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Bifunctional Resorcinarene-Based Organocatalysts Bearing 5-Imino Pyridyl and 4-OH Groups for CO_2 Cycloaddition to Epoxides

Yongzhu Hu, Min Zhang, Zhenjiang Li,* Ning Li, Yujia Wang, Haoyu Wang, Xin Yuan, Xin Zou, Chunyu Li, and Kai Guo

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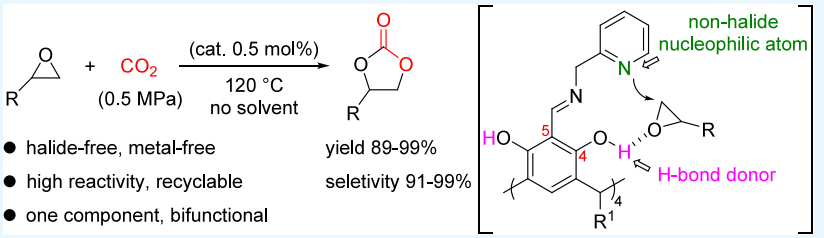

ABSTRACT: The cycloaddition of carbon dioxide to epoxide (CCE) reactions requires binary catalysts in which halide cocatalysts are predominant. However, halide is notorious for its corrosion to steel reactors, and halide residue is environmentally harmful. In the design of a halide-free catalyst for CCE reactions, we proposed resorcinarenes installed with the 5-(imino pyridyl) catalytic group, in cooperation with 4-OH on the same resorcinol unit, as a bifunctional organocatalyst. A series of resorcinarene pyridyl (**R-Py**) catalysts was designed and evaluated in CCE reactions of styrene oxide, of which the optimal catalyst **R-Py2** converted 15 terminal epoxide, 3 internal epoxides, and commercial epoxide bisphenol A diglycidyl ether into the corresponding cyclic carbonates in high yields and nearly quantitative selectivity (91−99%). Noticeably, epichlorohydrin transformed into its cyclic carbonate at atmospheric pressure of CO_2, at 100 °C, in 24 h with 99% conversion and 99% selectivity. The catalyst was recycled five times, while the conversion remained at 96%. Control experiments with analogue catalysts **R-Ph** (5-(imino phenyl)) and **R-Qu** (5-(imino 8-quinolyl)) and the 4-OH masked analogue catalyst **R-Py2** (4-OMe) showed no conversions or decreases, suggesting the indispensable pyridyl and phenolic OH groups in the bifunctional catalysis. These exemplified a first case of a calixarene-based halide-free organocatalyst for CO_2 cycloaddition and suggested an avenue of halide-free ion pair catalyst design for carbon dioxide activations.

INTRODUCTION

Carbon dioxide is a greenhouse gas and a nontoxic and abundant renewable resource; excessive accumulation of carbon dioxide will not only cause serious climate problems but also cause waste of carbon resources.[1] For the sustainable development of society, using carbon dioxide as a C1 building block to convert high-value-added chemicals is an ideal and promising strategy.[2] The cycloaddition of carbon dioxide to epoxide (CCE) reaction has attracted the interest of academia and industry due to its 100% atomic economics and commercial value.[3] Carbon dioxide is used as a raw material source to replace the traditional highly toxic and corrosive phosgene pathway, and the highly active substrate can compensate for the high energy input of the cycloaddition reaction process.[4] With its high boiling point, low toxicity, and biodegradability, the produced cyclic carbonate finds use as a good chemical intermediate,[5] polar aprotic solvent,[6] electrolyte solvent for lithium-ion batteries,[7] and monomers of polycarbonate[8] and nonisocyanate polyurethane.[9] However, the development of catalytic systems is necessary due to carbon dioxide's inherent chemical inertness and thermodynamic properties.[10] Various catalysts have been developed for the CCE reaction, including metal complexes[11] and organocatalysts.[12] As a more sustainable and environmentally acceptable alternative to metal complexes, organocatalysts have been developed increasingly in this field due to the procedure's simplicity, low toxicities of catalysts, and cost effectiveness.

Hydrogen bond donors (HBDs) are excellent organocatalysts in cycloaddition reactions and have been widely used to activate the substrate through noncovalent H-bonding interactions.[13] In general, the HBD alone does not exhibit activity while the halide does, and the catalytic activity of the binary catalytic system was significantly accelerated after the addition of HBDs.[12] In a recognized cyclic mechanism, the

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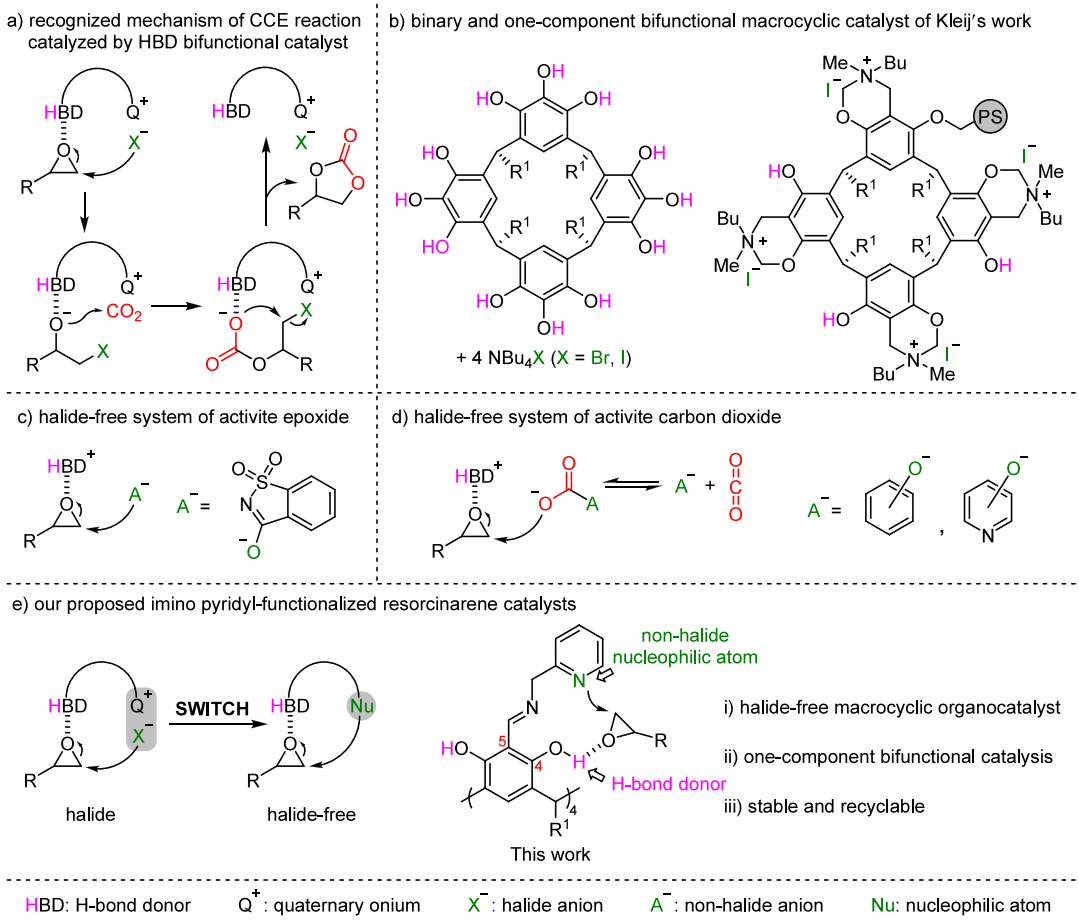
Scheme 1. H-Bond Donor Organocatalysis in CCE Reactions[a]



[a](a) Key steps of the CCE reaction of a one-component bifunctional catalyst (HBD/quaternary onium). (b) Macrocyclic organocatalytic systems have been reported by Kleij et al.[22,36] (c, d) Halide-free catalytic system of activated epoxide or carbon dioxide in our previous work.[39−42] (e) Imino pyridyl-functionalized resorcinarene as a halide-free macrocyclic organocatalyst replacing halide anions to attack epoxide ring opening.

coordination of the HBD with the substrate and the nucleophilic attack of the halide anion facilitate the formation of intermediate alkoxide compounds by ring opening of epoxides, which attack carbon dioxide to generate carbonate anions, and the departure of the halide anion promotes the formation of cyclic carbonates (Scheme 1a).[13] The development of bifunctional catalysts containing both HBDs and halides has extended the field of H-bonding catalysis, such as hydroxyl functionalized ammonium halides,[14] phosphorus halides,[15] and pyridine halides.[16] Nonclassical C−H hydrogen bond donors[17,18] and halogen bond donors[19] accompanied by cocatalyst halide anions were recently introduced by our group in the CCE reaction. Some macrocyclic compound catalysts rich in HBDs also showed good activity and selectivity in CCE reactions, such as crown ether,[20] β-cyclodextrin,[21] self-assembled calixarene,[22] and chiral macrocycles.[23]

Macrocyclic compounds are regarded as excellent mimic enzyme catalysts in the supramolecular chemistry field owing to high binding affinity and enzyme-like binding bags.[24−26] Many cavity-containing macrocycles and cages have been applied as catalytic vessels to accommodate substrates; functional groups near the cavities bind the reactants through secondary interactions, increase the local concentration of the reactants, and promote the reaction through proximity effects.[27] Resorcinarenes and their derivatives are used as molecular receptors,[28] drug carriers,[29] and host−guest complexes[30] due to their unique cavity structure and functional groups. Among the various applications of resorcinarenes, catalysis for organic reactions has been prominently used and is considered an important platform for constructing efficient, stable, easy-to-handle, and recyclable catalysts, which could be modified by introducing functional groups to multiple sites at the upper and lower rims.[31] Functionalized resorcinarene derivatives have shown good activity and selectivity as self-assembly catalysts in some reactions, such as hydrolysis of phosphorus acid esters,[32] azide−alkyne cycloaddition reaction,[33] and the formation of other compounds.[34] There have also been a few reports of CCE reactions. For instance, Dufaud et al. reported on the well-recognition ability of the tetraphosphate cavitand host for the quaternary ammonium guest to improve the catalytic reactivity by increasing the nucleophilicity of the halide.[35] Kleij et al. reported that a binary catalyst consisting of resorcin[4]arenes as HBDs and NBu_4I as cocatalysts showed high reactivity and a privileged substrate scope,[22] and polystyrene-supported bifunctional resorcin[4]-arenes as excellent stable and recyclable organocatalysts (Scheme 1b).[36] Ma et al. reported that a stable microporous MOF has been constructed by the new resorcin[4]arene-functionalized dodecacarboxylic acid and Cd(II) cations as a promising heterogeneous catalyst for the CCE reaction.[37]

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ACS Omega XXXX, XXX, XXX−XXX

Although these studies have promoted the development of supramolecular catalysis, these systems all include halide or metal as part of the catalyst system, and the corrosivity of these halides to standard stainless-steel reactors is an obvious disadvantage of such catalysts in commercial applications.[38] Our group has recently been devoted to the molecular design of halide-free organocatalyst systems for the conversion of epoxide and carbon dioxide.[39−42] Therefore, we wanted to develop a new halide-free macrocyclic organocatalyst system for the CCE reaction.

The key to the design of nonhalide catalysts is to search for nucleophilic nonhalide anions or atoms to replace halide anions to attack epoxides or carbon dioxide (Scheme 1c,d).[39−42] Recently, some halide-free catalysts with N bases as nucleophilic groups have been reported, such as pyridinium saccharinate,[40] salophen,[43] 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)/cellulose,[44] and pyridyl salicylimines.[45] In supramolecular chemistry, resorcinarene has been shown to introduce multiple types and quantities of specific functional groups into well-defined macrocyclic scaffolds to give the molecule new functions. There are three active sites in macrocyclic scaffolds of resorcinarene: (i) phenolic OH groups at the upper rim, (ii) active *C*-5 positions on the aromatic ring at the upper rim, and (iii) bridging methylene at the lower rim. The *C*-5 positions at the upper rim of the resorcinarene aromatic ring are electron-rich and are prone to electrophilic substitution.[34] The structural diversity of supramolecules is greatly enriched by introducing various functional groups, mainly including the functionalization with halide[46] and the nitrogen-,[47] phosphorus-,[48] and sulfur-containing groups.[49] The pyridyl group is one of the most common nitrogen-containing groups and can be introduced by a two-step production.[50] North et al. reported the application of pyridine−imine−phenol ligands in various metal-catalyzed polymerization and CCE reactions,[51] and Yavuz et al. reported on catalyzing cyclic carbonate formation in the presence of pyridyl salicylimines bearing the pyridine−imine−phenol pair moiety, revealing the catalytic mechanism of pyridine as a nucleophile to attack epoxides ring opening and phenolic OH as HBD.[45]

Based on these inspirations, we adopted a simple non-chromatographic synthesis method by introducing pyridine−imine pairs to resorcinarene *C*-5 positions to obtain the resorcinarene pyridyl (**R-Py**) bearing the 5-(imino pyridyl) catalytic group match with 4-OH.[50] The 4-OH groups in the resorcinarene scaffold are used as HBDs, and the 5-(imino pyridyl) groups are used as a halide-free nucleophile to attack the epoxide ring-opening reaction (Scheme 1e). The effects of various catalytic groups, reaction temperatures, CO_2 pressures, and catalyst loading parameters on the reaction performance and recycling ability were fully investigated. The resorcinarene pyridyl catalyst as a new one-component bifunctional halide-free organocatalyst has the advantages of noncorrosion, environmental safety, thermal stability, and chemical stability, which reflects the potential of this new model of macrocyclic organocatalyst.

EXPERIMENTAL SECTION

Materials. Epoxides were purchased from Alfa Aesar. Carbon dioxide with a purity of 99.999% was commercially available from Nanjing Shangyuan Co. Resorcinol, butyraldehyde, octanal, dodecyl aldehyde, trifluoroacetic acid, aniline, 2-picolylamine, 2-aminopyridine, and 8-aminoquinoline were purchased from Energy Chemical. All reagents were used without further purification.

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 selectivity of epoxides, and characterizations of catalysts and cyclic carbonates using $CDCl_3$ or DMSO-*d6* as the solvent. 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-*d6*; ^{13}C δ 77.16 for $CDCl_3$, δ 39.52 for DMSO-*d6*).

General Procedure for the Organocatalysts R-Ph, R-Py, and R-Qu. *Resorcinarene* ***3***.[35,52] To a solution of resorcinol (5.0 g, 45.4 mmol) in ethanol (50 mL) was added concentrated hydrochloric acid (7.6 mL, 90.8 mmol). The stirred solution was cooled to 0 °C, and aldehyde (45.4 mmol) was added dropwise over 30 min. The mixture was then stirred at 70 °C for 24 h and allowed to cool to room temperature. The mixture was added slowly to a beaker with plenty of water and stirred constantly; the residue was obtained and filtered. The solid was triturated with water, filtered, and recrystallized from ethanol−water to give resorcinarene **3** (63−75% yield).

Tetraformylresorcinarene ***4***.[50] Resorcinarene **3** (2.0 mmol) and urotropine (16.0 mmol) were placed in a 100 mL round-bottom flask. Trifluoroacetic acid (12.5 mL) was added, and the mixture was stirred vigorously until it became a dark solution. The mixture was then stirred and refluxed for 24 h. The resulting solution was transferred to a flask containing dichloromethane (100 mL) and aqueous HCl (100 mL, 1 M). The mixture was stirred vigorously overnight. The organic phase was separated, and the aqueous phase was washed three times with CH_2Cl_2. The combined CH_2Cl_2 extracts were dried over anhydrous $MgSO_4$ and evaporated to dryness. The resulting crude precipitate was washed with acetone (50 mL), filtered, and dried under vacuum to give the yellow product (53−68% yield).

Organocatalysts ***R-Ph, R-Py1−4, and R-Qu***.[50] A solution of tetraformylresorcinarene **4** (1.3 mmol) and dichloromethane (5 mL) was placed in a dry 20 mL vial, amine (5.2 mmol) was added slowly with a pipet, and the vial was sealed. The solution was stirred for 24 h at room temperature and dried by evaporation. The precipitate was ground in EtOH, filtered, and repeatedly rinsed with EtOH to produce a blood-red solid powder and dried by vacuum to obtain blood-red solid powder (>95% yield).

Organocatalyst ***R-Py5***.[53] Tetraformylresorcinarene **4a** (0.5 g, 0.64 mmol) was dissolved in acetonitrile (10 mL) by an experimental procedure. Potassium carbonate (1.4 g, 10.2 mmol) was added, followed by dimethyl sulfate (1.0 mL, 10.2 mmol). The resulting solution was refluxed for 26 h. The reaction was terminated, and the mixture was allowed to cool to room temperature. A solution of water (20 mL) was added to the crude reaction mixture and extracted with ethyl acetate (3 × 20 mL). The organic extracts were combined, dried with anhydrous magnesium sulfate, and filtered. The solvent was removed under vacuum, and the resulting solid was recrystallized from acetone to obtain octamethoxy resorcinarene (80% yield). Following the methodology outlined for synthesizing **R-Py1−4**, octamethoxy resorcinarene was reacted with 2-aminopyridine to afford **R-Py5**.

Monomeric Analogue of ***R-Py2***. A solution of 2,6-dihydroxybenzaldehyde (0.2 g, 1.43 mmol) and MeOH (5 mL) was placed in a dry 20 mL vial, 2-picolylamine (149 μL,

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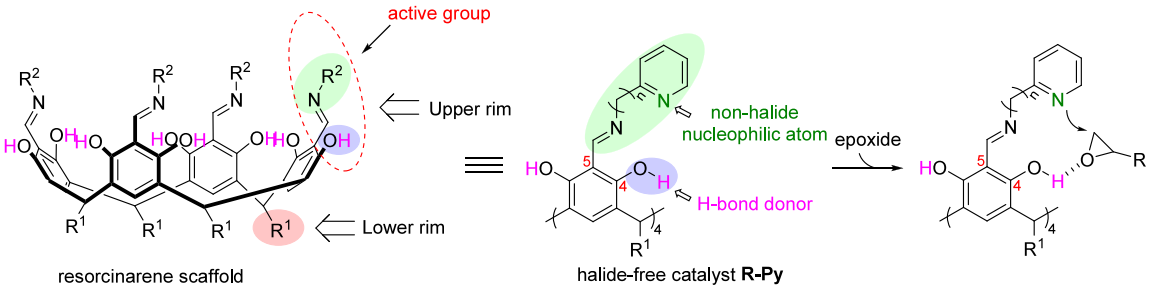
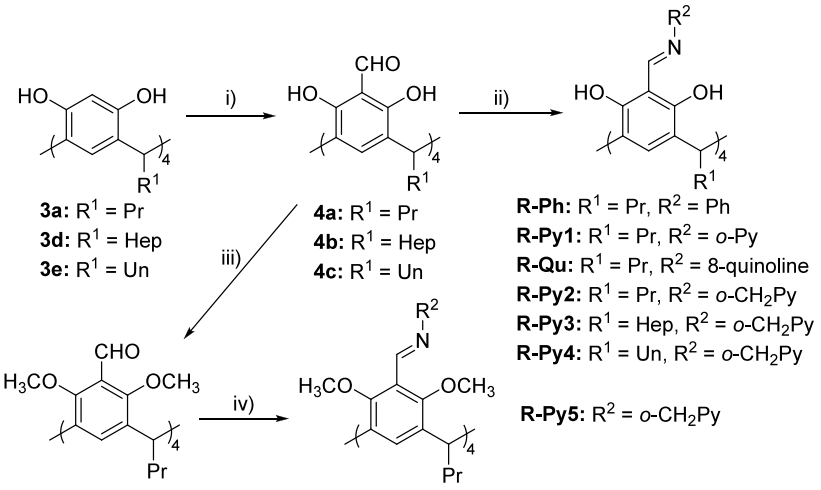
Scheme 2. Halide Organocatalysts R-Py Generated from the Resorcinarene Scaffold by Installed with 5-(Imino pyridyl) Catalytic Group for CCE Reactions



Scheme 3. Preparation of Resorcinarene 3a−c, Tetraformylresorcinarene 4a−c, and Organocatalysts R-Ph, R-Py, and R-Qu[a]



[a](i) HMTA, TFA, reflux, 24 h; (ii) CH_2Cl_2, r.t., 12 h; (iii) Me_2SO_4, K_2CO_3, MeCN, reflux, 26 h; (iv) DCM, r.t., 12 h.

1.43 mmol) was added slowly with a pipet, and the vial was sealed. The solution was stirred for 24 h at room temperature, filtered, and repeatedly rinsed with MeOH to obtain a yellow solid (85% yield).

General Procedure for the Cycloaddition of Epoxides and CO_2. The styrene oxide (0.57 mL, 5.0 mmol) and catalyst **R-Py2** (28.3 mg, 0.025 mmol, 0.5 mol %) were placed in a dry 25 mL stainless-steel reactor containing a magnetic stirring bar at room temperature, the reactor was continuously purged with CO_2 to remove air, and finally the pressure was maintained at 0.5 MPa. The reactor was placed in an oil bath at 120 °C and stirred for 12 h. When the reaction was complete, the reactor was placed in an ice water bath and cooled to 0 °C. The reactor was then slowly depressurized to atmospheric pressure. The conversions of cyclic carbonate obtained were determined by ^{1}H NMR spectroscopy with $CDCl_3$ as a solvent mixture with the supplementation of 1,3,5-trimethoxybenzene. The reaction mixture was filtered over silica gel (SiO_2) with petroleum ether:ethyl acetate = 30:1−5:1 to obtain the corresponding cyclic carbonate.

RESULTS AND DISCUSSION

Design of Resorcinarene Pyridyl Catalysts and Evaluation of the Catalytic Performances in CCE Reactions. The multiple catalytic groups are easily introduced into the bowl-shaped resorcinarene, resulting in efficient and stable self-assembled catalysts, which can be used as an excellent molecular platform for activating various organic reactions.[34] N-based molecules and ions have been used as cocatalysts to convert epoxides and carbon dioxide to cyclic carbonates, due to its nucleophilic and leaving abilities, replace the traditional halide ion, avoid the corrosion to the steel reactor and alleviate the environmentally harmful from halide residue.[40,43−45] A one-component bifunctional resorcinarene-based organocatalyst was proposed to be a representative halide-free catalyst in the CCE reaction, the 5-(imino pyridyl) groups were installed on the resorcinarene scaffold as a halide-free nucleophile moiety to attack the ring opening of the epoxide, and the 4-OH groups on the scaffold as HBDs activate the epoxide (Scheme 2).

The five halide-free catalysts **R-Py1−5** (5-(imino pyridyl)), control catalysts **R-Ph** (5-(imino phenyl)), and **R-Qu** (5-(imino 8-quinolyl)) were prepared according to chromatography-free procedures reported previously (Scheme 3). First, resorcinarene **3a−c** with different alkyl chain lengths at the lower rim (R^1) were prepared by reacting resorcinol with different aldehydes. Resorcinarene **3a−c** were combined with trifluoroacetic acid (TFA) and urotropine (HMTA) through Duff formylation to prepare the intermediate tetraformylresorcinarene **4a−c**. At room temperature, intermediates **3a−c** reacted with aniline, 2-aminopyridine, 2-aminomethylpyridine, and 8-aminoquinoline stirred in dichloromethane solvent for 12 h, respectively. The halide-free catalyst **R-Py** can be obtained by evaporation of the solvent without additional operation. The structure was characterized by ^{1}H/^{13}C NMR, TG, and melting point analyses.

The cycloaddition reaction of solvent-free styrene oxide (SO) with CO_2 was selected as the initial benchmark reaction

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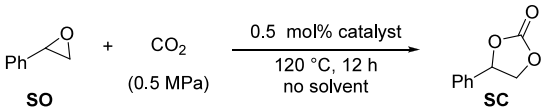
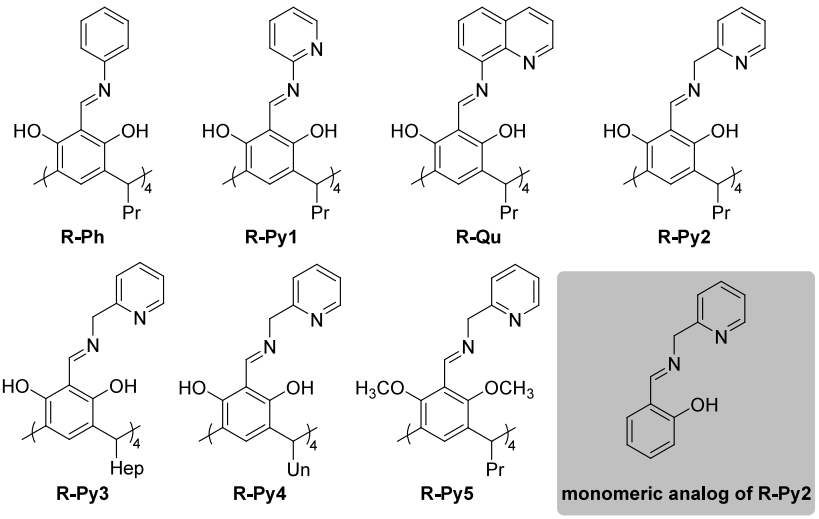
Table 1. Evaluation of the Performance of Halide-Free Organocatalysts in CCE Reactions of Styrene Oxide with Carbon Dioxide to Obtain Styrene Carbonate[d]



Catalysts



Entry	Catalysts	Conv.[a][%]	Sel.[a][%]	TOF[b]
1	**R-Ph**	trace	-	-
2	**R-Py1**	59	94	2.31
3	**R- Qu**	02	99	0.08
4	**R-Py2**	96	93	3.72
5	**R-Py3**	93	92	3.61
6	**R-Py4**	91	94	3.57
7	**R-Py5**	70	93	2.71
8[c]	**monomeric analog of R-Py2**	71	91	2.69

[a]Conversion and selectivity were determined via ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard[39,41] [b]Turnover frequency (TOF) = moles of product/ (moles of pyridyl unit in catalysts × time). [c]Catalyst loading (2.0 mol % = 4 × 0.5 mol %). [d]Reaction conditions: SO (5.0 mmol, 0.57 mL), catalyst loading (0.5 mol %), 120 °C, 0.5 MPa CO_2, 12 h, no solvent.

for evaluating halide-free catalyst **R-Py**. SO (5 mmol), catalyst (0.025 mmol, 0.5 mol %), and CO_2 (0.5 MPa) were added to the stainless-steel autoclave and stirred at 120 °C for 12 h. According to previous reports, the nucleophilic ring opening ability of pyridine and the nucleophilic ability of the basicity of pyridine-imine pairs were adjusted.[45] Therefore, we first considered the influence of different R^2 groups on the CCE reaction on resorcinarenes, and the results are shown in Table 1. The absence of strong nucleophilic atoms in catalyst **R-Ph** (5-(imino phenyl)), composed of phenyl, imine, and a phenolic OH group, results in its expected lack of activity (Table 1, entry 1). The results exclude the possible mechanism of the nucleophilic ring opening by the formation of a carbonic semicarbonate by phenolic OH groups activated carbon dioxide. The mechanism of this catalytic system is different from the salophen molecules previously reported in North et al.,[43] even though their structures both contain phenol and imine moiety. Comparing catalysts **R-Py1** (5-(imino pyridyl)) and **R-Qu** (5-(imino 8-quinolyl)), the former exhibits moderate catalytic activity (conversion % = 59%, TOF = 2.31), whereas the latter has barely catalytic activity in the conversion of epoxide to cyclic carbonate (conversion % = 2%, TOF = 0.08). Obviously, these results indicate that imino pyridyl was a good catalytic group in the conversion of epoxides, the larger volume of the 5-(imino 8-quinolyl) group may prevent contact with the substrate, or the weakening of the basicity of the quinoline−imine pairs may reduce the nucleophilicity of the N atoms. When the distance between the phenolic 4-OH group and pyridyl group of **R-Py1** was extended, better catalytic activity in **R-Py2** was observed (conv.% = 96%, TOF = 3.72).

Next, we tried to increase the alkyl chain length of the lower rim of resorcinarene (R^1 = Hep or Un). We predicted that the increase in alkyl chain length might reduce the solubility of the catalyst in the substrate. However, this phenomenon was not observed during the experiment, and the conversion of styrene oxide was not significantly decreased in the presence of **R-Py3** (R^1 = Hep) and **R-Py4** (R^1 = Un) compared with **R-Py2** (entries 5−6). The calixarenes are regarded as HBDs with excellent performance in CCE reactions attributable to the abundance of OH groups.[22,36,54,55] The masked 4-OH analogue catalyst, *R*-Py5 (4-OMe), was prepared via methyl protection for evaluation. Comparative analysis revealed a 26% reduction in conversion relative to the **R-Py2** catalyst (entry

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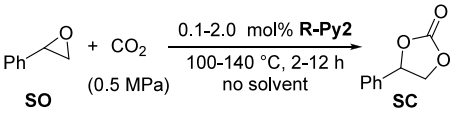
ACS Omega XXXX, XXX, XXX−XXX

7), thereby confirming that the 4-OH moiety, functioning as HBDs, significantly enhances the catalytic efficiency. Nevertheless, the overall activity of the catalytic system—comprising pyridyl, imine, and phenol motifs—is predominantly governed by the pyridyl group. In terms of a monomeric structural perspective, the phenolic OH group positioned on one side of the resorcinarene scaffold is more susceptible to steric constraints, which hinder its participation in substrate activation. Notably, under conditions of equivalent pyridyl and effective hydroxyl active groups, **R-Py2** exhibited superior catalytic activity compared to its monomeric analogue (entry 8), further underscoring the synergistic role of structural integration in catalytic performance.

The performance of the catalyst under different reaction conditions was studied to understand the effect of reaction parameters on the reaction rate; the results are shown in Table 2. Under the reaction conditions with a catalyst loading of 0.5 mol %, the initial CO_2 pressure in the reaction system decreased from 0.5 to 0.1 MPa (using a balloon), and after 12 h of stirring in an oil bath at 120 °C, the conversion of the epoxide substrate styrene oxide decreased from 96 to 23%. When the pressure was raised to 1.0 MPa, the conversion marginally improved to 98% (Table 2, entries 1−3). Under the conditions of low catalyst loading of 0.1 and 0.3 mol %, the conversion of SO decreased to 23 and 76%, respectively, and the selectivity of cyclic carbonate SC was greater than 98% (Table 2, entries 4−5). When the loading capacity was increased to 1 mol %, the conversion was 93%, and the selectivity decreased to 93% with the increase of catalyst loading (Table 2, entry 6). The kinetic curves of the preparation of carbonate SC from SO and CO_2 were determined at 120 °C (Figure 1). Next, the performance of the reaction at different temperatures was investigated. At the higher temperature of 140 °C, the SO was almost completely transformed and had a high selectivity of 99%, indicating the high-temperature stability of the catalyst (Table 2, entry 7).

Table 2. Optimization of the Reaction Conditions for the Cycloaddition of Carbon Dioxide to Epoxides[d]



entry	catalyst loading [mol %]	temp. (°C)	time (h)	P (CO_2) (MPa)	conv.[a] (%)	sel.[a] (%)	TOF[b]
1	0.5	120	12	0.1	23	89	3.41
2	0.5	120	12	0.5	96	93	14.88
3	0.5	120	12	1.0	98	91	14.86
4	0.1	120	12	0.5	23	99	18.89
5	0.3	120	12	0.5	76	98	20.69
6	1.0	120	12	0.5	91	93	7.05
7	0.5	140	12	0.5	98	99	16.17
8	0.5	100	12	0.5	04	99	0.66
9	0.5	100	12	0.1	61	99	10.07
10	0.5	100	24	0.1	99	99	8.17

[a]Conversion and selectivity were determined via ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [b]Turnover frequency (TOF) = moles of product/ (moles of pyridyl unit in catalysts × time). [c]ECH (5.0 mmol, 0.39 mL), **R-Py2** (0.025 mmol, 28.3 mg), no solvent. [d]Reaction conditions unless specified otherwise: SO (5.0 mmol, 0.57 mL), no solvent.

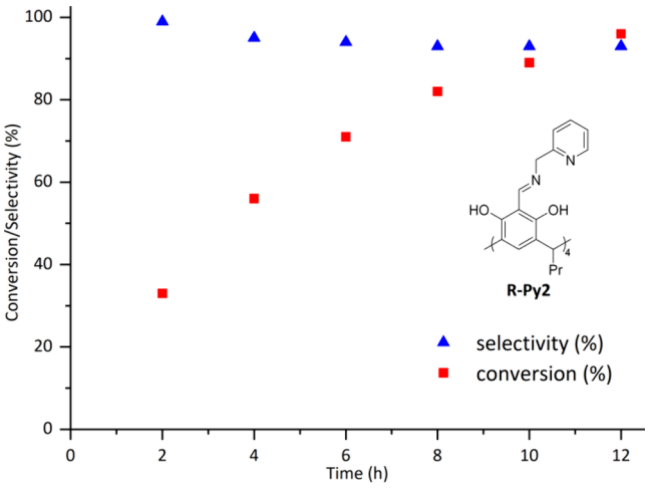


Figure 1. Kinetic profiles for the formation of cyclic carbonate **SC** at reaction temperatures of 120 °C using **R-Py2** as a halide-free catalyst.

Surprisingly, under the condition of 100 °C, the conversion of oxidized styrene was only 4%, which we suspect is related to the low activity of styrene oxide substrate; high temperature is more important for the conversion of low activity substrate. Previous experiments have also been reported accordingly. Therefore, we replaced the highly active epichlorohydrin as the substrate for the experiment and found that the substrate conversion reached 61% at 100 °C for 12 h, and it could be completely transformed at 24 h.

After optimizing the reaction conditions, the scope of terminal epoxides was evaluated under the initial reaction conditions of 120 or 100 °C, 0.5 mol % **R-Py2**, P (CO_2) = 0.5 MPa, and reaction time of 12 h; the results are shown in Table 3. The epoxides of various end substituents were used to obtain **2a−l** cyclic carbonate products with a conversion of 89−99%. The saturated substituents of glycerol derivatives containing aliphatic groups have higher selectivity than epoxides containing aryl groups (97−98% of **1a−j** vs 91−93% of **1k−l**). For the internal epoxide **1m−p**, the reaction time needs to be extended to 48 h and the CO_2 pressure increased to 1.0 MPa to achieve a 15−94% conversion (**1m−o** in Table 3). The substrate **1p** needs to be added to the solvent *n*-butanol due to the high melting point, but no corresponding carbonate ester is formed. In addition, the commercially significant epoxide bisphenol A diglycidyl ether resin was successfully converted to the corresponding cyclic carbonate **2q** with a conversion of 87%.

Proposition of the Mechanism of the CCE Reaction by Halide Organocatalyst R-Py2. The pyridine nitrogen atoms in the resorcinarene pyridyl catalyst are highly nucleophilic and might either attack the epoxide directly to ring opening or combine with carbon dioxide to form the intermediate semicarbonates and then attack the ring opening. Carbon dioxide adducts are easier to detect by ^{13}C NMR spectroscopy, so we placed the catalyst **R-Py2** in a stainless-steel reactor with 0.5 MPa CO_2 pressure, without epoxide, and DMSO-*d6* as solvent at 120 °C for 12 h. The peak shape of catalyst **R-Py2** was detected by ^{13}C NMR without chemical shift, which indicated that catalyst **R-Py2** did not react with carbon dioxide or thermal decomposition (Figure S1). The epoxide ring opening is more likely due to the direct attack of the pyridine nitrogen.

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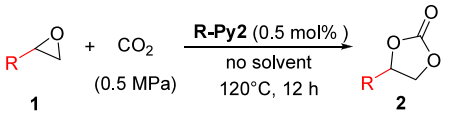
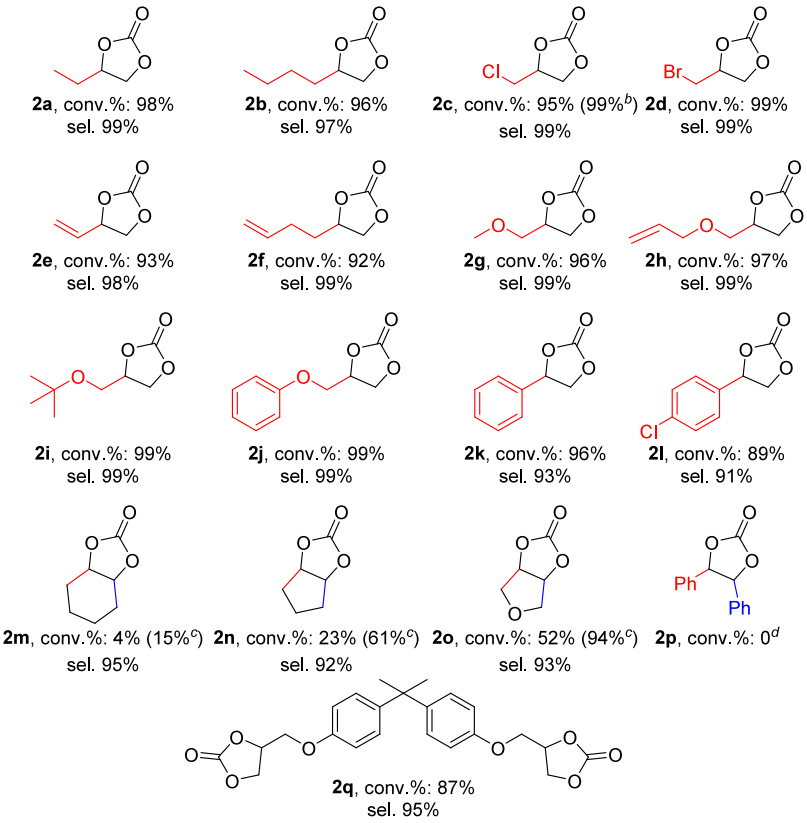
ACS Omega XXXX, XXX, XXX−XXX

Table 3. Substrate Scope in Converting Various Terminal and Internal Epoxides 1a−q to Cyclic Carbonates 2a−q Using R-Py2 as the Catalyst[a]



1 2



[a]Reaction conditions: 0.5 mol % **R-Py2**, 120 °C, 0.5 MPa CO_2, 12 h, no solvent. [b]100 °C, 0.1 MPa (use a balloon), 24 h. [c]120 °C, 1.0 MPa CO_2, 48 h. [d]*n*-Butanol was employed as a solvent, 1.0 M **R-Py2**, 120 °C, 1.0 MPa CO_2, 48 h.

The catalytic mechanism of the resorcinarene pyridyl catalyst in the CCE reaction was further determined by ^{1}H NMR titration experiments. The intramolecular H-bonding in **R-Py2** results in a chemical shift that is not observed at room temperature, so the monomeric analog catalyst of **R-Py2** was used with the substrate SO for ^{1}H NMR titration experiments. The ratio of SO to the monomeric analogue catalyst of **R-Py2** was gradually changed from 1:0.125 to 1:2 (Figure 2). With the increase of the concentration of the monomeric analog catalyst, the chemical shift value of the methyne proton of SO (blue squares) migrated from 2.815 to 2.823 ppm, and the chemical shift value of the proton of the phenolic OH groups (pink circle) was migrated from 14.463 to 14.424 ppm. The H-bond interaction between the catalyst and the epoxide promotes the progress of the CCE reaction, as evidenced by the migration phenomenon of these proton shifts.

Based on the above experimental results and previous reports,[45,56,57] the possible cycle mechanism of this reaction is proposed (Scheme 4). Epoxide **1** is activated under the action of the OH H-bonding of catalyst **R-Py2**, and the alkaline pyridine N atom carries out a nucleophilic attack on the carbon atom on the methylene side of the end epoxide, forming the intermediate alkoxide, which is stabilized by the H-bonding. Subsequently, the oxygen anion at the end of the intermediate attacks CO_2 to form a carbonate, and the ring is closed to yield the product cyclic carbonate **2.**

Catalyst Recycling of CCE Reaction Catalyzed by R-Py2. Thermogravimetric (TG) analysis showed that catalyst **R-Py2** did not lose more than 1.0 wt % of mass when maintained in an N_2 atmosphere at 120 °C for 2 h (Figure S3). The melting point test of catalyst **R-Py2** shows that the melting point >300 °C. The results show that catalyst **R-Py2** has high thermal stability. The recovery of ECH **1c**, 0.1 MPa, for 24 h catalyzed by **R-Py2** was studied (Figure 3). A total of five times reuse cycles were performed. Newly prepared dry catalyst **R-Py2** was added for the first time, and a small amount of reaction solution ^{1}H NMR was taken to detect the conversion. The first conversion of epoxide ECH **1c** was 99%, and the remaining product **2c** and raw material were separated from by vacuum distillation.[58] By the fifth cycle, the conversion of product **2c** was still 96%, which still maintains high catalytic activity.

CONCLUSIONS

In summary, we successfully applied resorcinarenes installed with a 5-(imino pyridyl) catalytic group, in cooperation with 4-OH on the same resorcinol unit, as a bifunctional organo-catalyst to the CCE reaction. The effects of R^1 and R^2 groups

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ACS Omega XXXX, XXX, XXX−XXX

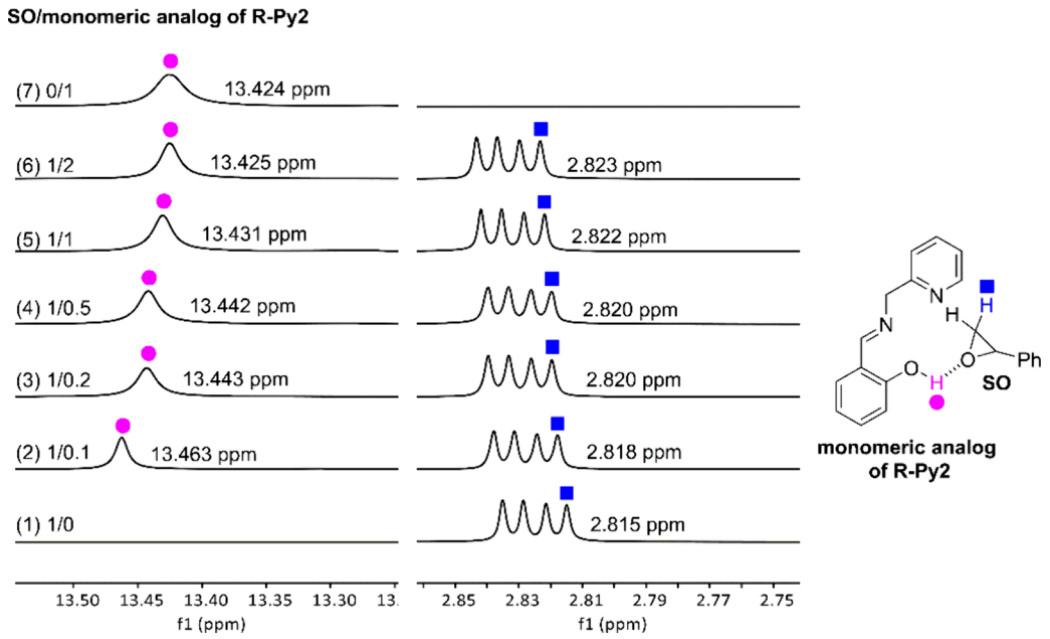
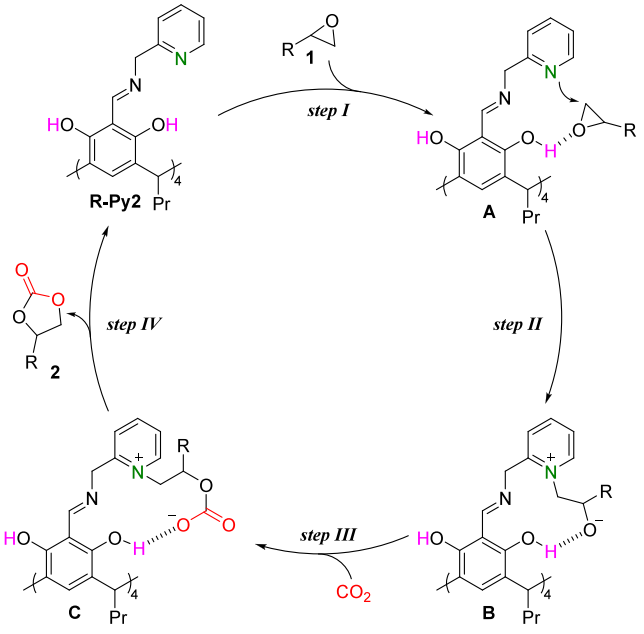


Figure 2. Chemical shifts of the O−H proton of the monomeric analog of catalyst **R-Py2** (pink circle) and methylene protons (blue squares) of the substrate SO in the titration in the ^{1}H NMR spectra (DMSO-*d6*), and series ratios of SO/monomeric analogue of **R-Py2** in (1) 1/0, (2) 1/0.1, (3) 1/0.2, (4)1/0.5, (5) 1/1, (6) 1/2, and (7) 0/1. The full ^{1}H NMR spectra of the titrations are shown in Figure S2.

Scheme 4. Proposed Mechanism for the Formation of Cyclic Carbonates from Epoxides and CO_2 Catalyzed by Halide-Free Catalyst R-Py2.



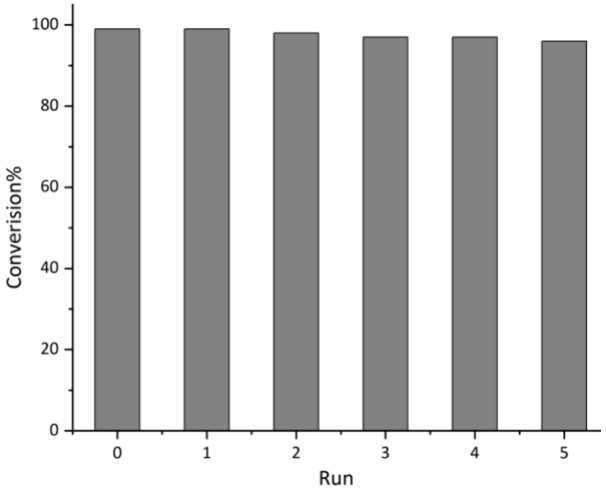


Figure 3. Recyclability study of halide-free catalyst **R-Py2**. Reaction conditions: ECH **1c** (10.0 mmol, 0.78 mL), **R-Py2** (0.05 mmol, 0.5 mol %, 56.5 mg), 100 °C, 0.1 MPa (use a balloon) of CO_2, 24 h, neat. Selectivity for cyclic carbonate **2c** was all >99%.

on the activity of resorcinarene pyridyl (**R-Py**) catalyst, **R-Ph** (5-(imino phenyl)), and **R-Qu** (5-(imino 8-quinolyl)) was investigated; the optimal catalyst **R-Py2** (5-(imino pyridyl)) showed the highest catalytic activity. The analysis of the influencing factors of reaction conditions showed that under the condition of 0.5 mol % catalyst loading, 0.1 MPa CO_2 pressure, and 100 °C, ECH was almost completely converted to the corresponding carbonate with conversion 99% and selectivity 99% after 24 h. Fifteen terminal epoxide substrates, three internal epoxides, and commercially significant epoxide bisphenol a diglycidyl ether resin were converted into corresponding cyclic carbonates at high selectivities of 89−99%. The designed analog catalysts **R-Ph** ruled out the possible mechanism of nucleophilic ring opening by activating carbon dioxide to form carbonic semicarbonates by phenolic OH groups; the control experiment and ^{1}H NMR titration experiment proved the importance of the synergistic effect of phenolic OH groups and pyridine in the catalytic cycle. The thermogravimetric analysis shows that the catalyst has high thermal stability and high reusability in the catalyst cycle experiment. The successful application of a one-component calixarene catalyst in the CO_2 fixation reaction provides strong evidence for further development of the halide-free catalyst.

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ACS Omega XXXX, XXX, XXX−XXX

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.5c03311.

NMR spectra for the catalyst and product and TGA thermogram of the catalyst (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Zhenjiang Li − *State Key Laboratory Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China;* orcid.org/0000-0002-1100-7297; Email: zjli@njtech.edu.cn

Authors

Yongzhu Hu − *State Key Laboratory Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China*

Min Zhang − *State Key Laboratory Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China*

Ning Li − *State Key Laboratory Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China*

Yujia Wang − *State Key Laboratory Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China*

Haoyu Wang − *State Key Laboratory Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China*

Xin Yuan − *State Key Laboratory Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China*

Xin Zou − *State Key Laboratory Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China*

Chunyu Li − *State Key Laboratory Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China*

Kai Guo − *State Key Laboratory Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China;* orcid.org/0000-0002-0013-3263

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.5c03311

Author Contributions

Yongzhu Hu: investigation, methodology, writing—original draft, and writing—review and editing. Min Zhang: writing—original draft and writing—review and editing. Zhenjiang Li: conceptualization, resources, funding acquisition, supervision, and writing—review and editing, Project administration. Ning Li: methodology. Yujia Wang: methodology. Haoyu Wang: methodology. Xin Yuan: methodology. Xin Zou: methodology. Chunyu Li: methodology. Kai Guo: funding acquisition, project administration, resources, and supervision.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Aresta, M.; Dibenedetto, A.; Angelini, A. Catalysis for the valorization of exhaust carbon: from CO_2 to chemicals, materials, and fuels. technological use of CO_2. *Chem. Rev.* **2014**, *114* (3), 1709−1742.

(2) Bushuyev, O. S.; De Luna, P.; Dinh, C. T.; Tao, L.; Saur, G.; van de Lagemaat, J.; Kelley, S. O.; Sargent, E. H. What should we make with CO_2 and how can we make it? *Joule* **2018**, *2* (5), 825−832.

(3) Martín, C.; Fiorani, G.; Kleij, A. W. Recent advances in the catalytic preparation of cyclic organic carbonates. *ACS Catal.* **2015**, *5* (2), 1353−1370.

(4) Martin, R.; Kleij, A. W. Myth or reality? Fixation of carbon dioxide into complex organic matter under mild conditions. *ChemSusChem* **2011**, *4* (9), 1259−1263.

(5) Clements, J. H. Reactive applications of cyclic alkylene carbonates. *Ind. Eng. Chem. Res.* **2003**, *42* (4), 663−674.

(6) Schäffner, B.; Schäffner, F.; Verevkin, S. P.; Börner, A. Organic carbonates as solvents in synthesis and catalysis. *Chem. Rev.* **2010**, *110* (8), 4554−4581.

(7) Etacheri, V.; Marom, R.; Elazari, R.; Salitra, G.; Aurbach, D. Challenges in the development of advanced Li-ion batteries: a review. *Energy Environ. Sci.* **2011**, *4*, 3243.

(8) Kamphuis, A. J.; Picchioni, F.; Pescarmona, P. P. CO_2-fixation into cyclic and polymeric carbonates: principles and applications. *Green Chem.* **2019**, *21* (3), 406−448.

(9) Maisonneuve, L.; Lamarzelle, O.; Rix, E.; Grau, E.; Cramail, H. Isocyanate-Free Routes to Polyurethanes and Poly(hydroxy Urethane)s. *Chem. Rev.* **2015**, *115* (22), 12407−12439.

(10) Pescarmona, P. P.; Taherimehr, M. Challenges in the catalytic synthesis of cyclic and polymeric carbonates from epoxides and CO_2. *Catalysis Science & Technology* **2012**, *2* (11), 2169−2187.

(11) Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kuhn, F. E. Transformation of carbon dioxide with homogeneous transition-metal catalysts: a molecular solution to a global challenge? *Angew. Chem., Int. Ed. Engl.* **2011**, *50* (37), 8510−8537.

(12) Steinbauer, J.; Kubis, C.; Ludwig, R.; Werner, T. Mechanistic study on the addition of CO_2 to epoxides catalyzed by ammonium and phosphonium salts: A combined spectroscopic and kinetic approach. *ACS Sustainable Chem. Eng.* **2018**, *6* (8), 10778−10788.

(13) Guo, L.; Lamb, K. J.; North, M. Recent developments in organocatalysed transformations of epoxides and carbon dioxide into cyclic carbonates. *Green Chem.* **2021**, *23* (1), 77−118.

(14) Büttner, H.; Lau, K.; Spannenberg, A.; Werner, T. Bifunctional one-component catalysts for the addition of carbon dioxide to epoxides. *ChemCatChem.* **2015**, *7* (3), 459−467.

(15) Alves, M.; Grignard, B.; Mereau, R.; Jerome, C.; Tassaing, T.; Detrembleur, C. Organocatalyzed coupling of carbon dioxide with epoxides for the synthesis of cyclic carbonates: catalyst design and

https://doi.org/10.1021/acsomega.5c03311
ACS Omega XXXX, XXX, XXX−XXX

mechanistic studies. *Catalysis Science & Technology* **2017**, *7* (13), 2651−2684.
(16) Rostami, A.; Mahmoodabadi, M.; Hossein Ebrahimi, A.; Khosravi, H.; Al-Harrasi, A. An electrostatically enhanced phenol as a simple and efficient bifunctional organocatalyst for carbon dioxide fixation. *ChemSusChem* **2018**, *11* (24), 4262−4268.
(17) Xu, J.; Xian, A.; Li, Z.; Liu, J.; Zhang, Z.; Yan, R.; Gao, L.; Liu, B.; Zhao, L.; Guo, K. A strained ion pair permits carbon dioxide fixation at atmospheric pressure by C-H H-bonding organocatalysis. *J. Org. Chem.* **2021**, *86* (4), 3422−3432.
(18) Gao, L.; Zhou, Y.; Li, Z.; He, J.; Qu, Y.; Zou, X.; Liu, B.; Ma, C.; Sun, J.; Guo, K. Nicotinamide onium halide bidentate hybrid H−bond donor organocatalyst for CO_2 fixation. *J. CO2 Util.* **2022**, No. 102196.
(19) Yan, R.; Chen, K.; Li, Z.; Qu, Y.; Gao, L.; Tong, H.; Li, Y.; Li, J.; Hu, Y.; Guo, K. Fixation of CO(2) into cyclic carbonates by halogen-bonding catalysis. *ChemSusChem* **2021**, *14* (2), 738−744.
(20) Steinbauer, J.; Spannenberg, A.; Werner, T. An in situ formed Ca^{2+}−crown ether complex and its use in CO_2-fixation reactions with terminal and internal epoxides. *Green Chem.* **2017**, *19* (16), 3769−3779.
(21) Wen, Q.; Yuan, X.; Zhou, Q.; Yang, H. J.; Jiang, Q.; Hu, J.; Guo, C. Y. Functionalized *β*-cyclodextrins catalyzed environment-friendly cycloaddition of carbon dioxide and epoxides. *Materials* **2022**, *16* (1), 53.
(22) Martínez-Rodríguez, L.; Otalora Garmilla, J.; Kleij, A. W. Cavitand-based polyphenols as highly reactive organocatalysts for the coupling of carbon dioxide and oxiranes. *ChemSusChem* **2016**, *9* (7), 749−755.
(23) Ema, T.; Yokoyama, M.; Watanabe, S.; Sasaki, S.; Ota, H.; Takaishi, K. Chiral macrocyclic organocatalysts for kinetic resolution of disubstituted epoxides with carbon dioxide. *Org. Lett.* **2017**, *19* (15), 4070−4073.
(24) Raynal, M.; Ballester, P.; Vidal-Ferran, A.; van Leeuwen, P. W. N. M. Supramolecular catalysis. Part 2: artificial enzyme mimics. *Chem. Soc. Rev.* **2014**, *43* (5), 1734−1787.
(25) Liu, Y.; Chen, Y.; Zhang, H.-Y.*Handbook of Macrocyclic Supramolecular Assembly*; Springer Singapore 2020.
(26) Guo, H.; Zhang, L. W.; Zhou, H.; Meng, W.; Ao, Y. F.; Wang, D. X.; Wang, Q. Q. Substrate-induced dimerization assembly of chiral macrocycle catalysts toward cooperative asymmetric catalysis. *Angew. Chem., Int. Ed.* **2020**, *59* (7), 2623−2627.
(27) Sachdeva, G.; Vaya, D.; Srivastava, C. M.; Kumar, A.; Rawat, V.; Singh, M.; Verma, M.; Rawat, P.; Rao, G. K. Calix[n]arenes and its derivatives as organocatalysts. *Coord. Chem. Rev.* **2022**, *472*, No. 214791.
(28) Szumna, A. Chiral encapsulation by directional interactions. Chemistry − A. *European Journal* **2009**, *15* (45), 12381−12388.
(29) Pedro-Hernández, L.; Martínez-Klimova, E.; Cortez-Maya, S.; Mendoza-Cardozo, S.; Ramírez-Ápan, T.; Martínez-García, M. Synthesis, characterization, and nanomedical applications of conjugates between resorcinarene-dendrimers and ibuprofen. *Nanomaterials* **2017**, *7* (7), 163.
(30) Martínez, G. M.; Teran, C. R.; Tlapanco, O. A.; Toscano, A.; Cruz-Almanza, R. Supramolecular complexes between fullerene [60]- and [70], and resorcinarene. *Fullerene Science and Technology* **2000**, *8* (6), 475−482.
(31) Gajjar, J. A.; Vekariya, R. H.; Parekh, H. M. Recent advances in upper rim functionalization of resorcin[4]arene derivatives: Synthesis and applications. *Synth. Commun.* **2020**, *50* (17), 2545−2571.
(32) Pashirova, T. N.; Lukashenko, S. S.; Kosacheva, E. M.; Leonova, M. V.; Vagapova, L. I.; Burilov, A. R.; Pudovik, M. A.; Kudryavtseva, L. A.; Konovalov, A. I. Aggregation behavior and catalytic properties of systems based on aminomethylated calix[4]-resorcinarenes and poly(ethylene) imines. *Russian Journal of General Chemistry* **2008**, *78* (3), 402−409.
(33) Lu, B.-B.; Yang, J.; Che, G.-B.; Pei, W.-Y.; Ma, J.-F. Highly Stable Copper(I)-Based Metal-Organic Framework Assembled with Resorcin[4]arene and Polyoxometalate for Efficient Heterogeneous Catalysis of Azide-Alkyne "Click" Reaction. *ACS Appl. Mater. Interfaces* **2018**, *10* (3), 2628−2636.
(34) Liu, J.-L.; Sun, M.; Shi, Y.-H.; Zhou, X.-M.; Zhang, P.-Z.; Jia, A.-Q.; Zhang, Q.-F. Functional modification, self-assembly and application of calix[4]resorcinarenes. *Journal of Inclusion Phenomena and Macrocyclic Chemistry* **2022**, *102* (3−4), 201−233.
(35) Mirabaud, A.; Mulatier, J.-C.; Martinez, A.; Dutasta, J.-P.; Dufaud, V. Investigating host−guest complexes in the catalytic synthesis of cyclic carbonates from styrene oxide and CO_2. *ACS Catal.* **2015**, *5* (11), 6748−6752.
(36) Jose, T.; Cañellas, S.; Pericàs, M. A.; Kleij, A. W. Polystyrene-supported bifunctional resorcinarenes as cheap, metal-free and recyclable catalysts for epoxide/CO_2 coupling reactions. *Green Chem.* **2017**, *19* (22), 5488−5493.
(37) Lu, B.-B.; Jiang, W.; Yang, J.; Liu, Y.-Y.; Ma, J.-F. Resorcin[4]arene-based microporous metal−organic framework as an efficient catalyst for CO_2 cycloaddition with epoxides and highly selective luminescent sensing of $Cr_2O_7^{2-}$. *ACS Appl. Mater. Interfaces* **2017**, *9* (45), 39441−39449.
(38) Kleij, A. W. Advancing halide-free catalytic synthesis of CO_2-based heterocycles. *Current Opinion in Green and Sustainable Chemistry* **2020**, *24*, 72−81.
(39) Yuan, X.; Liu, Z.; Li, Z.; Shi, Y.; Yang, B.; Zou, X.; Hu, Y.; Li, C.; Li, S.; Guo, K. Halide-free pyridinium base binary organocatalyst for the cycloaddition of carbon dioxide to epoxides. *New J. Chem.* **2024**, *48* (25), 11435−11446.
(40) Tong, H.; Qu, Y.; Li, Z.; He, J.; Zou, X.; Zhou, Y.; Duan, T.; Liu, B.; Sun, J.; Guo, K. Halide-free pyridinium saccharinate binary organocatalyst for the cycloaddition of CO_2 into epoxides. *Chem. Eng. J.* **2022**, *444*, No. 135478.
(41) Liu, B.; Yu, H.; Li, Z.; He, J.; Hu, Y.; Zou, X.; Lu, L.; Cao, S.; Ma, C.; Guo, K. Halide-free squaramide−phenolate organocatalyst for the cycloaddition of CO_2 into epoxides. *J. Enviro. Chem. Eng.* **2023**, *11*, No. 110886.
(42) Zhu, T.; Xu, Y.; Li, Z.; He, J.; Yuan, X.; Qian, D.; Chang, T.; Lu, L.; Chi, B.; Guo, K. Cholinium Pyridinolate ionic pair-catalyzed fixation of CO_2 into cyclic carbonates. *Journal of Organic Chemistry* **2024**, *89* (11), 7408−7416.
(43) Wu, X.; Chen, C.; Guo, Z.; North, M.; Whitwood, A. C. Metal- and halide-free catalyst for the synthesis of cyclic carbonates from epoxides and carbon dioxide. *ACS Catal.* **2019**, *9* (9), 1895−1906.
(44) Sun, J.; Cheng, W.; Yang, Z.; Wang, J.; Xu, T.; Xin, J.; Zhang, S. Superbase/cellulose: an environmentally benign catalyst for chemical fixation of carbon dioxide into cyclic carbonates. *Green Chem.* **2014**, *16*, 3071.
(45) Subramanian, S.; Park, J.; Byun, J.; Jung, Y.; Yavuz, C. T. Highly efficient catalytic cyclic carbonate formation by pyridyl salicylimines. *ACS Appl. Mater. Interfaces* **2018**, *10* (11), 9478−9484.
(46) Cram, D. J.; Karbach, S.; Kim, H. E.; Knobler, C. B.; Maverick, E. F.; Ericson, J. L.; Helgeson, R. C. Host-guest complexation. 46. Cavitands as open molecular vessels form solvates. *J. Am. Chem. Soc.* **1988**, *110* (7), 2229−2237.
(47) Aakeröy, C. B.; Schultheiss, N.; Desper, J. A pyridyl-functionalized cavitand: Starting point for hydrogen-bond driven assembly of heterodimeric capsules. *CrystEngComm* **2006**, *8* (7), 502−506.
(48) Kazakova, E. K.; Makarova, N. A.; Rakhmatullin, A. I.; Muslinkina, L. A.; Muslinkin, A. A. The molecular complexes of calix[4]resorcinolarene with diglycidylmethyl phosphonate. *Journal of Inclusion Phenomena and Macrocyclic Chemistry* **2000**, *36* (2), 153−162.
(49) Konishi, H.; Yamaguchi, H.; Miyashiro, M.; Kobayashi, K.; Morikawa, O. Functionalization at the extraannular positions of calix[4]resorcinarene using a Mannich-type thiomethylation. *Tetrahedron Lett.* **1996**, *37* (47), 8547−8548.
(50) Grajda, M.; Wierzbicki, M.; Cmoch, P.; Szumna, A. Inherently chiral iminoresorcinarenes through regioselective unidirectional tautomerization. *Journal of Organic Chemistry* **2013**, *78* (22), 11597−11601.

https://doi.org/10.1021/acsomega.5c03311
ACS Omega XXXX, XXX, XXX−XXX

(51) Cuesta-Aluja, L.; Campos-Carrasco, A.; Castilla, J.; Reguero, M.; Masdeu-Bultó, A. M.; Aghmiz, A. Highly active and selective Zn(II)-NN′O Schiff base catalysts for the cycloaddition of CO 2 to epoxides. *Journal of CO2 Utilization* **2016**, *14*, 10−22.
(52) Tunstad, L. M.; Tucker, J. A.; Dalcanale, E.; Weiser, J.; Bryant, J. A.; Sherman, J. C.; Helgeson, R. C.; Knobler, C. B.; Cram, D. J. Host-guest complexation. 48. Octol building blocks for cavitands and carcerands. *Journal of Organic Chemistry* **1989**, *54* (6), 1305−1312.
(53) Ngodwana, L.; Kleinhans, D. J.; Smuts, A. J.; van Otterlo, W. A. L.; Arnott, G. E. Selective derivatisation of resorcinarene ethers via an ortholithiation approach. *RSC Adv.* **2013**, *3*, 3873.
(54) Maeda, C.; Sasaki, S.; Takaishi, K.; Ema, T. Calix[4]pyrroles as macrocyclic organocatalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide. *Catalysis Science & Technology* **2018**, *8* (16), 4193−4198.
(55) Zhang, Y.; Su, K.; Hong, Z.; Han, Z.; Yuan, D. Robust Cationic Calix[4]arene polymer as an efficient catalyst for cycloaddition of epoxides with CO_2. *Ind. Eng. Chem. Res.* **2020**, *59* (15), 7247−7254.
(56) Giri, A.; Hussain, M. D. W.; Sk, B.; Patra, A. Connecting the dots: Knitting c-phenylresorcin[4]arenes with aromatic linkers for task-specific porous organic polymers. *Chem. Mater.* **2019**, *31* (20), 8440−8450.
(57) Hu, Y.; Du, X.; Li, Z.; He, J.; Chang, T.; Shi, N.; Li, N.; Zou, X.; Sun, J.; Guo, K. Monodentate H-bond donor bifunctional catalyst in fixation of atmospheric pressure carbon dioxide into cyclic carbonates. Molecular. *Mol. Catal.* **2024**, No. 113765.
(58) Kumatabara, Y.; Okada, M.; Shirakawa, S. Triethylamine hydroiodide as a simple yet effective bifunctional catalyst for CO_2 fixation reactions with epoxides under mild conditions. *ACS Sustainable Chem. Eng.* **2017**, *5* (8), 7295−7301.

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