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Research Paper

Monodentate H-bond donor bifunctional catalyst in fixation of atmospheric pressure carbon dioxide into cyclic carbonates

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ABSTRACT

The efficient conversion of epoxides and CO_2 into cyclic carbonates by employing H-bond donor (HBD) and nucleophilic halide cooperating catalysis under mild conditions is an attractive research topic. Herein, we report a new onium halide bearing a CO—N(H) moiety as a weak HBD catalyst to facilitate the cycloaddition reaction of epoxides and CO_2 under mild conditions. The structural influences on the catalytic activity were scrutinized, which included tunable substituents, the distance between functional groups, and counter anions. The result indicated that the catalyst of the bis-meta-substitutions on an aromatic ring exhibited excellent activity for converting epichlorohydrin into cyclic carbonate under atmospheric pressure at 25–70 °C. Twelve terminal epoxides were converted into corresponding cyclic carbonates in 72–99 % isolated yield. A reasonable activation mechanism was proposed and validated by using control experiments and NMR titrations. In addition, the good recyclability proves that the onium halide is a sustainable green organocatalyst.

Introduction

Sustainable and effective chemical fixation of CO_2 to synthesize various high-value-added products has become an attractive methodology to rationally utilize CO_2 in the atmosphere [1]. CO_2 is recognized as an abundant, inexpensive, and renewable C1 building block for the preparation of useful industrial products that contribute to reducing CO_2 emissions [2]. The actual utilization of CO_2 although significant for the chemical industry represents a minor fraction of the anthropogenic emission [3], primarily due to the intrinsic inertness of carbon in its highest oxidation state [4–6]. One viable strategy to overcome the extremely high thermodynamic energy barrier of CO_2 fixation is using highly active reactants to compensate for their chemical inertness and employing carefully designed catalysts to reduce the activation energy [7,8]. Given the above consideration, the cycloaddition of CO_2 into epoxides (CCE) to afford cyclic organic carbonates is the most popular strategy for CO_2 chemical fixation [9–11]. Cyclic organic carbonates have a wide range of applications, including applied as polar aprotic solvents [12–13], electrolytes in lithium batteries [14–16], raw materials for the synthesis of polymers [17–19] and intermediates for fine chemicals [20–22]. Various metal-complex catalysts [23–25] and organocatalysts [26–31] have been designed and evaluated for CCE reactions.

H-bond donor (HBD) catalysis was used as a remarkable metal-free platform for activating various organic molecules [32–34] and has recently been shown to be a key to activating the reactants through the formation of H-bonds with substrates, or/and stabilizing the charge of the transition states or intermediate products in organocatalytic CO_2 fixations [35]. The first systematic investigation of H-bonding catalysis in CCE reaction was reported by Kleij et al. (Scheme 1, a) [27]. Numerous binary catalytic systems containing a polyphenol compound and auxiliary nucleophile *n*Bu4NI showed good activity under 25–45 °C and 1.0 MPa of CO_2, and demonstrated the synergistic effects of multiphenolic systems increased H-bonding abilities towards epoxides. Lately, the development of HBD catalysts such as phenolic derivatives [35], fluorinated alcohols [36], boronic acids [37] carboxylic acids [38] and even water [39] with O–H moiety, and squaramides [40], hemisquaramide tweezers [41], ureas [42], and thioureas [43] with N–H moieties has extended the scope of this process. Compared with binary catalytic systems, H-bond donor-based bifunctional catalytic systems

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have been further developed by their excellent activity, several catalysts, including ammonium halides [28,44-45], phosphonium halides [46–48], imidazolium halides [49–50], and pyridinium halides [51] have been widely investigated for coupling CO_2 with epoxides. In 2014, Wu and co-workers reported that imidazolium bromide as protic ionic liquids catalyst satisfactorily demonstrated cyclic carbonate synthesis at 120 °C and 1.5 MPa (Scheme 1, a) [52]. In 2017, Werner and co-workers successfully designed an effective bifunctional quaternary ammonium salt triethylamine hydroiodide, achieving CO_2 fixation under 40 °C and atmospheric pressure [53]. In 2020, Rostami and Al-Harrasi an amino-pyridinium ionic liquid showed high activities under 40 °C and 1 atm of CO_2 without solvent reaction conditions [54]. In this regard, we recently reported that relatively weak HBDs [55–56] and analog halogen bond donors [57–58] as catalyst systems with interesting potential for terminal epoxide/CO_2 couplings, and that these systems convert terminal epoxides into corresponding carbonates under mild conditions.

A CO—N(H) moiety, which is a type of relatively weak but frequently seen amide H-bond donor, predominates in higher structures of proteins [59] and is widely used in neutral receptors for the recognition of anions [60], but is only occasionally appreciated as a design element in organocatalysts [61]. We suggest weak HBDs rather than strong ones are more appropriate in catalysis based on Dyson's observation [62] and our prior calculations [55] on the advantages of weak C—H-bond donors in rate-limiting steps in CCE reactions. Our team recently discovered that the nicotinamide onium halide bidentate hybrid HBD, which contains non-classical C—H HBD and relatively weak amide N—H, is crucial for the activation of epoxides (Scheme 1, c) [56].

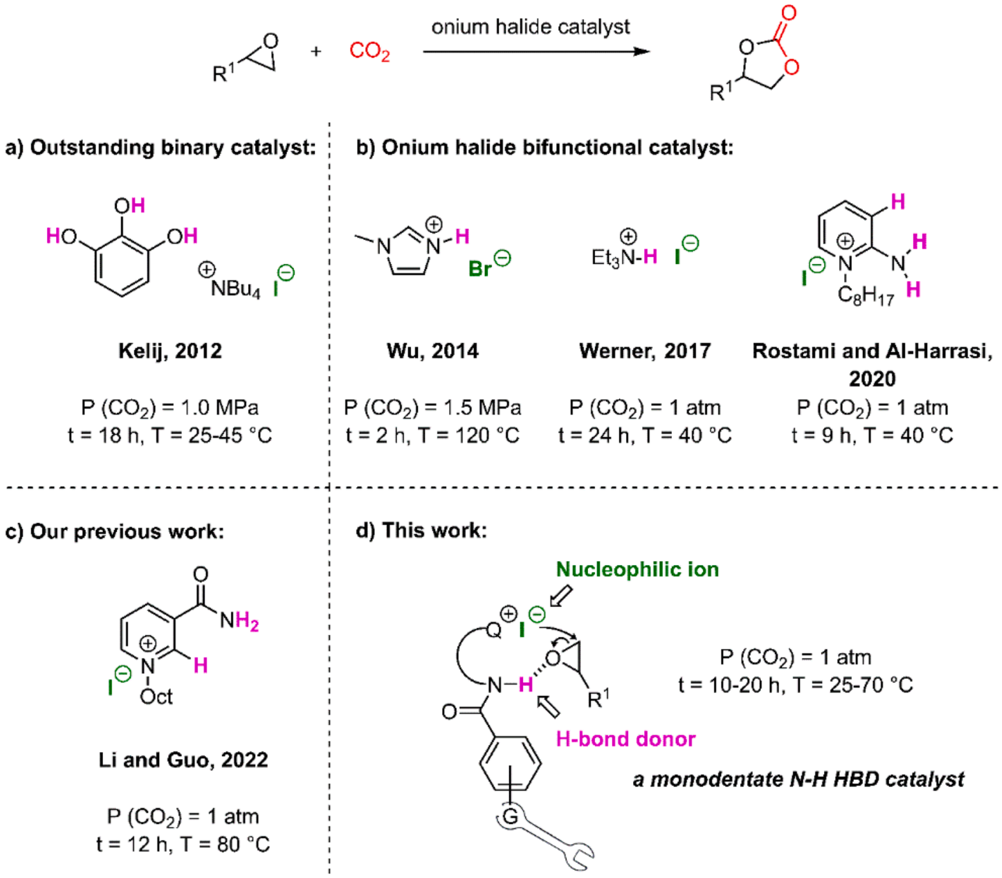
Furthering our focus on developing new weak HBD organic catalytic systems for ring-opening processes, we envision an onium halide bearing an amide CO—N(H) moiety in the side chain as a one-component monodentate HBD catalyst (Scheme 1, d). The aromatic ring of benzamide is easy to introduce tunable groups, which enhance the H-bonding interaction between catalyst and epoxide through the induction effect and conjugation effect, reduce the activation barrier for halide nucleophilic ring-opening processes, and thus promote the coupling of CO_2 and epoxide.

We designed a monodentate N—H HBD catalyst with tunable activity by introducing substituent groups into the aromatic ring, changing the substituent group on the positive nitrogen ion, the halide X and the distance between N—H portion and the nitrogen center (Scheme 1, d). This one-component bifunctional organocatalyst exemplified a new model of monodentate HBD and onium halide synergetic catalysis, typical CCE reactions were evaluated under the catalysis of **1**, and the plausible mechanism was proposed and validated.

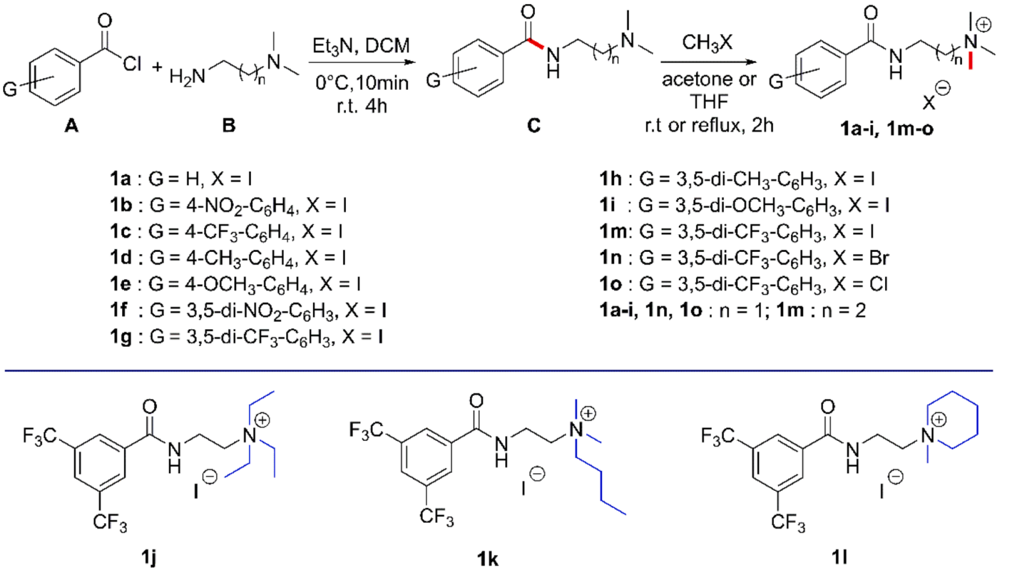
Results and discussion

Preparation of the onium halide catalysts

The structure of onium halide catalysts can be built up stepwise by substitution and alkylation in excellent yields [63], and tune easily (Scheme 2). The electronic groups on the aromatic ring can be modified in terms of type and number, the distance between the functional groups can be changed according to the number of carbon atoms between the nitrogen atoms in compound **B**, the substituent on the center of the nitrogen atom depends on compound **B** and alkylation reagents. Fully details of the preparation steps of the onium halide catalysts can be found in the Experiment Section. In general, the reaction conditions for the synthesis of these catalysts are similar. For the acylation reaction, the materials need to be added dropwise under 0 °C and stirred at room



Scheme 1. Design of onium halides for cycloaddition of carbon dioxide into epoxides (CCE) reactions. (a) H-bond donor (HBD)/onium halide ($Q^+ \cdot X^-$) binary cocatalysis [27]; (b) one-component catalysis of HBD/halide anion (X^-) [52–54]; (c) nicotinamide onium halide bidentate hybrid HBD organocatalyst [56]; (d) proposed one-component monodentate HBD catalysis, the catalytic capacity is affected by substituted groups.



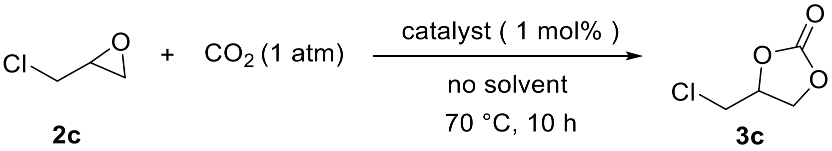
Scheme 2. Onium halide **1** with different groups were synthesized as candidate catalysts used in CCE reactions.

temperature for 4 h. Since the by-product carboxylic acid produced during the reaction, unreacted raw materials (**A** and/or **B**) and acid scavenger triethylamine (Et_3N) are easily soluble in the water phase, the impurities can be removed after the extraction process, and the clean intermediate **C** can be obtained without further purification. The only exception is that the Et_3N cannot be removed by extraction operation when preparing the intermediate of catalyst **1j**; however, a pure product can be obtained without adding any other acid scavenger. For alkylation reactions, most catalysts can be prepared in acetone solution at room temperature, and this step yields up to 99 % (**1a-i, 1m,** and **1l**). However, the preparation of chloride (**1o**) requires stirring for 2 h under reflux conditions due to the high dissociation energy of the C—Cl bond [64], the commercially available alkylation reagent chloromethane is dissolved in THF solution. The synthesis of iodide (**1j**) at room temperature requires a longer reaction time, prolonged from 1 h to 5 h. The synthesis of iodide (**1k**) requires changing the solvent to the highly polar solvent acetonitrile and refluxing for 6 h to obtain the desired yield.

Evaluation of the catalytic performance of onium halide catalysts in CCE reactions

The cycloaddition reaction between epichlorohydrin (ECH) and CO_2 without cosolvent was selected as the initial benchmark reaction to evaluate bifunctional catalysts **1a–o**. It is worth noting that the catalyst performed better solubility in the substrate ECH compared with widely used substrates styrene oxide (SO) and 1,2-epoxyhexane in preliminary experiments, similar phenomena were mentioned in previous reports [62]. Moreover, to develop a highly active catalyst under mild conditions, we chose to stir for 10 h at 70 °C and under atmospheric pressure (1 atm, using a balloon) without cosolvent as the screening experimental conditions (Table 1). No catalyst gave no formation of carbonate **3c**, as expected (entry 1). To our delight, a promising yield (80 %) of desired carbonate **3c** was observed in the presence of **1a** (entry 2). Next, four catalysts **1b–e** with different para-substituent on the aromatic ring were considered to learn if the Lewis acidity of the CO—N(H) group in **1** would affect the reaction progress. The experimental results show that only strong electron-withdrawing group CF_3 exhibits a relatively significant promotion in the yield of **3c**, electron-donating groups (G = CH_3

Table 1
Screening of Catalysts[a].



Entry	Catalyst	Yield[b] (%)	Entry	Catalyst	Yield[b] (%)
1	None	0	9	**1h**	78
2	**1a**	80	10	**1i**	74
3	**1b**	81(30)[c]	11	**1j**	89
4	**1c**	85	12	**1k**	88
5	**1d**	79	13	**1l**	89
6	**1e**	78	14	**1m**	84
7	**1f**	69(27)[c]	15	**1n**	81
8	**1g**	91(30)[c]	16	**1o**	72

[a] Reaction conditions unless specified otherwise: ECH (10.0 mmol, 0.78 mL), catalyst (1.0 mol%), 1 atm CO_2 (use a balloon), no solvent.

[b] Yield was determined via ^1H NMR analysis using mesitylene (0.14 mmol) as an internal standard, average yield from three runs, and selectivity for the cyclic carbonate product **3c** was > 99 %.

[c] Dimethyl sulfoxide was employed as a solvent, 1.0 M **2c**.

and OCH_3) hardly change the activity (79 %, 78 %, respectively; entries 5–6). Remarkably, the NO_2 group also does not change the activity because of the poor solubility of the catalyst **1b** in the substrate, even if it is a stronger electron-withdrawing group than the CF_3 group. To further enhance the influence of electronic groups on the catalytic activity, bis-meta-substitutions were considered (entries 7–10). As expected, the increase in the number of strong electron-withdrawing group CF_3 raised the yield again to 91 % (entry 8), and electron-donating groups resulted in a slight decrease in the yield of product **3c**. (entries 9–10). The comparative catalytic activity with onium halides **1a, 1f, 1g,** and **1i** are shown in Fig. 1. To our surprise is that the solubility of **1f** containing bis-meta-substitutions of NO_2 became extremely worse, and a large amount of catalyst **1f** was suspended in the mixture in the reaction process, which led to a decrease in yield to 69 % (entry 7). To explore whether the solubility of the catalyst will affect the performance of the catalyst, we choose dimethyl sulfoxide (1.0 M ECH) as the solvent of insoluble organocatalysts. Under the same other conditions, organocatalysts **1b, 1f**, and **1g** converted epoxides **2c** (30 %, 27 %, and 30 %, respectively) to the corresponding cyclic carbonates **3c** (entries 3, 7–8). Under solvent conditions, the catalytic performance difference between **1f** and **1g** becomes closer (3 % of solvent vs. 22 % of no solvent), which proves that the relative catalytic activity can be appropriately improved by increasing the solubility. The catalyst performance of catalyst **1b** increased to almost the same as catalyst **1g**, the catalytic performance of catalyst **1f** containing bis-meta-substitutions of NO_2 is still lower than that of catalysts **1b** and **1g**. These results indicated that the CO—N(H) moiety of catalyst **1** was crucial in the reaction progress, changing the substituents on the aromatic ring can enhance the catalytic activity by tuning the solubility of the catalyst in the epoxide and/or Lewis acidity of the HBD catalyst.

Subsequently, we also checked the influence of the counter anion on the catalytic activity. An exchange of the counter anion from iodide (**1g**) to bromide (**1n**) and chloride ion (**1o**), obtained yields in descending from **1g** > **1n** > **1o** (entries 8, 15−16), the result is identical to the previous reports of the one-component onium halide HBD catalysts [28, 46-47]. In addition, we also increased the distance between the functional group and the nitrogen center to three carbon atoms to synthesize the catalyst **1m**, and the product **3c** obtained a lower yield of 84 % (entry 14), the results showed that the distance of functional groups also slightly influence the activity of the catalyst.

In general, the nature of the cation is also an important factor that influences catalytic activity [65]. Three catalysts **1j–l** with different substituents on the nitrogen center were employed, and the yields of desired product **3c** were obtained respectively all marginally lower than the yield catalyzed by **1g** (entries 11−13). On the one hand, these experimental results are due to the number of atoms of the same substituent; on the other hand, the six-membered ring or longer alkyl chain on the cation increases the hydrophobicity of catalysts and reduces the solubility of the catalyst in the substrate.

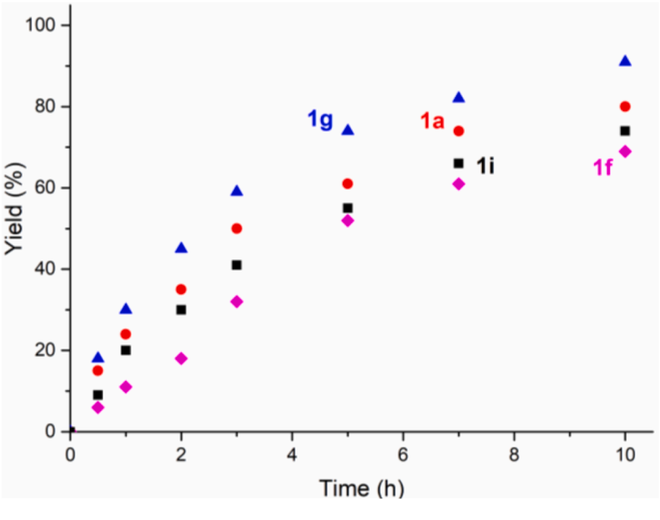


Fig. 1. Comparative catalytic activity in the formation of **3c** from ECH and CO_2 using **1a, 1f, 1g,** and **1i**. Reaction conditions: 10.0 mmol ECH, 1 mol% **1a, 1f, 1g** and **1i**, 70 °C, 1 atm CO_2 (use a balloon), no solvent.

Influence of reaction parameters on the conversions of the CCE reactions

In pursuit of more information under mild conditions, we investigated the performance of the catalyst **1g** at the lower reaction temperature and diffident catalyst loadings and conducted a kinetics study to understand the effect of reaction parameters on reaction rate. A series of experiments were performed at reaction temperatures of 25 °C, 40 °C, and 50 °C, catalyst loading of 1–10 mol% **1g**, reaction time of 20 h, and atmospheric pressure (Fig. 2(a)). Under the reaction conditions of 5 mol % **1g**, $P(CO_2) = 1$ atm, and the reaction temperature of 40 °C and 50 °C, the excellent conversion of **2c** was obtained at 97 % and 99 %, respectively. Further increasing the amount of the catalyst **1g**, substrate **2c** was given virtually full conversion; this result indicates that an excessive catalyst amount would not harm the reaction process. It is worth noting that at the amount of 5 mol% **1g**, 20 h, only in room temperature conditions more than half of substrate **2c** was converted and a conversion yield of 75 % was detected, indicating that the catalyst has a good catalyst activity under mild conditions.

The effect of the amount of catalyst on the reaction rate was further investigated, and the reaction kinetics graphs of epoxide **2c** catalyzed by **1g** were plotted. It was carried out at a stable temperature of 50 °C, 1–5 mol% **1g**, and without solvent, the conversion of ECH was determined by ^{1}H NMR spectroscopy (Fig. 2(b)). It is assumed that the concentration of catalyst and carbon dioxide during the reaction is a constant, because there is a large excess of carbon dioxide during the reaction, and it will not change [66]. Thus, the general rate law Eq. (1) of CCE reaction can be transformed in Eq. (1), where k is the rate constant and [ECH], $[CO_2]$, [CAT] are the concentrations of ECH, CO_2 and **1g**, respectively; a, b and c are the orders of reaction; $k_{obs} = k[ECH]^a[CO_2]^b[CAT]^c$, (Eq. (4)). Integrating Eq. (2) as a function of time deduces Eq. (3), take the natural logarithm of both sides of Eq. (4) to get Eq. (5), it can be used to express the effect of catalyst concentration on reaction rate.

$$\text{Rate} = k[\text{ECH}]^a[\text{CO}_2]^b[\text{CAT}]^c \tag{1}$$

$$\text{Rate} = -\frac{d[\text{ECH}]}{dt} = k_{obs}[\text{ECH}]^a \tag{2}$$

$$-\ln[\text{ECH}] = k_{obs}\cdot t \tag{3}$$

Where

$$k_{obs} = k[\text{CO}_2]^b[\text{CAT}]^c \tag{4}$$

$$\ln k_{obs} = \ln k + b\ln[\text{CO}_2] + c\ln[\text{CAT}] \tag{5}$$

Based on Eqs. (4) and (5), a first-order dependence reaction kinetics graph with a slope of 0.0692 ln[ECH] versus reaction time was drawn at 50 °C, 128 mM **1g** (1 mol% catalyst loading) and atmospheric pressure (Fig. 2(c)), the double logarithmic plot between k_{obs} and catalyst concentration indicates that the reaction rate depends on catalyst concentration in the first-order from 128 mM to 640 mM (Fig. 2(d)). This result suggests that only one molecule of bifunctional onium halide catalyst per epoxide is involved in the reaction mechanism [67–69].

A series of experiments investigated the effect of temperature on the reaction rate at 25–70 °C, while determining the thermodynamic and activation parameters of the reaction. According to the calculated reaction rate constant (k_{obs}), the reaction rate increases with the increase in reaction temperature. Arrhenius equation (Eq. (6)) is used to calculate the activation energy for the CCE reaction, where R is the universal gas

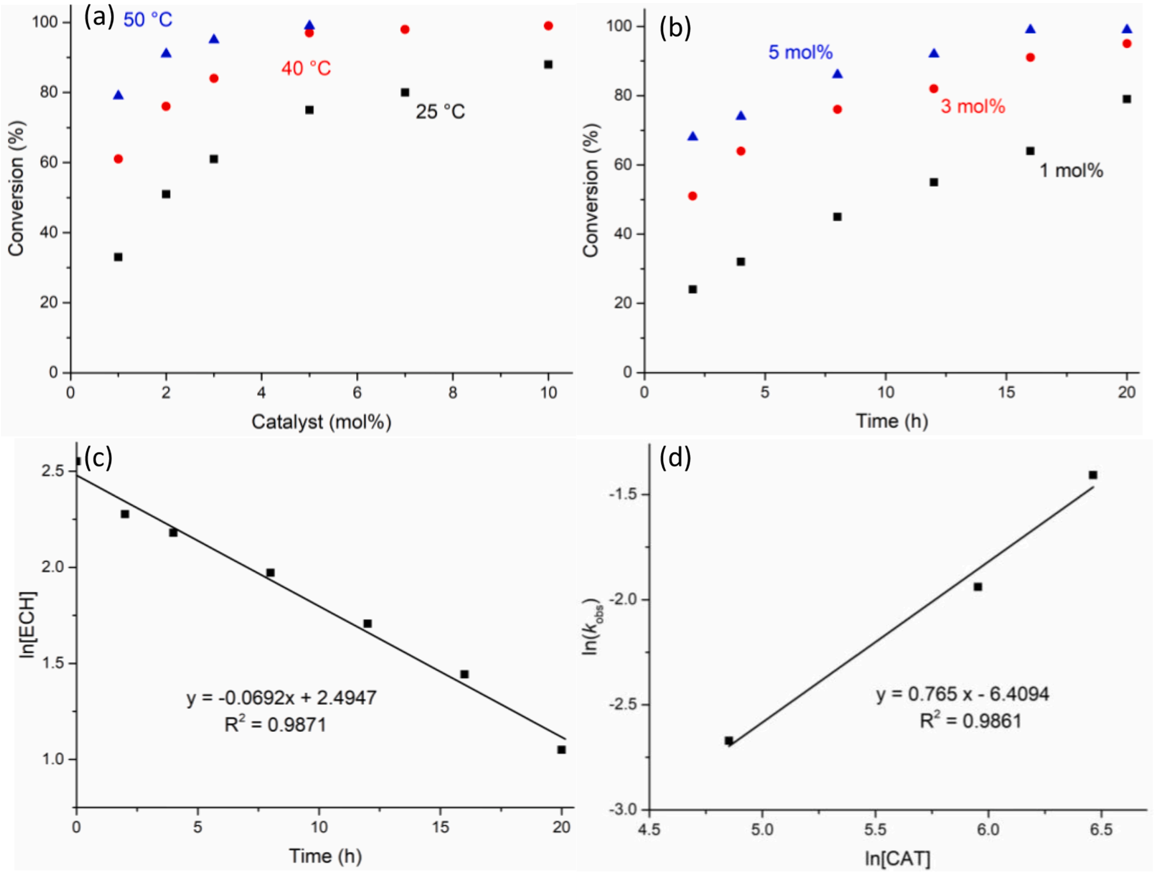


Fig. 2. (a) Effect of the reaction temperature on the conversion of **3c** in the presence of catalyst **1g**. Reaction conditions: 1–10 mol% **1g**, temperature = 25 °C, 40 °C or 50 °C, 1 atm CO_2 (use a balloon), 20 h; (b) Effect of the catalyst loading on the conversion of **3c** in the presence of catalyst **1g**. Reaction conditions: 1, 3, or 5 mol% **1g**, 50 °C, 1 atm CO_2, 20 h; (c) First order plot of ln[ECH] versus time. Reaction conditions: 1 mol% **1g**, temperature = 50 °C, 1 atm CO_2, 20 h; (d) Double logarithmic plot between k_{obs} and catalyst **1g** concentration. Reaction conditions: 128–640 mM **1g**, 50 °C, 1 atm CO_2, 20 h.

constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K), and A and E_a are the pre-exponential factor (h^{-1}) and activation energy (kJ mol^{-1}), respectively by linear Arrhenius plot of the ln(k_{obs}) versus 1/T (Fig. 3(a)), the activation energy was calculated with $E_a = 46.7$ KJ·mol^{-1} in the presence of catalyst **1g** (Eq. (7)). Further, a linear Eyring plot between ln(k_{obs}/T) and 1/T (Fig. 3(b)) was obtained by the Eyring equation (Eq. (8)), and the enthalpy ($\Delta H^{\ddagger}$) of activation was calculated to be 44.0 KJ·mol^{-1}.

$$k_{obs} = Ae^{-\frac{E_a}{RT}} \tag{6}$$

$$\ln(k_{obs}) = \ln A - \frac{E_a}{RT} \tag{7}$$

$$\ln\left(\frac{k_{obs}}{T}\right) = \frac{\Delta H^{\ddagger}}{RT} + \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R} \tag{8}$$

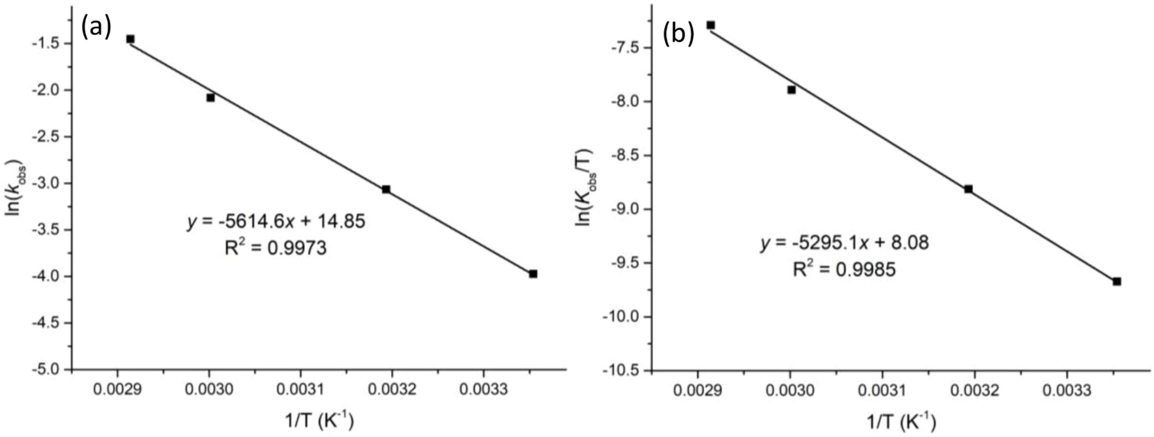


Fig. 3. (a) Arrhenius plots for activation energy estimation in the presence of catalyst **1g**. (b) Eyring plots for activation enthalpy estimation in the presence of catalyst **1g**. Reaction conditions: 1 mol% **1g**, temperature = 25–70 °C (T = 298.15–343.15 K), 1 atm CO_2 (use a balloon).

*Substrate scope of terminal epoxides with 1 atm of CO_2 in CCE reactions catalyzed by **1g***

After optimizing the reaction conditions, four common substrates were evaluated at the initial reaction condition of a reaction temperature of 40 °C or 50 °C, 5 mol% **1g**, P (CO_2) = 1 atm, and 20 h. However, the corresponding carbonates of CCE reactions were obtained in low yields at 40 °C (Table S1). This result is consistent with previous reports that epichlorohydrin is one of the most reactive epoxides for the CCE reaction [70], and it is more easily converted to cyclic carbonate than other epoxides under the same mild conditions even at room temperature. Hence, the reaction temperature was increased to 50 °C or 70 °C is necessary to further investigate the substrate scope of other terminal epoxides (Table 2). For the terminal epoxides with various aliphatic substituents, the corresponding cyclic carbonates **3a–f** were synthesized in good to excellent yields of 88–99 % yields at 50 °C. Due to the high activity of epichlorohydrin and epibromohydrin, the substrates were converted to cyclic carbonates for 16 h. All glycidyl derivatives were smoothly converted under mild conditions generating exclusively the desired carbonates **3g–j** in excellent yields from 92 % up to 99 %. It is worth mentioning that both saturated and unsaturated substituents of glycerin derivatives show good solubility for catalyst **1g**. Furthermore, the terminal epoxide **2k** bearing an aryl group was also examined and gave a high yield of 98 % at a higher reaction temperature of 70 °C. Similarly, the derivative **2l** reacted smoothly to afford a 73 % yield.

*Substrate scope of internal epoxides with 1.0 MPa of CO_2 in CCE reactions catalyzed by **1g***

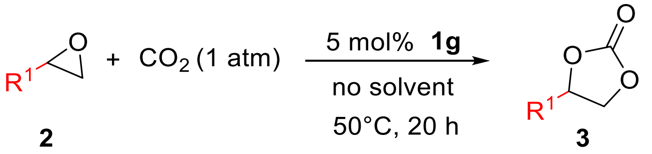
Internal epoxides are known to be low-reactivity substrates because of extremely high steric hindrance. Inspired by the above results, we then evaluate the more challenging substrate scope of internal epoxides (Table 3). Firstly, we tested the reaction of bicyclic cyclohexene oxide **4a** at 50 °C, P (CO_2) = 1 atm, 20 h. However, no corresponding product **5a** was obtained under this condition. Reaction temperature and CO_2 pressure factors were considered, and we switched to a stainless-steel autoclave for the CCE reaction, the CO_2 pressure was increased to 1.0 MPa, but still no corresponding product **5a** was obtained. The temperature was further increased and the reaction was performed at 80 °C and 4 mol% **1g** for 48 h to obtain a 74 % product yield. Then the two types of five-membered bicyclic epoxides **4b–c** were tested, obtaining carbonate **5b–c** of 76 % and 64 % isolated yield, respectively. Next, 1,2-dimethyloxirane and 2,3-diphenyloxirane was employed as substrates under 80 °C with a CO_2 pressure of 10 bar, and the cyclic carbonate product **5a** and **5e** was obtained with 61 % and 36 % yield, respectively. Limonene oxide is bio-based internal epoxides and represents an internal, trisubstituted epoxide motif and the kinetic barrier for its activation is significantly higher than for terminal epoxides and disubstituted epoxide [71]. Unfortunately, no corresponding product was obtained when the limonene oxide as a substrate.

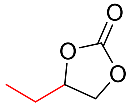
*Proposition and validation of the mechanism of the CCE reaction by catalyst **1g***

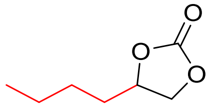
The activation mechanism of catalyst **1g** was investigated via a ^1H NMR titration experiment of a solution of ECH to a 0.1 M solution of catalyst **1g** in DMSO-*d6* at room temperature (Fig. 4) [51,55-56]. After adding ECH to the catalyst **1g**, the proton in the amide functional group shifted significantly. With the increasing concentration of ECH, the ratio of **1g**/ECH was from 1:0 to 1:10, and the chemical shift of protons to the bottom field was a total of 0.293 ppm. Relative to the substrate, as the concentration of the catalyst **1g** increases, both hydrogens on the CO—N(H) group and ECH migrated to the bottom field (Δδ = 0.009 ppm and 0.014 ppm, respectively). The migration phenomenon of these proton shifts proves that the H-bonding interaction between the catalyst and the epoxide promotes the progress of the cycloaddition reaction.

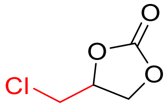
In order to further clarify both vital roles of the proton of the amide moiety and counter anion of the bifunctional catalyst in the CCE

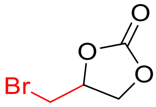
Table 2
Scope of Terminal Epoxides[a].

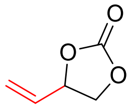


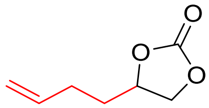

3a, Yield: 72%

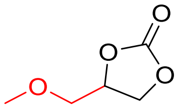

3b, Yield: 79%

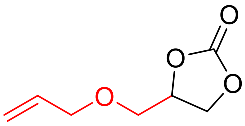

3c, Yield: 99%[b]

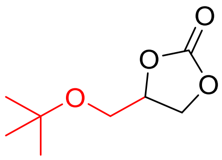

3d, Yield: 99%[b]

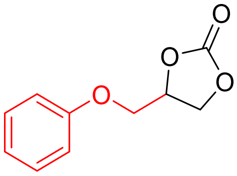

3e, Yield: 96%

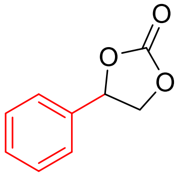

3f, Yield: 88%

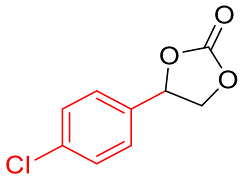

3g, Yield: 97%


3h, Yield: 96%


3i, Yield: 92%

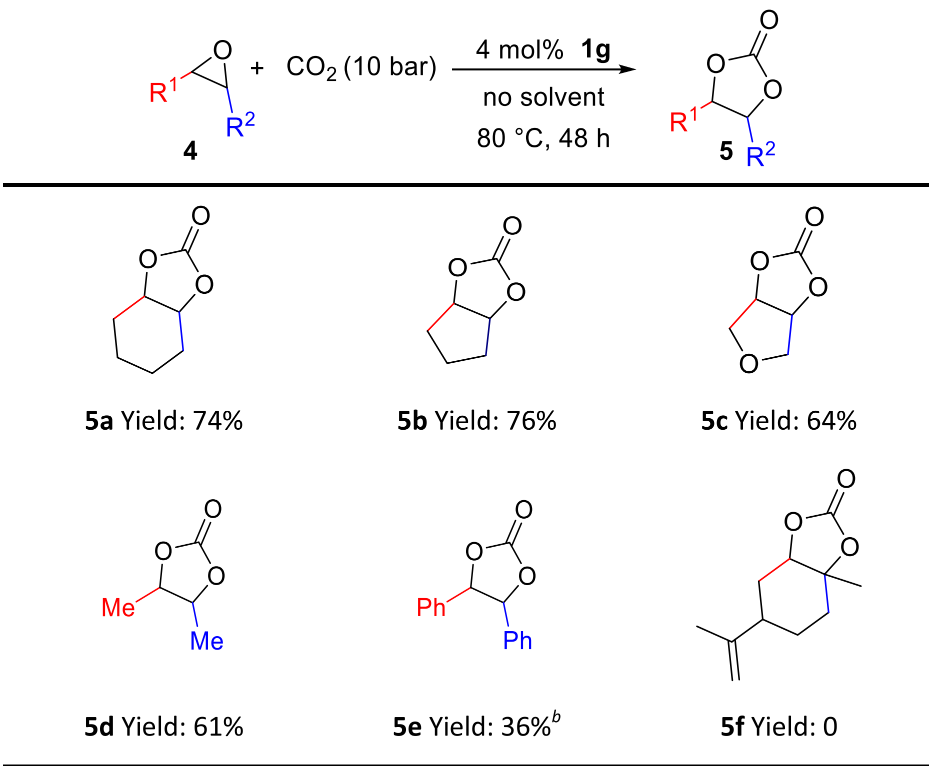

3j, Yield: 99%


3k, Yield: 98%[c]


3l, Yield: 73%[c]

[a] Reaction conditions: 5 mol% **1g**, 50 °C, 1 atm CO_2 (use a balloon), 20 h, no solvent. Isolated yields. Selectivity for cyclic carbonate products was all > 99 %. [b]16 h. [c]70 °C.

Table 3
Scope of Internal Epoxides[a].



[a]Reaction conditions: 4 mol% **1g**, 80 °C, P (CO_2) = 1.0 MPa, 48 h, no solvent. These reactions were carried out in 25 mL stainless steel reactors containing a magnetic stir bar. Isolated yields. Selectivity for cyclic carbonate products was all > 99 %. [b]*n*-Butanol was employed as a solvent, 1.0 M **4d**.

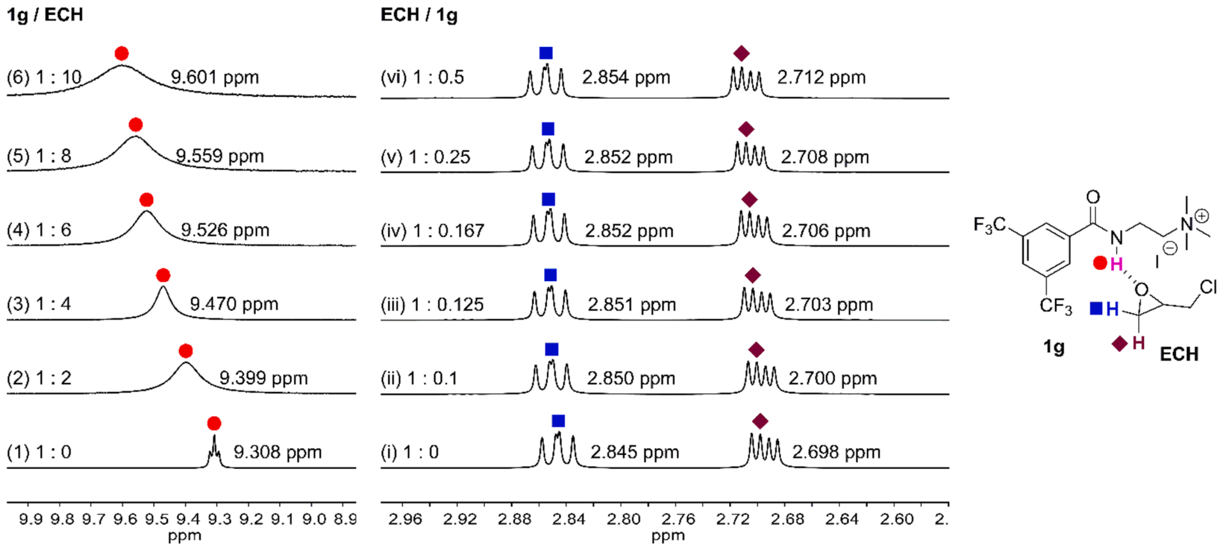
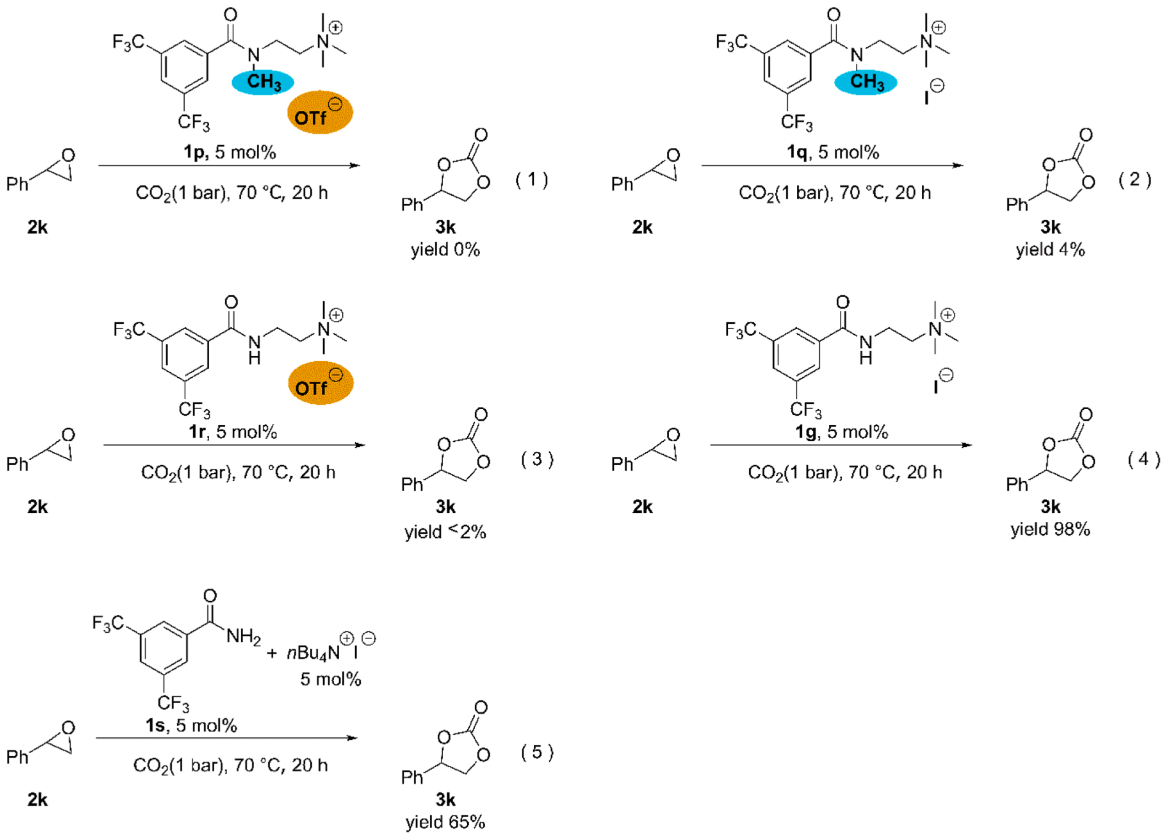


Fig. 4. The chemical shifts of the protons of **1g** in the ^1H NMR spectra (DMSO-d_6, 1.0×10^{-1} M) and two methylene protons of ECH observed by titrations of **1g** with ECH at room temperature: **1g** / ECH ratios (1) 1 / 0, (2) 1/ 2, (3) 1/ 4, (4) 1/ 6, (5) 1/ 8, (6) 1/ 10; ECH / **1g** ratios (i) 1 / 0, (ii) 1/ 2, (iii) 1/ 4, (iv) 1/ 6, (v) 1/ 8, (vi) 1/ 10.

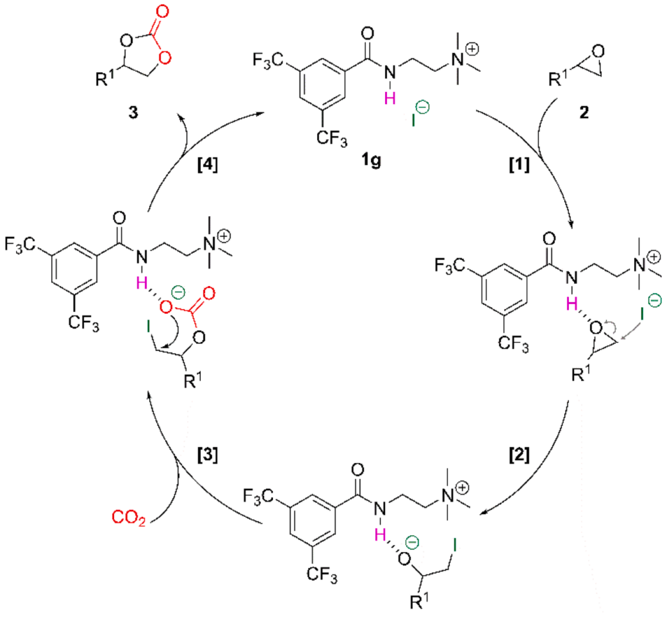
reaction, we introduced a methyl group to protect the proton of CO—N (H) group, generated catalyst derivatives **1q**, and the low nucleophilic counter anion triflate (TfO^-) replaced the strong nucleophilic ion iodide (I^-), generated catalyst derivatives **1r**. Both the proton and counter anion of catalyst **1g** were replaced and afford the compound **1p**. A fair comparison of the control experiment was investigated by the above catalysts and **1g**, which used styrene oxide (SO) as the substrate and employed a catalyst loading of 5 mol% reacted for 20 h under the atmospheric pressure at 70 °C (Scheme 3). The results show that in the absence of the iodide or the amide proton, the yield of the cyclic carbonate product **3k** decreases dramatically. Furthermore, in the absence of both protons and iodide, no product **3k** was observed. In the presence of a binary catalytic system consisting of 3,5-di(trifluoromethyl)benzamide **1s** and $nBu_4N^+I^-$ (in 1: 1 molar ratio), the product **3k** obtained in 65 % yield, which was much lower than the yield of 98 % of product **3k** catalyzed by **1g**. The results indicated that the synergistic effect of



Scheme 3. Investigate the catalytic performances of the optimal catalyst **1g**, the analog catalyst **1p-r** prepared by switching the cation of halide or/and blocking N—H, and a binary catalytic system of 1 s and $n\text{Bu}_4\text{N}^+\text{I}^-$ (in 1: 1 molar ratio) on the CCE reaction. Reaction conditions: styrene (10.0 mmol), catalyst (5 mol%), 1 atm CO_2 (use a balloon), 70 °C, 20 h, no solvent.

CO—N(H) proton and iodide ion in bifunctional catalyst **1g** was of vital importance in the catalytic reaction [72].

Attempting to detect intermediates produced by the interaction of onium halide **1g** with either an epoxide (via ^{1}H NMR) was unsuccessful. Based on the result in Table 2, ^{1}H NMR titration data in Fig. 4, and the control experimental results in Scheme 3, the hypothetical cycle mechanism of this reaction is proposed (Scheme 4). Epoxide **2** is activated under the action of the N–H-bonding of catalyst **1g** (step 1). The easily leaving iodide ion in the halide initiates a nucleophilic attack on the carbon atom on the less steric methylene side of terminal epoxides to form an intermediate alkoxide anion (step 2). Then the oxygen anions at the end of the intermediate attack CO_2 to form a carbonate anion (step 3). Finally, the ring is closed to form the product cyclic carbonate **3** (step 4) [73–75].



Scheme 4. Proposed mechanism for the formation of cyclic carbonates from epoxides and CO_2 catalyzed by onium iodide **1g**.

Catalyst recycling of CCE reaction catalyzed by ***1g***

The recovery rate of 1,2-epoxyhexane **2b** catalyzed by **1g** at 70 °C for 20 h under a CO_2 atmosphere was investigated (Fig. 5). A total of five reuse cycles were performed. For the first time, the freshly prepared dry catalyst **1g** was added, and a small amount of reaction solution was taken to detect the yield by ^{1}H NMR to obtain the first yield of product **3b** is 97 %, and the remaining product **3b** and the raw materials were separated by vacuum distillation [72]. In the first two cycles, no significant loss of activity was observed and **3b** was obtained in excellent yields up to 92 %. Until the fifth cycle, the yield of product **3b** was 82 % and still had high activity. The thermogravimetric analysis (TGA) test results found that the catalyst **1g** has high thermal stability, with the first mass loss of 5 % occurring at 220.8 °C (Fig. 6). However, the catalyst **1g** decomposition product trimethylamine was identified by NMR spectroscopy after five cycles, which was presumably generated as a result of high-temperature distillation [28,76].

Conclusions

To summarize, we have successfully developed a structure-tunable

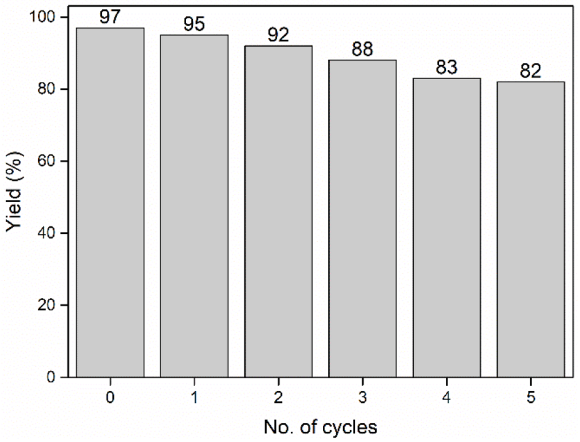


Fig. 5. Recycling study. Conditions: 1, 2-epoxyhexane **2b** (10.0 mmol, 1.21 mL), **1g** (0.5 mmol, 5 mol%, 235.0 mg), 70 °C, 1 atm of CO_2 (use a balloon), 20 h, neat. The yield was determined via ^1H NMR analysis using mesitylene as an internal standard.

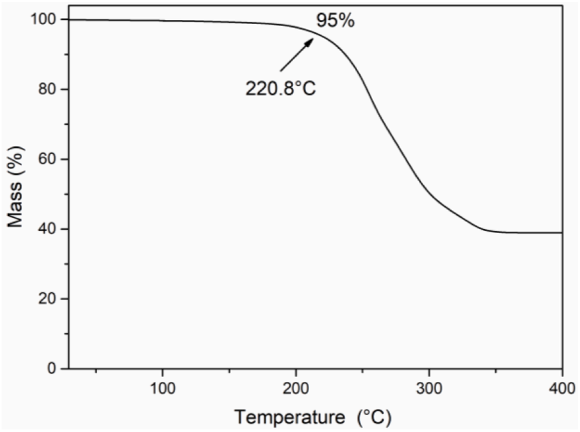


Fig. 6. TGA thermogram of catalyst **1g**. Determined by TGA at a heating rate of 10 °C/min from room temperature to 400 °C under a nitrogen atmosphere.

monodentate H-bond donor (HBD) bifunctional catalyst, which was evaluated in CO_2 fixation reaction with epoxides under mild conditions (room temperature, 1 atm CO_2). Fifteen types of halide catalysts were prepared from benzoyl chloride, diamine, and haloalkanes by substitution reaction and alkylation reaction. The substituent groups on the aromatic ring, the substituent group on the positive nitrogen ion, the halide X, and the N—H portion and the distance between nitrogen center on catalytic activity were investigated by using epichlorohydrin (ECH) as substrate, the results showed that bis-meta-ditrifluoromethyl substituted iodide was screened as the optimal catalyst and achieved 91 % yield of carbonate **3c** after 10 h at 1 mol% catalyst load, 1 atm CO_2 pressure, and 70 °C. A series of terminal epoxides and internal epoxides with large internal resistance were converted into corresponding cyclic carbonates with good to excellent yields. The cooperative catalysis mechanism of N–H HBD and onium halide anion of catalyst in the CO_2 fixation reactions was verified by the control experiment and ^1H NMR titration experiment. The thermogravimetric analysis indicated that the catalyst has high thermal stability, and the high reusability was in the catalyst recycle experiment. The successful application of the monodentate N—H HBD catalyst in the CO_2 fixation reaction provides strong proof for the further development of weak HBD catalysts.

Experimental section

General information

All materials were purchased from Energy Chemical with purities over 98 % and used without further purification. Carbon dioxide with a purity of 99.999 % was commercially available. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 and 100 MHz NMR spectrometer. ^1H NMR spectra of catalysts and product cyclic carbonate were recorded on the 400 MHz spectrometers utilizing DMSO-*d6* and Chloroform-*d* as solvent referenced to DMSO-*d6* (2.50 ppm) or Chloroform-*d* (7.26 ppm), respectively. ^{13}C NMR spectra were recorded on 100 MHz spectrometers using DMSO-*d6* or Chloroform-*d* as solvent referenced to DMSO-*d6* (39.52 ppm) or Chloroform-*d* (76.80 ppm). High resolution mass spectra (HRMS) were conducted using an Ionspec 7.0 T spectrometer. Thermal gravimetric analysis (TGA) was conducted using TGA550 instrument model.

*General procedure for the synthesis of catalysts **1a**–**i**[58]*

The substituted benzoyl chloride **A** (5.0 mmol, 1.0 equiv) and Et_3N (6.0 mmol, 1.2 equiv) were dissolved in dry CH_2Cl_2 (10 mL) at 0 °C, *N, N*-dimethylethylenediamine **B** (5.0 mmol, 1.0 equiv) was added dropwise and stirred for 10 min. The reaction solution was heated to room temperature, and stirred for 4 h, the mixture was quenched with saturated aqueous $NaHCO_3$, and organic compounds were extracted with CH_2Cl_2 (15 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to give **C**. Product **C** was dissolved in acetone added excessive Iodomethane and stirred for 1 h at room temperature, the resulting precipitate was collected by filtration, after further recrystallization and drying to afford catalysts **1a–i**.

*Synthesis of intermediate product N-(2-(dimethylamino)ethyl)-3,5-bis(trifluoromethyl)benzamide (**C-1g**) of catalyst **1g***

3,5-bis(trifluoromethyl)benzoyl chloride (5.0 mmol, 1.0 equiv) was dissolved in dry CH_2Cl_2 (10 mL) at 0 °C, *N, N*-dimethylethylenediamine (5.0 mmol, 1.0 equiv) was added dropwise and stirred for 10 min. The reaction solution was heated to room temperature, and stirred for 4 h, the mixture was quenched with saturated aqueous $NaHCO_3$, and organic compounds were extracted with CH_2Cl_2 (15 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to give the intermediate product as a white solid.

*Synthesis of catalyst **1j***

3,5-bis(trifluoromethyl)benzoyl chloride (5.0 mmol, 1.0 equiv) and Et_3N (6.0 mmol, 1.2 equiv) were dissolved in dry CH_2Cl_2 (10 mL) at 0 °C, *N, N*-diethylethylenediamine (5.0 mmol, 1.0 equiv) was added dropwise and stirred for 10 min. The reaction solution was heated to room temperature, and stirred for 4 h, the mixture was quenched with saturated aqueous $NaHCO_3$, and organic compounds were extracted with CH_2Cl_2 (15 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. Subsequently, the residue was dissolved in acetone and added to excessive Iodoethane and stirred for 5 h at room temperature, the resulting precipitate was collected by filtration, after further recrystallization and drying to afford the product as a white solid.

*Synthesis of catalyst **1k***

the intermediate **C-1g** was dissolved in acetonitrile and added excessive 1-Iodobutane and reflux for 6 h, the reaction solution was concentrated, and the residue further recrystallization and drying to afford the product as a white solid.

*Synthesis of catalyst **1l***

3,5-bis(trifluoromethyl)benzoyl chloride (5.0 mmol, 1.0 equiv) and Et_3N (6.0 mmol, 1.2 equiv) were dissolved in dry CH_2Cl_2 (10 mL) at 0 °C, *N, N*-diethylethylenediamine (5.0 mmol, 1.0 equiv) was added dropwise and stirred for 10 min. The reaction solution was heated to room temperature, and stirred for 4 h, the mixture was quenched with saturated aqueous $NaHCO_3$, and organic compounds were extracted with CH_2Cl_2 (15 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. Subsequently, the residue was dissolved in acetone added excessive Iodomethane, and stirred for 1 h at room temperature, the resulting precipitate was collected by filtration, after further recrystallization and drying to afford the product as a white solid.

*Synthesis of catalyst **1m***

3,5-bis(trifluoromethyl)benzoyl chloride (5.0 mmol, 1.0 equiv) and Et_3N (6.0 mmol, 1.2 equiv) was dissolved in dry CH_2Cl_2 (10 mL) at 0 °C, *N*-(2-aminoethyl)piperidine (5.0 mmol, 1.0 equiv) was added dropwise and stirred for 10 min. The reaction solution was heated to room temperature, and stirred for 4 h, the mixture was quenched with saturated aqueous $NaHCO_3$, and organic compounds were extracted with CH_2Cl_2 (15 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. Subsequently, the residue was dissolved in acetone added excessive Iodomethane, and stirred for 1 h at room temperature, the resulting precipitate was collected by filtration, after further recrystallization and drying to afford the product as a white solid.

*Synthesis of catalyst **1n***

The known intermediate product **C-1g** was dissolved in acetonitrile added excessive bromomethane and stirred for 1 h at room temperature, the resulting precipitate was collected by filtration, after further recrystallization and drying to afford the product as a white solid.

*Synthesis of catalyst **1o***

The known intermediate product **C-1g** was dissolved in tetrahydrofuran (THF) added excessive chloromethane (1.0 M in THF) and stirred for 6 h at 60 °C, the reaction solution was concentrated, the residue was further recrystallization and dried to afford the product as a white solid.

*Synthesis of catalyst **1p***

The known intermediate product **C-1g** was dissolved in THF (10 mL) was added sodium hydride (7.5 mmol, 1.5 equiv) at 0 °C, and stirred for 10 min. To this reaction mixture was added CH_3OTf (11.0 mmol, 2.1 equiv) at 0 °C, and then the solution was warmed to room temperature. After stirring for 1 h at room temperature, evaporation to remove THF. The mixture was quenched with a large amount of water, and the resulting white precipitate was collected by filtration and washed three times with water. The residue drying to afford the product as a white solid.

Synthesis of catalyst 1q

The known intermediate product **C-1g** was dissolved in THF (10 mL) was added sodium hydride (7.5 mmol, 1.5 equiv) at 0 °C, and stirred for 10 min. To this reaction mixture was added iodomethane (11.0 mmol, 2.1 equiv) at 0 °C, and then the solution was warmed to room temperature. After stirring for 1 h at room temperature, evaporation to remove THF. The mixture was quenched with a large amount of water, and the resulting white precipitate was collected by filtration and washed three times with water. The residue drying to afford the product as a white solid.

General procedure for the synthesis of catalyst 1r

The known intermediate product **C-1g** was dissolved in acetone and added methyl trifluoromethanesulfonate (4.8 mmol, 1.0 equiv) and stirred for 1 h at room temperature, the reaction solution was concentrated, the residue was further recrystallization and dried to afford the product as a white solid.

General procedure for the CCE reaction of terminal epoxides and CO_2

To a mixture of the terminal epoxide (10.0 mmol) and catalyst **1g** (235.0 mg, 0.5 mmol, 5 mol%) was placed in a dry 25 mL Schlenk reaction flask containing a magnetic stir bar, the flask was constantly purged with CO_2 under atmospheric pressure. The reaction mixture was warmed to 50 °C and stirred for 20 h under a CO_2 atmosphere (1 atm, using a balloon). After the flask cooled down to room temperature, the reaction mixture was filtered over silica gel (SiO_2) with petroleum ether: ethyl acetate = 30:1–5:1 to afford corresponding cyclic carbonate.

General procedure for the CCE reaction of internal epoxides and CO_2

The internal epoxide (10.0 mmol) and catalyst **1g** (188.0 mg, 0.4 mmol, 4 mol%) were placed in a dry 25 mL stainless steel reactor containing a magnetic stir bar, the reactor was constantly purged with 0.3 MPa CO_2 to remove air and finally maintain the pressure at 1.0 MPa. The reaction mixture was heated to 80 °C and stirred for 48 h. Then the reactor was cooled down to room temperature and slowly depressurized to atmospheric pressure. The reaction mixture was filtered over silica gel (SiO_2) with petroleum ether: ethyl acetate = 10:1–1:1 to afford the corresponding cyclic carbonate.

General procedure for the reaction of catalyst recycling

After the 1,2-epoxyhexane **2b** (1.21 mL, 10.0 mmol) and catalyst **1g** (235.0 mg, 0.5 mmol, 5 mol%) were stirred for 20 h at 70 °C under a CO_2 atmosphere (1 atm, using a balloon), the reaction solution was cooled to room temperature, the yield was determined by ^1H NMR spectroscopy with 1,3,5-trimethylbenzene as an internal standard. The product **3b** and residual raw materials were separated with a catalyst by vacuum distillation for 6–8 h under 100 °C. The fresh substrate **2b** was added to the residue, and then the next run was repeated under the same experimental conditions.

CRediT authorship contribution statement

Yongzhu Hu: Investigation, Methodology, Writing – original draft, Writing – review & editing. **Xinru Du:** Writing – original draft, Writing – review & editing. **Zhenjiang Li:** Conceptualization, Resources, Funding acquisition, Supervision, Writing – review & editing, Project administration. **Jun He:** Methodology. **Tong Chang:** Writing – original draft, Writing – review & editing. **Na Shi:** Methodology. **Ning Li:** Methodology. **Xin Zou:** Methodology. **Jie Sun:** Resources, Funding acquisition. **Kai Guo:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2023.113765.

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