Journal of Environmental Chemical Engineering 11 (2023) 110886

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

Halide-free squaramide–phenolate organocatalyst for the cycloaddition of CO_2 into epoxides

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ARTICLE INFO

Editor: <Chao He>

Keywords:
Carbon dioxide
Epoxide
Halide-free
Organocatalysis
Phenolate
Squaramide

ABSTRACT

The cycloaddition of CO_2 into epoxide (CCE) reaction was the few routes viable industrially in catalytic fixation of carbon dioxide into value-added chemicals in which cocatalyst halide was predominant. To obviate the harmful corrosion of halide anions to steel reactors, and to alleviate the environmental burden of halogen waste, halide-free catalyst was desirable. We propose a category of one-component H-bond donor (HBD) and nucleophilic anion (HBD–anion) bifunctional organocatalyst as representative halide-free catalyst in CCE reactions. Squaramide (Sq) in conjugation with phenolate constitutes a typical HBD–anion catalyst featured with the squaramide as the HBD moiety and the phenolate as the nucleophilic anion moiety. Series of pre-catalyst in structure of squaramide–phenol (Sq–PhOH) was designed and the active catalyst Sq–phenolate (Sq–PhO) was generated from the corresponding Sq–PhOH by deprotonating of the weakly acidic hydroxyl of the phenol by super strong Brønsted base. In an optimal *N*-benzyl squaramide *para*-phenol (Sq–PhOH-*p*) and P2 phosphazene (*t*-BuP_2) combination, CCE reactions proceed under mild conditions of 120 °C, and atmospheric pressure of 0.1 MPa, by 2.5 mol % loading of catalyst Sq–PhOH-*p*/*t*-BuP_2. Terminal epoxides were transformed with excellent conversions (86–99 %) and high selectivity (85–97 %) in 8 h. Bifunctional activations mechanisms were proposed and validated. ^1H and ^{13}C NMR titrations certified the coordination of H-bond donor squaramide to epoxide, and FT-IR spectra observed formation of phenyl carbonate anion from phenolate and carbon dioxide, these suggested unprecedent CCE reaction composed capture of CO_2 in carbonate anion followed by its intramolecular nucleophilic attack on the HBD coordinated epoxide as the key catalytic steps. The squaramide–phenolate catalytic dyad exemplified halide-free HBD–anion organocatalyst of wide scope for carbon dioxide activation and fixation.

1. Introduction

Chemical transformations of carbon dioxide (CO_2) into the value-added chemicals [1–4] have received increasing attention as it could reduce the accumulation of CO_2 in the atmosphere and mitigate climate changes [5]. The thermodynamic constraints [6,7] and kinetic hindrance [8] rendered the chemical fixation of CO_2 infeasible. A viable approach for CO_2 utilizations was reacting with high-energy reactants to compensate the barrier and employing suitable catalysis to reduce the activation energy [9,10]. The cycloaddition of CO_2 into epoxides (CCE) reaction producing cyclic carbonates [11,12] was the most discussed strategy under these considerations. These cyclic carbonates could be served as green solvents [13], electrolytes in lithium-ion batteries [14,15], synthon of isocyanate-free polyurethanes [16,17], and monomers in polymerizations [18,19]. Numerous catalysts have been developed for CCE reactions, including metal complexes [20,21] and metal-free organocatalysts [22–24]. Among the types organocatalysts for CCE reactions, the non-covalent hydrogen-bonding catalyst attracted extensive interests because the H-bond donor (HBD) could significantly accelerate the reaction by activating epoxides [25].

The general mechanism of H-bonding catalysts in CCE reactions was first systematically studied by Kleij [26], where the phenolic compounds worked as HBDs and an auxiliary nucleophile nBu_4NI as the cocatalyst. Series of HBDs in binary [23,27] or one-component bifunctional [27–29] catalysis were widely explored after that. In a well-established bifunctional catalysis [28,29], H-bond donor moiety (for epoxide

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https://doi.org/10.1016/j.jece.2023.110886
Received 9 June 2023; Received in revised form 23 August 2023; Accepted 28 August 2023
Available online 29 August 2023
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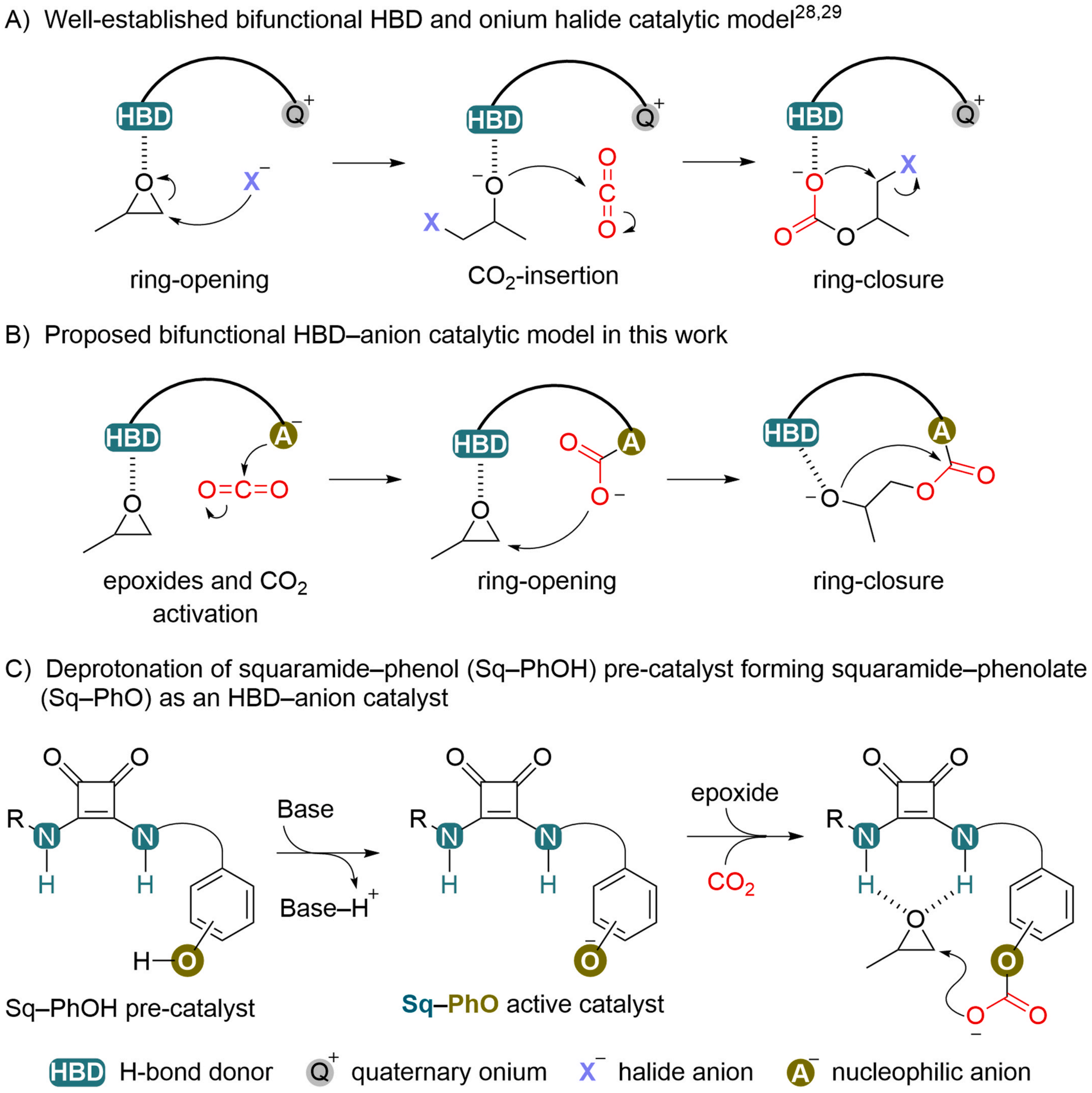
activation) and onium halide (Q^+X^-) moiety (for nucleophilic attack on epoxide) both installed in a molecular scaffold as a one-component HBD–Q^+X^- catalyst (Scheme 1, A). Cocatalyst halide anions were essential for most H-bond catalysts in CCE reactions [30–32]. Non-classical C–H hydrogen-bond donor [33,34] and halogen-bond donor [35,36,38] accompanied with cocatalyst halide anions were recently introduced by our group in the reaction of CO_2 and epoxides. Emerging HBD squaramides in CCE reactions have been reported as well [3,30,37], and the excellent catalytic performance showed that they could effectively promote the reactions with cocatalyst halide anions. However, due to the toxicity, corrosion to reactors, and non-green nature of halides [39,40], the catalysis comprised of HBDs and halide anions were limited in the green and sustainable conversions of CO_2. Halide-free organocatalysts [39–41] avoiding these disadvantages of halides have recently become an important objective in CCE reactions, and diverse homogeneous [42–49] or heterogeneous [50–56] halide-free catalysts were developed.

The key of designing halide-free catalysis was finding a non-halide nucleophile to replace halide anions in working synergistically with H-bond donors [41]. Previous work with pyridine salicylate [50], *N,*



Scheme 1. One-component bifunctional H-bond catalysis in CCE reactions. A). Well-established bifunctional catalysts composed of H-bond donors (HBDs) and onium halides (Q^+X^-) by Werner [28,29] in three key-steps of CCE reactions; B). Bifunctional HBD–anion catalyst composed of HBDs and non-halide anion (A^-) in three key-steps of CCE reactions proposed by this work; C). Deprotonation of squaramide–phenol (Sq–PhOH) pre-catalyst forming active catalyst squaramide–phenolate (Sq–PhO) in an HBD–anion catalytic model.

N'-phenylbis(5-*tert*-butylsalimide) [42,57], and PENDIs [49] proposed a promising way, in which the *N*-base worked as nucleophile moiety. Non-halide nucleophilic anions were also found to be efficient in nucleophilic attack on the HBD coordinated epoxides, such as the carboxylic anion (–COO$^-$) [54] and bicarbonate anion (HCO$_3^-$) [51]. Our group found that the pyridinium saccharinate [44] and tertiary ammonium saccharinate [45] binary cocatalyst could effectively promote the halide-free CCE reaction, where the nucleophilic saccharinate (Sac$^-$) played the role of the halide anions. A one-component HBD and nucleophilic anion (HBD–anion) bifunctional catalyst (Scheme 1, B) was thus proposed as a possible halide-free catalyst.

The inherent nucleophilicity of the oxygen atom of phenol [58] was considered to develop the phenolate as a non-halide nucleophile for CCE reactions [59]. The phenol was generally used as an H-bond donor to activate epoxides in CCE reactions [26,60,61], while the deprotonating phenol, that is phenolate, could play a promising role in absorbing CO$_2$ [62,63]. A phenyl carbonate anion would be formed after the CO$_2$ absorption by phenolate, which could nucleophilic attack the epoxide for initiating ring-opening [47,59,64,65]. An ammonium betaine was reported by Sakai [64] to produce cyclic carbonates from epoxides and CO$_2$ where the nucleophilic phenolate could capture CO$_2$ to give a useful reactive carbonate anion intermediate. A series 1,8-diazabicyclo-[5.4.0] undec-7-ene (DBU)-based phenolates and their inclusion complexes with β-cyclodextrin [65] were also developed as the supramolecular organocatalysts in carbonate synthesis. Eshghi [59] recently proved that the nucleophilic attack of the phenolate to the carbon atom of carbon dioxide was preferred instead of to the carbon atom of ethylene oxide. Dihydroxybenzene derived ionic liquids [47] also successfully promoted the halide-free CO$_2$ insertion reactions, where the phenolate anions nucleophilically attack on the CO$_2$ molecules at high CO$_2$ pressure ($\geq$ 1.0 MPa) and epoxides at low CO$_2$ pressure ($\leq$ 1.0 MPa). Employing anions such as phenolate that could capture CO$_2$ in HBD–anion catalytic model would promote unprecedent CCE reaction composed capture of CO$_2$ in anion–CO$_2$ (such as phenyl carbonate anion by phenolate) intermediate followed by its intramolecular nucleophilic attack on the HBD coordinated epoxide as the key catalytic steps (Scheme 1, B).

Squaramide (Sq) in conjugation with phenolate constituted a typical HBD–anion catalyst for homogeneous CCE reactions featured with the squaramide as the H-bond donor moiety and the phenolate as nucleophilic anion moiety (Scheme 1, C). The active catalyst Sq–phenolate (Sq–PhO) could be easily generated by deprotonating the weakly acidic hydroxyl of the phenol on the corresponding pre-catalyst in the structure of squaramide–phenol (Sq–PhOH) by super strong Brønsted base (Scheme 1, C). Unlike traditional bifunctional catalysts that required a quaternary onium (Q$^+$) to bind the free halide anions by electrostatic attraction (Scheme 1, A) for better synergy with HBDs [66–68], the Q$^+$ (Base–H$^+$) of Sq–PhO was free where the nucleophilic phenolate directly linked to the HBD squaramide (Scheme 1, C) as a true one-component bifunctional catalyst. NMR titrations and FT-IR spectra validated the possible bifunctional activation mechanisms of the HBD squaramide coordinated to epoxide and the phenolate captured CO$_2$ in forming phenyl carbonate anion. Different from the previous reported phenolate-based halide-free catalysts [47,64,65], the Sq–PhO catalyst was able to capture CO$_2$ under atmospheric pressure, which made the Sq–PhO performed good catalytic activity under milder temperature and/or pressure than other halide-free catalyst. The squaramide–phenolate bifunctional catalyst represented a general catalytic model of halide-free HBD–anion for wider scope of carbon dioxide activation and fixation.

2. Experimental section

2.1. Materials

Epoxides were purchased from Alfa Aesar. Carbon dioxide with a purity of 99.999 % was commercially available from Nanjing Shangyuan Co. 3,4-Diethoxy-3-cyclobutene-1,2-dione, benzylamine, 2-hydroxybenzylamine, 3-methoxybenzylamine, 4-hydroxybenzylamine, 1,1,2,2-tetrachloroethane, and BBr$_3$ (1 mol L^{-1} in dichloromethane) were purchased from Energy Chemical. (1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phos-phoranylidenamino]-2Λ^5,4Λ^5-catenadi(phosphazene) *t*-BuP$_4$) (0.8 mol L^{-1} in hexane), (1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2Λ^5,4Λ^5-catenadi(phosphazene) *t*-BuP$_2$) (2 mol L^{-1} in tetrahydrofuran), and (*tert*-butylimino-tri(pyrrolidino)phosphorane BTPP) were available from the Sigma-Aldrich Chemicals Co. 1,8-Diazabicyclo[5.4.0]-undec-7-ene (DBU, GC, >98 %, TCI), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, GC, >95 %, TCI), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, GC, >97 %, TCI) were purchased commercially. All reagents were used without any further purification.

2.2. Characterizations

^{1}H NMR and ^{13}C NMR spectra were carried out on a Bruker Ascend TM-400 (400 MHz) spectrometer for titration experiments, determinations for the conversions and selectivities of epoxides, and characterizations of the squaramide–phenols and cyclic carbonates using CDCl$_3$ or DMSO-*d*$_6$ as the solvent at 20 °C. Chemical shifts δ are reported in parts per million (ppm) relative to a residual undeuterated solvent as an internal reference (^{1}H δ 7.26 for CDCl$_3$, δ 2.50 for DMSO-*d*$_6$; ^{13}C δ 77.16 for CDCl$_3$, δ 39.52 for DMSO-*d*$_6$). FT-IR spectra were recorded on a Thermo Fisher Nicolet iS5 Fourier transform infrared spectrometer. High-resolution mass spectrometry (HRMS) was conducted using an Ionspec 7.0 T spectrometer.

2.3. Synthesis of squaramide–phenol pre-catalysts with different phenol substitution positions

***N*-Benzyl squaramide *ortho*-phenol (Sq–PhOH-*o*).** 3,4-Diethoxy-3-cyclobutene-1,2-dione (2.96 mL, 20 mmol) was first solved with 50 mL methanol in a 250 mL round bottom flask, the benzylamine (2.18 mL, 20 mmol) was added dropwise, and the reaction mixture was stirred for 24 h at room temperature. The reaction solution was filtered to remove solids, and 2-hydroxybenzylamine (2.46 g, 20 mmol) was added to the filtrate. The mixture was stirred for 24 h at room temperature. A brick-red solid product was obtained after filtering the mixture and washing the filter residue with methanol. Yield 64 %.

***N*-Benzyl squaramide *meta*-phenol (Sq–PhOH-*m*).** 3,4-Diethoxy-3-cyclobutene-1,2-dione (2.96 mL, 20 mmol) was first solved with 50 mL methanol in a 250 mL round bottom flask, the benzylamine (2.18 mL, 20 mmol) was added dropwise, and the reaction mixture was stirred for 24 h at room temperature. The reaction solution was filtered to remove solids, and 3-methoxybenzylamine (2.56 mL, 20 mmol) was added to the filtrate. The mixture was stirred for 24 h at room temperature. A white solid product was obtained after filtering the mixture and washing the filter residue with methanol. Then, the white solid (1.62 g, 5 mmol) was dissolved with 25 mL dichloromethane (DCM), and 20 mL BBr$_3$ (1 M in DCM) was added at −40 °C. The mixture was stirred at −40 °C for 30 min, and then stirred at 0 °C and room temperature for 4 h and 12 h, respectively. After that, 50 mL methanol was added slowly to quench the reaction, and the reaction solution was washed with saturated NaHCO$_3$ (2 ×100 mL) solution and water (2 ×100 mL) in order. A beige solid product was obtained after filtering the mixture and washing the filter residue with water. Yield 61 %.

***N*-Benzyl squaramide *para*-phenol (Sq–PhOH-*p*).** 3,4-Diethoxy-3-cyclobutene-1,2-dione (2.96 mL, 20 mmol) was first solved with 50 mL methanol in a 250 mL round bottom flask, the benzylamine (2.18 mL, 20 mmol) was added dropwise, and the reaction mixture was stirred for 24 h at room temperature. The reaction solution was filtered to remove solids, and 4-hydroxybenzylamine (2.46 g, 20 mmol) was added to the filtrate. The mixture was stirred for 24 h at room temperature. A white solid product was obtained after filtering the mixture and washing the filter residue with methanol. Yield 70 %.

2.4. General procedure for the cycloaddition of epoxides and CO_2

The cycloaddition of carbon dioxide into epoxides (CCE) reactions were conducted in a 10 mL Schlenk flask. After Schlenk operations, the water- and oxygen-free Schlenk flask was transferred into a glove box. The inert gas used was argon. The squaramide–phenol pre-catalyst, epoxide, and Brønsted base were added to the flask in the glove box. Then, the flask was transferred out from the glove box and the argon in the flask was replaced by CO_2. The flask was put into the oil bath pan and equipped with a CO_2 balloon. In a typical procedure, the Schlenk flask was charged with pre-catalyst Sq–PhOH-*p* (38.5 mg, 0.125 mmol), styrene oxide (0.6 mL, 5 mmol), and *t*-BuP$_2$ (62.5 μL, 0.125 mmol, 2 M in THF). The flask was subsequently inserted by a CO_2 balloon and put into the oil bath under 120 °C for reaction. The conversions of epoxides were determined by ^1H NMR spectra with $CDCl_3$ as a solvent, and the selectivity of cyclic carbonates were determined with 1,1,2,2-tetrachloroethane as the internal standard (see Supporting Information for details). The reaction mixture was cooled in ice before it was sampled for ^1H NMR spectra measurements. Pure carbonates were obtained by column chromatography with an eluent of petroleum ether (PE) and ethyl acetate (EA) (5:1).

3. Results and discussion

3.1. Design of squaramide–phenolate catalysts and evaluation of the catalytic performances in CCE reactions

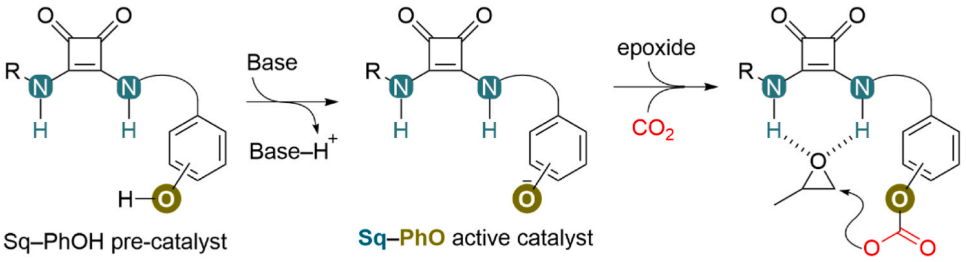
Halide-free organocatalyst for the cycloaddition of carbon dioxide into epoxides (CCE) reactions was highly desirable since currently prevalent strategy containing cocatalyst halide while the halide anion posed serious risk in reactor corrosion [39–41]. One-component HBD–anion bifunctional catalyst composed of H-bond donor (HBD) and nucleophilic anion was proposed to be a representative halide-free catalyst in CCE reaction. The nucleophilic anion required to have appropriate nucleophilicity and nucleofugality [69]. Phenolate has been introduced in CCE reaction due to its nucleophilic and leaving abilities [47,59,64,65], and it could capture CO_2 in forming phenyl carbonate anions [62,63]. Squaramide (Sq) in conjugation with phenolate constituted a typical HBD–anion catalyst featured with the Sq as the HBD moiety and the phenolate as the nucleophilic anion moiety (Scheme 2). In the squaramide–phenolate (Sq–PhO) catalyst, the Sq activated epoxide through H-bonding and the phenolate captured CO_2 in forming carbonate anion followed by its intramolecular nucleophilic attack on the squaramide coordinated epoxide. The active catalyst Sq–PhO was easily generated from the corresponding pre-catalyst in the structure of squaramide–phenol (Sq–PhOH) by deprotonating the weakly acidic hydroxyl of the phenol by super strong Brønsted base (Scheme 2).

Three new Sq–PhOH pre-catalysts with different phenolic hydroxyl substitution positions (Fig. 1), *N*-benzyl squaramide *ortho*-phenol (Sq–PhOH-*o*), *N*-benzyl squaramide *meta*-phenol (Sq–PhOH-*m*), and *N*-benzyl squaramide *para*-phenol (Sq–PhOH-*p*), were designed and synthesized from the 3,4-diethoxy-3-cyclobutene-1,2-dione, aminophenol, and amine. Brønsted bases for the deprotonation of Sq–PhOH were commercially available (Fig. 1), including 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), P1 phosphazene BTPP, P2 phosphazene *t*-BuP$_2$, and P4 phosphazene *t*-BuP$_4$.

The catalytic performances of Sq–PhOH pre-catalysts were firstly compared in the CCE reaction of styrene oxide (SO) by combing with DBU (Table 1, entries 1–3). The experiments were conducted with 5 mol % Sq–PhOH/DBU (the ratio of Sq–PhOH/DBU = 1/1) loading under conditions of 120 °C, 6 h, and 0.1 MPa CO_2. The Sq–PhO catalysts showed an order of the reactivity in *N*-benzyl squaramide *ortho*-phenolate (Sq–PhO-*o*) < *N*-benzyl squaramide *meta*-phenolate (Sq–PhO-*m*) < *N*-benzyl squaramide *para*-phenolate (Sq–PhO-*p*) and exhibited turnover frequencies (TOFs) of 1.98, 2.13, and 2.15 h^{-1} respectively, which may be related to the different substitution positions of the phenolates (Fig. S7). It was also worth mentioning that Sq–PhOH-*p* was easier to synthesize than Sq–PhOH-*m*, Sq–PhOH-*p* was thus selected as the optimal squaramide–phenol among three Sq–PhOHs. In addition, there was no significant increase in the conversion of SO observed by extending the reaction time of the cycloaddition catalyzed by Sq–PhOH-*p*/DBU from 6 h to 8 h (Table 1, entries 3 and 4, 86 % vs. 88 %).

All the reactions promoted by Sq–PhOHs and DBU showed poor selectivity (< 80 %). It was supposed that the basicity of DBU (pK_a (DBU–H$^+$) = 13.9 in DMSO [70]) was too weak to completely abstract the phenolic hydroxyl (pK_a (PhOH) = 18.0 in DMSO [71]) when the ratios of Sq–PhOH/DBU were 1/1, and the unreacted DBU directly attacked the epoxide as a nucleophile while the poor nucleofugality of DBU [72] led to low selectivity. The same phenomenon also appeared in the combination of Sq–PhOH-*p* with MTBD (pK_a (MTBD–H$^+$) = 14.8 in DMSO [70], TOF = 0.80 h^{-1}) and TBD (pK_a (TBD–H$^+$) = 15.3 in DMSO [70], TOF = 1.44 h^{-1}), both of which performed moderate selectivity (Table 1, entries 5 and 6, 84 % and 81 %).

This situation improved by using phosphazene bases, which preformed both strong Brønsted basicity and low nucleophilicity [73,74]. The pK_a of the conjugate acid of P1 phosphazene BTPP (pK_a (BTPP–H$^+$) = 17.4 in DMSO [70]) was similar to that of phenol [71]. However, it was also failed to completely deprotonate the phenolic hydroxyl of Sq–PhOH-*p*, and the nucleophilicity of BTPP was too poor to attack the epoxides like DBU in CCE reactions, resulting in low conversion (22 %) but high selectivity (99 %) (Table 1, entry 7, TOF = 0.54 h^{-1}). Further increasing the basicity of the Brønsted base, P2 phosphazene *t*-BuP$_2$ (pK_a (*t*-BuP$_2$–H$^+$) = 21.52 in DMSO [70]) was selected for the CCE reaction of SO and CO_2 in combination with Sq–PhOH-*p*, resulted in both high conversion and high selectivity (92 % and 94 %) (Table 1, entry 8, TOF = 2.16 h^{-1}). Compared with the previously reported halide-free phenolate catalyzed CCE reactions [47,64,65], the reaction promoted by Sq–PhOH-*p*/*t*-BuP$_2$ was conducted in less time with similar conversions under milder conditions of lower pressure (0.1 MPa) and/or temperature (120 °C). The experiment of recycling Sq–PhO catalyst was also tried in the Sq–PhOH-*p*/*t*-BuP$_2$ promoted CCE reactions of SO, however, it was failed. The Sq–PhO catalyst was difficult to separate from the reaction mixture due to its homogeneous molecular catalyst



Scheme 2. Sq–PhO catalyst generated from Sq–PhOH pre-catalyst by deprotonating the hydroxyl of phenol for CCE reactions.

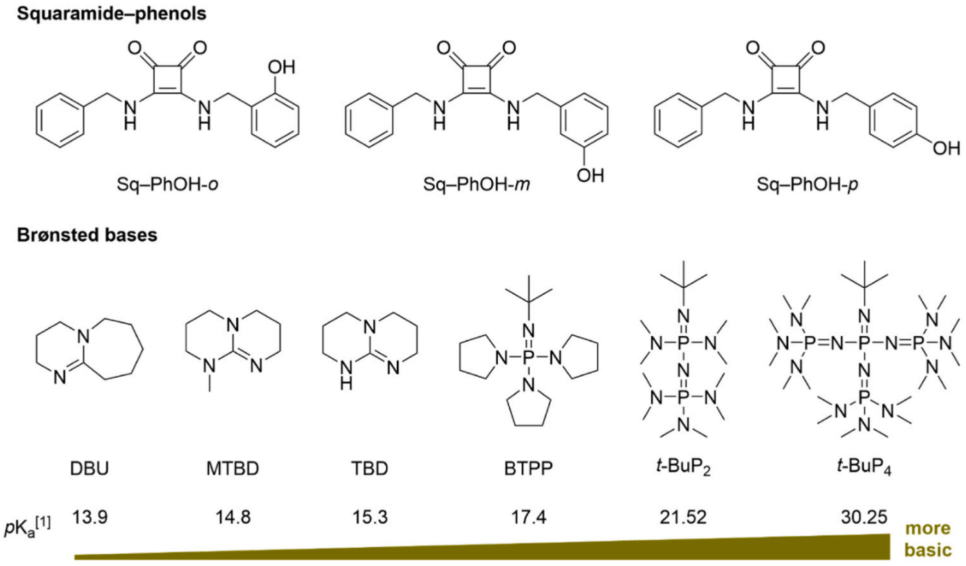
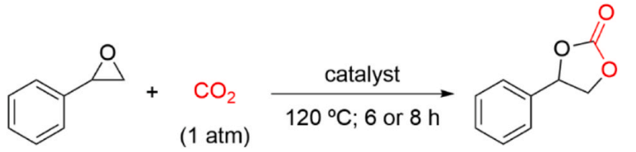


Fig. 1. The Sq–PhOHs screened in combination with Brønsted bases for CCE reactions. Note: [1] The pK_a values are from the conjugate acids of the respective Brønsted bases, in DMSO [70].

Table 1

The cycloaddition of styrene oxide (SO) and carbon dioxide catalyzed by different combinations of Sq–PhOHs and bases[a].



Entry	Catalyst	*t* [h]	Conv.[b] [%]	Sel.[b] [%]	TOF[c] [h^{-1}]
1	Sq–PhOH-*o*/DBU	6	75	79	1.98
2	Sq–PhOH-*m*/DBU	6	81	79	2.13
3	Sq–PhOH-*p*/DBU	6	86	75	2.15
4	Sq–PhOH-*p*/DBU	8	88	73	1.61
5	Sq–PhOH-*p*/MTBD	8	38	84	0.80
6	Sq–PhOH-*p*/TBD	8	71	81	1.44
7	Sq–PhOH-*p*/BTPP	8	22	99	0.54
8	Sq–PhOH-*p*/*t*-BuP$_2$	8	92	94	2.16
9	Sq–PhOH-*p*/*t*-BuP$_4$	8	64	80	1.28
10	Sq–PhOH-*p*/–	8	–	–	–
11	–/*t*-BuP$_2$	8	51	87	1.11

[a] Reaction conditions: SO (5 mmol), CO$_2$ (0.1 MPa), Sq–PhOH (5 mol %), Brønsted bases (5 mol %), 120 °C, solvent-free.

[b] Determined by ^{1}H NMR (CDCl$_3$) using 1,1,2,2-tetrachloroethane as internal standard.

[c] Turnover frequency (TOF) = moles of product/(moles of catalyst × time).

feature. Moreover, the formation of by-products such as polyether made the catalyst difficult to be recovered as well.

The basicity of *t*-BuP$_2$ was strong enough to deprotonate the phenolic hydroxyl, and it was validated by NMR titration experiments of Sq–PhOH-*p* and *t*-BuP$_2$. The NMR titration experiments conducted in DMSO-d_6 by changing the molar ratio of Sq–PhOH-*p*/*t*-BuP$_2$ to 1:0, 1:0.1, 1:0.2, 1:0.5, 1:0.8, and 1:1 (Fig. 2a). The results showed that the N–H and O–H signals of Sq–PhOH-*p* (9.412 and 7.653 ppm) were normalized after the addition of *t*-BuP$_2$. And the normalized peak shifted from upfield (8.147 ppm) to downfield (10.343 ppm) and its peak area gradually decreased with the increasing amount of *t*-BuP$_2$, which proved that the Sq–PhOH-*p* could be deprotonated by *t*-BuP$_2$ (Fig. 2b). Moreover, the peaks of the proton on the phenyl connecting hydroxyl presented obvious chemical shifts from downfield (7.120 and 6.738 ppm) to upfield (6.779 and 6.129 ppm) for the anion formation, and the signals of the proton on the phenyl without O–H attached (7.268–7.382 ppm) hardly shifted, further indicated that it was not N–H but O–H deprotonated in Sq–PhOH-*p* (Fig. 2c). These results meant that the Sq–phenolate composed of H-bond donors (N–Hs) and nucleophilic phenolate could be easily formed by combining the squaramide–phenol pre-catalysts with *t*-BuP$_2$, and could effectively promote CCE reactions as a halide- and metal-free organocatalyst.

Abnormality appeared at the use of more basic P4 phosphazene *t*-BuP$_4$ (pK_a (*t*-BuP$_4$–H$^+$) = 30.25 in DMSO [70]). The Sq–PhOH-*p*/*t*-BuP$_4$ catalysis displayed lower conversion and selectivity than Sq–PhOH-*p*/*t*-BuP$_2$ in the CCE reaction (Table 1, entry 9, TOF = 1.28 h^{-1}). The deviant behavior of *t*-BuP$_4$ probably attributed to the bigger cation radius of *t*-BuP$_4$H$^+$ (4.7 Å) than *t*-BuP$_2$H$^+$ (3.3 Å) [75], which caused different ionic pairs (tight or loose) with different anionic reactivity [76]. Sq–PhOH-*p* and *t*-BuP$_2$ were also examined individually for their catalytic activities. Sq–PhOH-*p* (Table 1, entry 10) was not capable of promoting the CCE reaction in the absence of nucleophiles, while the control experiment of using *t*-BuP$_2$ (Table 1, entry 11, TOF = 1.11 h^{-1}) as the catalyst realized a lower conversion and selectivity (51 % and 87 %).

The catalytic performances of the Sq–PhO catalyst derived from Sq–PhOH-*p*/*t*-BuP$_2$ in CCE reactions of SO and CO$_2$ were probed in more detail. Different ratios of Sq–PhOH-*p*/*t*-BuP$_2$ were compared in the benchmark CCE reaction of SO (Table 2, entries 1–4). As the ratio of Sq–PhOH-*p*/*t*-BuP$_2$ increased from 1/1–1.5/1, the conversion of SO was not improved (90 %) and the selectivity decreased (82 %). Furtherly increasing the equivalent of Sq–PhOH-*p* into the ratio of 2/1 and 3/1, SO converted to SC faster (6 h, 94 % and 90 %) but the selectivity deteriorated sharply (64 % and 41 %). The reaction was conducted homogeneously at 120 °C with 5 mol % Sq–PhOH-*p*/*t*-BuP$_2$ added in the ratio of 1/1, while the excess Sq–PhOH-*p* made the mixture to be homogeneous later. These results suggested that the higher equivalents of Sq–PhOH-*p* had a slight gain in promoting CCE reactions, but the excess Sq–PhOH-*p* preformed a severe negative impact on the selectivity of CCE reactions, probably due to the poor solubility of Sq–PhOHs in SO.

The catalyst loading was tuned into four series with a fixed ratio of Sq–PhOH-*p*/*t*-BuP$_2$ at 1/1 to study its effect on the cycloaddition (Table 2, entries 1 and 5–7). A higher catalyst loading of 10 mol % (Table 2, entry 5) speeded up the transformation of SO (6 h, 93 %), but a lower selectivity (60 %) was observed, which demonstrated that too much Sq–PhO was unfavorable for the selectivity of the reaction as well. The decreased catalyst loading of 2.5 mol % (Table 2, entry 6) afforded

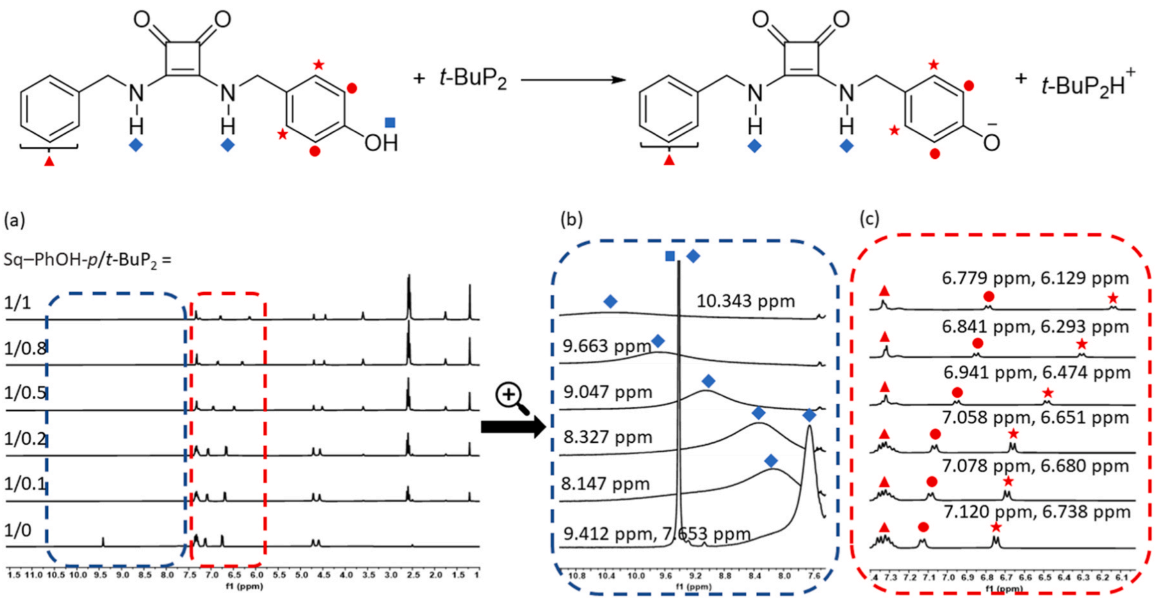
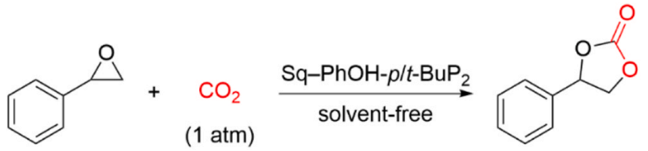


Fig. 2. The chemical shifts of protons on Sq–PhOH-*p*/*t*-BuP_2 in the ^1H NMR spectra (DMSO-d_6, room temperature) with changing the molar ratio of Sq–PhOH-*p*/*t*-BuP_2 as 1/0, 1/0.1, 1/0.2, 1/0.5, 1/0.8, and 1/1.

Table 2
Optimization of reaction conditions for the cycloaddition of carbon dioxide into epoxides[a].



Entry	Sq–PhOH-*p*/*t*-BuP_2	Catalyst loading [mol %]	*T* [°C]	*t* [h]	Conv.[b] [%]	Sel.[b] [%]
1	1/1	5	120	8	92	94
2	1.5/1	5	120	8	90	82
3	2/1	5	120	6	94	64
4	3/1	5	120	6	90	41
5	1/1	10	120	6	93	60
6	1/1	2.5	120	8	90	95
7	1/1	1	120	8	45	99
8	1/1	2.5	100	8	62	94
9	1/1	2.5	80	8	10	99
10	1/1	2.5	60	8	3	99

[a] Reaction conditions: SO (5 mmol), CO_2 (0.1 MPa), Sq–PhOH-*p*/*t*-BuP_2.

[b] Determined by ^1H NMR ($CDCl_3$) using 1,1,2,2-tetrachloroethane as internal standard.

virtually the same result in the conversion (90 %) and selectivity (95 %) compared with those of 5 mol % catalyst loading (92 % conv., 94 % sel.) (Table 2, entry 1), while the lower catalyst loading of 1 mol % (Table 2, entry 7) presented much lower conversion (45 %) in 8 h.

The CCE reactions of SO also conducted in a staged reduction of the temperature from 120 °C to 60 °C (Table 2, entries 1 and 8–10) under the conditions of Sq–PhOH-*p*/*t*-BuP_2 = 1/1 and 2.5 mol % catalyst loading, and the catalytic activities decreased steadily. The results suggested that a temperature of 100 °C was still feasible, and the SO converted 62 % with a high selectivity (94 %) in 8 h. The reactions were also proceeded at 80 °C and 60 °C, but it was less efficient, and the conversions were 10 % and 3 % at 8 h, respectively. Overall, Sq–PhOH-*p*/*t*-BuP_2 in the ratio of 1/1, 2.5 mol % catalyst loading, and 120 °C were considered as the optimal conditions for CCE reactions and used in subsequent studies.

3.2. *Substrate scope studies for cycloaddition of epoxides into CO_2 catalyzed by Sq–PhOH-p/t-BuP_2*

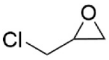
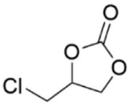
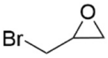
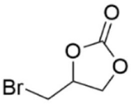
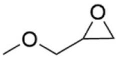
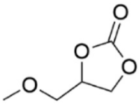
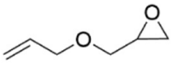
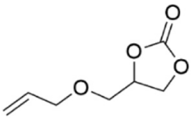
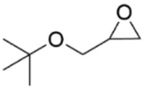
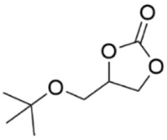
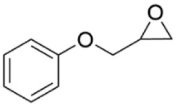
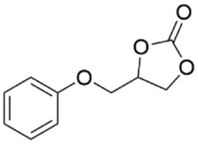
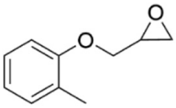
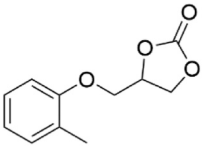
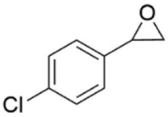
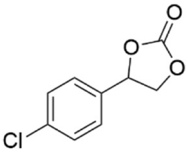
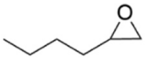
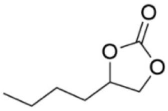
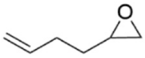
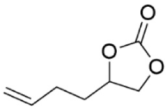
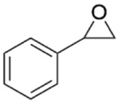
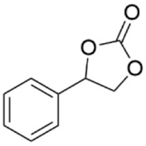
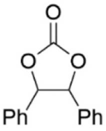
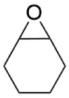
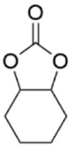
Different epoxides were investigated in the optimal conditions for extending the substrate scope of this catalysis, and the results summarized in Table 3. All terminal epoxides (Table 3, entries 1–10) converted into the corresponding cyclic carbonate with high conversions (86–99 %), good selectivity (85–97 %), and considerable TOFs (≥ 4 h^{-1}) in 8 h, including the sterically hindered epoxide 2-[(2-methylphenoxy)methyl] oxirane (entry 7, TOF = 4.41 h^{-1}). Internal epoxides cyclohexene (Table 3, entry 11) and stilbene (Table 3, entry 12), which were generally difficult to activate [30,66], were also studied under these mild conditions but resulted in no formation of cyclic carbonate. All the prepared cyclic carbonates were simply isolated by column chromatography and their structures were determined by ^1H and ^{13}C NMR spectra. Compare with other halide-free organocatalysts, the squaramide–phenolate catalyst could achieve good catalytic performance under milder conditions of lower pressure (0.1 MPa) and/or temperature (120 °C) (Table S2).

3.3. *Proposed mechanism for CCE reactions catalyzed by Sq–PhOH-p/t-BuP_2*

The phenolic hydroxyl of squaramide–phenol pre-catalyst was first deprotonated by strong Brønsted base to give a one-component squaramide–phenolate bifunctional catalyst featured with the squaramide as H-bond donor and the phenolate as basic anion. The deprotonation of the phenolic hydroxyl in Sq–PhOH by *t*-BuP_2 was validated by ^1H NMR titration experiments showed above (Fig. 2).

^1H NMR titration experiments were also performed to certify the mechanism of the Sq–PhO-*p* (derived from Sq–PhOH-*p*/*t*-BuP_2) catalyzed CCE reactions. The chemical shifts of methine protons on SO shifted upfield from 3.921 to 3.908 ppm with increasing ratios of Sq–PhOH-*p*/*t*-BuP_2/SO from 0/0/1–1/1/1 (Fig. 3). The shielding effect of the methine protons on SO was ascribed to the H-bonds between the squaramide moiety of Sq–PhO-*p* and SO. ^{13}C NMR spectra were studied to furtherly evaluate the H-bonds between the Sq–phenolate and SO. As the ratio of ratios of Sq–PhOH-*p*/*t*-BuP_2/SO increased from 0/0/1–1/1/1, the methine carbon on SO shifted upfield from 51.524 to 51.477 ppm (Fig. 4). These experiments suggested that the CCE reactions were

Table 3
Synthesis of cyclic carbonates under optimal conditions[a].

Entry	Substrate	Product	Conv.[b] [%]	Sel.[b] [%]	TOF[c] [h^{-1}]	Yield[d] [%]
1			90	89	4.01	79
2			98	97	4.75	93
3			96	91	4.37	86
4			86	95	4.09	80
5			99	97	4.80	93
6			99	89	4.41	88
7			98	90	4.41	87
8			95	87	4.13	82
9			98	85	4.17	81
10			93	86	4.00	77
11			90	95	4.28	85
12			–	–	–	–
13			–	–	–	–

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[a] Reaction conditions: epoxide substrates (5 mmol), CO_2 (0.1 MPa), Sq–PhOH-*p*/*t*-BuP_2 = 1/1, 2.5 mol % of Sq–PhOH-*p*/*t*-BuP_2, 120 °C, 8 h.

[b] Determined by ^1H NMR ($CDCl_3$) using 1,1,2,2-tetrachloroethane as internal standard.

[c] Turnover frequency (TOF) = moles of product/(moles of catalyst × time).
[d] Isolated yields by column chromatography.

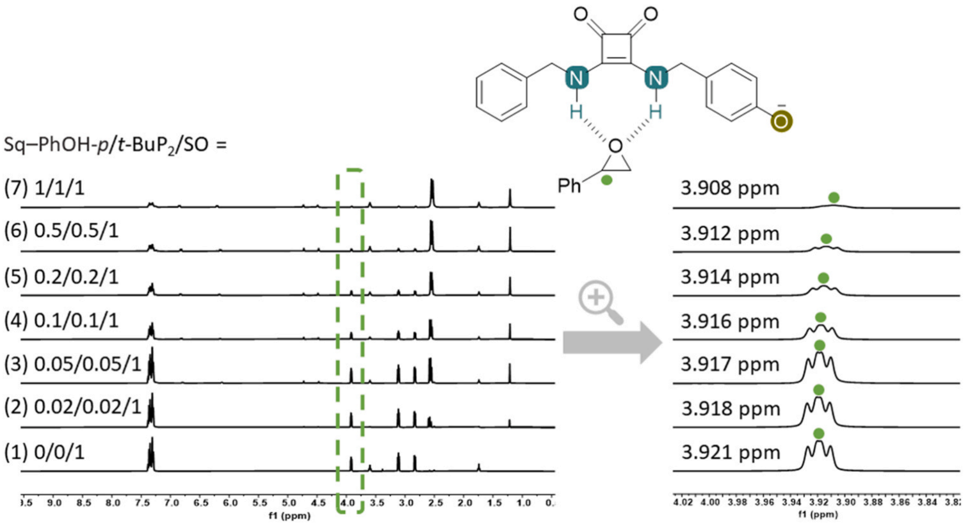


Fig. 3. Chemical shifts of the methine proton of SO in the ^1H NMR spectra (DMSO-d_6, room temperature) with different ratios of Sq–PhOH-*p*/*t*-BuP_2/SO: (1) 0/0/1, (2) 0.02/0.02/1, (3) 0.05/0.05/1, (4) 0.1/0.1/1, (5) 0.2/0.2/1, (6) 0.5/0.5/1, and (7) 1/1/1.

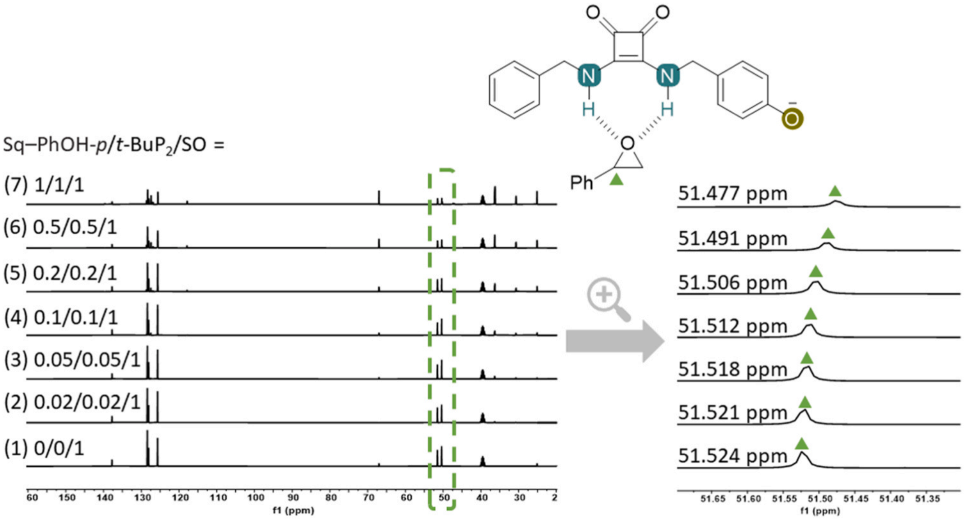


Fig. 4. Chemical shifts of the methine carbon of SO in the ^{13}C NMR spectra (DMSO-d_6, room temperature) with different ratios of Sq–PhOH-*p*/*t*-BuP_2/SO: (1) 0/0/1, (2) 0.02/0.02/1, (3) 0.05/0.05/1, (4) 0.1/0.1/1, (5) 0.2/0.2/1, (6) 0.5/0.5/1, and (7) 1/1/1.

promoted with the Sq–PhOH-*p*/*t*-BuP_2 by forming H-bonds between the Sq–PhO-*p* and SO.

The capture of CO_2 by the phenolate moiety of Sq–PhO-*p* catalyst was also investigated to furtherly clarify the reaction mechanism. In the FT-IR spectroscopy (Fig. 5), a new peak at $\tilde{\nu} = 1638$ cm^{-1} appeared for the Sq–PhO-*p* after interacting with CO_2 due to the formation of phenyl carbonate anions [63,64]. The experimental results emphasized the capture of CO_2 played an important role in the subsequent conversion.

A plausible mechanism of the squaramide–phenolate (derived from Sq–PhOH-*p*/*t*-BuP_2) catalyzed CCE reactions was proposed based on the NMR titration and FT-IR experimental results (Scheme 3). First, the nucleophilic phenolate of the Sq–PhO-*p* captured CO_2 yielding a phenyl carbonate anion (step **1**). The squaramide moiety of the Sq–PhO-*p* coordinated with the oxygen of epoxide by H-bonds for activating epoxide (step **2**). An alkoxide was subsequently produced due to the intramolecular nucleophilic attack of the phenyl carbonate anion formed in step **1** to the methylene carbon of the Sq coordinated epoxide, opening the epoxide ring (step **3**). The H-bonds stabilized transient alkoxide intramolecularly substituted the Sq–PhO-*p*, achieving the ring-closure of cyclic carbonate and releasing the Sq–PhO-*p* for another catalytic cycle (step **4**).

4. Conclusions

Halide-free organocatalyst was highly desirable in the cycloaddition of CO_2 into epoxide (CCE) reaction for obviating the harmful corrosion of prevalent cocatalyst halide to steel reactors and the environmental burden of halogen waste [39–41,44,45]. Nucleophilic anion in place of halide anion and H-bond donor (HBD) composed a one-component HBD–anion bifunctional catalyst was a promising way of promoting halide-free CCE reactions. Squaramide (Sq) in conjugation with phenolate represented a typical HBD–anion catalyst, where the

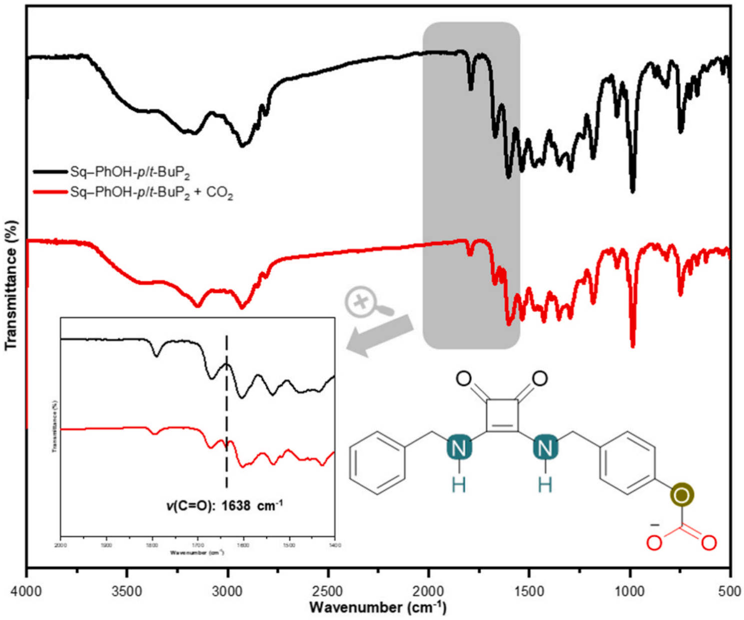
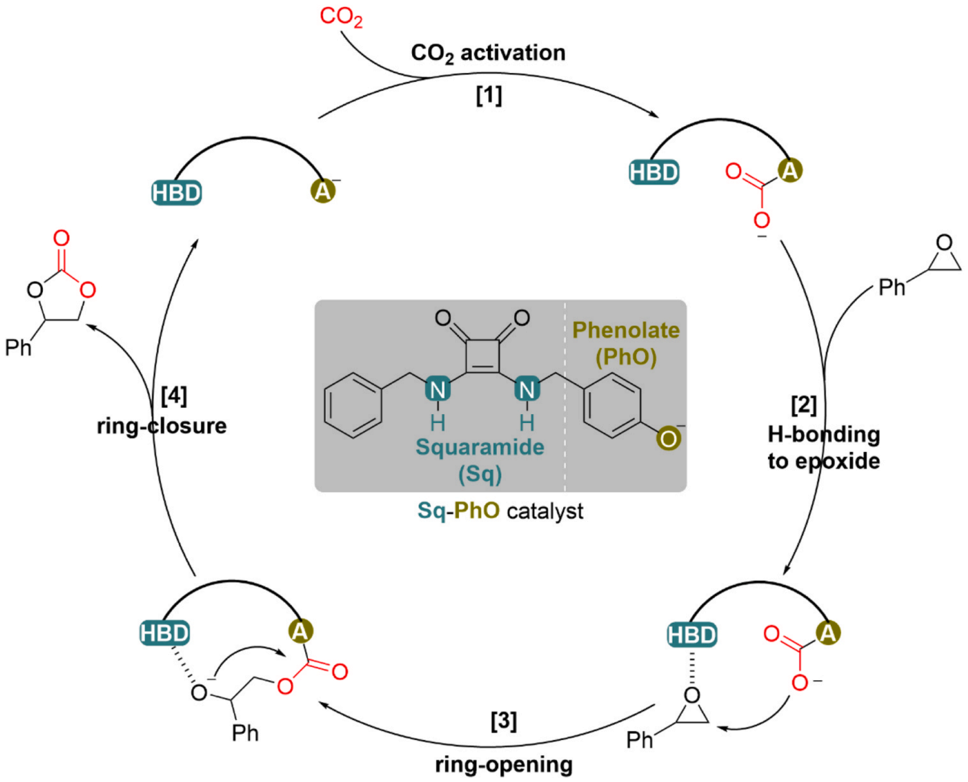


Fig. 5. FT-IR spectra of Sq–PhOH-*p*/*t*-BuP$_2$ (black) and Sq–PhOH-*p*/*t*-BuP$_2$ + CO$_2$ (red). Reaction conditions: 0.2 mmol of Sq–PhOH-*p*, 0.2 mmol of *t*-BuP$_2$, 2 mL of solvent (CH$_2$Cl$_2$:MeOH = 10:1), CO$_2$ balloon, 25 °C, 6 h.



Scheme 3. Plausible activation mechanisms of the Sq–PhOH-*p*/*t*-BuP$_2$ catalyzed CCE reaction. The catalytic cycle was in four steps: step **1**, nucleophilic phenolate captured CO$_2$ forming a phenyl carbonate anion; step **2**, the squaramide moiety coordinated to the oxygen on epoxide by H-bonds for activating the epoxide; step **3**, the ring-opening was initiated by the intramolecular nucleophilic attack of the phenyl carbonate anion on the methylene carbon of epoxide, and the generated alkoxide anion was stabilized by the H-bonds; step **4**, the ring-closure was finished by an intramolecular nucleophilic substitution of the alkoxide anion onto carbonyl, the cyclic carbonate was produced and released, and the catalyst Sq–PhO-*p* was regenerated.

squaramide was an emerging HBD and the phenolate worked as a nucleophilic anion. Different squaramide–phenolate (Sq–PhO) active catalysts were easily generated by the deprotonation of the weakly acidic hydroxyl of the phenol in the corresponding squaramide–phenol (Sq–PhOH) pre-catalysts by super strong Brønsted bases. The combination of *N*-benzyl squaramide *para*-phenol (Sq–PhOH-*p*) and P2 phosphazene (*t*-BuP$_2$) was selected as the optimal catalysis because of the suitable phenol substitution position of Sq–PhOH-*p* and the appropriate basicity and nucleophilicity of *t*-BuP$_2$. The deprotonation of the phenolic hydroxyl on Sq–PhOH-*p* by *t*-BuP$_2$ was validated by the ^{1}H NMR titration experiments. The CCE reactions could be conducted under mild conditions of 120 °C, and 0.1 MPa of CO$_2$, by 2.5 mol % loading of catalyst Sq–PhOH-*p*/*t*-BuP$_2$. Terminal epoxides were transformed with excellent conversions (86–99 %) and high selectivity (85–97 %) in 8 h, while the internal epoxides cyclohexene and stilbene were not viable under these conditions. ^{1}H and ^{13}C NMR titrations also certified the coordination of HBD squaramide to epoxide for epoxide activation, and FT-IR spectra observed formation of phenyl carbonate anion from phenolate and carbon dioxide. A bifunctional activations mechanisms were proposed in this way. The Sq–PhO catalyst promoted an unprecedent CCE reaction with key catalytic steps of capturing CO_2 in carbonate anion for its subsequent intramolecular nucleophilic attack on H-bond donor coordinated epoxide. The halide-free nature of Sq–PhO catalyst indicated that it was able to be employed in commercial processes avoiding risk in reactor corrosion. Heterogous version of this kind of halide-free HBD–anion organocatalyst for carbon dioxide utilization was under investigation, which might be recovered and used in industry. The one-component squaramide–phenolate bifunctional catalyst exemplified halide-free HBD–anion catalyst of wide scope for carbon dioxide activation and fixation, and the diversified nucleophilic anions would provide possibility in developing more halide-free catalysis.

Supporting Information

The Supporting Information is available free of charge on the publisher's website.

CRediT authorship contribution statement

Bo Liu: Investigation, Methodology, Writing - review & editing. **Hui Yu**: Writing - review & editing. **Zhenjiang Li**: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing. **Jun He**: Validation, Investigation. **Yongzhu Hu**: Investigation. **Xin Zou**: Investigation. **Longlin Lu**: Investigation. **Shaoju Cao**: Investigation. **Canliang Ma**: 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

This work was supported by the National Natural Science Foundation of China (22078150), the Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), the project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), the Jiangsu Synergetic Innovation Center for Advanced Bio-Manufacture (XTB2201), and the Top-Notch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2023.110886.

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