.66 $(3M+Na)^+$.

*4.5.8. 3-Cyclopropyl-5-phenyloxazolidin-2-one (**2g**)*

White crystals, mp 52–55 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.75 (s, 4H), 2.55–2.59 (m, 1H), 3.43 (t, ^3J=8.1 Hz, 1H), 3.88 (t, ^3J=8.7 Hz, 1H), 5.42 (t, ^3J=8.1 Hz, 1H), 7.28–7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 5.4, 5.8, 25.7, 53.3, 74.3, 125.4, 128.6, 128.7, 138.5, 157.9; ESI-MS calcd for $C_{12}H_{13}NO_2$ 203.09, found 429.27 $(2M+Na)^+$, 631.80 $(3M+Na)^+$.

*4.5.9. 3-Cyclohexyl-5-phenyloxazolidin-2-one (**2h**)*

White crystals, mp 92–93 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.0–1.8 (m, 10H), 3.38 (t, ^3J=8.4 Hz, 1H), 3.70–3.73 (m, 1H), 3.88 (t, ^3J=8.7 Hz, 1H), 5.45 (t, ^3J=8.4 Hz, 1H), 7.35–7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.1, 25.2, 29.9, 30.3, 48.1, 52.4, 74.4, 125.3, 128.5, 128.7, 138.9, 157.0; ESI-MS calcd for $C_{15}H_{19}NO_2$ 245.14, found 246.27 $(M+H)^+$, 757.70 $(3M+Na)^+$.

*4.5.10. 3-Cyclohexyl-5-p-tolyloxazolidin-2-one (**2i**)*

White crystals, mp 89–91 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03–1.86 (m, 10H), 2.36 (s, 3H), 3.38 (t, ^3J=8.0 Hz, 1H), 3.71–3.75 (m, 1H), 3.85 (t, ^3J=8.7 Hz, 1H), 5.43 (t, ^3J=8.0 Hz, 1H), 7.17–7.26 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 25.2, 25.3, 25.4, 30.1, 30.5, 48.3, 52.5,

74.5, 125.5, 129.5, 136.0, 138.6, 157.3; ESI-MS calcd for $C_{16}H_{21}NO_2$ 259.16, found 260.02 $(M+H)^+$, 799.55 $(3M+Na)^+$. HRMS calcd for $C_{16}H_{21}NO_2$ $(M+H)^+$ 260.1645, found 260.1652.

4.5.11. 5-(4-Chlorophenyl)-3-cyclohexyloxazolidin-2-one (**2j**)

White crystals, mp 94–96 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 1.05–1.83 (m, 10H), 3.34 (t, ^3J=8.0 Hz, 1H), 3.69–3.76 (m, 1H), 3.89 (t, ^3J=8.7 Hz, 1H), 5.44 (t, ^3J=8.0 Hz, 1H), 7.27–7.38 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.2, 25.3, 30.0, 30.4, 48.2, 52.6, 73.8, 126.8, 129.0, 134.5, 137.6, 156.8; APCI-MS calcd for $C_{15}H_{18}ClNO_2$ 279.10, found 839.62 $(3M+H)^+$, 859.60 $(3M+Na)^+$. HRMS calcd for $C_{15}H_{18}ClNO_2$ $(M+H)^+$ 280.1099, found 280.1101.

4.5.12. 3-Benzyl-4-(cholomethyl)oxazolidin-2-one (**3l**)

Colorless liquid. ^1H NMR (300 MHz, $CDCl_3$) δ 3.52 (d, 2H), 3.86–3.94 (m, 1H), 4.17 (d, ^2J=15.3 Hz, 1H), 4.24 (t, ^3J=8.9 Hz, 1H), 4.23 (q, ^3J=9.0 Hz, ^3J=5.3 Hz, 1H), 4.82 (d, ^2J=15.3 Hz, 1H), 7.29–7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.4, 46.5, 54.8, 65.3, 128.1, 128.3, 129.0, 135.5, 158.0; ESI-MS calcd for $C_{11}H_{12}NO_2Cl$ 225.67, found 472.90 $(2M+Na)^+$. HRMS calcd for $C_{11}H_{12}NO_2Cl$ $(M+Na)^+$ 248.0449, found 248.0454.

4.5.13. 1,4-Diethyl-2,5-diphenyl-piperazine (**4a**)

White crystals, mp 116–119 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, ^3J=7.2 Hz, 6H), 1.99–2.05 (m, 2H), 2.30 (t, ^3J=10.8 Hz, 2H), 2.54–2.62 (m, 2H), 3.08 (dd, ^2J=11.6 Hz, ^3J=2.4 Hz, 2H), 3.45 (dd, ^3J=2.0 Hz, ^2J=12.0 Hz, 2H), 7.29–7.43 (m, 10H); LC–MS calcd for $C_{20}H_{26}N_2$ 294.21, found 295.35 $(M+H)^+$. HRMS calcd for $C_{20}H_{26}N_2$ $(M+H)^+$ 295.2169, found 295.2164.

4.5.14. 1,4-Diethyl-2,3-diphenyl-piperazine (**5a**)

Colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, ^3J=7.2 Hz, 6H), 2.17–2.26 (m, 2H), 2.33–2.26 (m, 2H), 2.65–2.69 (m, 2H), 2.95–2.99 (q, ^3J=6.0 Hz, 2H), 3.73 (s, 2H), 7.27–7.38 (m, 6H), 7.69–7.71 (d, ^3J=7.2 Hz, 4H); LC–MS calcd for $C_{20}H_{26}N_2$ 294.21, found 295.31 $(M+H)^+$. HRMS calcd for $C_{20}H_{26}N_2$ $(M+H)^+$ 295.2169, found 295.2167.

Acknowledgements

Financial support from the National Natural Science Foundation of China (Grant Nos. 20421202, 20672054, and 20872073) and the 111 project (B06005) and Tianjin Natural Science Foundation is gratefully acknowledged. We also thank the reviewers for their valuable suggestions regarding revision.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.05.034.

References and notes

1. As representative examples see: (a) Barbachyn, M. R.; Ford, C. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 2010–2023; (b) Colca, J. R.; McDonald, W. G.; Waldon, D. J.; Thomasco, L. M.; Gadwood, R. C.; Lund, E. T.; Cavey, G. S.; Mathews, W. R.; Adams, L. D.; Cecil, E. T.; Pearson, J. D.; Bock, J. H.; Mott, J. E.; Shinabarger, D. L.; Xiong, L.; Mankin, A. S. *J. Biol. Chem.* **2003**, *278*, 21972–21979; (c) Hoellman, D. B.; Lin, G.; Ednie, L. M.; Rattan, A.; Jacobs, M. R.; Appelbaum, P. C. *Antimicrob. Agents Chemother.* **2003**, *47*, 1148–1150; (d) Rubinstein, E.; Isturiz, R.; Standiford, H. C.; Smith, L. G.; Oliphant, T. H.; Cammarata, S.; Hafkin, B.; Le, V.; Remington, J. *Antimicrob. Agents Chemother.* **2003**, *47*, 1824–1831; (e) Fluit, A. C.; Schmitz, F. J.; Verhoef, J.; Milatovic, D. *J. Antimicrob. Chemother.* **2002**, *50*, 271–276.
2. As representative examples using oxazolidinones as chiral auxiliaries, see: (a) Prashad, M.; Liu, Y. G.; Kim, H. Y.; Repic, O.; Blacklock, T. J. *Tetrahedron: Asymmetry* **1999**, *10*, 3479–3482; (b) Gawley, R. E.; Campagna, S. A.; Santiago, M.; Ren, T. *Tetrahedron: Asymmetry* **2002**, *13*, 29–36; (c) Phoon, C. W.; Abell, C. *Tetrahedron Lett.* **1998**, *39*, 2655–2658.
3. As representative examples using oxazolidinones as intermediates, see: (a) Makhtar, T. M.; Wright, G. D. *Chem. Rev.* **2005**, *105*, 529–542; (b) Aurelio, L.; Brownlee, R. T. C.; Hughus, A. B. *Chem. Rev.* **2004**, *104*, 5823–5846; (c) Shi, Z. D.; Liu, H. P.; Zhang, M. C.; Yang, D. J.; Burke, T. R., Jr. *Synth. Commun.* **2004**, *34*, 3883–3889; (d) Andreou, T.; Costa, A. M.; Esteban, L.; Gonzalez, L.; Mas, G.; Vilarrasa, J. *Org. Lett.* **2005**, *7*, 4083–4086; (e) Watson, R. J.; Batty, D.; Baxter, A. D.; Hannah, D. R.; Owen, D. A.; Montana, J. G. *Tetrahedron Lett.* **2002**, *43*, 683–685.
4. (a) Ben-Ishai, D. *J. Am. Chem. Soc.* **1956**, *78*, 4962–4965; (b) Vo, L.; Ciula, J.; Gooding, O. W. *Org. Process Res. Dev.* **2003**, *7*, 514–520; (c) Close, W. J. *J. Am. Chem. Soc.* **1951**, *73*, 95–98; (d) Lynn, J. W. U.S. Patent 2,975,187, 1961; (e) Steele, A. B. U.S. Patent 2,868,801, 1959; (f) Yoshida, T.; Kambe, N.; Ogawa, A.; Sonoda, N. *Phosphorus Sulfur Silicon Relat. Elem.* **1988**, *38*, 137–148.
5. (a) Costa, M.; Chiusoli, G. P.; Rizzardi, M. *Chem. Commun.* **1996**, 1699–1700; (b) Shi, M.; Shen, Y. M. *J. Org. Chem.* **2002**, *67*, 16–21; (c) Feroci, M.; Orsini, M.; Sotgiu, G.; Rossi, L.; Inesi, A. *J. Org. Chem.* **2005**, *70*, 7795–7798; (d) Gu, Y. L.; Zhang, Q. H.; Duan, Z. Y.; Zhang, J.; Zhang, S. G.; Deng, Y. Q. *J. Org. Chem.* **2005**, *70*, 7376–7380.
6. The cycloaddition of CO_2 and aziridines to give oxazolidinones, see: (a) Miller, A. W.; Nguyen, S. T. *Org. Lett.* **2004**, *6*, 2301–2304; (b) Shen, Y. M.; Duan, W. L.; Shi, M. *Eur. J. Org. Chem.* **2004**, *14*, 3080–3089; (c) Hancock, M. T.; Pinhas, A. R. *Tetrahedron Lett.* **2003**, *44*, 5457–5460; (d) Sudo, A.; Morioka, Y.; Sanda, F.; Endo, T. *Tetrahedron Lett.* **2004**, *45*, 1363–1365; (e) Sudo, A.; Morioka, Y.; Koizumi, E.; Sanda, F.; Endo, T. *Tetrahedron Lett.* **2003**, *44*, 7889–7891; (f) Kawanami, H.; Ikushima, Y. *Tetrahedron Lett.* **2002**, *43*, 3841–3844; (g) Kawanami, H.; Matsumoto, H.; Ikushima, Y. *Chem. Lett.* **2005**, *34*, 60–61; (h) Tascedda, P.; Dunach, E. *Chem. Commun.* **2000**, 449–450; (i) Ihata, O.; Kayaki, Y.; Ikariya, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 717–719; (j) Ihata, O.; Kayaki, Y. *Macromolecules* **2005**, *38*, 6429–6434; (k) Du, Y.; Wu, Y.; Liu, A. H.; He, L. N. *J. Org. Chem.* **2008**, *73*, 4709–4712.
7. (a) Shen, Y. M.; Duan, W. L.; Shi, M. *J. Org. Chem.* **2003**, *68*, 1559–1562; (b) Shi, M.; Shen, Y. M. *Curr. Org. Chem.* **2003**, *7*, 737–745.
8. Farnworth, F.; Jones, S. L.; McAlpine, I. *Speciality Inorganic Chemicals Special Publication No. 40*; Royal Society of Chemistry: London, 1980.
9. Shirini, F.; Zolfigol, M. A.; Mollarazi, E. *Synth. Commun.* **2005**, *35*, 1541–1545.
10. Shi, M.; Cui, S. C.; Yin, W. P. *Eur. J. Org. Chem.* **2005**, *11*, 2379–2384.
11. Ghosh, R.; Maiti, S.; Chakraborty, A. *Tetrahedron Lett.* **2005**, *46*, 147–151.
12. (a) Mantri, K.; Komura, K.; Sugi, Y. *Green Chem.* **2005**, *7*, 677–782; (b) Nakayama, M.; Sato, A.; Ishihara, K.; Yamamoto, H. *Adv. Synth. Catal.* **2004**, *346*, 1275–1279; (c) Sun, H. B.; Hua, R. M.; Yin, Y. W. *Molecules* **2006**, *11*, 263–271.
13. Firouzabadi, H.; Iranpoor, N.; Jafarpour, M.; Ghaderi, A. J. *Mol. Catal. A: Chem.* **2006**, *252*, 150–155.
14. Rodriguez-Dominguez, J. C.; Bernardi, D.; Kirsch, G. *Tetrahedron Lett.* **2007**, *48*, 5777–5780.
15. Eftekhari-Sis, B.; Abdollahifar, A.; Hashemi, M. M.; Zirak, M. *Eur. J. Org. Chem.* **2006**, *22*, 5152–5157.
16. (a) Moghaddam, F. M.; Ismaili, H.; Bardajee, G. R. *Heteroat. Chem.* **2006**, *17*, 136–141; (b) Mohammad poor-Baltork, I.; Khosropour, A. R.; Hojati, S. F. *Catal. Commun.* **2007**, *8*, 200–204; (c) Mohammadpoor-Baltork, I.; Khosropour, A. R.; Hojati, S. F. *Catal. Commun.* **2007**, *8*, 1865–1870; (d) Zhang, Z. H.; Yin, L.; Wang, Y. M. *Catal. Commun.* **2007**, *8*, 1126–1131.
17. Ghosh, R.; Maiti, S.; Chakraborty, A.; Chakraborty, S.; Mukherjee, A. K. *Tetrahedron* **2006**, *62*, 4059–4064.
18. Zhang, Z. H.; Li, T. S.; Li, J. J. *Catal. Commun.* **2007**, *8*, 1615–1620.
19. Bhagat, S.; Chakraborti, A. K. *J. Org. Chem.* **2008**, *73*, 6029–6032.
20. Shen, W.; Wang, L. M.; Feng, J. J.; Tian, H. *Tetrahedron Lett.* **2008**, *49*, 4047–4049.
21. Xie, Y.; Zhang, Z. F.; Jiang, T.; He, J. L.; Han, B. X.; Wu, T. B.; Ding, K. L. *Angew. Chem. Int. Ed.* **2007**, *46*, 7255–7258.
22. (a) Benaliouche, F.; Boucheffa, Y.; Ayrault, P.; Mignard, S.; Magnoux, P. *Micropor. Mesopor. Mat.* **2008**, *111*, 80–88; (b) Oliveira, A. C.; Essayem, N.; Tuel, A.; Clacens, J.-M.; Taarit, Y. B. J. *Mol. Catal. A: Chem.* **2008**, *293*, 31–38.
23. The amount of Lewis acid sites is defined as the corresponding peak area divided by the sample weight.
24. Based on the BET measurement, pore channel was not found in the fresh catalyst; while the recovered one could show a small pore structure with the surface area of 3 $m^2 g^{-1}$), pore volume of 0.0368 $cm^3 g^{-1}$), and average pore diameter (24.79 nm), being well agreement with the results of catalytic activity.
25. (*S*) -**1c** was synthesized according to a literature procedure: Calet, S.; Urso, F.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 931–934 The reaction of (*S*)-**1c** with CO_2 in the presence of 5 mol % catalyst affords (*S*)-**2c** in 99.8% ee with 86% yield and (*S*)-**3c** in 99.9% ee with 7% yield.
26. The zirconyl group consists of a complex cation in which four zirconium atoms are at the corners of a slightly distorted square, and are linked along each edge of the square by two OH groups. Each zirconium is bound to four water molecules. There are no zirconium–halogen bonds in this structure. Clearfield, A.; Vaughan, P. A. *Acta Crystallogr.* **1956**, *9*, 555–558.
27. (a) Capriati, V.; Florio, S.; Luisi, R.; Musio, B. *Org. Lett.* **2005**, *7*, 3749–3752; (b) Chakraborti, A. K.; Rudrawar, S.; Kondaskar, A. *Eur. J. Org. Chem.* **2004**, *17*, 3597–3600; (c) Chamchaang, W.; Pinhas, A. R. *J. Org. Chem.* **1990**, *55*, 2531–2533; (d) Calet, S.; Urso, F.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 931–934.
28. (a) Bergmann, E. D.; Goldschomidt, Z. *J. Med. Chem.* **1968**, *11*, 1121–1125; (b) Herweh, J. E. *J. Org. Chem.* **1968**, *33*, 4029–4033; (c) Das, J. *Synth. Commun.* **1988**, *18*, 907–915; (d) Orito, K.; Miyazawa, M.; Nakamura, T.; Horibata, A.; Ushito, H.; Nagasaki, H.; Yuguchi, M.; Yamashitan, S.; Yamazaki, T.; Tokuda, M. *J. Org. Chem.* **2006**, *71*, 5951–5958.