

Chemical Fixation of Carbon Dioxide Co-Catalyzed by a Combination of Schiff Bases or Phenols and Organic Bases

Yu-Mei Shen,^[a] Wei-Liang Duan,^[b] and Min Shi*^[a]

Keywords: Aziridines / Carbon dioxide fixation / Epoxides / Schiff bases

Binaphthyldiamino, ethyldiamino and cyclohexyldiamino Schiff bases can catalyze the reaction of epoxides with carbon dioxide in the presence of catalytic amounts of various organic bases to give the corresponding cyclic carbonates in high yields. The simplest binaphthyldiamino Schiff base, derived from the reaction of binaphthyldiamine with salicylaldehyde, gave the highest yield of cyclic carbonate. This catalytic system can be further simplified by use of a phenol in-

stead of the Schiff base to give the corresponding cyclic carbonates in high yields as well. Mechanistic insights were obtained based on a deuterium labeling experiment. The reaction of aziridines with CO₂ and epoxide with CS₂ were also examined under the same reaction conditions.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

Carbon dioxide is the earth's most abundant carbon resource and is used by green plants and anaerobic bacteria for chemical production on a massive scale. In contrast, man's industrial and laboratory utilization of carbon dioxide as a chemical feedstock is extremely small. During the last two decades of the twentieth century, the chemical fixation of carbon dioxide received much attention from the viewpoint of carbon resources and environmental problems.^[1] In particular, the fixation of carbon dioxide by transition metal catalysts has seen significant progress.^[2–4] One of the major successes is the utilization of epoxides and carbon dioxide as the starting materials to prepare the corresponding five-membered cyclic carbonate in the presence of a transition metal catalyst.^[5,6] For example, De Pasquale has reported a number of coordinatively unsaturated nickel(0) complexes, such as Ni(PPh₃)₂ and Ni(PCy₃)₂, that are excellent catalysts for this reaction.^[7a,7b] Copper, tin and tantalum systems also catalyze this reaction.^[7c,7d] Kisch has developed a catalyst system which can be applied at room temperature and under normal pressure.^[8] Vinyl ethylene carbonate can be formed from the monoepoxide of butadiene in 96% yield at room temperature, normal pressure and with a reaction time of 15 minutes if Pd(PPh₃)₄ is used as the catalyst.^[9] Kruper performed this

reaction using Cr^{III} porphyrins as a catalyst.^[10] In addition, Floriani has reported that Co salen-type complexes can react with carbon dioxide to afford a Co-CO₂ salen-type complex.^[11] Later, Nguyen reported that ethyldiamino or cyclohexyldiamino Cr^{III} salen-type complex can efficiently catalyze the reaction of epoxide with carbon dioxide to give the five-membered cyclic carbonate in high turnover number (TON) and turnover frequency (TOF).^[12] These results stimulated us to explore other Cu^{II}, Zn^{II}, and Co^{II} salen-type complexes derived from binaphthyldiamino Schiff bases to catalyze the reaction of epoxides with carbon dioxide.^[13] Moreover, main group compounds such as aluminum porphyrins or salen-type aluminum complexes,^[14] tin compounds^[15] and organoantimony compounds^[16] are also suitable to be used as a catalyst for the synthesis of cyclic carbonates from epoxides with carbon dioxide. Several organic compounds, such as ammonium salts,^[17] amines,^[18] halides,^[19] alkali salt/phase transfer system,^[20] guanidine or cyanamide salts,^[21] and phosphanes,^[22] can also be used as catalysts for the production of cyclic carbonates from the reaction of epoxides with carbon dioxide.

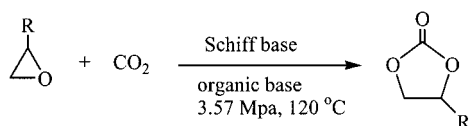
While the advances have been significant, the development of an efficient chemical process for the chemical fixation of CO₂ is still attracting much interest in view of the so-called “sustainable society” and “green chemistry” concepts. In the course of synthesis of the binaphthyldiamino salen-type zinc(II) or copper(II) complexes^[13] as catalysts for the reaction of epoxide with CO₂, we incidentally found that the Schiff base **1** itself also can catalyze this reaction efficiently in the presence of organic bases such as 4-(dimethylamino)pyridine (DMAP), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO),

^[a] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences Shanghai 200032, China
Fax: +86-21-6416-6128
E-mail: mshi@pub.sioc.ac.cn

^[b] East China University of Science and Technology
130 Mei Long Lu, Shanghai 200237, China

Supporting information for this article is available on the WWW under <http://www.eurjoc.org> or from the author.

or triethylamine (NEt₃; Scheme 1).^[23] Upon further investigation we confirmed that many common Schiff bases, including ethyldiamino Schiff bases or cyclohexyldiamino Schiff bases, and even phenols,^[24] can catalyze the reaction of epoxides with carbon dioxide to give the corresponding cyclic carbonates in excellent yields under relatively mild conditions in the presence of organic bases. Herein, we wish to report the full details of this unprecedented Schiff base or phenols and organic base co-catalyzed reaction of epoxides with carbon dioxide. The reaction of aziridines with CO₂ and epoxide with CS₂ were also examined under the same conditions with the same catalysts. Based on a deuterium labeling experiment, a plausible mechanism of this novel catalytic system has been proposed.



Scheme 1

Results and Discussion

The binaphthyldiamino, ethyldiamino and cyclohexyldiamino Schiff bases **1**–**7** shown in Figure 1 were synthesized according to the literature procedures.^[25] The scope and limitations of these catalysts under different reaction conditions were carefully examined in the reaction of propylene oxide (PO) **8a** with CO₂. The results are summarized in Table 1. No reaction occurred when using either the Schiff base or the organic base on its own (Table 1, entries 5 and 7). The presence of both Schiff base (0.1 mol %) and organic base (0.2 mol %) is therefore required in order to al-

low the reaction to take place (Table 1, entries 1–4, 6 and 8–14).

These Schiff bases have poor solubilities in most organic solvents, although a small amount of organic solvent such as CH₂Cl₂ or ClCH₂CH₂Cl is required to give the cyclic carbonate **9a** in higher yields. Among the organic bases examined in this reaction DMAP or DBU showed the best results under similar conditions (Table 1, entries 1–8). We found that with Schiff base **1** and DMAP as the catalysts in 5.0 mL of 1,2-dichloroethane (DCE) at 120 °C the cyclic carbonate **9a** could be obtained in 89% yield (Table 1, entry 6). The use of binaphthyldiamino Schiff bases **1**–**3** or cyclohexyldiamino Schiff base **6** as a catalyst in the presence of DMAP gave the cyclic carbonate **9a** in similarly high yields (84–89%; Table 1, entries 6, 9, 10 and 13), while the sterically hindered binaphthyldiamino Schiff base **4** decreased the yield of cyclic carbonate **9a** under the same conditions (Table 1, entry 10). The ethyldiamino Schiff base **5** also has lower reactivity. If the Schiff base has no phenolic hydroxyl group, such as Schiff base **7**, the yield of product is lower under the same conditions (Table 1, entry 14). The best reaction conditions are Schiff base **1** and DMAP as the co-catalysts at 120 °C under a high pressure of CO₂ (3.57 Mpa) with 5 mL of solvent (DCE; Table 1, entry 6).

Having optimized the reaction conditions, we then tried the reaction of other epoxides with carbon dioxide in the presence of **1** (1.0 mol %) and DMAP (2.0 mol %). These results are summarized in Table 2, where we can see that almost all of the terminal epoxides **8** react with carbon dioxide to give the corresponding cyclic carbonates **9** in good to excellent yields with high selectivity (Table 2, entries 1–6). To the best of our knowledge, this is the first example

Table 1. Reaction of propylene oxide with CO₂ in the presence of Schiff base and organic base

Entry	Schiff base	Organic base ^[a]	Temp/[°C]	Solvent	Yield (%) ^[b]	TON
1	1	DABCO	100 ^[c]	CH ₂ Cl ₂	17	169
2	1	Et ₃ N	100 ^[c]	CH ₂ Cl ₂	20	204
3	1	DBU	100 ^[c]	CH ₂ Cl ₂	31	308
4	1	DMAP	100 ^[c]	CH ₂ Cl ₂	25	254
5	1	None	100 ^[c]	CH ₂ Cl ₂	0	0
6	1	DMAP	120 ^[d]	ClCH ₂ CH ₂ Cl	89	887
7	none	DMAP	120 ^[d]	ClCH ₂ CH ₂ Cl	0	0
8	1	DBU	120 ^[d]	ClCH ₂ CH ₂ Cl	80	801
9	2	DMAP	120 ^[d]	ClCH ₂ CH ₂ Cl	84	841
10	3	DMAP	120 ^[d]	ClCH ₂ CH ₂ Cl	89	887
11	4	DMAP	120 ^[d]	ClCH ₂ CH ₂ Cl	15	153
12	5	DMAP	120 ^[d]	ClCH ₂ CH ₂ Cl	38	382
13	6	DMAP	120 ^[d]	ClCH ₂ CH ₂ Cl	84	838
14	7	DMAP	120 ^[d]	ClCH ₂ CH ₂ Cl	14	138

^[a] Reaction conditions: PO (2.6 g, 45 mmol), solvent (5 mL), Schiff base (0.045 mmol) and organic base (0.09 mmol). ^[b] Isolated yield. ^[c] The reaction time was 24 h. ^[d] The reaction time was 48 h.

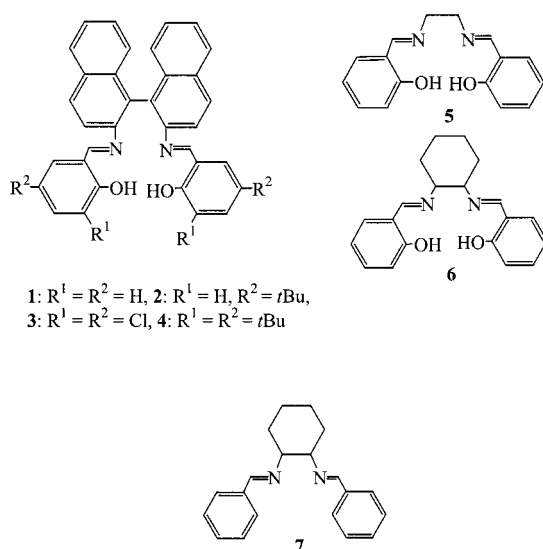


Figure 1. Structures of the Schiff bases

where a Schiff base combined with an organic base can catalyze the reaction of various terminal epoxides with carbon dioxide. More importantly, the catalysts are stable during the reaction and can be easily recovered by distilling off the formed cyclic carbonates **9** and then reused for the next run of the same reaction without loss of efficiency (Table 2, entry 7).

Table 2. Reaction of various epoxides with CO₂ in the presence of Schiff Base **1** and DMAP^[a]

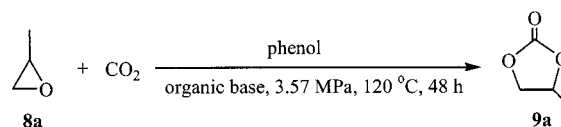
Entry ^[a]	Epoxide	Product	Yield (%) ^[b]
1	 8a	 9a	100
2	 8b	 9b	89
3	 8c	 9c	95
4	 8d	 9d	99
5	 8e	 9e	89
6	 8f (<i>m</i> - and <i>p</i> -mixture)	 9f (<i>m</i> - and <i>p</i> -mixture)	70
7 ^[c]	 8a	 9a	98

^[a] Reaction conditions: epoxide (4.5 mmol), ClCH₂CH₂Cl (5 mL), catalyst (0.045 mmol), DMAP (0.09 mmol). ^[b] Isolated yields.

^[c] Recovered catalysts were used.

Based on the above results, we decided that this catalytic system could be simplified by use of phenol instead of the Schiff bases **1**–**6** because only the phenolic hydroxy group plays an important role in this reaction based on the results shown in Table 1 (entries 7 and 14). Thus, we carried out the reaction of epoxide **8a** with CO₂ in the presence of phenol and organic base under similar conditions (Scheme 2). We found that five-membered cyclic carbonate **9a** could be obtained in excellent yield in the presence of phenol (0.4 mol %) and organic base (0.4 mol %) from the reaction of epoxide **8a** with carbon dioxide under similar reaction conditions (3.57 MPa CO₂, 120 °C, 48 h; Scheme 2); phenol on its own gave no product. Therefore the presence of both

phenol and an organic base is required in order to get a high yield of cyclic carbonate **9a**.



Scheme 2

The scope and limitations of both catalysts and reaction conditions were also carefully examined. Many phenols (phenol: $pK_a = 10.0$; *m*-nitrophenol: $pK_a = 7.15$; *p*-methoxyphenol: $pK_a = 10.21$; binol: $pK_a = 10.64$; naphthol: $pK_a = 10.12$) combined with organic bases (DMAP, DBU, NEt₃, or pyridine) are catalysts for this reaction. These results are summarized in Table 3. 4-(Dimethylamino)pyridine (DMAP) is the best organic base (Table 3, entries 3, 7–10) and *p*-methoxyphenol is the most effective phenol under otherwise identical reaction conditions (Table 3, entries 1–6). These results suggest that both the pK_a of the phenol and the structure of the organic base play important roles in this reaction; the combination of either an alcohol or carboxylic acid with the organic base shows no reactivity. We also examined the reaction system using *p*-toluenesulfonic acid as a co-catalyst with DMAP, but found that the cyclic carbonate **9a** was obtained in only 10% yield under the same conditions as for DMAP and phenol. The best combination is *p*-methoxyphenol (0.4 mol %) with DMAP (0.4 mol %) in this reaction.

Table 3. Reaction of propylene oxide with CO₂ in the presence of phenol and organic base

Entry ^[a]	Phenol	Base	Yield (%) ^[b]	TON ^{[c][d]}
1	PhOH	DMAP	91	228
2	<i>m</i> -NO ₂ C ₆ H ₄ OH	DMAP	59	149
3	<i>p</i> -MeOC ₆ H ₄ OH	DMAP	98	246
4	β -naphthol	DMAP	90	224
5	binol	DMAP	94	235
6	8-hydroxyquinoline	DMAP	55	138
7	<i>p</i> -MeOC ₆ H ₄ OH	DABCO	13	34
8	<i>p</i> -MeOC ₆ H ₄ OH	Et ₃ N	24	61
9	<i>p</i> -MeOC ₆ H ₄ OH	DBU	69	173
10	<i>p</i> -MeOC ₆ H ₄ OH	pyridine	20	50
11 ^[c]	<i>p</i> -MeOC ₆ H ₄ OH	DMAP	97	245

^[a] Reaction conditions: propylene oxide (PO) (2.6 g, 45 mmol), CH₂Cl₂ (0.5 mL), phenol (0.18 mmol), organic base (0.18 mmol).

^[b] Isolated yield. ^[c] Moles of propylene carbonate produced per mol of catalyst. ^[d] The reaction time was 24 h. ^[e] Recovered catalysts were used.

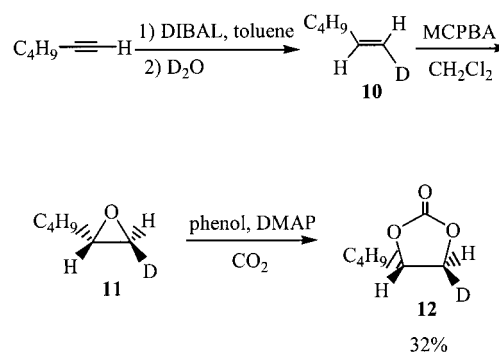
Under the optimized reaction conditions (*p*-methoxyphenol/DMAP, 3.57 MPa, 120 °C, 48 h), we examined the reactions of other epoxides **8** with carbon dioxide. These results are summarized in Table 4. We found that, by using 4 mol % of both *p*-methoxyphenol and DMAP, many monosubstituted terminal epoxides can be quantitatively transformed into the corresponding cyclic carbonates **9** (Table 4, entries 1–6). The catalysts are stable during the reaction and can be easily recovered by distilling off the formed cyclic carbonate **9a** and then reused for the next run of the same reaction with no loss of efficiency (Table 3, entry 11).

Table 4. Reaction of epoxide with CO₂ in the presence of *p*-methoxyphenol and DMAP

Entry ^[a]	Epoxide	Product	Yield (%) ^[b]
1	 8a	 9a	100
2	 8b	 9b	96
3	 8c	 9c	94
4	 8d	 9d	99
5	 8e	 9e	96
6	 8f	 9f	74

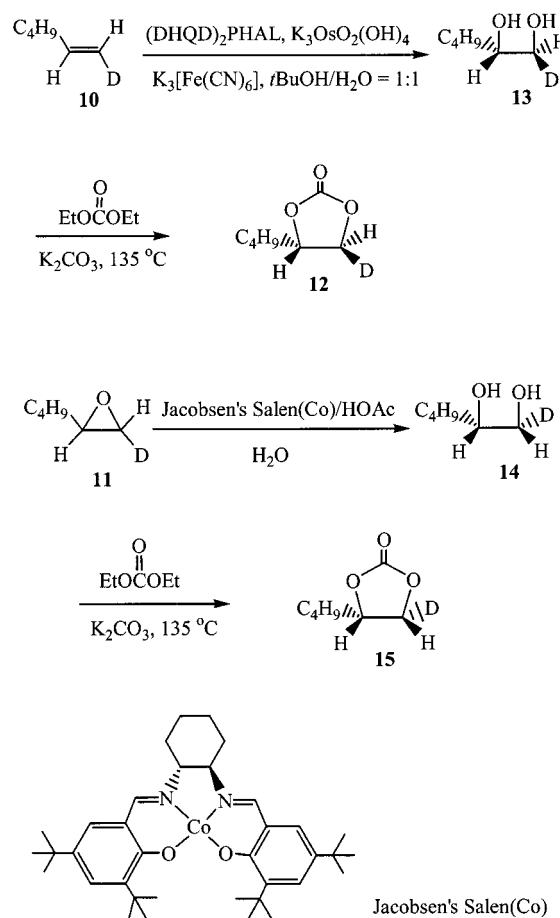
^[a] Reaction conditions: epoxides (4.5 mmol), CH₂Cl₂ (0.5 mL), *p*-methoxyphenol (0.18 mmol), DMAP (0.18 mmol). ^[b] Isolated yield.

Considering the reaction mechanism, Kim has shown, on the basis of an X-ray crystal structure, that in the reaction of epoxide with CO₂ in the presence of ZnBr₂ and pyridine, the epoxy ring, activated by the Lewis acidic ZnBr₂, is opened by the pyridine.^[26] Then, the zinc complexes bridged by the alkoxy pyridinium ion rapidly interact with CO₂ to give zinc carbonate species, which, in turn, react with additional epoxides to regenerate the zinc complexes and cyclic carbonates. However, it is also well-known that an organic base can activate CO₂ as a Lewis base^[27] and the zwitterion [R₃N⁺C(O)O[−]] can open the aziridinyll ring.^[28] In order to clarify the reaction mechanism, we synthesized *trans*-deuterioethylene oxide **11**, as shown in

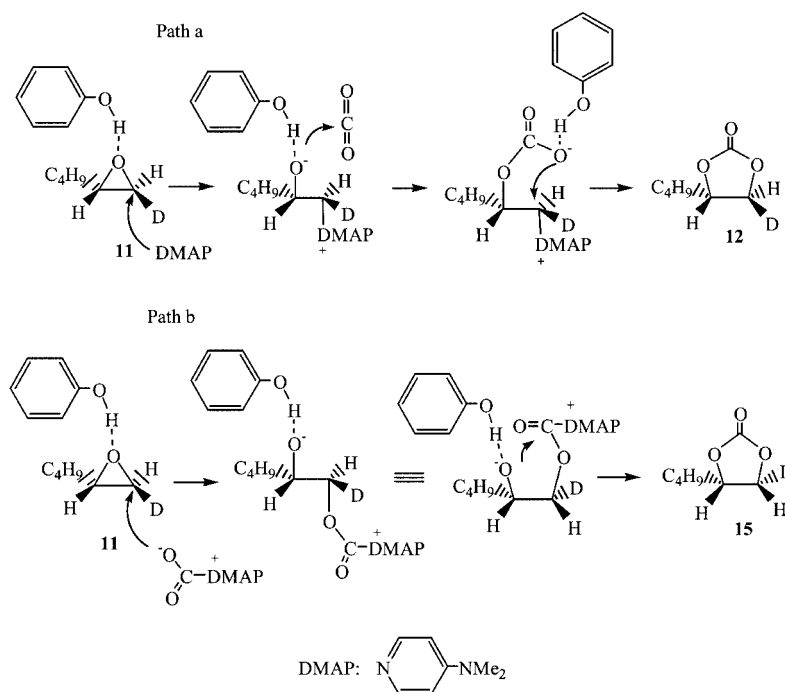


Scheme 3

Scheme 3, according to a literature procedure,^[29] and utilized it as the substrate in the DMAP and phenol co-catalyzed reaction of epoxides with CO₂ (Scheme 3). The deuterated ethylene carbonate **12** formed was analyzed by ¹H NMR spectroscopy and the spectrum compared with those of authentic samples prepared according to literature procedures (Scheme 4).^[30,31] We found that deuterated ethylene carbonate **12** was exclusively formed (the lower yield compared to **8c** may be caused by a secondary isotope effect).^[32] This result suggests that the formation of the cyclic carbonate in our reaction system proceeds via path a as shown in Scheme 5: the epoxy ring, activated by the phenol through hydrogen bonding, is first opened by the amine (DMAP)



Scheme 4



Scheme 5

and then reacts with CO_2 to give the corresponding deuterated ethylene carbonate **12**. If the reaction proceeded via path b, another deuterated ethylene carbonate **15**, with the opposite configuration of deuterium atoms to **12**, should be exclusively formed (Scheme 5).

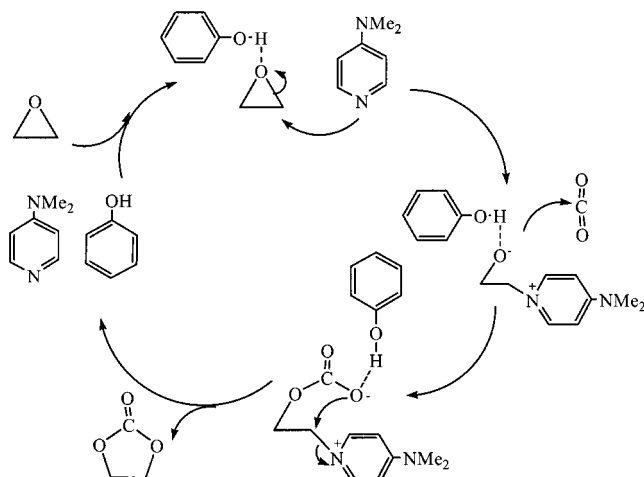
Based on the above results, in Scheme 6 we propose a plausible mechanism for this chemical fixation reaction of CO_2 . We believe that, in fact, this is a Lewis base (amine) and Lewis acid (phenol; through hydrogen bonding) co-catalyzed reaction system. The Lewis base and Lewis acid work together to open the epoxy ring and then react with CO_2 to give the corresponding cyclic carbonate in a ring opening and recyclization process. Previous reports also suggest the parallel requirement of both Lewis base and

Lewis acid in the fixation of CO_2 .^[2,6,33] Alcohols have low Lewis acidity and cannot activate CO_2 , whereas it is well-known that acids will react with organic bases to give a salt. Only phenols with $\text{p}K_{\text{a}}$'s of 7.0–10.5 can selectively activate CO_2 . *m*-Nitrophenol ($\text{p}K_{\text{a}} = 7.15$) can combine with organic bases to some extent as well because of its higher acidity. Thus, it has the lowest activity for the chemical fixation of CO_2 under our reaction conditions.

Using aziridines **16** as substrates,^[34] we examined the reaction with CO_2 under our optimized conditions. We found that the corresponding oxazolidines **17** were obtained in moderate to good yields (Table 5, entries 1–5). For aziridine **16a**, the corresponding oxazolidine **17a** was produced in 90% yield (Table 5, entry 1). The configuration of **17a** was determined by X-ray crystallography (Figure 2).^[35] For aziridine **16b**, two oxazolidines **17b-1** and **17b-2** were formed in 86% yield in a 1:1 ratio (Table 5, entry 2).^[34a–34f,36] Their structures were determined by ^1H NMR and ^{13}C NMR spectroscopy. The aziridines **16c–e** furnished the corresponding oxazolidines **17c–e** in moderate yields (Table 5, entries 3–5).

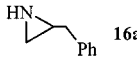
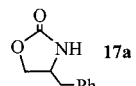
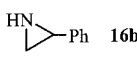
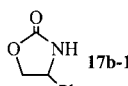
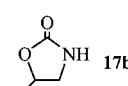
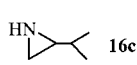
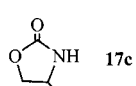
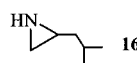
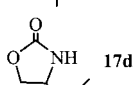
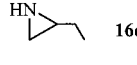
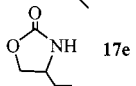
Epoxide **8a** can also react with carbon disulfide (CS_2) to give the corresponding oxathiolane-2-thione **18a** in moderate yield under the same conditions (Scheme 7). The reaction of ethylene sulfide with CO_2 under the same conditions gave a complex mixture of products (Scheme 7).

In conclusion, we have found that cyclic carbonates **9** can be obtained quantitatively (3.57 MPa of CO_2 initial pressure; reaction temperature 120 °C) from the reaction of epoxides **8** with carbon dioxide in the presence of a catalytic amount of a Schiff base or a phenol and an organic base. This is a very efficient organic Lewis acid (phenol) and Lewis base (amine) co-catalyzed system without metal cata-



Scheme 6. Plausible reaction mechanism

Table 5. Reaction of aziridines with CO₂ in the presence of *p*-methoxyphenol and DMAP

$\text{R} \begin{array}{c} \diagup \\ \text{N} \\ \diagdown \end{array} + \text{CO}_2 \xrightarrow[\text{DMAP, 3.57 MPa, 120 }^\circ\text{C, 48 h}]{p\text{-methoxyphenol}} \begin{array}{c} \text{O} \\ \parallel \\ \text{O} \text{---} \text{NH} \text{---} \text{R} \end{array}$			
Entry ^[a]	Epoxide	Product	Yield (%) ^[b]
1			90
2		 	86
3			34
4			50
5			30

^[a] Reaction conditions: epoxides (4.5 mmol), CH₂Cl₂ (0.5 mL), *p*-methoxyphenol (0.18 mmol), DMAP (0.18 mmol). ^[b] Isolated yield.

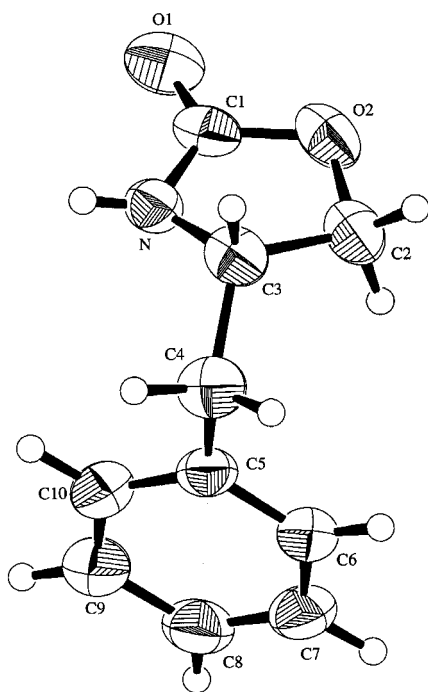
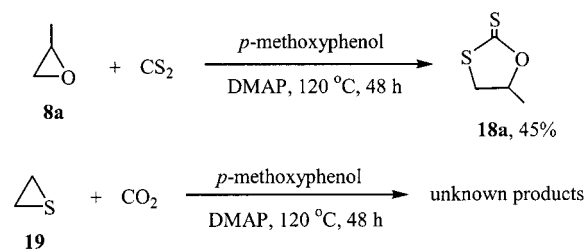


Figure 2. ORTEP drawing of 17a



Scheme 7

lyst; the cyclic carbonates **9** were obtained in excellent yields as the sole product. In addition, aziridines **16** can react with CO₂ to give the corresponding oxazolidines **17** in moderate to good yields under the same conditions. The reaction mechanism has been determined on the basis of deuterium labeling experiments. Efforts are currently underway to elucidate the further mechanistic details of this reaction and to identify systems enabling the carboxylation of other substrates and subsequent transformations thereof.

Experimental Section

General Methods. Melting points are uncorrected. ¹H and ¹³C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI methods, and HRMS was measured on a Finnigan MA+ mass spectrometer. The organic solvents used were dried by standard methods when necessary. All solid compounds reported in this paper gave satisfactory CHN microanalyses. Commercially obtained reagents were used without further purification. Schiff bases^[25] and aziridines^[37] were prepared according to literature procedures. All reactions were monitored by TLC with Huanghai GF254 silica-gel-coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

General Procedure for the Formation of Binaphthyl Schiff Bases:^[25a,25b] A mixture of 3,5-dichlorosalicylaldehyde (0.32 g, 1.67 mmol) and 1,1'-binaphthyl-2,2'-diamine (0.2 g, 0.7 mmol) in ethanol (10 mL) was stirred at room temperature for 3 h. During the reaction, the diimine Schiff base **1** formed precipitated as an orange solid. The crude product was filtered off, washed with ethanol and recrystallized from dichloromethane/diethyl ether give an orange crystalline solid (0.36 g, 81.2%).

Schiff base **1** is a known compound. ¹H NMR (300 MHz, CDCl₃, TMS): δ = 6.66 (d, *J* = 8.2 Hz, 2 H, ArH), 6.78–6.80 (m, 2 H, ArH), 7.17–7.29 (m, 8 H, ArH), 7.43–7.48 (m, 2 H, ArH), 7.63 (d, *J* = 8.7 Hz, 2 H, ArH), 7.96 (d, *J* = 8.5 Hz, 2 H, ArH), 8.10 (d, *J* = 8.7 Hz, 2 H, ArH), 8.67 (s, 2 H, HC=N). 12.10 (s, 2 H, OH) ppm. The ¹H NMR spectroscopic data are consistent with those reported in the literature.^[25c,25d]

Schiff base **2** is a known compound. ¹H NMR (300 MHz, CDCl₃, TMS): δ = 1.29 [s, 18 H, C(CH₃)₃], 6.64 (d, *J* = 8.8 Hz, 2 H, ArH), 7.25–7.29 (m, 8 H, ArH), 7.41–7.46 (m, 2 H, ArH), 7.64 (d, *J* = 8.8 Hz, 2 H, ArH), 7.94 (d, *J* = 8.8 Hz, 2 H, ArH), 8.08 (d, *J* = 8.8 Hz, 2 H, ArH), 8.71 (s, 2 H, HC=N). 11.87 (s, 2 H, OH) ppm. The ¹H NMR spectroscopic data are consistent with those reported in the literature.^[25a,25b]

Schiff base **3** is a known compound. ¹H NMR (300 MHz, CDCl₃, TMS): δ = 7.12–7.32 (m, 8 H, ArH), 7.46–7.51 (m, 2 H, ArH), 7.60 (d, *J* = 9.2 Hz, 2 H, ArH), 7.97 (d, *J* = 7.9 Hz, 2 H, ArH),

8.12 (d, $J = 9.2$ Hz, 2 H, ArH), 8.64 (s, 2 H, HC=N), 12.77 (s, 2 H, OH), 11.87 (s, 2 H, OH). The ^1H NMR spectroscopic data are consistent with those reported in the literature.^[25a,25b]

Schiff base **4** is a known compound. ^1H NMR (300 MHz, CDCl_3 , TMS): $\delta = 1.22$ (s, 36 H, CMe_3), 7.05 (d, $J = 1.5$ Hz, 2 H, ArH), 7.24–7.49 (m, 6 H, ArH), 7.42–7.46 (m, 2 H, ArH), 7.56 (d, $J = 8.6$ Hz, 2 H, ArH), 7.97 (d, $J = 8.0$ Hz, 2 H, ArH), 8.03 (d, $J = 9.1$ Hz, 2 H, ArH), 8.66 (s, 2 H, HC=N), 12.72 (s, 2 H, OH). The ^1H NMR spectroscopic data are consistent with those reported in the literature.^[25c]

Schiff bases **5–7** are also known compounds.^[25f,25g] Their physical and spectroscopic data are consistent with those reported in the literature.

Representative Procedure for the Coupling Reaction of Epoxide with Carbon Dioxide: A 100 mL stainless-steel pressure reactor was charged with binaphthylidiamino Schiff base **1** (22 mg, 0.045 mmol), propylene oxide (0.26 g, 45 mmol), DMAP (11 mg, 0.09 mmol), and $\text{ClCH}_2\text{CH}_2\text{Cl}$ (5 mL). The reaction vessel was placed under a constant pressure of carbon dioxide for 5 min to allow the system to equilibrate and then heated to 120 °C for 48 h. The vessel was then cooled to ambient temperature, the pressure released, and the contents transferred to a 50 mL round-bottomed flask. Unchanged substrate and solvent were removed in vacuo, and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 1:4) to give the cyclic carbonate as a colorless liquid.

4-Methyl-1,3-dioxolan-2-one (9a): This is a known compound.^[38] IR (neat): $\tilde{\nu} = 1800$ (C=O) cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): $\delta = 1.51$ (d, $J = 6.2$ Hz, 3 H, CH_3), 4.04 (t, $J = 8.1$ Hz, 1 H, CH), 4.57 (t, $J = 8.1$ Hz, 1 H, CH), 4.84–4.91 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): $\delta = 19.34, 70.83, 73.85, 155.33$ (C=O) ppm.

4-Ethyl-1,3-dioxolan-2-one (9b): IR (neat): $\tilde{\nu} = 1798$ (C=O) cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): $\delta = 1.0$ (t, $J = 7.1$ Hz, 3 H, CH_3), 1.74–1.95 (m, 2 H, CH_2), 4.14 (dd, $J = 8.1, 7.1$ Hz, 1 H, CH), 4.54 (t, $J = 8.1$ Hz, 1 H, CH), 4.64–4.78 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): $\delta = 9.2, 27.6, 69.8, 78.8, 155.9$ (C=O) ppm. MS (EI): $m/z = 117$ [$\text{M}^+ + 1$]. HRMS (EI): calcd. for $\text{C}_5\text{H}_8\text{O}_3$ 116.0473; found 116.0465.

4-Butyl-1,3-dioxolan-2-one 9c. IR (neat): $\tilde{\nu} = 1800$ (C=O) cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): $\delta = 0.95$ (t, $J = 7.1$ Hz, 3 H, CH), 1.20–1.54 (m, 4 H, CH_2), 1.60–2.0 (m, 2 H, CH_2), 4.09 (dd, $J = 8.1, 7.4$ Hz, 1 H, CH), 4.54 (t, $J = 8.1$ Hz, 1 H, CH), 4.65–4.80 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): $\delta = 14.0, 22.5, 26.6, 33.7, 69.7, 77.4, 155.5$ (C=O) ppm. MS (EI): $m/z = 144$ [M^+]. HRMS (EI): calcd. for $\text{C}_7\text{H}_{12}\text{O}_3$ 144.0786; found 144.0789.

4-Chloromethyl-1,3-dioxolan-2-one (9d): IR (neat): $\tilde{\nu} = 1801$ (C=O) cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): $\delta = 3.71$ –3.82 (m, 2 H, CH_2), 4.43 (dd, $J = 8.6, 5.5$ Hz, 1 H, CH), 4.61 (t, $J = 8.6$ Hz, 1 H, CH), 4.94–5.02 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): $\delta = 44.1, 66.6, 74.3, 154.4$ (C=O) ppm. MS (EI): $m/z = 136$ [M^+]. HRMS (EI): calcd. for $\text{C}_4\text{H}_5\text{ClO}_3$ 135.9927; found 135.9915.

4-Phenyl-1,3-dioxolan-2-one (9e): M.p. 50–51 °C. IR (neat): $\tilde{\nu} = 1814$ (C=O) cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): $\delta = 4.36$ (t, $J = 8.6$ Hz, 1 H, CH), 4.82 (t, $J = 8.6$ Hz, 1 H, CH), 5.68 (t, $J = 8.6$ Hz, 1 H, CH), 7.27–7.46 (m, 5 H, Ar) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): $\delta = 71.1, 125.8, 129.1, 129.6, 135.7, 154.8$

(C=O) ppm. MS (EI): $m/z = 164$ [M^+]. $\text{C}_9\text{H}_8\text{O}_3$: calcd. C 65.85, H 4.88; found C 65.91, H 5.02.

4-(3-Chloromethylphenyl)-1,3-dioxolan-2-one and 4-(4-chloromethylphenyl)-1,3-dioxolan-2-one (9f): IR (neat): $\tilde{\nu} = 1801$ (C=O) cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): $\delta = 4.36$ (dd, $J = 8.6, 8.0$ Hz, 1 H, CH), 4.62 (s, 2 H, CH_2), 4.84 (dd, $J = 8.6, 8.0$ Hz, 1 H, CH), 5.71 (dd, $J = 8.0, 8.0$ Hz, 1 H, CH), 7.40–7.48 (m, 5 H, Ar) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): $\delta = 43.0, 71.3, 77.8, 126.1, 130.1, 136.2, 138.9, 177.8$ (C=O) ppm. MS (EI): $m/z = 212$ [M^+], HRMS (EI): calcd. for $\text{C}_{10}\text{H}_9\text{ClO}_3$ 212.0240; found 212.0241.

trans-1-Deuterio-1-hexene (**10**) and *trans*-1-deuterio-1,2-hexene oxide (**11**) were prepared according to literature procedures.^[29]

threo-1-Deuterio-1,2-hexanediol (13): This compound was prepared from *trans*-1-deuterio-1-hexene (**10**) by a Sharpless dihydroxylation reaction.^[30] *trans*-1-Deuterio-1-hexene (255 mg, 3.0 mmol) was added at 0 °C to a solution of $\text{K}_3\text{Fe}(\text{CN})_6$ (2.96 g, 9.0 mmol), K_2CO_3 (1.24 g, 9.0 mmol), MeSO_2NH_2 (285 mg, 3.0 mmol), hydroquinidine 1,4-phthalazinediyl diether (DHQD)₂PHAL (23 mg, 0.03 mmol), and $\text{K}_2\text{OsO}_2(\text{OH})_4$ (4 mg, 0.011 mmol) in *t*BuOH/ H_2O (1:1; 30 mL) and the mixture was vigorously stirred for 11 h at 0 °C. The reaction was then quenched by slow addition of Na_2SO_3 (4.2 g, 33.3 mmol). After stirring for 0.5 h at room temperature, the mixture was filtered. The solvent was removed from the filtrate under reduced pressure and the residue was extracted with EtOAc (3 × 20 mL). The extracted organic layer was washed with 5% H_2SO_4 (20 mL) and brine (40 mL), then dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1) to give the corresponding diol **13** as a colorless oil. 280 mg (79%). IR (neat): $\tilde{\nu} = 3369, 2931, 2151, 1466, 1061$ cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): $\delta = 0.91$ (t, $J = 6.9$ Hz, 3 H, CH_3), 1.25–1.43 (m, 6 H, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 2.50 (br. s, 1 H, OH), 3.41 (d, $J = 7.5$ Hz, 1 H, CHD), 3.72 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): $\delta = 14.0, 22.7, 27.8, 32.7, 66.2$ (t, $J_{\text{C,D}} = 20.18$ Hz), 72.2 ppm. MS (EI): m/z (%) = 87 (33.7) [$\text{M}^+ - \text{HCDOH}$].

erythro-1-Deuterio-1,2-hexanediol (14): This compound was prepared from *trans*-1-deuterio-1,2-hexene oxide (**11**) by a Jacobsen reaction.^[31] H_2O (90 μL , 5.0 mmol) was added in one portion to a solution of racemic Co(salen) (15 mg, 0.025 mmol), HOAc (6.0 μL , 0.1 mmol) and *trans*-1-deuterio-1,2-hexene (325 mg, 3.2 mmol) at 0 °C and the mixture was vigorously stirred for 16 h at 0 °C. The organic product was extracted with diethyl ether (3 × 20 mL). The extracted organic layer was washed with water (20 mL) and brine (40 mL), then dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 2:1) to give the corresponding diol **14** as a colorless oil. Yield: 309 mg (81%). IR (neat): $\tilde{\nu} = 3317, 2932, 2169, 1466, 1085$ cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): $\delta = 0.91$ (t, $J = 6.9$ Hz, 3 H, CH_3), 1.26–1.47 (m, 6 H, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 2.67 (br. s, 2 H, OH), 3.64 (d, $J = 7.5$ Hz, 1 H, CHD), 3.70 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): $\delta = 14.0, 22.7, 27.8, 32.8, 66.3$ (t, $J_{\text{C,D}} = 21.0$ Hz), 72.3 ppm. MS (EI): m/z (%) = 87 (30.71) [$\text{M}^+ - \text{HCDOH}$].

trans-4-Butyl-5-deuterio-1,3-dioxolane-2-one (12): A mixture of *threo*-1-deuterio-1,2-hexanediol (**13**; 238 mg, 2.0 mmol), K_2CO_3 (28 mg, 0.2 mmol) and $(\text{EtO})_2\text{C}=\text{O}$ (15 mL) was heated to reflux (at 135 °C) for 5 h. The unchanged $(\text{EtO})_2\text{C}=\text{O}$ was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 6:1) to give **12** as

a colorless oil. Yield: 192 mg, 66%. IR (neat): $\tilde{\nu}$ = 1801 (C=O) cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): δ = 0.93 (t, J = 7.2 Hz, 3 H, CH_3), 1.33–1.45 (m, 4 H, $-\text{CH}_2\text{CH}_2-$), 1.68–1.85 (m, 2 H, CH_2), 4.07 (d, J = 6.9 Hz, 1 H, CHD), 4.72 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): δ = 13.8, 22.2, 26.4, 33.5, 69.2 (t, $J_{\text{C,D}}$ = 23.78 Hz), 77.1, 155.2 (C=O) ppm. MS (EI): m/z (%) = 145 (0.93) [M^+]. HRMS (EI) calcd. for $\text{C}_7\text{H}_{11}\text{DO}_3$ 145.0848; found 145.0910.

cis-4-Butyl-5-deuterio-1,3-dioxolane-2-one (15): This compound was prepared in the same manner as described above from erythro-1-deuterio-1,2-hexanediol (**14**) as a colorless oil. Yield: 190 mg, 65%. IR (neat): $\tilde{\nu}$ = 1801 (C=O) cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): δ = 0.92 (t, J = 7.2 Hz, 3 H, CH_3), 1.33–1.44 (m, 4 H, $-\text{CH}_2\text{CH}_2-$), 1.68–1.85 (m, 2 H, CH_2), 4.52 (dt, J = 7.8, 1.2 Hz, 1 H, CHD), 4.69 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): δ = 13.6, 22.1, 26.3, 33.3, 69.1 (t, $J_{\text{C,D}}$ = 22.95 Hz), 77.1, 155.2 (C=O) ppm. MS (EI): m/z (%) = 146 (3.36) [$\text{M}^+ + 1$]. HRMS (EI) calcd. for $\text{C}_7\text{H}_{11}\text{DO}_3$ 145.0848; found 145.0910.

4-Benzylloxazolidin-2-one (17a): M.p. 72–74 °C. IR (CHCl_3): $\tilde{\nu}$ = 1753 (C=O) cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): δ = 2.88 (dd, J = 6.7, 8.6 Hz, 2 H), 4.05–4.18 (m, 2 H, CH_2), 4.47 (t, J = 8.6 Hz, 1 H, CH), 5.41 (s, 1 H, NH), 7.13–7.38 (m, 5 H, Ar) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): δ = 41.4, 53.8, 69.1, 127.3, 129.0, 129.1, 136.0, 159.8 (C=O) ppm. MS (EI): m/z = 177 [M^+]. $\text{C}_{10}\text{H}_{11}\text{NO}_2$: calcd. C 67.80, H 6.21, N 7.91; found C 67.47, H 6.32, N 7.77%.

4-Phenylloxazolidin-2-one (17b-1): M.p. 136–138 °C. IR (CHCl_3): $\tilde{\nu}$ = 1752 (C=O) cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): δ = 4.21 (dd, J = 8.6, 7.0 Hz, 1 H), 4.76 (dd, J = 8.6, 8.6 Hz, 1 H), 4.98 (dd, J = 8.6, 7.0 Hz, 1 H), 5.69 (s, 1 H, NH), 7.34–7.46 (m, 5 H, Ar) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): δ = 56.6, 72.8, 126.3, 129.1, 129.4, 139.7, 160.0 (C=O) ppm. MS (EI): m/z = 163 [M^+]. $\text{C}_9\text{H}_9\text{NO}_2$: calcd. C 66.25, H 5.56, N 8.58; found C 66.31, H 5.56, N 8.59.

5-Phenylloxazolidin-2-one (17b-2): M.p. 98–99 °C. IR (CHCl_3): $\tilde{\nu}$ = 1752 (C=O) cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): δ = 3.56 (dd, J = 8.4, 8.0 Hz, 1 H, CH), 3.98 (dd, J = 8.4, 8.4 Hz, 1 H, CH), 5.64 (dd, J = 8.4, 8.0 Hz, 1 H, CH), 5.84 (s, 1 H, NH), 7.35–7.47 (m, 5 H, Ar) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): δ = 48.6, 78.2, 126.0, 129.1, 129.1, 138.7, 160.6 (C=O) ppm. MS (EI): m/z = 163 [M^+]. $\text{C}_9\text{H}_9\text{NO}_2$: calcd. C 66.25, H 5.56, N 8.58; found C 65.74, H 5.63, N 8.5%.

4-Isopropylloxazolidin-2-one (17c): Colorless oil. IR (CHCl_3): $\tilde{\nu}$ = 1755 (C=O) cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): δ = 0.91 (d, J = 6.9 Hz, 3 H, CH_3), 0.97 (d, J = 6.9 Hz, 3 H, CH_3), 1.65–1.80 (m, 1 H, CH), 3.63 (ddd, J = 8.7, 6.3, 0.9 Hz, 1 H, CH), 4.15 (dd, J = 8.7, 6.3 Hz, 1 H, CH), 4.46 (dd, J = 8.7, 8.7 Hz, 1 H, CH), 6.42 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): δ = 17.9, 18.2, 32.9, 58.6, 68.8, 160.6 (C=O) ppm. MS (EI): m/z = 129 [M^+]. HRMS (EI): calcd. for $\text{C}_6\text{H}_{11}\text{NO}_2$ 129.0790; found 129.0774.

4-Isobutylloxazolidin-2-one (17d): Colorless oil. IR (CHCl_3): $\tilde{\nu}$ = 1751 (C=O) cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): δ = 0.92 (d, J = 6.9 Hz, 3 H, CH_3), 0.93 (d, J = 6.9 Hz, 3 H, CH_3), 1.30–1.42 (m, 1 H, CH), 1.43–1.65 (m, 2 H, 2CH), 3.85–4.02 (m, 2 H, 2CH), 4.50 (dd, J = 7.8, 7.8 Hz, 1 H, CH), 6.71 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): δ = 22.2, 23.2, 25.0, 44.7, 51.2, 71.0, 160.8 (C=O) ppm. MS (EI): m/z = 143 [M^+]. HRMS (EI): calcd. for $\text{C}_7\text{H}_{13}\text{NO}_2$ 143.0946; found 143.0930.

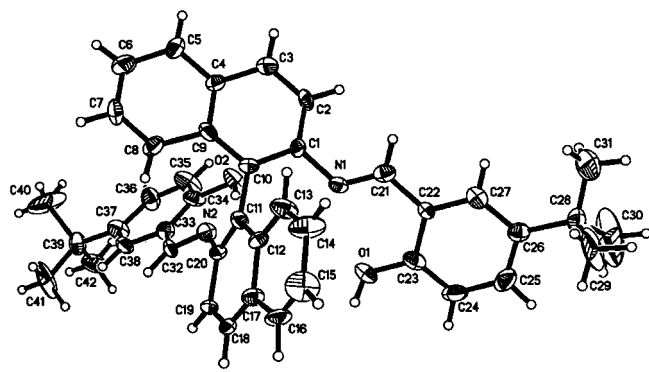
4-Ethylloxazolidin-2-one (17e): Colorless oil. IR (CHCl_3): $\tilde{\nu}$ = 1751 (C=O) cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): δ = 0.99 (d, J = 7.2 Hz, 3 H, CH_3), 1.66 (dq, J = 7.2, 7.2 Hz, 2 H, CH_2), 3.80–3.91 (m, 1 H, CH), 4.08 (dd, J = 8.4, 5.7 Hz, 1 H, CH), 4.52 (dd, J = 8.4, 8.4 Hz, 1 H, CH), 5.96 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): δ = 9.4, 28.3, 54.1, 70.2, 160.9 (C=O) ppm. MS (EI): m/z = 116 [M^+]. HRMS (EI): calcd. for $\text{C}_5\text{H}_9\text{NO}_2$ 115.0633; found 115.0650.

5-Methyl-1,3-oxathiolane-2-thione (18a): Colorless oil. IR (CHCl_3): $\tilde{\nu}$ = 1438 (C=S) cm^{-1} . ^1H NMR (300 MHz, TMS, CDCl_3): δ = 1.64 (d, J = 7.2 Hz, 3 H, CH_3), 3.73 (dd, J = 11.9, 7.6 Hz, 1 H, CH_2), 4.02 (dd, J = 11.9, 5.4 Hz, 1 H, CH), 4.46–4.60 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, CDCl_3 , TMS): δ = 19.3, 50.4, 55.5, 228.3 (C=S) ppm. MS (EI): m/z = 134 [M^+]. HRMS (EI): calcd. for $\text{C}_4\text{H}_6\text{OS}_2$ 133.9860; found 133.9857.

Acknowledgments

We thank the State Key Project of Basic Research (Project 973) (No. G2000048007), Shanghai Municipal Committee of Science and Technology, and the National Natural Science Foundation of China for financial support (20025206, 203900502, and 20272069).

- [1] [1a] A. Behr, in *Catalysis in C_1 Chemistry* (Ed.: W. Keim), Reidel, Dordrecht, **1983**. [1b] *The Rio Declaration*, United Nations Conference on Environment and Development, Rio de Janeiro, June 3–14, **1992**. [1c] *Green Chemistry* (Eds.: P. T. Anastas, T. C. Williamson), ACS Symposium Series 626; American Chemical Society, Washington, DC, **1996**.
- [2] [2a] V. Amarnath, A. D. Broom, *Chem. Rev.* **1977**, 77, 183. [2b] S. Inoue, Y. Yamazaki, *Organic and Bio-organic Chemistry of Carbon Dioxide*, Kodansha Ltd., Tokyo, **1982**.
- [3] A. Behr, *Carbon Dioxide Activation by Metal Complexes*, VCH, Weinheim, Germany, **1988**.
- [4] D. H. Gibson, *Chem. Rev.* **1996**, 96, 2063.
- [5] A. A. G. Shaikh, S. Sivaram, *Chem. Rev.* **1996**, 96, 951.
- [6] [6a] D. J. Darensbourg, M. W. Holtcamp, *Coord. Chem. Rev.* **1996**, 153, 155. [6b] H. S. Kim, J. J. Kim, B. G. Lee, O. S. Jung, H. G. Jang, S. O. Kang, *Angew. Chem. Int. Ed.* **2000**, 39, 4096. [6c] H. Kawanami, Y. Ikushima, *Chem. Commun.* **2000**, 2089. [6d] A. Fujita, *Catal. Lett.* **2002**, 79, 95.
- [7] [7a] R. J. De Pasquale, *J. Chem. Soc., Chem. Commun.* **1973**, 157. [7b] R. J. De Pasquale, *U. S. Patent* 3,748,345. [7c] E. Backvall, O. Karlsson, S. O. Ljunggren, *Tetrahedron Lett.* **1980**, 21, 4985. [7d] H. Matsuda, A. Ninagawa, R. Nomura, T. Tsuchida, *Chem. Lett.* **1979**, 73. [7e] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, *J. Am. Chem. Soc.* **1999**, 121, 4526. [7f] T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima, *Chem. Commun.* **1997**, 1129.
- [8] [8a] M. Ratzenhofer, H. Kisch, *Angew. Chem. Int. Ed. Engl.* **1980**, 19, 317. [8b] H. Kisch, R. Millini, I.-J. Wang, *Chem. Ber.* **1986**, 119, 1090. [8c] W. Dumler, H. Kisch, *Chem. Ber.* **1990**, 123, 277.
- [9] T. Fujinami, T. Suzuki, M. Namiya, *Chem. Lett.* **1985**, 199.
- [10] W. J. Kruper, D. V. Dellar, *J. Org. Chem.* **1995**, 60, 725.
- [11] S. Gambarotta, F. Arena, C. Floriani, P. F. Zanazzi, *J. Am. Chem. Soc.* **1982**, 104, 5082.
- [12] R. L. Paddock, S. T. Nguyen, *J. Am. Chem. Soc.* **2001**, 123, 11498 and references cited therein.
- [13] Y.-M. Shen, W.-L. Duan, M. Shi, *J. Org. Chem.* **2003**, 68, 1559 and references cited therein.
- [14] [14a] N. Takeda, S. Inoue, *Bull. Chem. Soc. Jpn.* **1978**, 51, 3564. [14b] T. Aida, S. Inoue, *J. Am. Chem. Soc.* **1983**, 105, 1304. [14c] D.-J. Ji, X.-B. Lu, R. He, *Appl. Catal. A: General* **2000**, 203, 329. [14d] X.-B. Lu, Y.-Z. Pan, D.-F. Ji, R. He, *Chin. Chem. Lett.* **2000**, 11, 589.
- [15] [15a] J. Harada, A. Kimura, S. Tagami, K. Watanabe, *Jpn. Pat-*

- ent 76,19,722 (17,2,1976); *Chem. Abstr.* **1976**, 85, 32452v. [15b] J. Harada, A. Kimura, Y. Takeshita, K. Watanabe, H. Sugahara, *Jpn. Patent* 76,141,871 (7,12,1976); *Chem. Abstr.* **1978**, 87, 38863t. [15c] H. Matsuda, A. Ninagawa, R. Nomura, T. Tsuchida, *Chem. Lett.* **1979**, 573. [15d] Mitsubishi Petrochemical Co., *Jpn. Kokai Tokyo Koho* 57,183,784 (12,11,1982); *Chem. Abstr.* **1984**, 100, 51588p.
- [16] [16a] H. Matsuda, A. Ninagawa, R. Nomura, T. Tsuchida, *Chem. Lett.* **1979**, 1261. [16b] R. Nomura, A. Ninagawa, H. Matsuda, *J. Org. Chem.* **1980**, 45, 3735.
- [17] [17a] Y. Deng, T. Peng, *New. J. Chem.* **2001**, 25, 639. [17b] V. Calo, A. Nacci, A. Monopoli, A. Fanizzi, *Org. Lett.* **2002**, 4, 2561. [17c] L. N. He, H. Yasuda, T. Sakakura, *Green. Chem.* **2003**, 5, 92. [17d] H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima, *Chem. Commun.* **2003**, 896.
- [18] Y. Fujita, T. Morimura, T. Nakano, *Jpn. Patent* 7,201,625 (17,1,1972); *Chem. Abstr.* **1972**, 76, 85406d.
- [19] [19a] N. Kihara, N. Hara, T. Endo, *J. Org. Chem.* **1993**, 58, 6198. [19b] T. Iwasaki, N. Kihara, T. Endo, *Bull. Chem. Soc. Jpn.* **2000**, 73, 713. [19c] W. C. Mills, *U. S. Patent* 2,907,771 (6,10,1959); *Chem. Abstr.* **1960**, 54, 3205f. [19d] Y. Fujita, T. Morimura, T. Nakano, *Jpn. Patent* 7,236,738 (14,9,1972); *Chem. Abstr.* **1972**, 77, 139417z. [19e] S. Fumasoni, F. Pochetti, *Rass. Chim.* **1975**, 27, 23; *Chem. Abstr.* **1975**, 83, 113625q.
- [20] G. Rokicki, W. Kuran, B. Pogorzelska-Marciniak, *Monatsh. Chem.* **1984**, 115, 205.
- [21] [21a] G.m.b.H. Erdölchemie, *French Patent* 1,543,832 (25,10,1968); *Chem. Abstr.* **1970**, 72, 12085f. [21b] G. Schnuchel, L. Bruns, O. Juebermann, *DOS*, 1,543,555 (6,3,1975); *Chem. Abstr.* **1975**, 83, 2170A.
- [22] [22a] Y. Fujita, T. Morimoto, T. Takanoichi, *Jpn. Patent* 7,322,702 (7,7,1973); *Chem. Abstr.* **1973**, 79, 146007k. [22b] M. J. Green, *PCT Int. Appl. WO* 84,03,701 (27,9,1984); *Chem. Abstr.* **1985**, 102, 166729u.
- [23] In one experiment on the use of the recovered binaphthyldiamino salen-type Zn^{II} catalyst in the same reaction of epoxide with CO₂, we incidentally found that the binaphthyldiamino Schiff base itself, derived from the decomposition of the Zn^{II} metal catalyst, can also catalyze this reaction to give the corresponding cyclic carbonate in the presence of organic base, although it is not as effective as the Zn^{II} metal catalyst. We confirmed that the decomposition of binaphthyldiamino salen-type Zn^{II} catalyst produces the corresponding Schiff base on the basis of X-ray diffraction.
- 
- Crystal data for **2**: empirical formula: C₄₂H₄₀N₂O₂; molecular mass: 604.76; color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: *a* = 22.365(2) Å, *b* = 14.6279(16) Å, *c* = 12.1375(13) Å, *a* = 90°, *β* = 120.187(2)°, *γ* = 90°, *V* = 3432.3(6) Å³; space group: *Cc*; *Z* = 4; *D*_{calcd.} = 1.170 g/cm³; *F*₀₀₀ = 1288; diffractometer: Rigaku AFC7R; residuals: *R*, *R*_w: 0.0366, 0.0502. CCDC-217653 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].
- [24] Previously we reported the phenol and organic base co-catalyzed chemical fixation of carbon dioxide with terminal epoxides to form cyclic carbonates in a short communication: Y.-M. Shen, W.-L. Duan, M. Shi, *Adv. Synth. Catal.* **2003**, 345, 337.
- [25] [25a] G. M. Chen, F. H. Chen, C. H. Zhou, *Chem. J. Chin. Univ.* **1995**, 16, 216; *Chem. Abstr.* **1996**, 123, 101213k. [25b] C.-W. Ho, W.-C. Cheng, M.-C. Cheng, S.-M. Peng, H.-F. Cheng, C.-M. Che, *J. Chem. Soc., Dalton Trans.* **1996**, 405 and references cited therein. [25c] H. Sakiyama, N. Okawa, N. Oguni, *Bull. Chem. Soc. Jpn.* **1992**, 65, 606. [25d] M. Shi, C.-J. Wang, A. S. C. Chan, *Tetrahedron: Asymmetry* **2001**, 12, 3105. [25e] N. Takenaka, Y. Huang, V. H. Rawal, *Tetrahedron* **2002**, 58, 8299. [25f] N. Kise, H. Oike, E. Okazaki, M. Yoshimoto, T. Shono, *J. Org. Chem.* **1995**, 60, 3980. [25g] U. Downing, *J. Am. Chem. Soc.* **1970**, 92, 5861.
- [26] [26a] H. S. Kim, J. J. Kim, B. G. Lee, O. S. Jung, H. G. Jang, S. O. Kang, *Angew. Chem. Int. Ed.* **2000**, 39, 4096. [26b] H. S. Kim, J. J. Kim, S. D. Lee, M. S. Lah, D. Moon, H. G. Jiang, *Chem. Eur. J.* **2003**, 9, 678.
- [27] It is well-known that organic bases (R₂NH) can coordinate to CO₂ to give an R₂NCO₂⁻ complex. See: [27a] S. Inoue, Y. Yamazaki, *Organic and Bio-organic Chemistry of Carbon Dioxide*, Kodansha Ltd., Tokyo, **1982**, p. 31. [27b] M. Abla, J.-C. Choi, T. Sakakura, *Chem. Commun.* **2001**, 2238. [27c] M. George, R. G. Weiss, *J. Am. Chem. Soc.* **2001**, 123, 10393. Very recently a molecular complex of DBU and CO₂ was isolated: E. R. Perez, M. O. Silva, V. C. Costa, U. P. Rodrigues-Filho, D. W. Franco, *Tetrahedron Lett.* **2002**, 43, 4091.
- [28] [28a] T. Kagiya, T. Matsuda, *Polym. J.* **1971**, 2, 398. [28b] W. A. Rokichi, D. Romanowsleca, *J. Polym. Sci., Polym. Chem. Ed.* **1979**, 17, 2003. [28c] L. D. Field, W. J. Shaw, P. Turner, *Chem. Commun.* **2002**, 46.
- [29] [29a] V. H. Krauledat, H. H. Brintzinger, *Angew. Chem. Int. Ed. Engl.* **1990**, 29, 1412. [29b] G. Wilke, H. Muller, *Ann.* **1958**, 618, 267. [29c] P. S. Skell, P. K. Freeman, *J. Org. Chem.* **1964**, 29, 2524. [29d] M. D. Refrik, R. D. J. Froese, J. D. Goddard, H. H. Pham, M. F. Pippert, A. L. Schwan, *J. Am. Chem. Soc.* **1995**, 117, 184. [29e] A. L. Schwan, M. R. Roche, J. F. Gallagher, G. Ferguson, *Can. J. Chem.* **1994**, 72, 312.
- [30] K. P. Vanheesche, K. B. Sharpless, *J. Org. Chem.* **1996**, 61, 7978.
- [31] S. E. Schaus, B. D. Brandes, J. F. Larrow, M. Tokunaga, K. B. Hansen, A. E. Gould, M. E. Furrow, E. N. Jacobsen, *J. Am. Chem. Soc.* **2002**, 124, 1307.
- [32] [32a] For a review of secondary isotope effects see: E. A. Halevi, *Prog. Phys. Org. Chem.* **1963**, 1, 109. [32b] A. J. Streitwieser, R. H. Jagow, R. C. Fahey, S. Suzuki, *J. Am. Chem. Soc.* **1958**, 80, 2326.
- [33] [33a] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, *J. Am. Chem. Soc.* **1999**, 121, 4526. [33b] T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima, *Chem. Commun.* **1997**, 1129.
- [34] [34a] K. Soga, S. Hosoda, H. Nakamura, S. Ikeda, *J. Chem. Soc., Chem. Commun.* **1976**, 617. [34b] H. Matsuda, A. Ninagawa, H. Hasegawa, *Bull. Chem. Soc. Jpn.* **1985**, 58, 2717. [34c] T. Nomura, T. Nakano, S. Nishio, S. Ogawa, A. Ninagawa, H. Matsuda, *Chem. Ber.* **1989**, 122, 2407. [34d] M. R. Banks, J. I. G. Cadogan, L. Gosney, K. G. Hodgson, D. E. Thomsen, *J. Chem. Soc., Perkin Trans. 1* **1991**, 961. [34e] P. Tascadda, E. Dunaeh, *Chem. Commun.* **2000**, 449. [34f] H. Kawanami, Y. Ikushima, *Tetrahedron Lett.* **2002**, 43, 3841.
- [35] Crystal data of **17a**: empirical formula: C₁₀H₁₁NO₂; molecular weight: 177.20; color, habit: colorless, prismatic; crystal dimensions: 0.20 × 0.20 × 0.30 mm; crystal system: monoclinic; lattice type: primitive; lattice parameters: *a* = 5.895(1) Å, *b* = 8.771(1) Å, *c* = 8.769(2) Å, *β* = 91.98(2)°, *V* = 453.1(2) Å³; space group: *P*₂₁ (no. 4); *Z* = 2; *D*_{calcd.} = 1.299 g/cm³; *F*₀₀₀ =

188; diffractometer: Rigaku AFC7R; residuals: R , R_w : 0.066, 0.086.

CCDC-178964 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

^[36] The formation of **17b-2** may be attributed to the reaction of a 1,3-dipole derived from phenylaziridine with CO₂ in the presence of phenol as it is known that phenylaziridine can react with an olefin to give a cyclized product via a formal [3+2] dipolar cycloaddition in the presence of a Lewis acid. ^[36a] I.

Ungureanu, C. Bologa, S. Chayor, A. Mann, *Tetrahedron Lett.* **1999**, 40, 5315. ^[36b] I. Ungureanu, P. Klota, A. Mann, *Angew. Chem. Int. Ed.* **2000**, 39, 4615. See also ref. 34e.

^[37] ^[37a] M. M. El-Abadelah, S. S. Sabri, A. A. Jarrar, M. H. Abu Zarga, *J. Chem. Soc., Perkin Trans. 1* **1979**, 2881. ^[37b] H. Rubinstein, B. Feibush, E. Cil-Av, *J. Chem. Soc., Perkin Trans. 2* **1973**, 2094. ^[37c] J. X. Xu, *Tetrahedron: Asymmetry* **2002**, 13, 1129.

^[38] ^[38a] W. J. Kruper, D. V. Dellar, *J. Org. Chem.* **1993**, 58, 1945–1948. ^[38b] A. Baba, T. Nozaki, H. Matsuda, *Bull. Chem. Soc. Jpn.* **1987**, 60, 1552–1554.

Received February 9, 2004