

論 文 主 題 目

Title of Dissertation

Chemical Fixation of CO₂ into Cyclic Carbonates Catalyzed by Efficient
Organocatalytic Systems under Metal-free and Mild Conditions
(金属を用いず温和な条件下でCO₂を環状炭酸エステルに
化学固定する効率的な有機触媒系の開発)

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Chemical Fixation of CO₂ into Cyclic Carbonates

Catalyzed by Efficient Organocatalytic Systems under Metal-free and Mild Conditions

Abstract

The synthesis of cyclic carbonates through coupling of carbon dioxide with epoxides is 100% atom economical and is already performed on an industrial scale. Its impact regarding the use of carbon dioxide as a renewable carbon source is expected to grow significantly in the near future, so that the development of efficient catalysts is of high interest in academia and industry. To improve the carbon footprint and sustainability of the cycloaddition reaction, the use of organocatalytic systems is a promising approach. In this thesis, during our study on the reaction of CO₂ with epoxides, we focused on developing organocatalytic systems using inexpensive and readily available compounds and employing ambient CO₂ pressure.

Herein, three different types of organocatalytic systems with enhanced properties for the chemical fixation of CO₂ into cyclic carbonates were developed. Firstly, using 1 mol% of benzyl halide as the nucleophilic catalyst and 3-5 *equiv.* of DMF as the recyclable solvent and activator. Under ambient CO₂ and 120 °C, the catalyst system smoothly converted diverse terminal epoxides up to 99% yields. A plausible mechanism for the coupling reaction of epoxide with CO₂ catalyzed by benzyl bromide and DMF was proposed. The ring opening of epoxide can be attributed to the electrophilic activation of epoxides by benzyl cations and the nucleophilic activation of CO₂ by DMF. Moreover, the activation of benzyl bromide by DMF was observed by ¹H NMR study.

Secondly, a simple, inexpensive and efficient binary organocatalytic system consisting of DBU and benzyl bromide was developed. A diverse range of epoxides was transformed into the corresponding cyclic carbonates with good to excellent yields (81-95%) under very mild conditions (65 °C, 1 atm CO₂). Furthermore, optically pure epoxides were also investigated, and a plausible mechanism for the coupling reaction of

epoxide with CO₂ was proposed.

Thirdly, a new, metal- and solvent-free, binary catalyst system consisting of commercially available pyridinemethanol as the hydrogen bond donors (HBDs) containing an organonitrogen component (pyridine) and *n*Bu₄NI as the co-catalyst for the cycloaddition of epoxides to ambient CO₂, affording five-membered cyclic carbonates under ambient conditions. Furthermore, optically pure epoxides were converted to the corresponding cyclic carbonates with minimal loss in the *ee* values. Notably, the binary catalytic system, 2,6-pyridinedimethanol/*n*Bu₄NI, is recyclable at least six times without any significant loss of activity, making this catalytic system sustainable and economical.

Keywords

Chemical fixation of CO₂, cyclic carbonates, ambient pressure, organocatalytic system

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Abbreviations

CO ₂	carbon dioxide
TON	turnover number
TOF	turnover frequency
Salen	<i>N,N'</i> -ethylenebis(salicylimine)
<i>ee</i>	enantiomeric excess
HBDs	hydrogen bond donors
DMSO	dimethyl sulfoxide
DMF	<i>N,N</i> -dimethylformamide
BnBr	benzyl bromide
SO	styrene oxide
DMAc	<i>N,N</i> -dimethylacetamide
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DABCO	1,4-diazabicyclo[2.2.2]octane
DMAP	<i>N,N</i> -dimethylaminopyridine
Py	pyridine
TEA	triethylamine
Im	imidazole
MIm	<i>N</i> -methylimidazole

List of Publications

This thesis is based on the following papers, referred to in the text by their Roman numerals I-III.

I. “Synthesis of cyclic carbonates from CO₂ and epoxides catalyzed by low loadings of benzyl bromide/DMF at ambient pressure”

Lin Wang, Li Lin, Guangyou Zhang, Koichi Kodama, Mikio Yasutake, and Takuji Hirose

Chem. Commun., **2014**, 50, 14813-14816.

II. “DBU/benzyl bromide: an efficient catalytic system for the chemical fixation of CO₂ into cyclic carbonates under metal- and solvent-free conditions”

Lin Wang, Koichi Kodama and Takuji Hirose

Catal. Sci. Technol., **2016**, 6, 3872-3877.

III. “An efficient metal- and solvent-free organocatalytic system for chemical fixation of CO₂ into cyclic carbonates under mild conditions”

Lin Wang, Guangyou Zhang, Koichi Kodama and Takuji Hirose

Green Chem., **2016**, 18, 1229-1233.

1. Introduction

1.1 Emission of CO₂

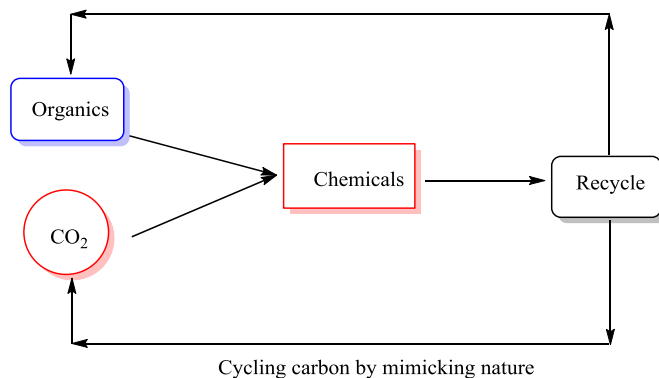
The increasing emission of carbon dioxide (CO₂) into the Earth's atmosphere has raised several concerns about the environmental impact of this greenhouse gas, thus necessitating the need for mitigating CO₂ emission.¹

In 2010, it was reported that the emission of CO₂ from human activities reached to *ca.* 30, 000 million tons, of which 43% was from coal combustion, 36% from oil, and 20% from gas.² It is very different for the growth of consumption of the above fuels. From 2009, coal is filling much of the world energy demand, due to the vast use in countries like India, China and where energy intensive productive activities based on this form of fossil carbon.

In 2012, without additional abatement measures, the World Environment Organization presents that in 2035 emissions from coal will grow to 15, 300 million tons of CO₂ compared to 13, 100 million tons in 2010, which shows substantially increasing CO₂ emissions is caused from the intensified use of coal.³

1.2 CO₂ as a Green C1 Resource

It is predicted that the current carbon-based raw materials from fossil fuels will be depleted in the decades to come;⁴ thus, renewable resources should be utilized for a sustainable society. Recently, the utilization of CO₂ has been raised considerable attention as it could either apply to cycling carbon, mimicking nature that makes thousands of value-added compounds from atmospheric CO₂, or lessen the climate change impact by employing CO₂ instead of chemicals. In recent years, CO₂ has been regarded as a renewable, nontoxic, economical, and abundant C1 feedstock for organic synthesis.⁵ CO₂ is also attractive as an environmentally friendly chemical reagent (especially useful as a phosgene substitute). However, the development of efficient catalysts for CO₂ activation and fixation is hindered by its inherent thermodynamic stability and kinetic inertness.⁶



CO₂ is involved as a building block, such as (i) production of chemicals, (ii) production of fuels (methanol, HCOOH), (iii) preparation of polycarbonates through copolymerization of epoxides and CO₂ and so on (as shown in Fig. 1). CO₂ has low energy level, in other words, a large energy input is required for transformation of CO₂. Thus, the development of high-performance catalysts is a key strategy. Recently, lots of catalytic reactions using high-energy starting materials such as hydrogen, unsaturated compounds, and organometallics were investigated considerably. Alternatively, as a promising possibility, we choose oxidized low-energy synthetic targets such as organic cyclic carbonates.

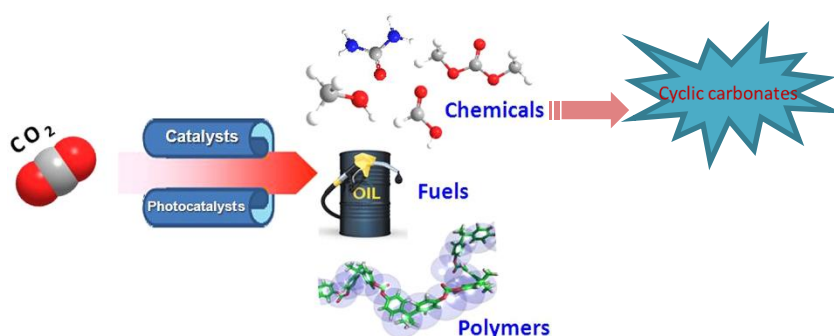


Fig. 1 CO₂ as the building block. Adapted from ref 3.³

1.3 CO₂ as a feedstock for synthesis of cyclic carbonates

The development of an efficient chemical process for the chemical fixation of this greenhouse gas into value-added organic chemicals under mild, metal-free reaction conditions is currently a very attractive prospect from the viewpoint of sustainability and green chemistry. Many efficient methods for the transformation of CO₂ have emerged.⁷ In addition to the elimination of highly toxic phosgene during the catalytic route, the atom-efficient addition of CO₂ to epoxides to form cyclic carbonates is one of the most effective strategies (as described in Fig. 2).⁸

Cyclic carbonates have been synthesized (application of CO₂ as a synthon) since the 1950s and also find applications as green polar aprotic solvents,⁹ fuel additives, electrolytes for lithium-ion batteries, monomers in polymerization reactions, and intermediates for fine chemicals and pharmaceuticals. Additionally, another possibility for further transformation into their linear analogues is to carry out transesterification reactions.¹⁰

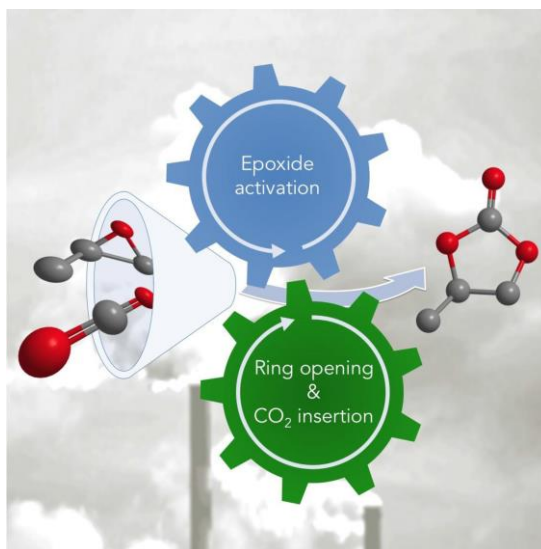


Fig. 2 Cycloaddition of CO₂ to epoxides.⁸

1.3.1 Metal-based catalytic systems for the synthesis of cyclic carbonates

In recent years, a variety of highly selective and reactive metal-based catalytic systems were developed. And representative systems are summarized in Fig. 3.^{7d}

In 1983, Inoue *et al.* described in their pioneering work that a (TPP)AlOMe complex can catalyze the reaction of CO₂ with epoxide at ambient conditions affording the corresponding cyclic carbonates.¹¹ After that, diverse metalloporphyrin catalysts were developed for this reaction. For example, Jing *et al.* in 2007, reported a Co(TPP)(OAc)/PTAT catalytic system to achieve this CO₂ fixation at room temperature and relatively low pressure (7 bar).¹² In 2012, Sakai *et al.* developed a highly active bifunctional porphyrin catalyst, which integrates Mg^{II} with an organocatalytic group (quaternary ammonium bromide). A high turnover number (TON=103,000) was achieved in the coupling of carbon dioxide with epoxides for obtaining the corresponding cyclic carbonates under solvent-free conditions.¹³ Salen-based complexes represent the different kind of efficient metal catalysts for the cycloaddition of CO₂ to epoxides. In 2001, Nguyen *et al.* reported the highly efficient, air stable and commercially available Cr^{III} salen complexes for the synthesis of cyclic carbonates under relatively mild conditions.¹⁴ While most of the work in this area employed pressurized carbon dioxide, Kleij *et al.* developed inexpensive and structurally simple Zn (salphen) catalysts, which can be employed as efficient catalysts for the synthesis of cyclic carbonates from terminal epoxides and CO₂ (2 bar).¹⁵ A noteworthy protocol for conversion 1 atm CO₂ into cyclic carbonates at room temperature employing bimetallic

Al^{III}-salen complexes was reported by North and coworkers.¹⁶ In 2013, Kleij *et al.* presented an amino triphenolate complex based on Al^{III} metal centre.¹⁷ It is shown that the complex is a highly active catalyst for the formation of organic carbonates. Strikingly, TOF as high as 36,000 per hour and TON over 100,000 were obtained. Except for the above-mentioned sophisticated metal complexes, simple onium salts can also act as efficient catalysts. For instance, a combination of ZnCl₂ and [Bmim]Br reported by Xia's group is a practical, highly efficient and environmentally benign catalytic system for the chemical fixation of CO₂ into cyclic carbonates.¹⁸ Additionally, in 2014, an efficient, recyclable catalytic system consists of ZnBr₂ and Poly(4-vinylimidazolium)s was also presented by Chung *et al.*, which could catalyze a broad scope of epoxides into cyclic carbonates.¹⁹

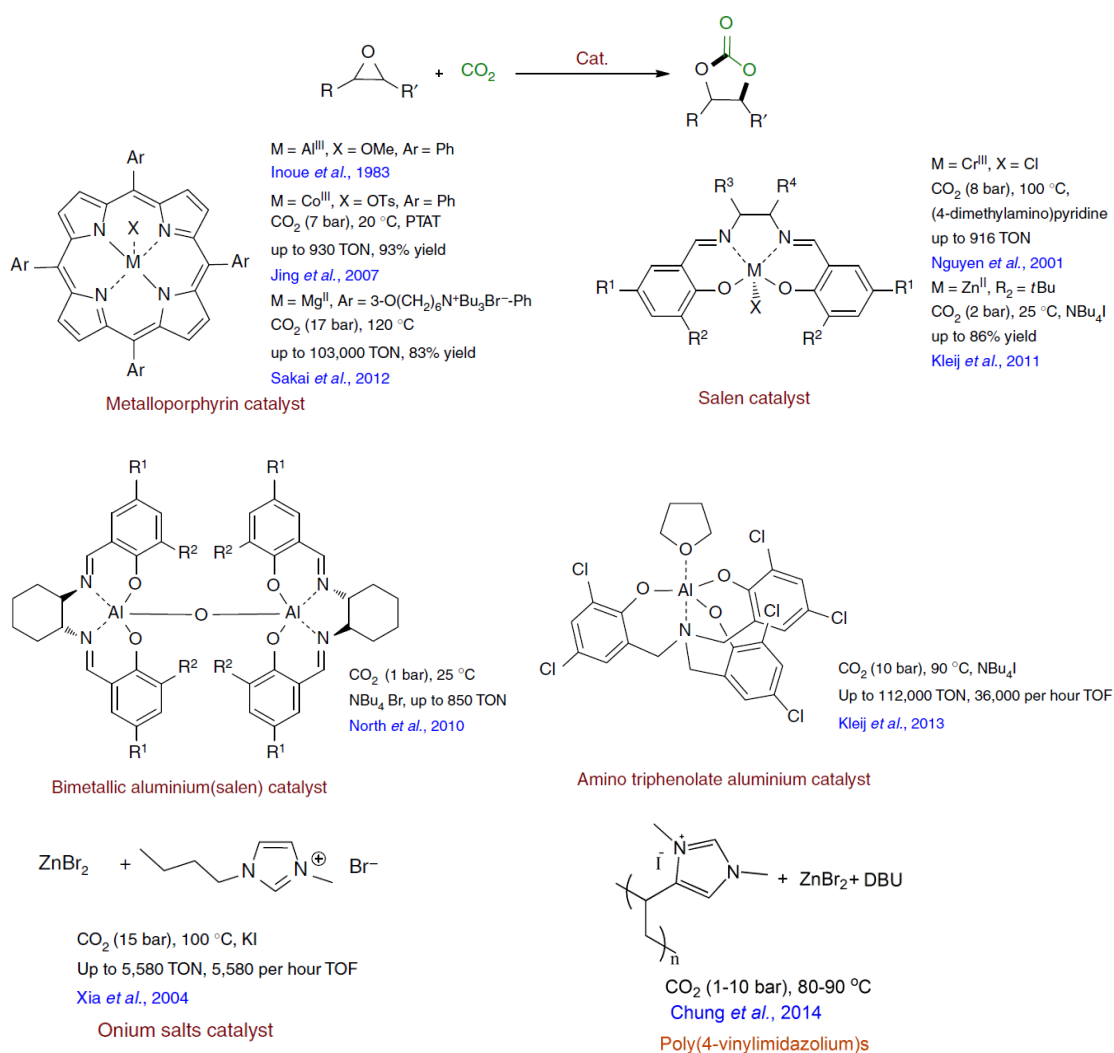
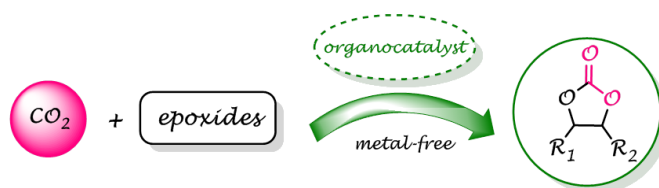


Fig. 3 Representative metal-based catalytic systems for synthesis of cyclic carbonates.^{7d}

1.3.2 Metal-free organocatalytic systems for the synthesis of cyclic carbonates



Metal-free organocatalysts for the synthesis of cyclic carbonates from CO₂ and epoxides could represent an attractive alternative, which are usually more cost-efficient, readily available, and less toxic.²⁰ Furthermore, with respect to green processes, metal waste should be avoided by using metal-free catalysts.

Until now, several metal-free catalysts (organocatalysts) based on pyridinium,²¹ imidazolium,²² ammonium,²³ and phosphonium salts²⁴ as well as *N*-heterocyclic carbenes²⁵ have been developed as both single catalysts and co-catalysts. However, most of these organocatalysts often require harsh reaction conditions (significantly higher temperatures and pressures than metal catalysts). Recently, several efficient binary catalytic systems have been developed, such as a mixture of hydrogen-bond donors (phenols,²⁶ glycerol,²⁷ pentaerythritol,²⁸ chitosan,²⁹ lignin,³⁰ cellulose,³¹) and a halide. Noteworthy, Kleij (T = 25-45 °C, pCO₂ = 10 atm),²⁶ Cokoja (T = 70 °C, pCO₂ = 4 atm)²⁸ and Werner (T = 90 °C, pCO₂ = 10 atm)³² reported relatively mild conditions; however, the reactions still require a high CO₂ pressure.

More recently, much milder reaction conditions were reached by the developing of efficient organocatalysts. For example, in 2013, Chatelet *et al.* employed azaphosphatranes as organocatalysts for the synthesis of cyclic carbonates under 1 atm CO₂ and 100 °C.³³ In the same year, a combination of bromine and DMF reported by Jamison and co-workers is an attractive and practical flow reactor system under 120 °C.³⁴ Notably, in 2014, Mattson *et al.* presented a silanediol-catalyzed system under ambient conditions (room temperature, 1 atm CO₂).³⁵ In 2015, Cokoja and co-workers also presented hydroxy-functionalized imidazolium bromides as catalysts for the cycloaddition of CO₂ and epoxides under relative mild conditions (T = 70 °C, pCO₂ = 4 atm), moreover, this organocatalytic system could be recycled very well.³⁶

It is worth mentioning that Han *et al.* in 2011 presented that cellulose/KI was a very active, selective and recyclable catalytic system for this reaction.³⁷ In 2014, Zhang *et al.* also employed cellulose as the catalyst combined with DBU as the cocatalyst, which is also an active and recyclable organocatalytic system.³⁸

Homogeneous organocatalysts are often difficult to isolate from the reaction mixture

due to the good product or catalyst solubility, which complicates recycling process. Thus, a very promising approach is to immobilize these homogeneous organocatalysts: not only separation is facilitated, but also a higher reaction rate can also be reached by using a suitable carrier material. For instance, in 2014, Kleij *et al.* presented THB-functionalized triazolium iodide on PS resin, which is an efficient and highly recyclable catalytic system for the cycloaddition of CO₂ and epoxides to afford corresponding cyclic carbonates under relatively mild conditions (T = 45 °C, pCO₂ = 10 atm).³⁹ In 2014, Zhang and co-workers developed imidazolium halides on silica supports, which exhibited efficient metal-free heterogeneous catalysts (TOF = 90 h⁻¹) for the fixation of CO₂ with epoxides into cyclic carbonates under mild conditions (T = 110 °C, pCO₂ = 10 atm).⁴⁰

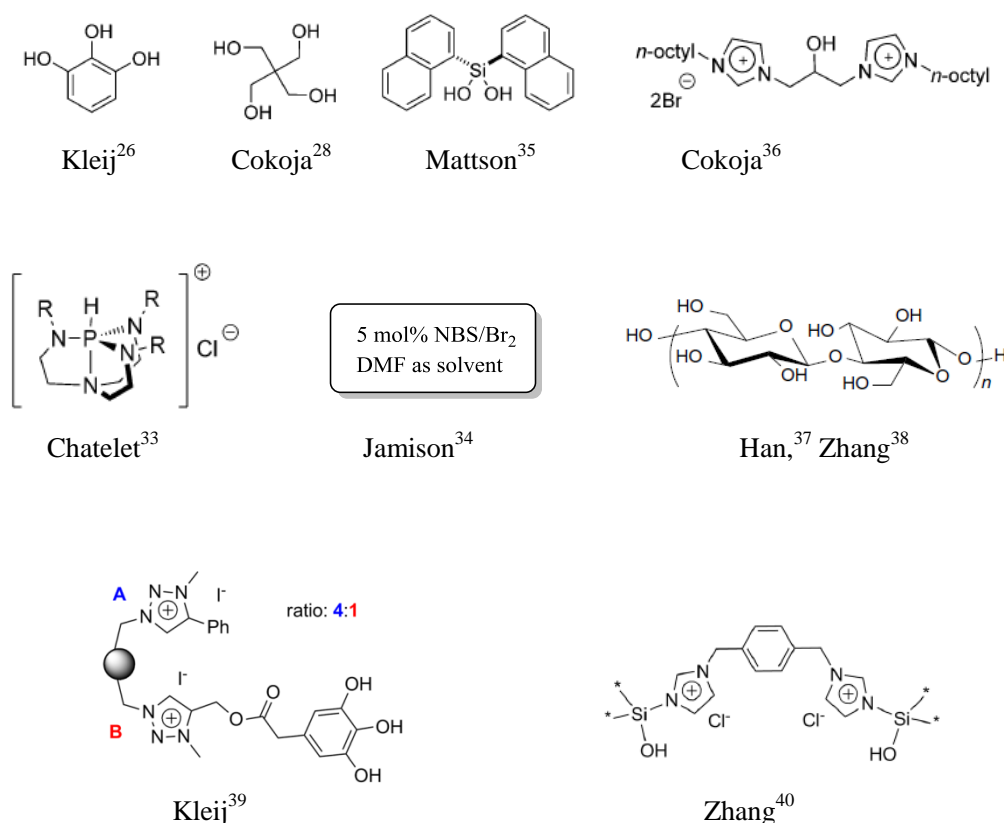


Fig. 4 Representative metal-free catalytic systems for chemical fixation of CO₂ into cyclic carbonates.

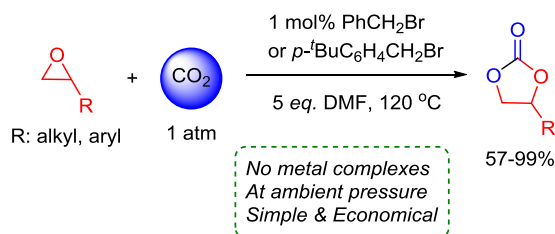
1.4 Aim of the Thesis

From the perspective of so-called “sustainable society” and “green chemistry”, efficient chemical processes should be developed for the chemical fixation of CO₂ into

value-added organic chemicals under mild reaction conditions.

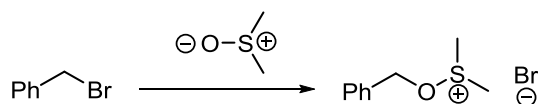
To date, the chemical fixation of CO₂ at ambient CO₂ pressure and ambient temperature has been a great challenge. Hence, simple, metal-free catalytic systems with enhanced properties remain to be developed for the efficient conversion of CO₂ to cyclic carbonates under mild reaction conditions. Therefore, during our study on the reaction of CO₂ with epoxides, we focused on developing a catalyst system using inexpensive and readily available compounds and without employing harsh reactions (significantly higher temperatures and CO₂ pressures than metal catalysts).

2. Low loadings of benzyl bromide/DMF as organocatalytic system



2.1 Background

Many organic reactions are known in which a combination of simple compounds forms a reactive intermediate or a new reagent like in the Swern oxidation and the Vilsmeier reaction. We noticed that a benzyloxysulfonium ion is formed from DMSO and benzyl halide (BnX) in the Kornblum oxidation (Scheme 1).⁴¹ Inspired by the Kornblum reaction, we conceived that if the benzyl cation could be transferred to epoxide and allowed for the formation of an oxonium ion species, it would undergo reaction with CO₂.



Scheme 1 Benzyloxysulfonium ion from BnBr and DMSO in Kornblum reaction.

More recently, Jamison *et al.* reported the nucleophilic activation of CO₂ by DMF,³⁴ which is shown in Fig. 5. Considering the activation of CO₂ by DMF, a combination of DMSO and DMF was expected to further enhance the reaction.

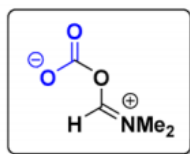


Fig. 5 Nucleophilic activation of CO₂ by DMF.³⁴

2.2 Results and discussion

Herein, we report an easy and mild procedure for the cycloaddition of epoxides to ambient CO₂ affording five-membered cyclic carbonates using a catalytic amount of benzyl halide and a small excess amount of DMF as a recyclable solvent.

Table 1 Influence of Various Parameters on the Cycloaddition of CO₂ to Styrene Oxide (SO).^a

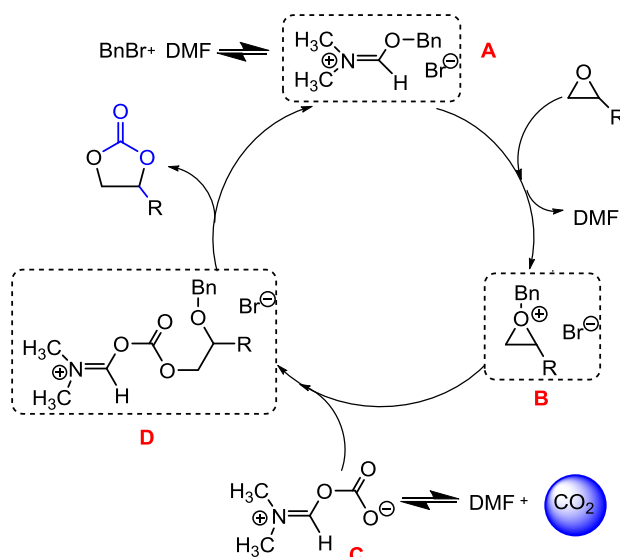
Entry	PhCH ₂ Br (mol%)	Solvent	T (°C)	Yield (%) ^b
1	5	DMSO (5 mL)	120	6
2	0	DMSO (5 mL)	120	0
3	5	DMF (2.5 mL)/DMSO (2.5 mL)	120	59
4	5	DMF (5 mL)	120	73
5	0	DMF (5 mL)	120	0
6	5	Toluene (5 mL)	120	0
7	5	DMF (5 mL)	100	62
8	5	DMF (5 mL)	80	0

^aReaction conditions: SO (5 mmol, 0.6008 g), CO₂ (99.999%, balloon), time 24 h. ^b Isolated yield.

The reaction of styrene oxide (SO) with CO₂ was used as the model reaction to systematically study the effect of various parameters on the reaction outcome (Table 1). At ambient CO₂ pressure, the reaction in DMSO afforded the corresponding cyclic carbonate (entry 1, Table 1). Although the yield was low (6%, 24 h), the promising results encouraged us to further investigate the benzyl cation as an important intermediate. Because no reaction occurred in the absence of BnBr (entry 2), BnBr was

confirmed to be a neutral and mild catalyst for the formation of cyclic carbonates from epoxides and CO₂. Recently, the nucleophilic activation of CO₂ by DMF was reported and this type of activation seemed to be appropriate for our study. As shown in entry 3, when DMSO and DMF were used as a mixed solvent system, the yield improved by about 10 times (59%), indicating that the nucleophilic activation of CO₂ by DMF was also feasible in the present system. When only DMF was used as the solvent (entry 4), the yield further improved to 73% with no detectable formation of by-products, indicating that DMF could activate CO₂ and BnBr in this reaction. The control experiments, without BnBr (entry 5) and in toluene (entry 6), revealed that the cycloaddition of SO to CO₂ proceeded with assistance from BnBr and DMF. Notably, this change makes it easier to recycle the solvent given that DMF has a lower boiling point than DMSO.

Temperature was also found to have a significant effect on this reaction (entries 4, 7, and 8). When the temperature was decreased to 100 °C, a lower yield of 62% was obtained with 5 mol% of BnBr (entry 7), and no conversion was observed at 80 °C (entry 8).



Scheme 2 A Plausible Mechanism for the Coupling Reaction of Epoxide with CO₂ Catalyzed by BnBr and DMF.

Based on the present and previous results,³⁴ the plausible catalytic mechanism is

shown in Scheme 2. Similar to the formation of a benzyl cation in the reaction with DMSO (Scheme 1), probably DMF also interacts with BnBr to generate iminium salt **A**. The interactions between BnBr and DMF were studied by the ^1H NMR spectrum of their 1 : 1 mixture at room temperature (Fig. 6). All the ^1H NMR signals of DMF (a, b, and c) in the mixture shifted up-field relative to those of pure DMF (from $\delta = 8.04$, 2.969, and 2.804 (Fig. 6A) to 7.44, 2.180, and 2.175 (Fig. 6B), respectively), indicating that BnBr was activated by DMF. The benzyl group of **A** transfers as a benzyl cation, activating the epoxide and generating a benzyl-oxonium species (**B**).

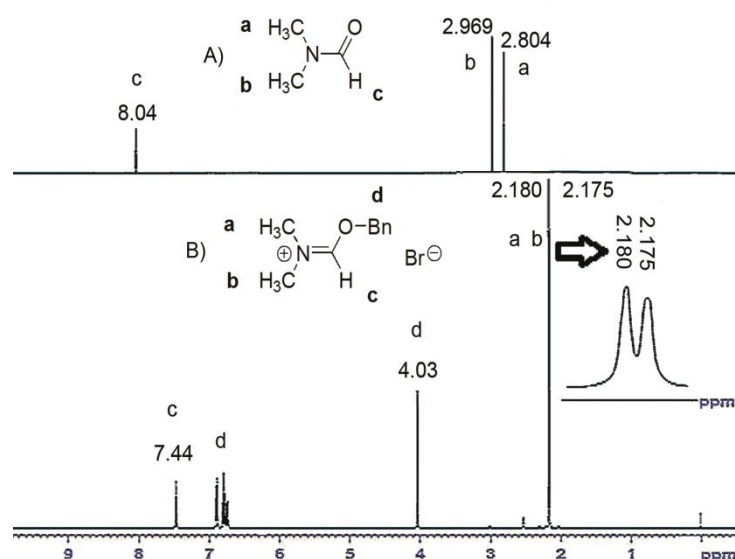


Fig. 6 ^1H NMR spectra of pure DMF (A) and a mixture of benzyl bromide and DMF (molar ratio=1:1) (B). (298 K, Dual NMR cell. The samples were placed in the inner cell, while DMSO- d_6 was placed in the outer cell as the external standard.)

On the other hand, CO_2 is activated by DMF to form $\text{C}^{34,42}$ which then reacts with **B** to afford intermediate **D**. According to the mechanism, the efficient ring-opening reaction is attributed to both the electrophilic activation of epoxide by the benzyl cation and the nucleophilic activation of CO_2 by DMF. Two possible mechanisms can account for the formation of the product. First the benzyl ether oxygen of **D** may attack the carbonyl carbon, forming a carbonate oxonium species and liberating DMF. Then a bromide ion (Br^-) cleaves the O-Bn bond regenerating BnBr. Alternatively, the O-Bn bond of **D** may be cleaved by Br^- , thus regenerating BnBr. Simultaneously, an alkoxide anion is liberated and undergoes cyclization to form the carbonate and release DMF. In

both scenarios, smooth cyclization of **D** and regeneration of DMF are important for negligible by-product formation.

The reaction conditions were optimized and the results are summarized in Table 2. The reaction yield was improved when DMF and SO were stirred at 120 °C for 4 h (86%, entry 2) rather than at room temperature for 30 min (73%, entry 1). The nucleophilic activation of CO₂ by DMF seems to be important in this reaction. It can be seen that 1 mol% of BnBr was sufficient as a catalyst. Moreover, the amount of DMF was successfully decreased to 5 *equiv.* without affecting the yield (86%, entry 3). When DMF was decreased to 3 *equiv.*, the yield also decreased (29%, entry 4), but a longer reaction time afforded a satisfactory result (81%, entry 5). Thus, DMF is expected to work as a solvent for CO₂ as well.

Table 2 Optimization of Reaction Conditions.^a

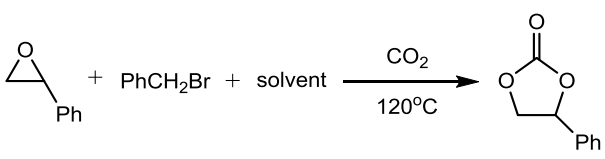
Entry	PhCH ₂ X (mol%)	DMF	Method	Yield (%) ^b
1	PhCH ₂ Br (5)	~13 <i>eq.</i> [5 mL]	a	73
2	PhCH ₂ Br (5)	~13 <i>eq.</i> [5 mL]	b	86
3	PhCH ₂ Br (1)	5 <i>eq.</i>	b	86
4	PhCH ₂ Br (1)	3 <i>eq.</i>	b	29
5	PhCH ₂ Br (1)	3 <i>eq.</i>	c	81
6	PhCH ₂ Cl (1)	5 <i>eq.</i>	b	81

^a Reaction conditions: SO (5 mmol, 0.6008 g), CO₂ (99.999%, balloon). Method a: After DMF and SO were stirred at room temperature for 30 min under CO₂, BnBr was added and stirred for 23.5 h at 120 °C. Method b: After DMF and SO were stirred at 120 °C for 4 h under CO₂, benzyl halide was added and stirred for 20 h at 120 °C. Method c: The reaction time was 48 h (4 h + 44 h) under the same reaction conditions as those of method b. ^b Isolated yield.

With the above results in hand, BnCl was investigated to compare the effect of the halogen atom (81%, entry 6). Under the same reaction conditions, the yield decreased

slightly (vs. entry 3), while being comparable to the reaction with 1 mol% BnBr (entry 5). This is mainly due to the lower reactivity of BnCl because Cl⁻ constitutes a poorer leaving group than Br⁻.

Table 3 Screening of Solvents.^a



Entry	Solvent	Yield (%) ^b
1	DMF	86
2	DMAc	83
3	<i>N</i> -Formylpiperidine	68
4	<i>N</i> -methylpyrrolidone	51
5	<i>N</i> -Formylmorpholine	47
6	<i>N,N,N',N'</i> -Tetramethylurea	71


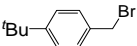
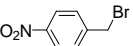
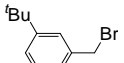
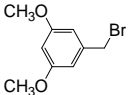




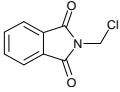
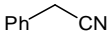
^a Reaction conditions: PhCH₂Br (1 mol%), epoxide (5 mmol), DMF (5 equiv.), CO₂ (99.999%, balloon), temperature 120 °C, total reaction time 24h. ^b Isolated yield.

The solvent effect on the reaction was further investigated for some amide-type solvents and the results are summarized in Table 3. All commercially available amides, DMAc, *N*-formylmorpholine, *N*-methylpyrrolidone, and *N*-formylpiperidine, afforded styrene carbonate in moderate-to-high yields (47-83%), but DMF gave the best result (86% yield). It is interesting that *N,N,N',N'*-tetramethylurea also resulted in a good yield of 71% (entry 6). The results support the mechanistic role of the amide-type carbonyl group, as shown in Scheme 2.³⁴

The structural effect of the catalyst was investigated for some benzyl bromides and halomethane derivatives, and the results are summarized in Table 4. Although the reactions of all benzyl bromides afforded styrene carbonate in high yields (>80%), benzyl bromides with an electron-donating group gave better results than those with an electron-withdrawing group or a branched structure (entries 2, 4, and 5 vs. 3, 6 and 7).

Interestingly, some halomethane derivatives, bromoacetonitrile, chloroacetone, and *N*-chloromethylphthalimide, also resulted in good yields of 72-88% (entries 8-10); however, no reaction occurred when using benzyl cyanide (entry 11).

Table 4 Screening of Catalysts.^a

Entry	Catalyst	Yield (%) ^b
1		86
2		92
3		80
4		88
5		89
6		85
7		86
8		72
9		82
10		88
11		0

^a Reaction conditions: catalyst (1 mol%), epoxide (5 mmol), DMF (5 equiv.), CO₂ (99.999%, balloon), temperature 120 °C, total reaction time 24h. ^b Isolated yield.

To evaluate the substrate scope of the catalytic system, various epoxides were reacted with CO₂ using 1 mol% BnBr and *p*-*tert*-butylbenzyl bromide in 5 equiv. of DMF at

120 °C as the optimal conditions. As shown in Table 5, most of the substrates were smoothly converted to the corresponding cyclic carbonates in good-to-excellent yields up to 99%. As shown in Table 5, *p*-*tert*-butylbenzyl bromide resulted in better yields for all the substrates studied.

Table 5 Synthesis of cyclic carbonates from CO₂ and epoxides^{a,b}

1b 75 ^c 78 ^d	2b 79 ^c	3b 82 ^c 85 ^d
4b 74 ^c 78 ^d	5b 57 ^c 59 ^d	6b 82 ^c
7b 90 ^c 99 ^d	8b 86 ^c 92 ^d	(R)-8b 85 (69 % ee) ^c 91 (63 % ee) ^d

^a Reaction conditions: epoxide (5 mmol except for **1a** (10 mmol) and **2a**, **4a**, and **5a** (6 mmol)), benzyl bromide (1 mol%), DMF (5 equiv.), CO₂ (99.999%, balloon), temperature 120 °C, total reaction time 24 h. ^b Isolated yield. ^c By BnBr. ^d By *p*-*tert*-butylbenzyl bromide.

Under the optimal conditions disubstituted epoxides such as cyclohexene oxide and trans-stilbene oxide were not converted to cyclic carbonates, presumably owing to the high steric hindrance.⁴³ This steric effect was more likely to hinder the nucleophilic attack on the epoxide rather than the coordination of the benzyl cation. Compared to the

previous metal-free catalytic systems under atmospheric CO₂ pressure,^{33, 34} the present system gave comparable yields and scope of various cyclic carbonates with low loading of an inexpensive catalyst.

Enantiomerically pure epoxide, (*R*)-**8a**, was transformed into (*R*)-**8b** with some *ee* loss in 85% yield (entry 9, 69% *ee*) by BnBr. When *p*-*tert*-butylbenzyl bromide was used, a further decrease in optical purity (63% *ee*) was observed despite higher chemical yield. On the other hand, negligible racemization of (*R*)-**8b** (from 69% *ee* to 67% *ee*) was confirmed at 120 °C for 24 h. Based on these results, the reaction at the less-hindered side of epoxide seems to be favorable as shown in Scheme 2. The stabilization of the positive charge at the tertiary 2-position of **B** is expected to be the main cause of the decrease in optical purity by direct attack of activated CO₂,³⁴ and thus more reactive *p*-*tert*-butylbenzyl bromide resulted in less regioselectivity (entry 9, 63% *ee*).

2.3 Conclusions

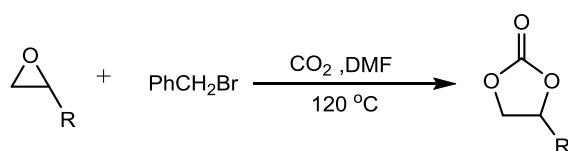
In summary, a new metal-free system for the conversion of CO₂ to cyclic carbonates was developed using commercially available and inexpensive materials: 1 mol% of benzyl halide as the nucleophilic catalyst and 3-5 *equiv.* of DMF as the recyclable solvent and activator. Under ambient CO₂, the catalyst system smoothly converted diverse terminal epoxides up to 99% yields. This procedure has a broad substrate scope. The ring opening of epoxide can be attributed to the electrophilic activation of epoxides by benzyl cations and the nucleophilic activation of CO₂ by DMF. Further study is currently underway to develop more economical and mild procedures for the cycloaddition of CO₂ to epoxides in our laboratory.

2.4 Experimental Section and ¹H and ¹³C NMR Spectral Charts

All starting materials and solvents commercially available were purchased at the highest quality from Sigma-Aldrich or Wako and used as received unless otherwise indicated. Reactions were monitored by thin layer chromatography using 0.25-mm E. Merck silica gel coated on aluminum plates (60F-254) with UV light to visualize the course of the reaction. Chemical yields refer to the pure isolated substances. ¹H (500 MHz) and ¹³C (125 MHz) NMR spectra were obtained using a Bruker AV-500 (500

MHz) spectrometer. The chemical shifts of the products were reported in ppm with reference to Me₄Si as the internal standard in CDCl₃ solution. The data were reported in the following order: chemical shift, multiplicity, coupling constants in Hz and integration. On the other hand, the spectra of the reaction system materials were taken using a coaxial dual NMR cell. The inner cell contained DMF, the DMF-BnBr mixture, and the reaction mixture, while the outer cell contained DMSO-d₆ as the external standard. Enantiomeric excesses of the carbonates were determined by HPLC analyses with a Daicel Chiralcel OD-3 with detection at 254 nm or 205 nm.

Representative procedure for the Cyclic Carbonate Formation



4-Phenyl-1,3-dioxolan-2-one (8b)

In a 20 mL two-neck flask, styrene oxide **8a** (5 mmol, 0.601 g) and DMF (5 equiv., 25 mmol, 1.827 g, flushed with CO₂ for 10 min) were stirred at 120 °C for 4 h under an atmosphere of CO₂ (99.999%, balloon), and then PhCH₂Br (0.05mmol, 0.0086 g) was added. The reaction mixture was stirred for 20 h at the same temperature and DMF was removed under reduced pressure. The residue was dissolved in ethyl acetate (50 mL) and washed with water (15 ml) and brine (15 mL × 2), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane : ethyl acetate = 3 : 1) to afford the desired cyclic carbonate 0.705 g (yield: 86.0%).

¹H NMR (500 MHz, CDCl₃): 7.42–7.37 (m, 2H), 7.37–7.30 (m, 3H), 5.70–5.60 (m, 1H), 4.81–4.70 (m, 1H), 4.31–4.20 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): 155.0, 135.9, 129.7, 129.2, 126.0, 78.0, 71.2.

Propylene carbonate (1b)

Propylene oxide (**1a**, 10 mmol, 0.581g), DMF (5 equiv., 50 mmol, 3.655 g), benzyl bromide (0.1 mmol, 0.0171 g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column

chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.766 g (yield: 75.0%).

^1H NMR (500 MHz, CDCl_3): 4.92–4.80 (m, 1H), 4.62–4.51 (m, 1H), 4.10–3.95 (m, 1H), 1.55–1.40 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3): 155.2, 73.7, 70.7, 19.3.

4-Butyl-1,3-dioxolan-2-one (2b)

1,2-Epoxyhexane (**2a**, 6 mmol, 0.601 g), DMF (5 equiv., 30 mmol, 2.193 g), benzyl bromide (0.06 mmol, 0.0103 g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.618 g (yield: 78.6%).

^1H NMR (500 MHz, CDCl_3): 4.80–4.65 (m, 1H), 4.60–4.50 (m, 1H), 4.18–4.01 (m, 1H), 1.85–1.62 (m, 2H), 1.55–1.22 (m, 4H), 0.93 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): 155.2, 77.2, 69.4, 33.4, 26.4, 22.2, 13.7.

4-Hexyl-1,3-dioxolan-2-one (3b)

1,2-Epoxyoctane (**3a**, 5 mmol, 0.641 g), DMF (5 equiv., 25 mmol, 1.827 g), benzyl bromide (0.05 mmol, 0.0086 g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 3 : 1) to afford the desired cyclic carbonate 0.666 g (yield: 81.5%).

^1H NMR (500 MHz, CDCl_3): 4.79–4.68 (m, 1H), 4.61–4.50 (m, 1H), 4.15–4.02 (m, 1H), 1.85–1.62 (m, 2H), 1.55–1.21 (m, 8H), 0.89 (t, J = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): 155.2, 77.2, 69.4, 33.7, 31.5, 28.7, 24.3, 22.4, 13.9.

4-(Chloromethyl)-1,3-dioxolan-2-one (4b)

Epichlorohydrin (**4a**, 6 mmol, 0.556 g), DMF (5 equiv., 30 mmol, 2.193 g), benzyl bromide (0.06 mmol, 0.0103 g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.602 g (yield: 73.5%).

¹H NMR (500 MHz, CDCl₃): 5.12–5.01 (m, 1H), 4.69–4.55 (m, 1H), 4.48–4.35 (m, 1H), 3.89 (dd, *J* = 12.5, 4.0 Hz, 1H), 3.77 (dd, *J* = 12.5, 3.5 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): 154.8, 74.7, 67.0, 44.6.

4-(But-3-en-1-yl)-1,3-dioxolan-2-one (5b)

1,2-Epoxy-5-hexene (**5a**, 6 mmol, 0.589 g), DMF (5 equiv., 30 mmol, 2.193 g), benzyl bromide (0.06 mmol, 0.0103 g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.490 g (yield: 57.4%).

¹H NMR (500 MHz, CDCl₃): 5.89–5.63 (m, 1H), 5.18–4.90 (m, 2H), 4.79–4.60 (m, 1H), 4.59–4.42 (m, 1H), 4.15–3.95 (m, 1H), 2.30–2.01 (m, 2H), 1.95–1.65 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): 155.1, 136.3, 116.0, 76.5, 69.4, 32.8, 28.6.

4-Allyloxymethyl-1,3-dioxolan-2-one (6b)

Allyl glycidyl ether (**6a**, 5 mmol, 0.571 g), DMF (5 equiv., 25 mmol, 1.827 g), benzyl bromide (0.05 mmol, 0.0086 g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.648 g (yield: 81.9%).

¹H NMR (CDCl₃, 500 MHz): 5.95–5.80 (m, 1H), 5.35–5.12 (m, 2H), 4.93–4.80 (m, 1H), 4.60–4.45 (m, 1H), 4.44–4.30 (m, 1H), 4.11–3.99 (m, 2H), 3.75–3.65 (m, 1H), 3.64–3.52 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): 155.2, 133.9, 117.3, 75.4, 72.3, 68.9, 66.2.

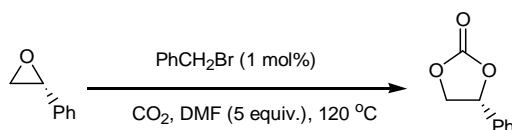
4-(Phenoxymethyl)-1,3-dioxolan-2-one (7b)

1,2-Epoxy-3-phenoxy propane (**7a**, 5 mmol, 0.750 g), DMF (5 equiv., 25 mmol, 1.827 g), benzyl bromide (0.05 mmol, 0.0086 g) were combined in a 20 mL two-neck flask according to the representative procedure. The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.870 g (yield: 89.6%).

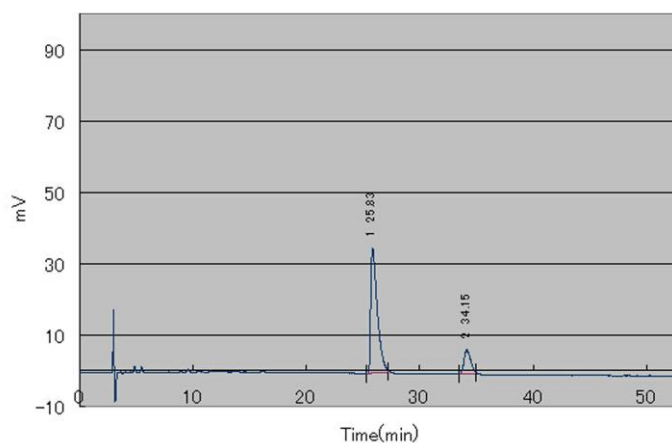
^1H NMR (500 MHz, CDCl_3): 7.36–7.22 (m, 2H), 7.06–6.92 (m, 1H), 6.91–6.85 (m, 2H), 5.06–4.95 (m, 1H), 4.65–4.56 (m, 1H), 4.55–4.46 (m, 1H), 4.22 (dd, $J = 10.5$, 4.0 Hz, 1H), 4.12 (dd, $J = 10.5$, 3.5 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): 157.8, 154.8, 129.7, 122.0, 114.7, 74.2, 66.9, 66.2.

Reaction of chiral epoxide

(*R*)-4-Phenyl-1,3-dioxolan-2-one ((*R*)-8b)

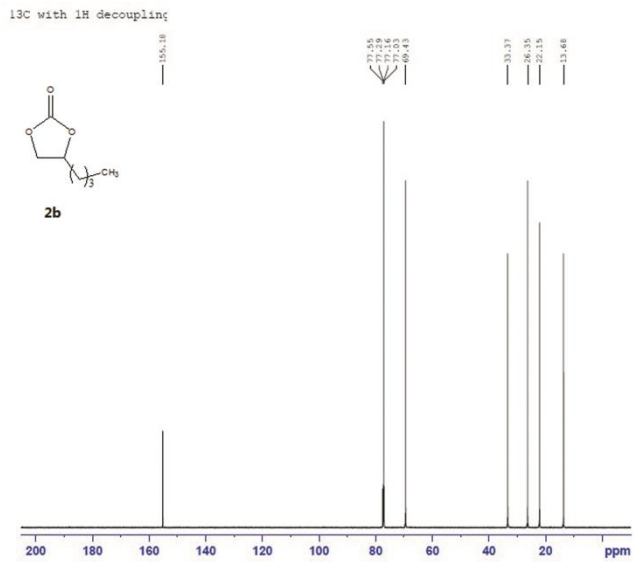
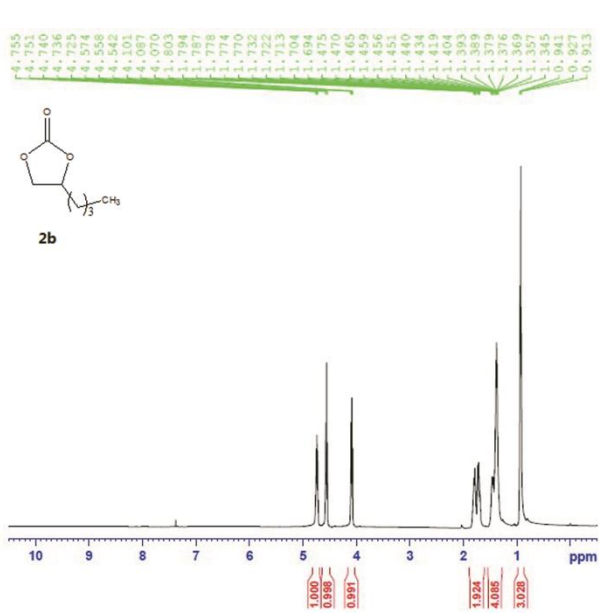
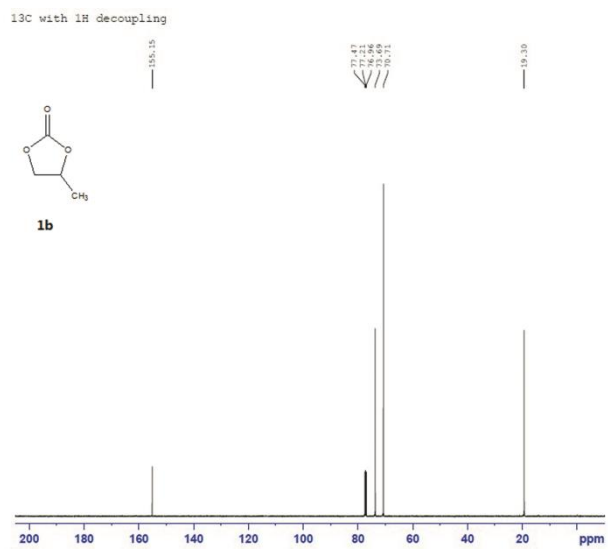
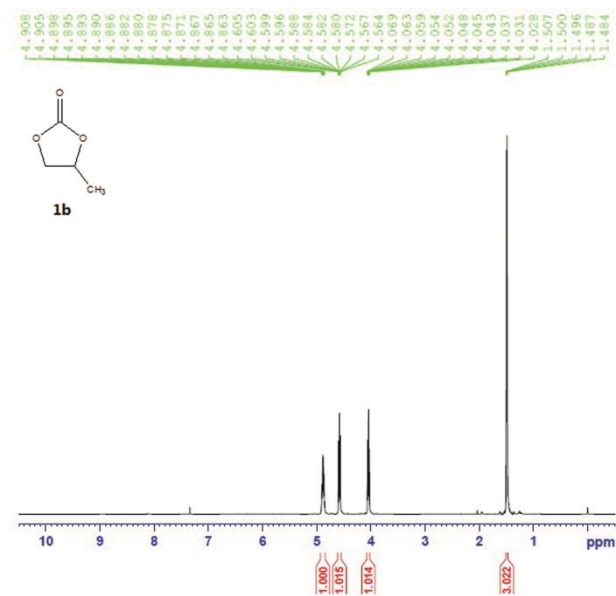


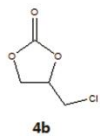
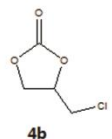
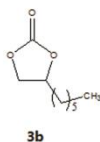
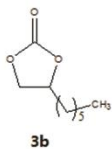
Reaction of (*R*)-styrene oxide was conducted according to the representative procedure, and the *ee* of the product was determined by chiral HPLC measurement using Chiralcel OD-3, 10% IPA/hexanes, 1 mL/min, $t_R=25.83$ min, $t_S=34.15$ min, 254 nm. Partial racemization of the product relative to the starting material was observed (68.6% *ee*). The DMF solution of the isolated product was kept for 24 h at $120\text{ }^\circ\text{C}$ and negligible change of optical purity was observed (66.6 % *ee*).

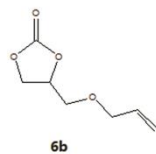
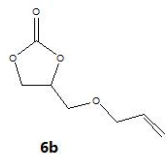
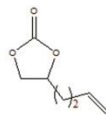
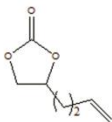


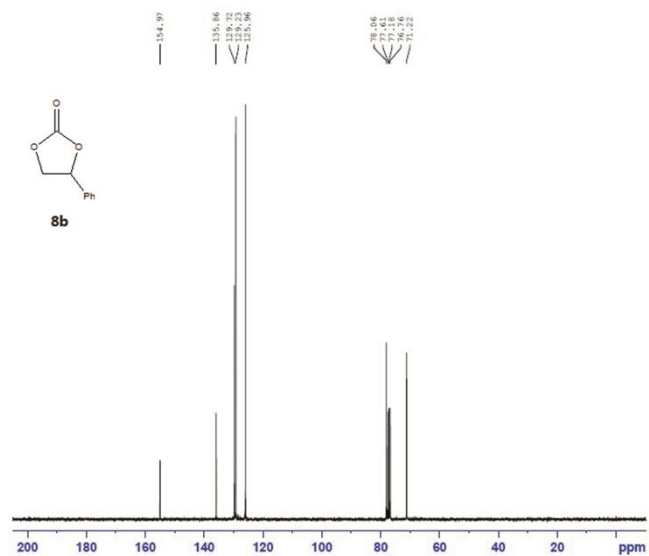
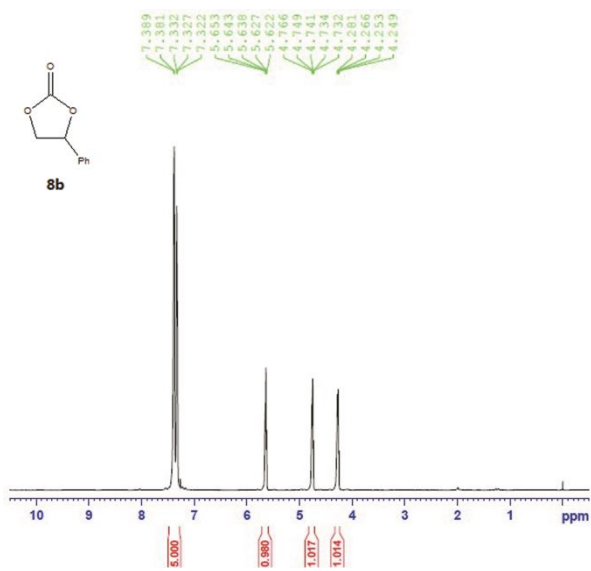
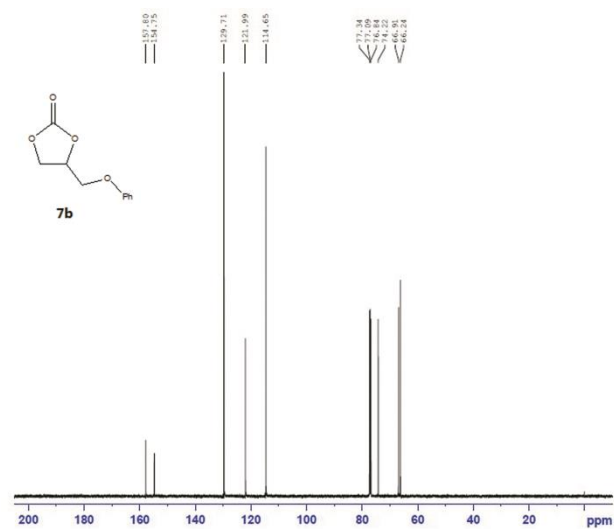
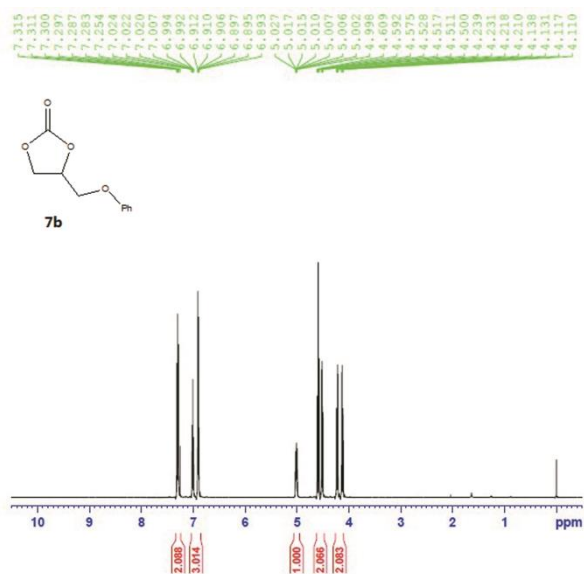
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2	34.15	262952.4	15.7029	6639	16073	1.343

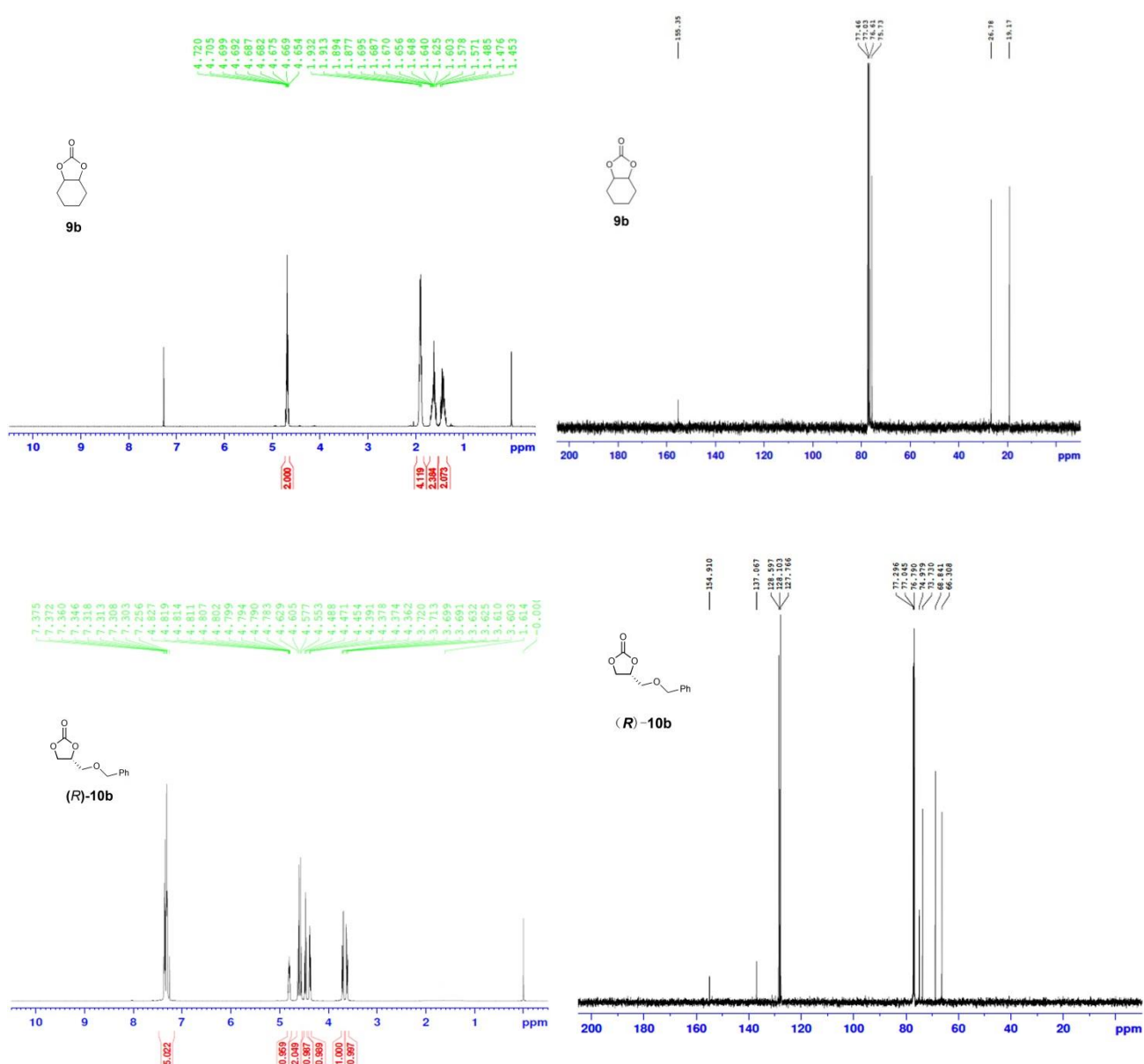
¹H and ¹³C NMR Spectral Charts:











3. Metal- and solvent-free catalytic system: DBU/benzyl bromide



Solvent-free
 No metal complexes
 Operationally simple
 At ambient pressure

3.1 Background

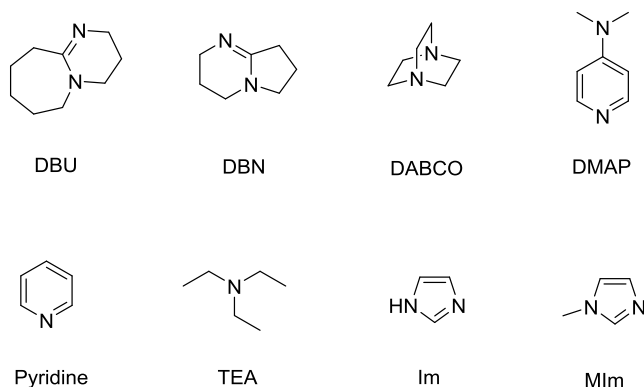
As mentioned before, many challenges must be overcome to increase the value of CO₂ as a chemical feedstock because the inherent kinetic and thermodynamic stability of CO₂ hampers the development of high performance catalysts that effect CO₂ activation and transformation.

To overcome the thermodynamics of CO₂, the use of organic bases has recently emerged. Among these materials, superbases, which provide new opportunities for CO₂ activation, are attracting ever-increasing attention in green chemistry.^{44, 45} Organic bases have recently been used in the conversion of CO₂ into cyclic carbonates in works such as those by the groups of Shi (T = 100-120 °C, pCO₂ = 35 atm),^{45a,b} Zhang (T = 120 °C, pCO₂ = 20 atm),³⁸ and Chung (T = 80 °C, pCO₂ = 1 atm).¹⁹ However, high CO₂ pressures or metallic ions are still required. Thus, metal-free synthetic methods using CO₂ under low pressure (optimally at 1 atm) are still highly desired.

As above-mentioned benzyl bromide/DMF catalytic system, the efficient conversion of CO₂ and epoxides to cyclic carbonates under mild and metal-free conditions (1 atm, 120 °C) was developed, but to realize the reaction at low temperature is still a great challenge.

Herein, we present a one-pot process for the combination of benzyl halides and organic bases as catalytic systems for the cycloaddition of epoxides to ambient CO₂. The reaction affords five-membered cyclic carbonates without the need for organic solvents or metal catalysts.

3.2 Results and discussion



Scheme 3 Chemical structures and designations of the organic bases used in this work.

To investigate the effects of organic bases and halides on the CO₂ conversion, several typical organic bases (Scheme 3) and halides were selected and explored. The bases were 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,4-diazabicyclo[2.2.2]octane (DABCO), *N,N*-dimethylaminopyridine (DMAP), pyridine (Py), triethylamine (TEA), imidazole (Im) and *N*-methylimidazole (MIm).

Table 6 Optimization of reaction conditions.^a

Entry	Catalytic system (mol)	T(°C)	Time (h)	Yield ^b (%)
1	5% DBU	65	24	48
2	5% PhCH ₂ Br	65	24	0
3	5% PhCH ₂ Br + 5% DBU	65	24	95
4	5% PhCH ₂ Br + 10% DBU	65	24	96
5	2.5% PhCH ₂ Br + 5% DBU	65	24	64
6	5% PhCH ₂ Br + 5% DBU	45	24	85
7	5% PhCH ₂ Br + 5% DBU	25	24	54
8	5% PhCH ₂ Br + 5% DBU	65	22	95
9	5% PhCH ₂ Br + 5% DBU	65	20	89

^a Reaction conditions: epichlorohydrin (6 mmol), CO₂ (99.999%, balloon).^b Isolated yield

First, the superbase DBU was employed in combination with benzyl bromide to systematically study the effect of various parameters on the model reaction of epichlorohydrin and CO₂ to produce the cyclic carbonate (chloromethyl)ethylene carbonate. The corresponding results are summarized in Table 6. At ambient CO₂ pressure, 5 mol% DBU alone afforded the corresponding cyclic carbonate in 48% yield (entry 1, Table 6), which might be due to the nucleophilic capability of DBU and its CO₂ activation effect.⁴⁶ When only benzyl bromide was used as the catalyst, negligible yield was observed (entry 2). However, a combination of DBU and benzyl bromide realized a significant enhancement in catalytic activity

(95%, entry 3) compared to that of each component individually, indicating the highly positive synergistic effect of DBU and benzyl bromide. No increase in the product yield was observed upon increasing the amount of DBU from 5 to 10 mol% (entries 3 and 4). However, an obvious decrease in the yield was observed when the amount of benzyl bromide decreased to 2.5 mol% (64%, entry 5), indicating that 5 mol% of DBU/benzyl bromide was the optimal catalyst loading. Additionally, upon lowering the temperature to 45 °C, a moderate yield (85%, entry 6) was obtained. However, further decrease of the temperature from 45 °C to 25 °C led to an unsatisfactory yield (54%, entry 7). Thus, 65 °C was selected as the optimal temperature.

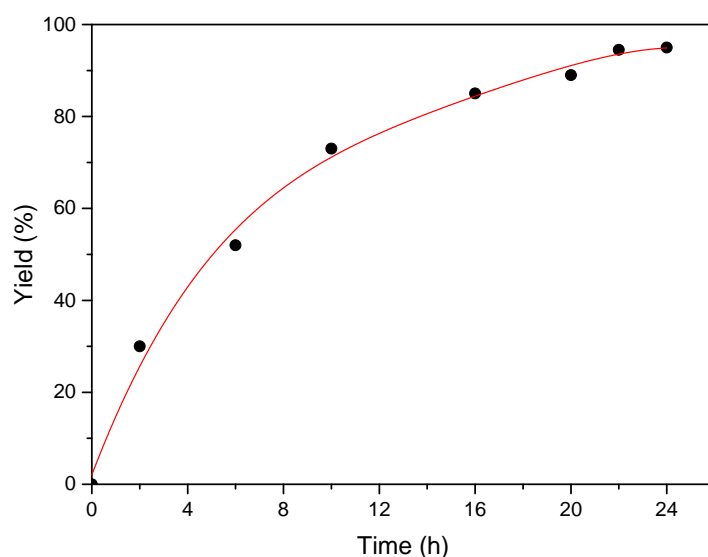


Fig. 6 Dependence of product yield on reaction time. Reaction conditions: epichlorohydrin (6 mmol), PhCH₂Br (0.3 mmol), DBU (0.3 mmol), CO₂ (99.999%, balloon), isolated yield.

In addition, the time dependence of product yield was also evaluated. As shown in Fig. 6, it can be seen that reaction time has a significant influence on the reaction yield and that the cycloaddition reaction proceeds rapidly within the first 10 h, during which time the product yield increases from 0% to 74%. Further extending the reaction time results

in relatively little improvement because the concentration of the starting materials decreases gradually with reaction time. As a result, reaction times of 22 and 24 h give almost the same yield of 95%, but a slightly lower yield of 89% is observed when the reaction time is 20 h (Fig. 6; entries 3, 8, and 9, Table 6). Hence, 22 h was chosen as the optimum reaction time. Moreover, the selectivity of the reaction for the desired product remained above 99% throughout.

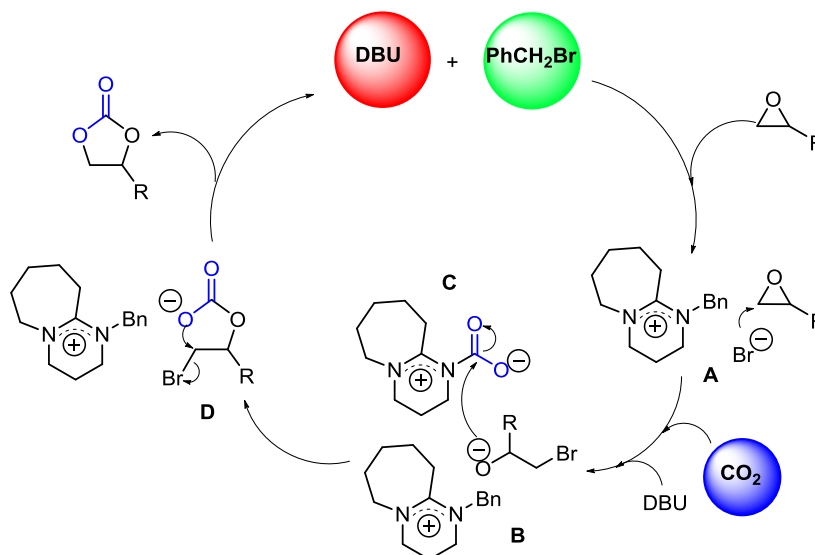
Table 7 The effect of organic bases on the cycloaddition^a

Entry	Base	pK _a ^b	T(°C)	Yield ^c (%)
1	DBU	24.3	65	95
2	DBN	23.7	65	91
3	DMAP	18.0	65	83
4	DABCO	(8.7)	65	54
5	Pyridine	12.5	65	85
6	TEA	18.8	65	84
7	MIm	(7.1)	65	81
8	Im	(7.0)	65	75

^a Reaction conditions: epichlorohydrin (6 mmol), PhCH₂Br (0.3 mmol, 5 mol%), time 22h, CO₂ (99.999%, balloon). ^b The pK_a value of the conjugated acid in acetonitrile or water (in parentheses)^{38,45} ^c Isolated yield (average of 2 runs).

Table 7 shows the effects of the different organic bases employed on the reaction in the presence of 5 mol% benzyl bromide. It can be seen that DBU is the most effective among the organic bases (entry 1, Table 7). Heldebrant *et al.* reported that organic bases with a lower pK_a value possess a lower negative Gibbs free energy to activate CO₂.^{46a} Consequently, the ability of the organic bases to form carbamate salts with CO₂ is in accordance with the order of the pK_a values. Notably, the results in Table 7 are largely consistent with this order. However, the presence of DABCO affords an unsatisfactory result (entry 4), which might be related to its high steric hindrance due to its rigid spherical shape. The results indicate that the strength of the base is a key factor for its

catalytic activity in the reaction and that steric hindrance of the base is also an important factor.



Scheme 4. Proposed mechanism for the coupling reaction of epoxide with CO₂ catalyzed by PhCH₂Br and DBU.

Based upon previous mechanistic studies on related systems^{45a,47,48} and the above results, we propose a plausible mechanism, as shown in Scheme 4. It is known that benzyl halides can react with organic bases easily to form quaternary onium salts. In the present DBU/PhCH₂Br system, the amidinium salt Bn-DBU⁺Br⁻ (**A**) is initially formed and catalyzes the ring-opening reaction through nucleophilic attack of its bromide ion at the less sterically hindered β -carbon atom of the epoxide, which results in oxanion species **B**. Simultaneously, DBU coordinates reversibly with CO₂,^{45d} affording carbamate salt **C**, an activated form of CO₂. Subsequently, nucleophilic attack by **B** on **C** forms alkylcarbonate anion **D**. Finally, the ring-closing of intermediate **D** affords the corresponding cyclic carbonate and regenerates the catalyst; thus the catalytic cycle is completed. According to this mechanism, when salt **C** is formed from DABCO and CO₂, the approach of **B** should be hindered due to its ball-like shape, leading to the lower yield observed in this system.

To investigate the reaction mechanism in detail, kinetic studies of the catalytic conversion of CO₂ and epichlorohydrin to cyclic carbonate were carried out using

PhCH₂Br and DBU as co-catalysts. As shown in Fig. 6, the product yield and reaction time almost have a linear relationship in the first 4 hours. Thus, the first 3 hours were chosen to investigate the reaction. The resulting kinetic curves of three different concentrations of DBU on the reaction are shown in Fig. 7. Notably, the concentration of DBU has a positive effect on the reaction rate, indicating the importance of the step of DBU coordinating reversibly with CO₂ to afford carbamate salt **C** in the proposed mechanism (Scheme 4). However, when using an excess amount of DBU (10 mol%; PhCH₂Br: 5 mol%), no drastic increase in the reaction rate was observed (line B and line C). This behavior may indirectly indicate that the step of forming CO₂ activated species by DBU (**C**, Scheme 4) is not the rate-determining step in the proposed mechanism. Additionally, the kinetic curves of three different concentrations of PhCH₂Br on the reaction were also investigated (Fig. 8). It can be clearly seen from Fig. 8 that the concentration of PhCH₂Br plays a significant role in the reaction. However, when using an excess amount of PhCH₂Br (7.5 mol%; DBU: 5 mol%), no significant increase in the reaction rate was observed. This further indicates the important role of the initially formed complex of DBU and PhCH₂Br (Bn-DBU⁺Br⁻ (**A**)) in the catalytic cycle, that is, the ring-opening reaction is through nucleophilic attack of its bromide ion on the epoxide rather than sole PhCH₂Br.

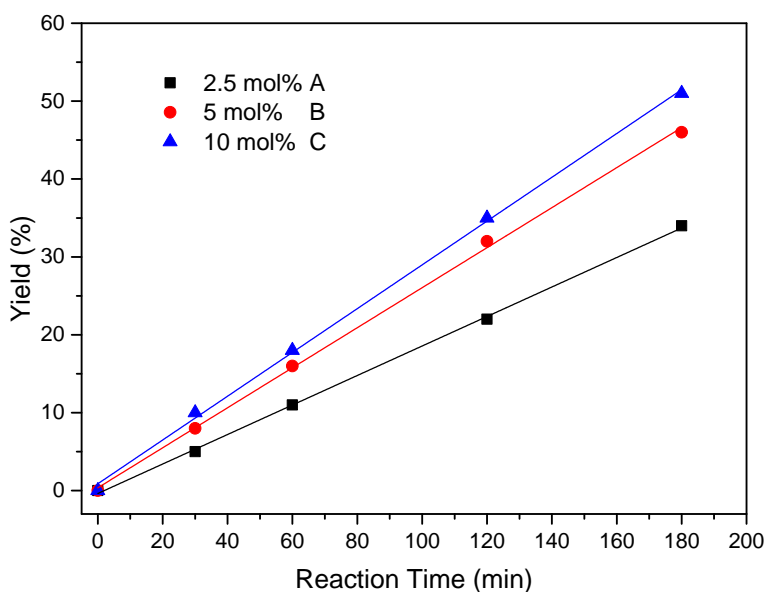


Fig. 7 Effect of DBU concentration on the reaction; Reactions were carried out under 1 atm CO₂ without solvent. Epichlorohydrin 6 mmol, PhCH₂Br 5 mol%, T = 65 °C, isolated yield. Line A: n[DBU] = 2.5 mol%, $y = 0.1893x$, $R^2 = 0.9997$; line B: n[DBU] = 5 mol%, $y = 0.2569x$, $R^2 = 0.9988$; line C: n[DBU] = 10 mol%, $y = 0.2810x$, $R^2 = 0.9986$.

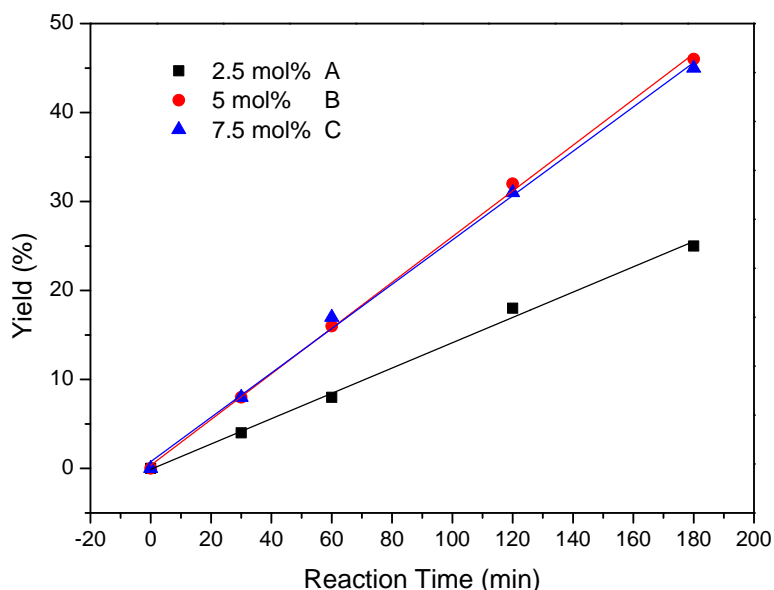


Fig. 8 Effect of PhCH₂Br concentration on the reaction; Reactions were carried out under 1 atm CO₂ without solvent. Epichlorohydrin 6 mmol, DBU 5 mol%, T = 65 °C, isolated yield. Line A: n[PhCH₂Br] = 2.5 mol%, $y = 0.1422x$, $R^2 = 0.9952$; line B: n[PhCH₂Br] = 5 mol%, $y = 0.2569x$, $R^2 = 0.9988$; line C: n[PhCH₂Br] = 7.5 mol%, $y = 0.2499x$, $R^2 = 0.9971$.

The present results (entries 1, 3, and 5, Table 6) and the above mechanism indicate that the role of the halide anion is important to the reaction rate. It is known that the order of nucleophilicity is $\text{Cl}^- > \text{Br}^-$, while the order of leaving ability is $\text{Br}^- > \text{Cl}^-$. Thus, the balance between the two conflicting factors is important. The proposed mechanism also indicates that the nucleophilicity of **A** and the leaving ability of halide anions from **D** are important for the catalytic activity. Hence, we investigated the effect of the halide anions on the catalytic activity, and the results are summarized in Table 8.

It can be seen that the activity increased in the order $\text{Cl}^- < \text{Br}^-$ (entries 1 and 2, Table

8). Additionally, the benzyl bromide derivatives with an electron-donating group gave better results than those with an electron-withdrawing group (entries 3, 4, and 5), presumably due to electron-withdrawing groups decreasing the leaving ability of the bromide anion from the amidinium center. Notably, in the presence of benzyl bromide, the reaction yield was better than those in the presence of *p*-^tBuPhCH₂Br and α-bromodiphenylmethane (entries 1, 3, and 5), indicating that the bulkiness of the formed quaternary onium salts also affected the reaction. When the arylmethyl halide is replaced by an alkyl halide, the yield decreases significantly (entries 6 and 7). For comparison with the ammonium salts formed using arylmethylbromide derivatives, *n*Bu₄NBr was employed as the bromide anion donor under the same conditions as the model reaction (entry 8). However, the yield was significantly lower than that using benzyl bromide as the bromide anion source, which is presumably due to the electrostatic interaction between the bromide anion and the ammonium center decreasing with the bulkiness of the cation.⁴⁷ Thus, the nucleophilicity of the bromide anion is weaker for *n*Bu₄NBr than the salts (Bn-DBU⁺Br⁻).

Table 8 The effect of halides on the cycloaddition^a

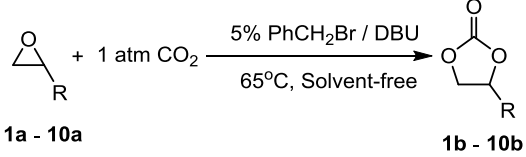
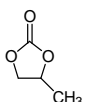
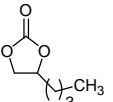
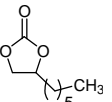
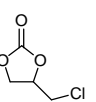
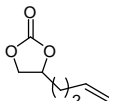
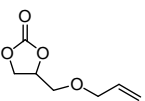
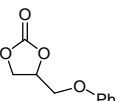
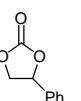
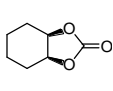

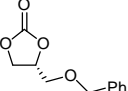
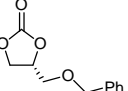
Entry	Halide	Yield ^b %
1	PhCH ₂ Br	95
2	PhCH ₂ Cl	71
3	<i>p</i> - ^t BuPhCH ₂ Br	92
4	4-Nitrobenzyl bromide	83
5	α-Bromodiphenylmethane	86
6	CH ₃ CH ₂ CH ₂ CH ₂ Br	68
7	CH ₃ CH ₂ CH ₂ CH ₂ I	27
8	<i>n</i> Bu ₄ NBr	72 (58) ^c

^a Reaction conditions: epichlorohydrin (6 mmol), DBU (0.3 mmol, 5 mol%), CO₂ (99.999%, balloon), T= 65 °C, time 22h. ^b Isolated yield (average of 2 runs). ^c without DBU.

In order to examine the substrate scope of the present dual catalyst system, a wide range of epoxides was investigated under the optimal reaction conditions (Table 9). The

results show that diverse epoxides are converted to the corresponding cyclic carbonates under ambient conditions with good to excellent yields.

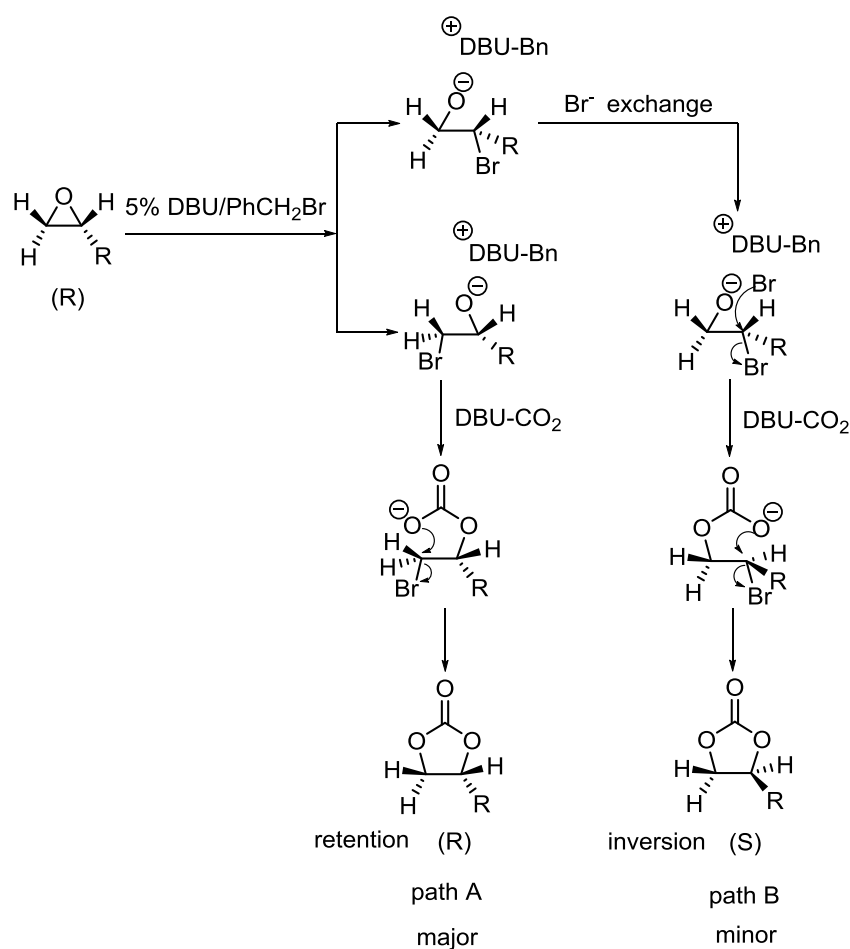
Table 9 Cycloaddition of CO₂ to various epoxides catalyzed by PhCH₂Br/DBU^a

	
	
1b 82 ^d	2b 85 ^b
	
3b 55 ^b 88 ^c	4b 95 ^b
	
5b 81 ^b	6b 85 ^b
	
7b 94 ^b	8b 82 ^b
	
cis-9b	(R)-8b 83 ^b
31 ^c	(98% <i>ee</i>)
	
(R)-10b	(R)-10b
89 ^b	35 ^e
(84% <i>ee</i>)	(99% <i>ee</i>)

^a Reaction conditions: epoxide (6mmol), binary catalyst (5 mol%), CO₂ (99.999%, balloon), reaction time 22 h, isolated yield. ^b T = 65 °C. ^c T = 95 °C. ^d Experiment reacted in 6M toluene, T = 45 °C. ^e DBU as a sole catalyst, T = 65 °C.

Among them, epichlorohydrin **4a** gave the best result, probably due to the electron-withdrawing properties of the chlorine atom. Similarly, the epoxides with an oxymethylene moiety (**6a**, **7a**, and **10a**, Table 9) afforded higher yields than those with alkyl groups. These substituents resulted in facilitated nucleophilic attack at the epoxide ring carbon atoms. Additionally, the other functional groups on the epoxide were stable in the reaction, indicating the outstanding efficiency of the catalytic system. The epoxides with large steric hindrance (**2a**, **3a**, and **8a**) were also converted to the

corresponding carbonates in good yields. Due to the higher steric hindrance of epoxide **3a** compared to the other epoxides, a higher reaction temperature (95 °C) was necessary to obtain a higher product yield. On the other hand, cyclohexene oxide, which is known to undergo cycloaddition with CO₂ poorly due to its steric hindrance, was converted to the corresponding carbonate **9b** in 31% yield at 95 °C, which was confirmed to be exclusively the *cis* isomer by ¹H NMR and ¹³C NMR spectra.^{18,49}



Scheme 5 Possible reaction pathways for the conversion of configuration.

This commercially inexpensive catalytic system can also be applied in the coupling of CO₂ and enantiomerically pure epoxides. (*R*)-**8a** was transformed to (*R*)-**8b** in 98% enantiomeric excess (*ee*), while (*R*)-**10b** was obtained with some loss in optical purity (84% *ee*) (Table 9). It can be concluded that the reaction at the β-carbon of epoxide seems favorable (Scheme 5, path A). Epoxide (*R*)-**10a** has lower potential steric

hindrance and higher reactivity than (*R*)-**8a**; thus, as for (*R*)-**10b**, the *ee* loss may be attributed to the nucleophilic attack on the α -carbon of the epoxide by the bromide anion, which may also be followed by a bromide–bromide ion exchange process to eventually afford the (*S*)-**10b** product (Scheme 5, path B).⁴⁸ When only DBU was used as a catalyst, (*R*)-**10b** was obtained in 35% yield, but with retention of stereochemistry (>99% *ee*), which indicates that direct nucleophilic attack of carbamate salt **C** on the epoxide proceeds exclusively at the less sterically hindered carbon atom.⁵⁰ This further demonstrates the possible role of the bromide anion in path B for the ring-opening process.

3.3 Conclusions

In summary, a simple, inexpensive and efficient binary organocatalytic system consisting of DBU and benzyl bromide was developed for the synthesis of cyclic carbonates from epoxides and CO₂ under metal- and solvent-free conditions. A diverse range of epoxides was transformed into the corresponding cyclic carbonates with good to excellent yields (81-95%) under very mild conditions (65 °C, 1 atm CO₂). Furthermore, optically pure epoxides were also investigated, and a plausible mechanism for the coupling reaction of epoxide with CO₂ was proposed. The proposed protocol provides an example of an easily handled, practical, and environmentally benign alternative for chemical fixation of CO₂ into 5-membered cyclic carbonates.

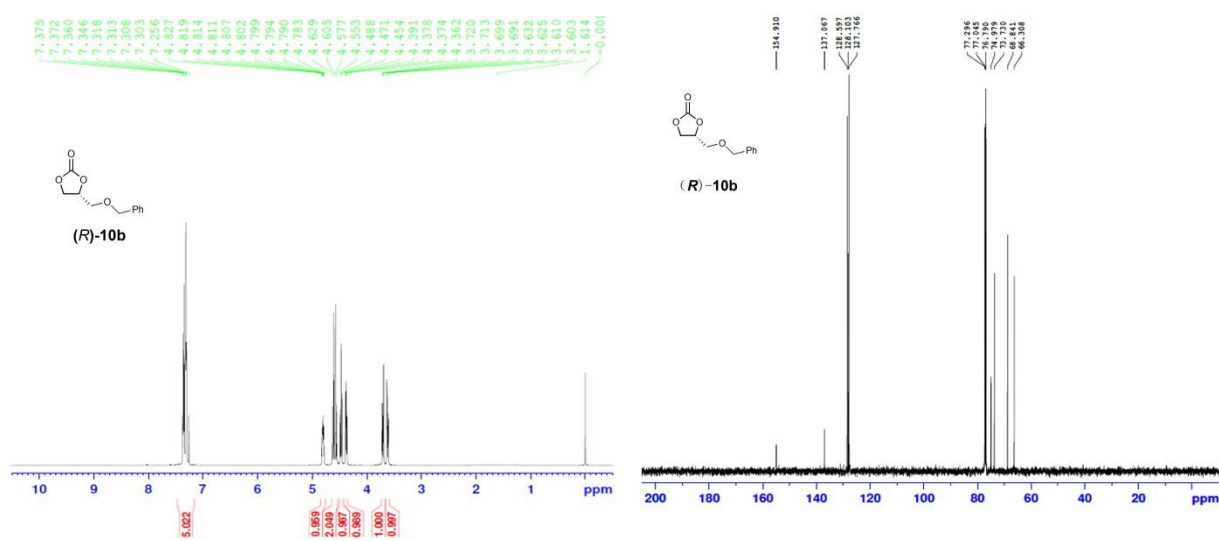
3.4 Experimental Section and ¹H and ¹³C NMR Spectral Charts

All starting materials and solvents commercially available were purchased at the highest quality from Sigma-Aldrich or Wako and used as received unless otherwise indicated. Chemical yields refer to the pure isolated substances. ¹H (500 MHz) and ¹³C (125 MHz) NMR spectra were obtained using a Bruker AV-500 (500 MHz) spectrometer. The chemical shifts of the products were reported in ppm with reference to Me₄Si as the internal standard in CDCl₃ solution. Enantiomeric excesses of the carbonates were determined by HPLC analyses with a Daicel Chiralcel OD-3 with detection at 254 nm.

Representative procedure for the cyclic carbonate formation (**4b**): In a 20 mL two-neck flask, epichlorohydrin **4a** (6 mmol, 0.555 g), DBU (5 mol%, 0.046 g) and PhCH₂Br (5 mol%, 0.051 g) were added under N₂ gas and then stirred at 65 °C for 22 h under an atmosphere of CO₂ (99.999%, balloon). After completion, the reaction mixture was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate (0.778 g, yield: 95.0%).

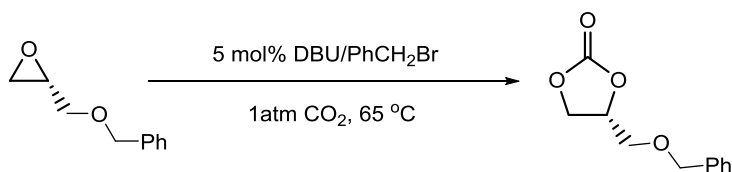
¹H NMR (500 MHz, CDCl₃): 5.12-5.01 (m, 1H), 4.69-4.55 (m, 1H), 4.48-4.35 (m, 1H), 3.89 (dd, J = 12.5, 4.0 Hz, 1H), 3.77 (dd, J = 12.5, 3.5 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): 154.8, 74.7, 67.0, 44.6. All the data are consistent with that previously reported.

As for the ¹H and ¹³C NMR Spectral Charts, the new supplementary spectra are for compound (*R*)-**10b**. And they are as follows:

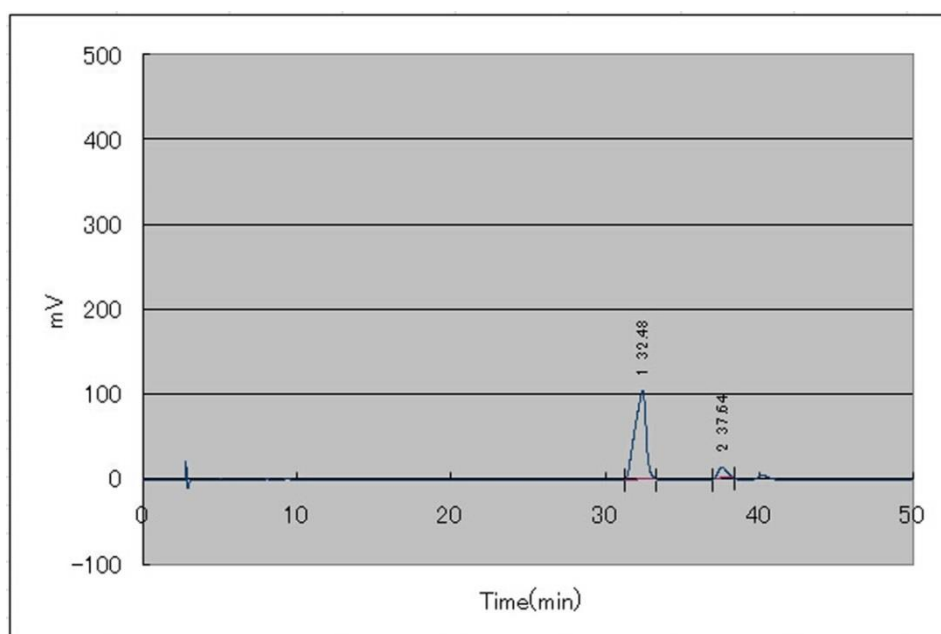


Moreover, the newly supplemented data are the ee value determination of (*R*)-**10b**

(*R*)-4-Benzyloxymethyl-1,3-dioxolan-2-one ((*R*)-**10b**)

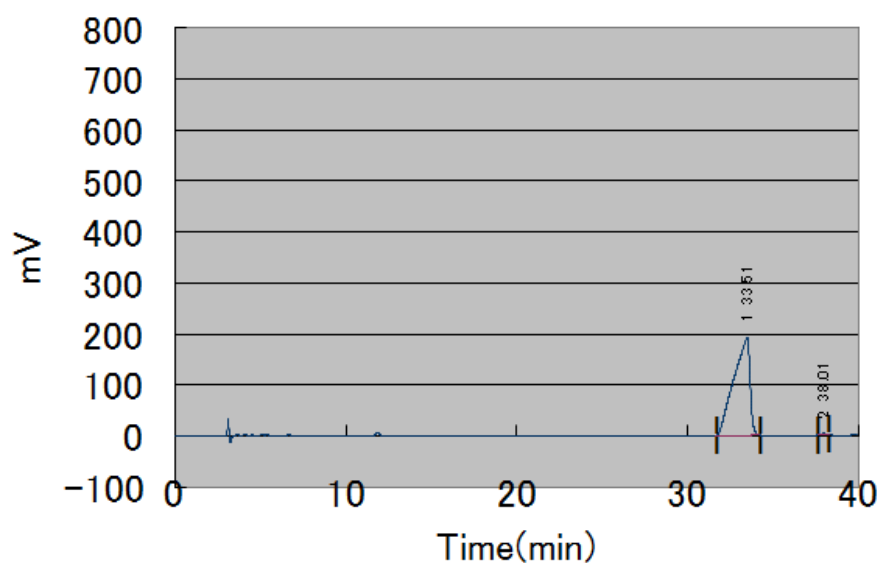


Reaction of (*R*)-Glycidyl benzyl ether was conducted according to the representative procedure, and the *ee* of the product was determined by chiral HPLC measurement using Chiralcel OD-3, 10% IPA/hexanes, 1 mL/min, t_R =32.48 min, t_S =37.64 min, 254 nm. Some racemization of the product (84% *ee*) relative to the starting material (99% *ee*) was observed.



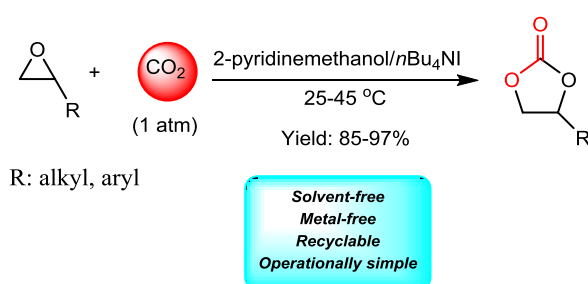
No.	Rt	Area	Area (%)	Height	NTP	Tf
1	32.48	5129703.029	91.9748	103839	9651.7	0.782
2	37.64	447591.732	8.0252	12465	25039	1.181

When only DBU was used as catalyst, (*R*)-**10b** was obtained in 35% yield with retention of stereochemistry (>99% *ee*), and the *ee* of the product was determined under the same condition.



No.	Rt	Area	Area (%)	Height	NTP	Tf
1	33.51	12645098.2	99.5874	191849	5619.8	0.639
2	38.01	52386.3	0.4126	2211	25032	1.091

4. An efficient and recyclable catalytic system under room temperature



4.1 Background

The development of an efficient chemical process for the chemical fixation of this greenhouse gas into value-added organic chemicals under mild, metal-free reaction conditions is currently a very attractive prospect from the viewpoint of sustainability and green chemistry.

As mentioned above, recently, several efficient binary catalytic systems have been developed, such as a mixture of hydrogen-bond donors (phenols,²⁶ glycerol,²⁷ pentaerythritol,²⁸ chitosan,²⁹ lignin,³⁰ cellulose,³¹ silanols,³⁵) and a halide. However, the reactions still require a high CO₂ pressure. To date, the chemical fixation of CO₂ at ambient CO₂ pressure and ambient temperature has been a great challenge.

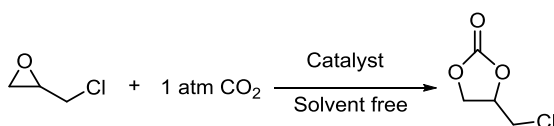
Hydrogen bond donors (HBDs) and the halogen anion play the most important role in the catalytic process.²⁶⁻³¹ It is well known that HBDs activate epoxides and facilitate the reaction with CO₂. Herein, we report the activation of CO₂ to further facilitate the fixation reaction. Well-known catalysts for activating CO₂ are organonitrogen compounds,^{44a,51} such as organic bases DBU, tri-*n*-butylamine, and pyridine.



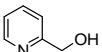
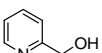
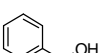
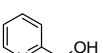
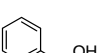
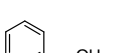
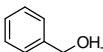
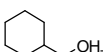
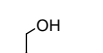
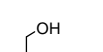
Compared to the number of reported metal-based catalyst systems, the number of organocatalytic systems is relatively low. Moreover, most of the reported systems typically require higher temperatures and pressures, challenging the applicability of these catalysts. For potential application in an economical and green process, the recyclability of the catalyst is an important feature. The recently reported organocatalytic systems could not be recycled very well. This is because, on the one hand, the catalyst is difficult to isolate from the reaction mixture; on the other hand, the catalyst is not stable under high temperatures and pressures.

Herein, we report a new, metal- and solvent-free, binary catalyst system consisting of commercially available pyridinemethanol as the HBD (methanol) containing an organonitrogen component (pyridine) and *n*Bu₄NI as the co-catalyst for the cycloaddition of epoxides to ambient CO₂, affording five-membered cyclic carbonates under ambient conditions. To the best of our knowledge, this catalytic system is the mildest and most efficient metal-free catalyst for this conversion among the recyclable catalytic systems (T = 25-45 °C, 1 atm CO₂).

4.2 Results and discussion

Table 10 Catalyst screening for the reaction conditions^a



Entry	Catalyst	T (°C)	Yield (%) ^b
1		25	3
2		60	39
3		25	18
4		60	73
5		60	0
6	 + $n\text{Bu}_4\text{NCl}$	25	52
7	 + $n\text{Bu}_4\text{NBr}$	25	67
8	 + $n\text{Bu}_4\text{NI}$	25	92
9	$n\text{Bu}_4\text{NI}$	25	26
10	 + $n\text{Bu}_4\text{NI}$	25	78
11	 + $n\text{Bu}_4\text{NI}$	25	58
12	 + $n\text{Bu}_4\text{NI}$	25	73
13	 + $n\text{Bu}_4\text{NI}$	25	92

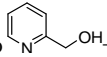
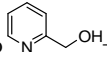
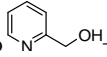
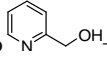
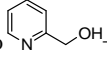
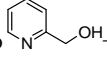
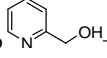
^a Reaction conditions: epichlorohydrin (6 mmol), catalyst (0.3 mmol, mol%), CO₂ (99.999%, balloon), 24h. ^b Isolated yield.

The reaction of epichlorohydrin with CO₂ was used as the model reaction to study the effect of various parameters on the reaction outcome (Table 10). At atmospheric pressure of CO₂, when only pyridine was used as the catalyst, the corresponding cyclic carbonate was obtained (entries 1 and 2, Table 10). Although the yield was low (39%, 60 °C), the result indicates that pyridine can activate CO₂ in this reaction. When 2-pyridinemethanol was used, a higher yield was obtained (entries 3 and 4, Table 10). The results indicate that the OH group of 2-pyridinemethanol plays a crucial role in promoting the reaction. Recently, Park *et al.* reported the synergistic catalysis of a N atom and OH group for the cycloaddition of epoxides to CO₂.⁵² They reported that the OH group initiated the epoxide ring-opening reaction, and the N atom of amine activated the inert CO₂ molecule. Similar results were obtained by our catalytic system and at a lower temperature and CO₂ pressure; however, the catalytic activity was not enough (entries 3 and 4, Table 10). Moreover, when benzyl alcohol was used as the catalyst no reaction occurred (entry 5, Table 10), further indicating the important role of N atom in pyridinemethanol. Nevertheless, when pyridinemethanol was combined with a halide ion as the binary catalytic system, a significantly higher yield was obtained under ambient conditions (entries 6-8, Table 10). However, when only *n*Bu₄NI was used, a low yield was obtained (26%, entry 9, Table 10), indicating the excellent synergistic effect of HBD bearing a N atom and halide in catalyzing the reaction. The results of the binary catalytic system entries 6–8, Table 10) show that the yield increased in the order: Cl[−] < Br[−] < I[−]; however, the intrinsic activity and nucleophilicity decreased in the order: Cl[−] > Br[−] > I[−]. This is probably because of stronger hydrogen-bond interactions between the alcohol moiety and chloride ion compared to bromide and iodide ions.^{28, 53} Furthermore, when other HBDs bearing no N atom were used as the dual catalytic system, the yields clearly decreased (entries 10–12, Table 10). Notably, the results obtained in entries 12 and 13 also indicate the crucial role of N atom in pyridinemethanol. As shown in entry 13, 2,6-pyridinedimethanol and *n*Bu₄NI were used as the dual catalytic system, resulting in the same yield (92%) as in entry 8. Moreover, the catalytic system was almost insoluble in epoxide, and thus could be easily recycled.

Nevertheless, all the above results indicate the acceleration of the ambient CO₂ cycloaddition to epoxides due to synergistic effects. The reaction conditions were

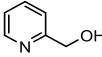
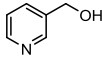
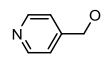
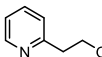
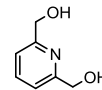
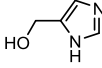
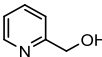

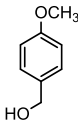
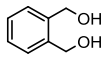
optimized; the results are shown in Table 11. First, the effect of catalyst concentration was investigated under ambient conditions (1 atm CO₂, 25 °C) for 24 h (entries 1–5, Table 2). The results indicate that the catalytic activity of the binary system strongly depends on the concentration of the catalysts. The almost quantitative conversion of epichlorohydrin with a catalyst loading of 8 mol% (entry 4, Table 11) decreased to 78% yield when the concentration of the catalysts was 3 mol% (entry 1, Table 11). The yield of the product did not increase with a further increase in the catalyst loading from 8% to 10% (entries 4 and 5, Table 11). Therefore, 8% was the optimum catalyst loading for this reaction. Moreover, a shortening of the reaction time from 24 h to 20 h maintained the yield of 97% (entries 4 and 6, Table 11); however, a further decrease in the reaction time to 18 h lowered the yield to 91% (entry 7, Table 11).

Table 11 Optimization of reaction conditions^a

Entry	Binary system (mol)	Time (h)	Yield (%) ^b
1	3%  + 3% <i>n</i> Bu ₄ NI	24	78
2	5%  + 5% <i>n</i> Bu ₄ NI	24	92
3	7%  + 7% <i>n</i> Bu ₄ NI	24	95
4	8%  + 8% <i>n</i> Bu ₄ NI	24	97
5	10%  + 10% <i>n</i> Bu ₄ NI	24	97
6	8%  + 8% <i>n</i> Bu ₄ NI	20	97
7	8%  + 8% <i>n</i> Bu ₄ NI	18	91

^a Reaction conditions: epichlorohydrin (6 mmol), CO₂ (99.999%, balloon), 25 °C. ^b Isolated yield.

Table 12 Model reaction and screening results for various co-catalysts^a

Entry	Co-catalyst 1	Co-catalyst 2	Yield ^b %
1		<i>n</i> Bu ₄ NI	97 (71)
2		<i>n</i> Bu ₄ NI	90 (62)
3		<i>n</i> Bu ₄ NI	89 (57)
4		<i>n</i> Bu ₄ NI	87 (51)
5		<i>n</i> Bu ₄ NI	97 (68)
6		<i>n</i> Bu ₄ NI	78 (50)
7 ^c		NaI	89 (54)
8		<i>n</i> Bu ₄ NI	65
9		<i>n</i> Bu ₄ NI	77
10		<i>n</i> Bu ₄ NI	82 (47)

^a Reaction conditions: epichlorohydrin (6 mmol), catalyst (0.48 mmol, 8 mol%), CO₂ (99.999%, balloon), 20 h. ^b Isolated yield, reaction time: 8 h (in parentheses). ^c KI was used as co-catalyst 2, yield: 90%, 20h.

A family of organocatalytic systems was screened under the optimized reaction conditions shown in entry 6, Table 11. The results are summarized in Table 12. A series of commercially available pyridinealcohols combined with *n*Bu₄NI as the co-catalyst were also screened as the organocatalysts (entries 2–5, Table 12). The cyclic carbonate was obtained in a high yield, indicating that all of them are efficient co-catalysts for promoting the reaction. Moreover, 2-pyridinemethanol and 2,6-pyridinedimethanol afforded the cyclic carbonate in almost the same excellent yield. However, when

imidazolemethanol was used as the catalyst, a lower yield was observed (entry 6, Table 12). Notably, NaI and KI were also very active for the cycloaddition of CO₂ and epichlorohydrin (entry 7, Table 12). Shortened reaction time (8 h) was also investigated, and the relevant isolated yields were summarized in Table 12, which clearly show the different performance of the catalysts but with almost the same trend. Interestingly, the catalytic system, pyridine/*n*Bu₄NI, also afforded the cyclic carbonate in a moderate yield (65%, entry 8); therefore, pyridine/*n*Bu₄NI is more efficient than only pyridine (3%, entry 1, Table 10). This further indicates the excellent role of iodide anion in facilitating the nucleophilic attack in the ring opening.

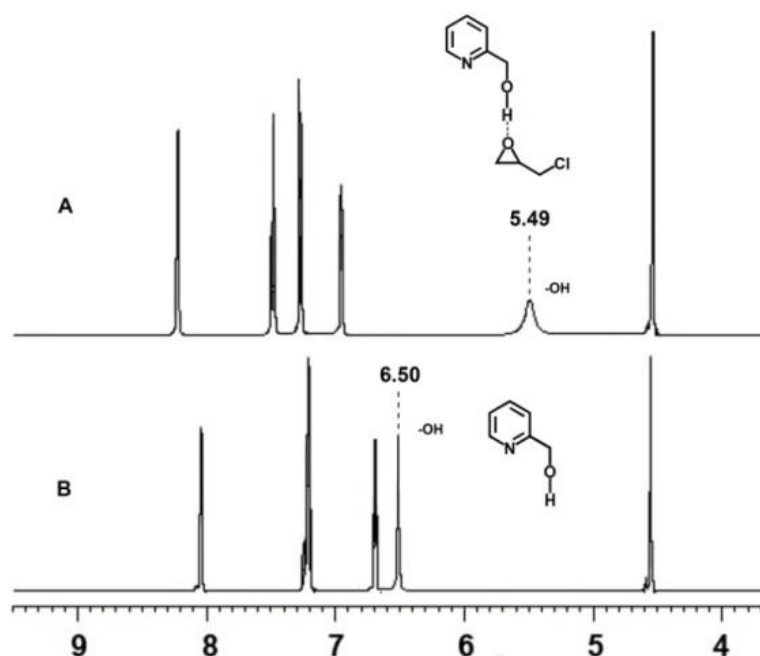


Fig. 8 ¹H NMR spectra of a mixture of 2-pyridinemethanol and epichlorohydrin (molar ratio = 1 : 2) (A) and 2-pyridinemethanol (B) at 298 K, dual NMR cell. The samples were placed in the inner cell, whereas CDCl₃ was placed in the outer cell as the external standard.

Hydrogen bonding has been reported to activate epoxide, as observed by ¹H NMR.^{35,37} Fig. 8 shows the ¹H NMR spectra of 2-pyridinemethanol with and without epichlorohydrin; a clear upfield shift in the 2-pyridinemethanol OH proton signal was observed (from $\delta = 6.50$ to 5.49 ppm), indicating that epoxide forms a hydrogen bond with the OH group.

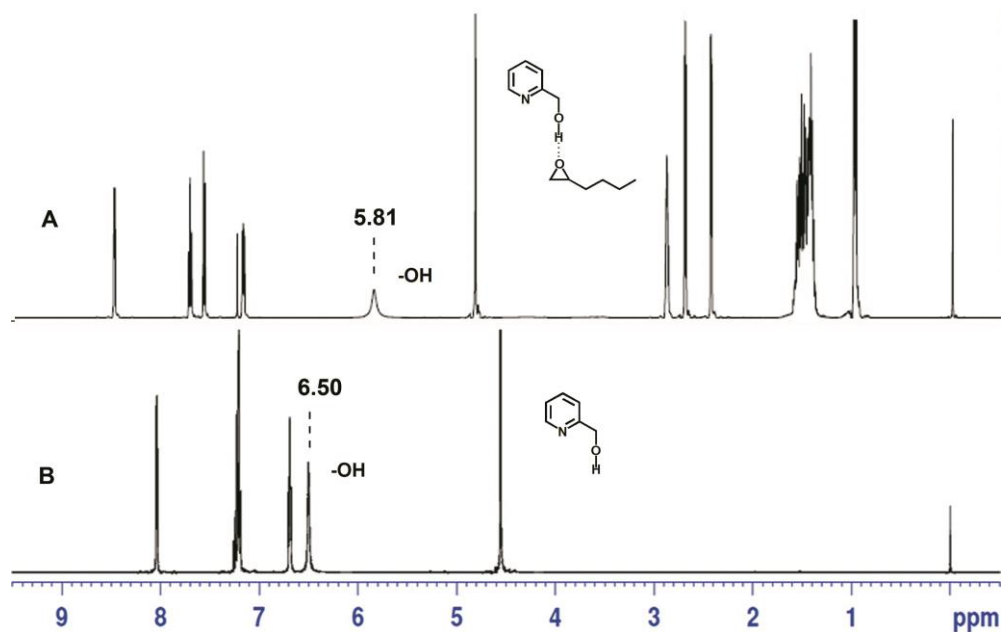


Fig. 9 ^1H NMR spectra of a mixture of 2-pyridinemethanol and 1,2-epoxyhexane (molar ratio = 1 : 2) (A) and 2-pyridinemethanol (B) at 298 K, Dual NMR tube. The samples were placed in the inner tube, whereas CDCl_3 was placed in the outer tube as the external standard.

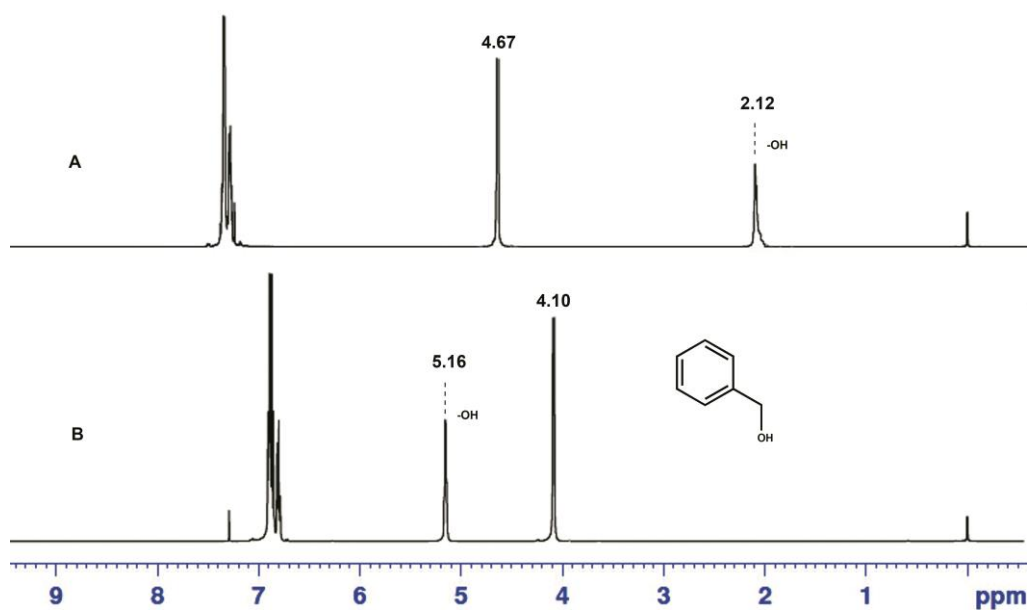
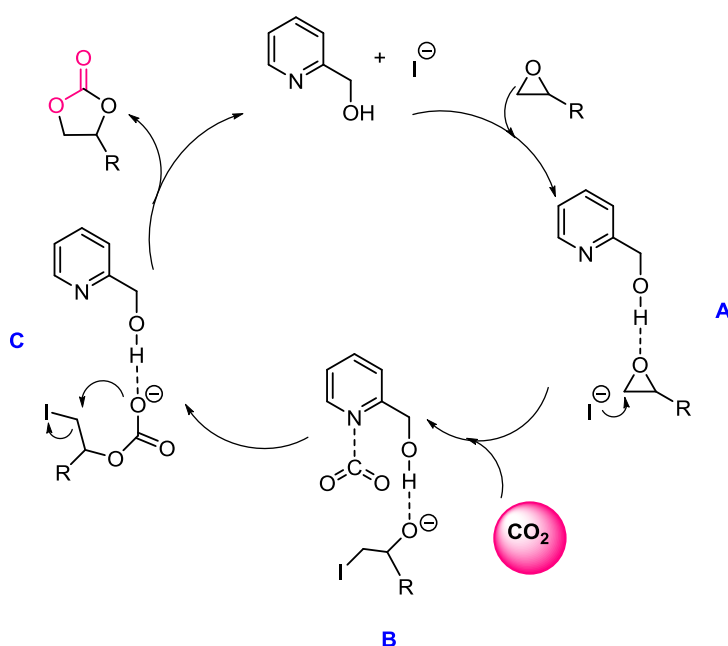


Fig. 10 ^1H NMR spectra of benzyl alcohol in CDCl_3 at 298 K, in a normal NMR tube (A) and benzyl alcohol at 298 K, in a dual NMR tube, where only benzyl alcohol was placed in the inner tube, whereas CDCl_3 was placed in the outer tube as the external standard (B).

To eliminate the effect of methylene chloride interaction with the nitrogen of 2-pyridinemethanol, 1,2-epoxyhexane was used instead of epichlorohydrin for the same

^1H NMR experiment (see Fig. 9); a similar upfield shift of the OH proton signal was observed. The downfield shift of the protons in the pyridine ring (A, Fig. 8) can be attributed to the epoxide-weakened intramolecular and/or intermolecular hydrogen bonding of pyridinemethanol. When benzyl alcohol was used for the same ^1H NMR experiment (see Fig. 10), a similar downfield shift of the phenyl proton signals was observed, indicating that the intermolecular hydrogen bonding was weakened by CDCl_3 .



Scheme 6 A proposed mechanism for the coupling reaction of an epoxide with CO_2 catalyzed by 2-pyridinemethanol and $n\text{Bu}_4\text{NI}$

Based on the previous mechanistic studies on related systems^{26–31} and the current results, a plausible catalytic mechanism is proposed as shown in Scheme 6. The epoxide ring is activated by the coordination of the OH group in 2-pyridinemethanol with the O atom of the epoxide through a hydrogen bond; simultaneously, the I^- anion nucleophilically attacks the less sterically hindered carbon atom of the epoxide ring to form intermediate **A**. This results in the ring opening of the epoxide, forming the corresponding alcoholate. CO_2 is activated by the N atom of pyridine, producing a new intermediate (**B**). The nucleophilic addition of the alcoholate to CO_2 forms an

alkylcarbonate anion (**C**); the ring-closing of intermediate **C** affords the corresponding cyclic carbonate and regenerates the catalyst, thus completing the catalytic cycle.

Table 13 Cycloaddition of CO₂ to various epoxides catalyzed by 2-pyridinemethanol/*n*Bu₄NI^a

	1b	86 ^b	
	2b	65 ^b	89 ^c
	3b	87 ^c	
	4b	97 ^b	
	5b	85 ^b	
	6b	88 ^b	
	7b	91 ^b	
	8b	73 ^b	85 ^c
	<i>cis</i> - 9b	15 ^c	
	(<i>R</i>)- 8b	85 ^c	
		(94% <i>ee</i>)	
	(<i>R</i>)- 10b	87 ^b	
		(98% <i>ee</i>)	

^a Reaction conditions: epoxide (6 mmol), binary catalyst (8 mol%), CO₂ (99.999%, balloon), reaction time 20 h. ^b T = 25 °C, isolated yield. ^c T = 45 °C, isolated yield.

Under the optimal reaction conditions, various epoxides were investigated in the presence of 2-pyridinemethanol/ *n*Bu₄NI (Table 13). The results show that diverse epoxides were converted to the corresponding cyclic carbonates under ambient conditions in high-to-excellent yields. Epichlorohydrin gave the best result because of the electron-withdrawing effect of the substituent, favouring the nucleophilic attack at the epoxide ring carbon atom, and the functional group was stable in the reaction, indicating the excellent efficiency of the catalytic system. However, because of the higher steric hindrance of the epoxides (**2b**, **3b**, and **8b**; Table 13) than the other epoxides, a slightly higher reaction temperature (45 °C) was required for higher product

yields. Moreover, cyclohexene oxide, a challenging substrate because of its steric hindrance, was converted to the corresponding carbonate **9b** in 15% yield, which was confirmed as the *cis* isomer by ^1H NMR and ^{13}C NMR spectra.^{18,49} Moreover, this inexpensive catalytic system was also used in the coupling reaction of CO_2 and enantiomerically pure epoxides. (*R*)-**8a** and (*R*)-**10a** were transformed to (*R*)-**8b** and (*R*)-**10b** in 94% and 98% enantiomeric excess (*ee*), respectively (Table 13). It can be concluded that the reaction is favorable at the less hindered side of epoxide. The ring opening of epoxide by iodide anion has been evidenced.⁴⁸ This environmentally friendly process affords enantioenriched cyclic carbonates with a minimal racemization of the initial epoxides.

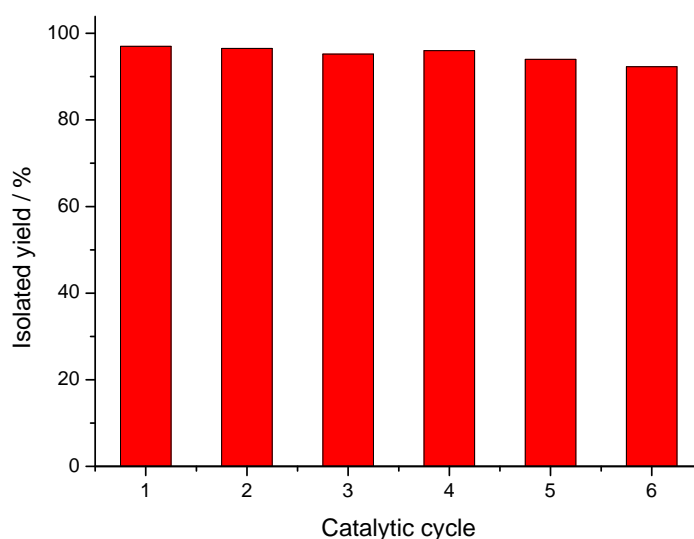


Fig. 11 Recycling of the catalyst 2,6-pyridinedimethanol in the coupling reaction of epichlorohydrin and CO_2 under optimized reaction conditions: catalyst amount (8 mol%), 1 atm CO_2 , 25 °C, 20 h.

For a potential application in an economic and green process, the recyclability of the catalyst is an important feature. The recently reported organocatalytic systems could not be recycled very well. This is because, on one hand, the catalyst is difficult to isolate from the reaction mixture; on the other hand, the catalyst is not stable under high temperatures and pressures. However, the present reaction conditions are very mild, and

2,6-pyridinedimethanol is almost insoluble in epoxide, thus easily recyclable. The reusability and stability of the binary catalytic system, 2,6-pyridinedimethanol/*n*Bu₄NI, were investigated. The reaction of CO₂ with epichlorohydrin was carried out under the above-mentioned reaction conditions (25 °C, 1 atm CO₂, 20 h). After the extraction of cyclic carbonate with diethyl ether, the catalysts were dried in vacuo and used for the next run under the same reaction conditions. The results show no significant loss of activity after six catalytic cycles, indicating that the organocatalytic system is very stable (see Fig. 11). Hence, 2,6-pyridinedimethanol/*n*Bu₄NI is a very practical and reusable catalytic system for the cycloaddition of CO₂ to epoxides.

4.3 Conclusions

In summary, a simple and efficient binary organocatalytic system was developed for the synthesis of cyclic carbonates from epoxides and CO₂ under metal- and solvent-free conditions. The excellent binary organocatalytic system, 2-pyridinemethanol/*n*Bu₄NI, is one of the few metal-free systems that allows less energy-demanding and more environmentally friendly chemical fixation of CO₂ into value-added chemicals under rather mild reaction conditions (T = 25-45 °C, 1 atm CO₂). Diverse epoxides were transformed into the corresponding cyclic carbonates in high-to-excellent yields under almost ambient conditions. Furthermore, optically pure epoxides were converted to the corresponding cyclic carbonates with a minimal loss in the *ee* values. Notably, the binary catalytic system, 2,6-pyridinedimethanol/*n*Bu₄NI, is recyclable for at least six times without any significant loss of activity, making this catalytic system sustainable and economical. Efforts are underway to further elucidate the mechanism of this reaction in detail.

4.4 Experimental Section and ¹H and ¹³C NMR Spectral Charts

Catalyst recycling studies:

Catalyst recycling experiments of the binary catalytic system, 2,6-pyridinedimethanol/*n*Bu₄NI, were investigated. The reaction of CO₂ with epichlorohydrin was carried out under the optimal reaction conditions (25 °C, 1 atm CO₂, 20 h). After completion, the unreacted substrate was removed under vacuum, and then added dry diethyl ether. After the extraction of cyclic carbonate with diethyl ether, the precipitated catalysts were filtered, dried in vacuum and used for the next run under

the same reaction conditions. Note: The 2,6-pyridinedimethanol was easily recycled from the reaction system, but some amount of TBAI may be dissolved in the crude carbonate, but after 4 times of recrystallization from the concentrated crude product by dry diethyl ether, the catalysts can be recycled without no significant loss (see Table 14).

Table 14 The amount of the recovered catalysts^a

Catalytic system	Total amount
2,6-pyridinedimethanol/ (8 mmol%) 0.052 g	0.229 g
TBAI/(8 mmol%) 0.177 g	
1 st Recovered catalysts	0.210 g
2 nd Recovered catalysts	0.196 g

^a Notes: The catalysts were filtered and washed by dry diethyl ether, then 3mL diethyl ether was added in the concentrated crude product, all the catalysts were collected after 4 times of recrystallization.

The reaction procedures and spectral data for the cyclic carbonates are the same with above-mentioned two catalytic systems that we have developed.

5. Summary and outlook

We have developed three different types of organocatalytic systems for the chemical fixation of CO₂ into cyclic carbonates under mild conditions. In particular, a recyclable organocatalytic system was developed under ambient conditions. Diverse epoxides were transformed into the corresponding cyclic carbonates in high-to-excellent yields under very mild conditions. Herein, the developed three proposed protocols provide examples of easily handled, practical, and environmentally benign alternative for chemical fixation of CO₂ into 5-membered cyclic carbonates.

The 100% atom-economical reaction employs epoxides and carbon dioxide to obtain cyclic carbonates has great potential for a future green chemicals industry. The cyclic carbonate products already have various applications; moreover, these applications will surely develop further as the importance of green and sustainable chemistry increases in the near future. The aim is to develop a metal-free catalyst that operates at room

temperature, under atmospheric pressure CO₂, a low catalyst loading and accompanying short reaction time. These criteria should reduce the carbon footprint as much as possible for obtaining sustainable CO₂ conversion conditions, also including recyclable catalysts for long-term use.

Future research should focus on organocatalysts that are comparable with the current metal catalysts. The catalyst should also be easily recycled with the long-term use to convert CO₂ on a strikingly larger scale than the currently case.

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