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

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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 instead 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 CO_2 and epoxide with CS_2 were also examined under the same reaction conditions.

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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 $Ni(PPh_3)_2$ and $Ni(PCy_3)_2$, 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 $Pd(PPh_3)_4$ 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-CO_2 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 CO_2 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 CO_2, 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),

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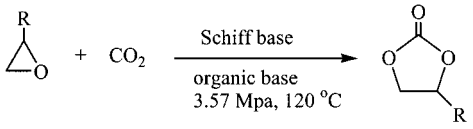
or triethylamine (NEt_3; Scheme 1).[23] Upon further investigation we confirmed that many common Schiff bases, including ethyldiamino Schiff bases or cyclohexyldiamino Schiff bases, and even phenols,[24] can catalyze the reaction of epoxides with carbon dioxide to give the corresponding cyclic carbonates 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 CO_2 and epoxide with CS_2 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 CO_2. 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 allow the reaction to take place (Table 1, entries 1−4, 6 and 8−14).

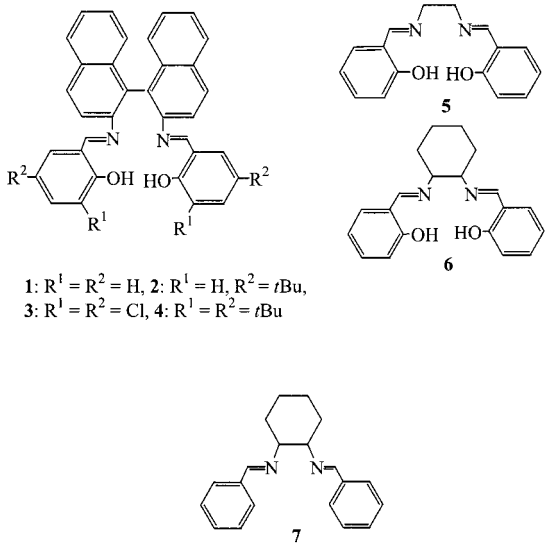
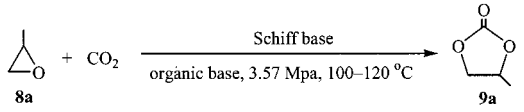


Figure 1. Structures of the Schiff bases

These Schiff bases have poor solubilities in most organic solvents, although a small amount of organic solvent such as CH_2Cl_2 or $ClCH_2CH_2Cl$ 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 CO_2 (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 CO_2 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_2Cl_2	17	169
2	**1**	Et_3N	100[c]	CH_2Cl_2	20	204
3	**1**	DBU	100[c]	CH_2Cl_2	31	308
4	**1**	DMAP	100[c]	CH_2Cl_2	25	254
5	**1**	None	100[c]	CH_2Cl_2	0	0
6	**1**	DMAP	120[d]	$ClCH_2CH_2Cl$	89	887
7	none	DMAP	120[d]	$ClCH_2CH_2Cl$	0	0
8	**1**	DBU	120[d]	$ClCH_2CH_2Cl$	80	801
9	**2**	DMAP	120[d]	$ClCH_2CH_2Cl$	84	841
10	**3**	DMAP	120[d]	$ClCH_2CH_2Cl$	89	887
11	**4**	DMAP	120[d]	$ClCH_2CH_2Cl$	15	153
12	**5**	DMAP	120[d]	$ClCH_2CH_2Cl$	38	382
13	**6**	DMAP	120[d]	$ClCH_2CH_2Cl$	84	838
14	**7**	DMAP	120[d]	$ClCH_2CH_2Cl$	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.

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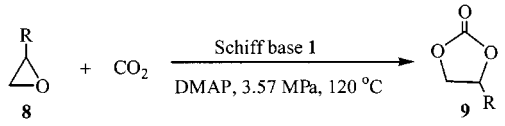
where a Schiff base combined with an organic base can catalyze the reaction of various terminal epoxides with carbon dioxide. More importantly, the catalysts are stable during the reaction and can be easily recovered by distilling off the formed cyclic carbonates **9** and then reused for the next run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

Table 2. Reaction of various epoxides with CO_2 in the presence of Schiff Base **1** and DMAP[a]

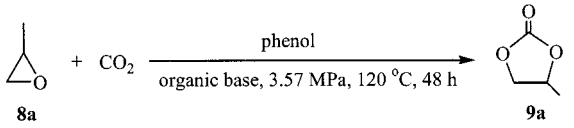


8 9

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	C_6H_4-CH_2Cl **8f** (*m*- and *p*-mixture)	**9f** C_6H_4-CH_2Cl (*m*- and *p*-mixture)	70
7[c]	**8a**	**9a**	98

[a] Reaction conditions: epoxide (4.5 mmol), $ClCH_2CH_2Cl$ (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 CO_2 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 CO_2, 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**.



8a **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, NEt_3, 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 CO_2 in the presence of phenol and organic base

Entry[a]	Phenol	Base	Yield (%)[b]	TON[c][d]
1	PhOH	DMAP	91	228
2	*m*-$NO_2C_6H_4OH$	DMAP	59	149
3	*p*-$MeOC_6H_4OH$	DMAP	98	246
4	*β*-naphthol	DMAP	90	224
5	binol	DMAP	94	235
6	8-hydroxyquinoline	DMAP	55	138
7	*p*-$MeOC_6H_4OH$	DABCO	13	34
8	*p*-$MeOC_6H_4OH$	Et_3N	24	61
9	*p*-$MeOC_6H_4OH$	DBU	69	173
10	*p*-$MeOC_6H_4OH$	pyridine	20	50
11[e]	*p*-$MeOC_6H_4OH$	DMAP	97	245

[a] Reaction conditions: propylene oxide (PO) (2.6 g, 45 mmol), CH_2Cl_2 (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.

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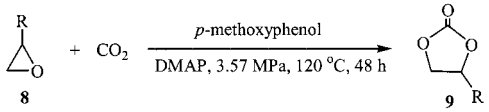
Under the optimized reaction conditions (*p*-methoxyphenol/DMAP, 3.57 MPa, 120 °C, 48 h), we examined the reactions of other epoxides **8** with carbon dioxide. These results are summarized in Table 4. We found that, by using 4 mol % of both *p*-methoxyphenol and DMAP, many monosubstututed terminal epoxides 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).

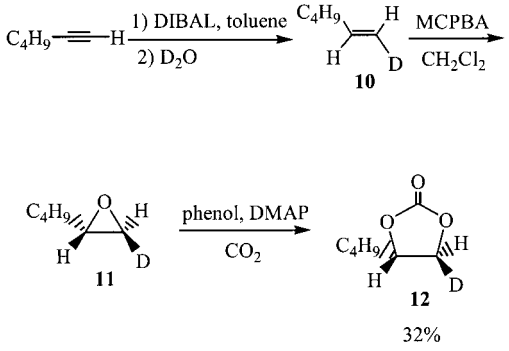
Table 4. Reaction of epoxide with CO_2 in the presence of *p*-methoxyphenol and DMAP



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	C_6H_4−CH_2Cl (*m*- and *p*-mixture) **8f**	**9f** C_6H_4-CH_2Cl (*m*- and *p*-mixture)	74

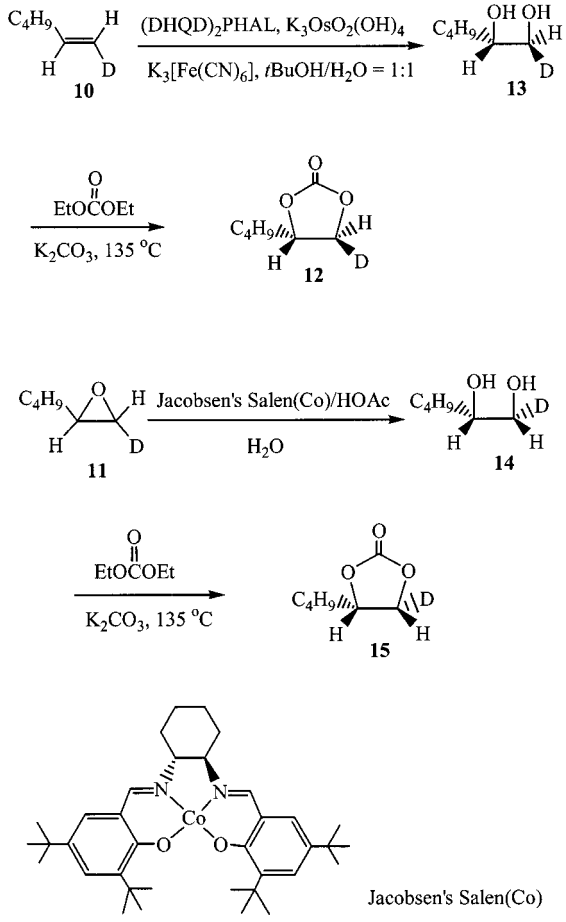
[a] Reaction conditions: epoxides (4.5 mmol), CH_2Cl_2 (0.5 mL), *p*-methoxyphenol (0.18 mmol), DMAP (0.18 mmol). [b] Isolated yield.

Considering the reaction mechanism, Kim has shown, on the basis of an X-ray crystal structure, that in the reaction of epoxide with CO_2 in the presence of $ZnBr_2$ and pyridine, the epoxy ring, activated by the Lewis acidic $ZnBr_2$, is opened by the pyridine.[26] Then, the zinc complexes bridged by the alkoxypyridinium ion rapidly interact with CO_2 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 CO_2 as a Lewis base[27] and the zwitterion $[R_3N^+C(O)O^-]$ can open the aziridinyl 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 CO_2 (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

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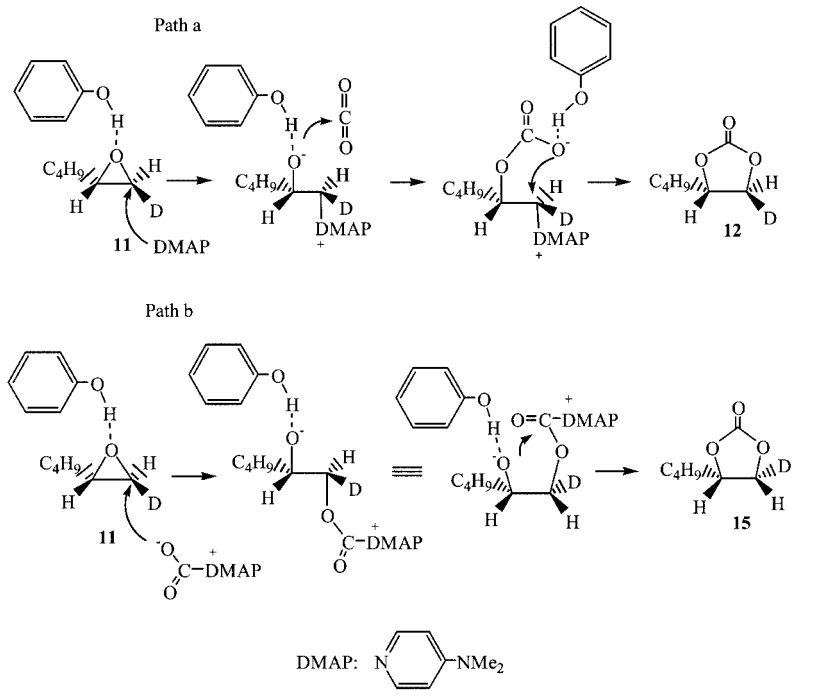
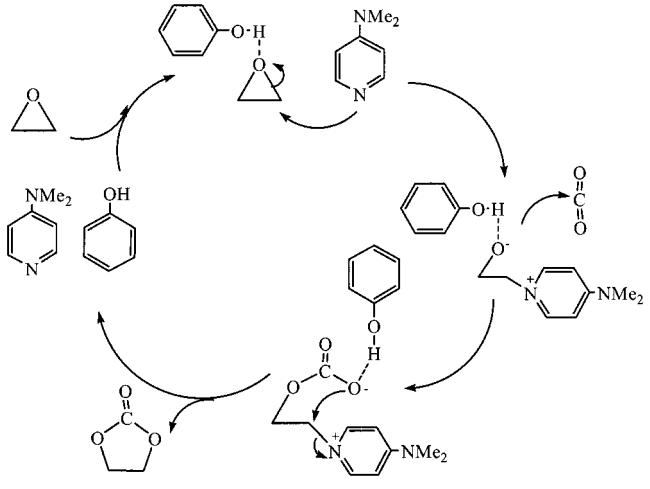


Scheme 5

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 pK_a's of 7.0−10.5 can selectively activate CO_2. *m*-Nitrophenol (pK_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.



Scheme 6. Plausible reaction mechanism

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 ^{1}H 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-

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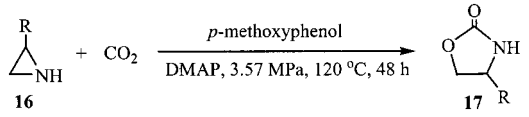
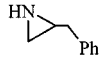
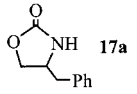
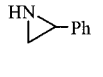
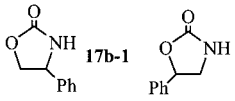
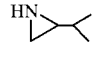
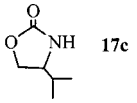
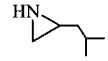
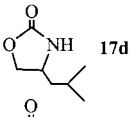
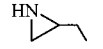
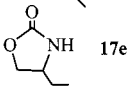
Table 5. Reaction of aziridines with CO_2 in the presence of *p*-methoxyphenol and DMAP



Entry[a]	Epoxide	Product	Yield (%)[b]
1	 **16a**	 **17a**	90
2	 **16b**	 **17b-1** **17b-2**	86
3	 **16c**	 **17c**	34
4	 **16d**	 **17d**	50
5	 **16e**	 **17e**	30

[a] Reaction conditions: epoxides (4.5 mmol), CH_2Cl_2 (0.5 mL), *p*-methoxyphenol (0.18 mmol), DMAP (0.18 mmol). [b] Isolated yield.

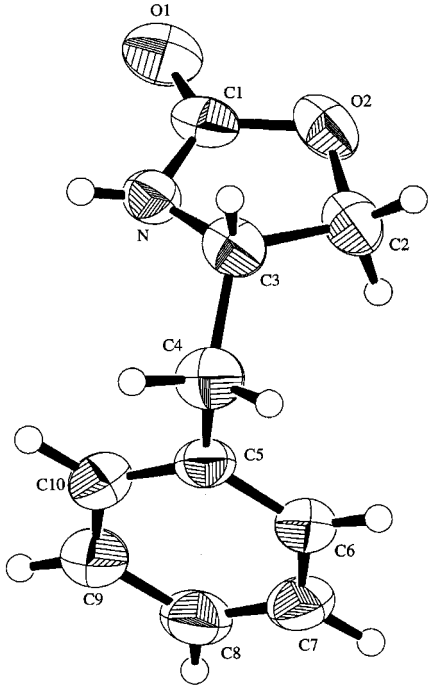
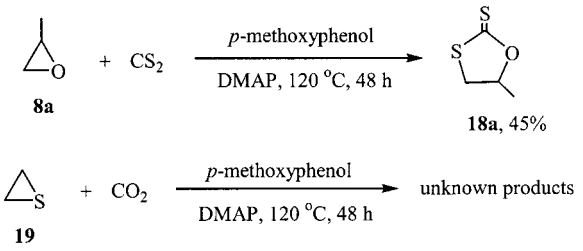


Figure 2. ORTEP drawing of **17a**



Scheme 7

lyst; the cyclic carbonates **9** were obtained in excellent yields as the sole product. In addition, aziridines **16** can react with CO_2 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 ^{13}C 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, $CDCl_3$, 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, $CDCl_3$, TMS): δ = 1.29 [s, 18 H, $C(CH_3)_3$], 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, $CDCl_3$, 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),

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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 ^{1}H NMR spectroscopic data are consistent with those reported in the literature.[25a,25b]

Schiff base **4** is a known compound. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 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 ^{1}H NMR spectroscopic data are consistent with those reported in the literature.[25e]

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 binaphthyldiamino Schiff base **1** (22 mg, 0.045 mmol), propylene oxide (0.26 g, 45 mmol), DMAP (11 mg, 0.09 mmol), and $ClCH_2CH_2Cl$ (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}. ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ = 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): δ = 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}. ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ = 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): δ = 9.2, 27.6, 69.8, 78.8, 155.9 (C=O) ppm. MS (EI): m/z = 117 [M^+ + 1]. HRMS (EI): calcd. for $C_5H_8O_3$ 116.0473; found 116.0465.

4-Butyl-1,3-dioxolan-2-one 9c. IR (neat): $\tilde{\nu}$ = 1800 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ = 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): δ = 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 $C_7H_{12}O_3$ 144.0786; found 144.0789.

4-Chloromethyl-1,3-dioxolan-2-one (9d): IR (neat): $\tilde{\nu}$ = 1801 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ = 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): δ = 44.1, 66.6, 74.3, 154.4 (C=O) ppm. MS (EI): m/z = 136 [M^+]. HRMS (EI): calcd. for $C_4H_5ClO_3$ 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}. ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ = 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): δ = 71.1, 125.8, 129.1, 129.6, 135.7, 154.8 (C=O) ppm. MS (EI): m/z = 164 [M^+]. $C_9H_8O_3$: 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}. ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ = 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): δ = 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 $C_{10}H_9ClO_3$ 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 proceduers.[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 $K_3Fe(CN)_6$ (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 $K_2OsO_2(OH)_4$ (4 mg, 0.011 mmol) in tBuOH/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}. ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ = 0.91 (t, J = 6.9 Hz, 3 H, CH_3), 1.25−1.43 (m, 6 H, -$CH_2CH_2CH_2$-), 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): δ = 14.0, 22.7, 27.8, 32.7, 66.2 (t, $J_{C,D}$ = 20.18 Hz), 72.2 ppm. MS (EI): m/z (%) = 87 (33.7) [M^+ − 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}. ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ = 0.91 (t, J = 6.9 Hz, 3 H, CH_3), 1.26−1.47 (m, 6 H, -$CH_2CH_2CH_2$-), 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): δ = 14.0, 22.7, 27.8, 32.8, 66.3 (t, $J_{C,D}$ = 21.0 Hz), 72.3 ppm. MS (EI): m/z (%) = 87 (30.71) [M^+ − 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 $(EtO)_2C=O$ (15 mL) was heated to reflux (at 135 °C) for 5 h. The unchanged $(EtO)_2C=O$ 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

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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, -CH_2CH_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, $J_{C,D}$ = 23.78 Hz), 77.1, 155.2 (C=O) ppm. MS (EI): m/z (%) = 145 (0.93) [M^+]. HRMS (EI) calcd. for $C_7H_{11}DO_3$ 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, -CH_2CH_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, $J_{C,D}$ = 22.95 Hz), 77.1, 155.2 (C=O) ppm. MS (EI): m/z (%) = 146 (3.36) [M^+ + 1]. HRMS (EI) calcd. for $C_7H_{11}DO_3$ 145.0848; found 145.0910.

4-Benzyloxazolidin-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^+]. $C_{10}H_{11}NO_2$: calcd. C 67.80, H 6.21, N 7.91; found C 67.47, H 6.32, N 7.77%.

4-Phenyloxazolidin-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^+]. $C_9H_9NO_2$: calcd. C 66.25, H 5.56, N 8.58; found C 66.31, H 5.56, N 8.59.

5-Phenyloxazolidin-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^+]. $C_9H_9NO_2$: calcd. C 66.25, H 5.56, N 8.58; found C 65.74, H 5.63, N 8.5%.

4-Isopropyloxazolidin-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 $C_6H_{11}NO_2$ 129.0790; found 129.0774.

4-Isobutyloxazolidin-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 $C_7H_{13}NO_2$ 143.0946; found 143.0930.

4-Ethyloxazolidin-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 $C_5H_9NO_2$ 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 $C_4H_6OS_2$ 133.9860; found 133.9857.

Acknowledgments

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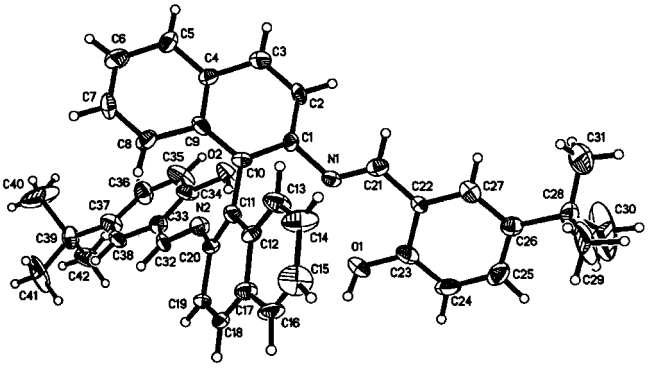

Crystal data for **2**: empirical formula: $C_{42}H_{40}N_2O_2$; molecular mass: 604.76; color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: a = 22.365(2) Å, b = 14.6279(16) Å, c = 12.1375(13) Å, α = 90°, β = 120.187(2)°, γ = 90°, V = 3432.3(6) Å^3; space group: *Cc;* Z = 4; $D_{calcd.}$ = 1.170 g/cm^3; F_{000} = 1288; diffractometer: Rigaku AFC7R; residuals: *R, Rw:* 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].

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188; diffractometer: Rigaku AFC7R; residuals: *R, Rw:* 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].

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