Sustainable Chemistry and Pharmacy 46 (2025) 102102

Contents lists available at ScienceDirect

Sustainable Chemistry and Pharmacy

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

Zwitterionic resorcinarene bifunctional organocatalyst for the cycloaddition of carbon dioxide to epoxide

Yongzhu Hu, Haoyu Wang, Zhenjiang Li [*], Jiahui Ma, Yue Xu, Ziqi Liu, Yanqi Shi, Xiaolong Huang, Hui Zhao, Kai Guo

State Key Laboratory Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, 30 Puzhu Road South, Nanjing, 211816, China

ARTICLE INFO

Handling Editor: Fabio Aricò

Keywords:
Carbon dioxide
Halide-free
Organocatalyst
Resorcinarene

ABSTRACT

The cycloaddition of carbon dioxide (CO_2) to epoxide (CCE) reaction is a highly attractive sustainable process due to its high atom economy and the versatility applications of the resulting cyclic carbonates. Conventional catalysts for CCE reactions were indispensable of halide cocatalyst, however, halides posed risk of corrosion to process steel equipment and the residue halide was environmentally harmful. To obviate halide, a new halide-free resorcinarene-based zwitterion (**RES-Z**) catalyst was designed and synthesized as organocatalyst for CCE reactions. The **RES-Z** catalyst exhibited excellent performance at 120 °C and 0.5 mol% catalyst loading under 1.0 MPa CO_2 pressure for 12 h, the commercially epoxide bisphenol A diglycidyl ether and 12 terminal epoxides were converted into the corresponding cyclic carbonates with 73–99 % conversion and 99 % selectivity. Bifunctional catalytic mechanism was proposed and validated by NMR titrations where the cationic moiety activated the epoxide and the anionic moiety activated the CO_2. Moreover, the catalyst demonstrated exceptional recyclability, exhibiting no decline in catalytic activity over five consecutive reaction cycles. These findings not only substantiate the efficacy of resorcinarene-based organocatalysts in halide-free catalytic systems but also advance the sustainable utilization of CO_2 in chemical synthesis.

1. Introduction

Carbon dioxide (CO_2) as an abundant, cheap, and renewable C1 building block for the synthesis of value-added chemicals is one of the most active areas of research today, with the promise of reducing CO_2 emissions and replacing petroleum-based feedstocks for the synthesis of fine chemicals (Artz et al., 2018). Nevertheless, this strategy presents considerable challenges, as merely 0.1 % of atmospheric CO_2 is currently utilized in chemical synthesis, primarily due to the thermodynamic stability of carbon in its highest oxidation state (Cokoja et al., 2011a). The cycloaddition of CO_2 to epoxides (CCE) was considered a promising conversion route (Cokoja et al., 2015). The products cyclic carbonates are an important class of compounds that can be used aas green solvents (Schäffner et al., 2010), electrolytes in lithium-ion batteries (Vivek et al., 2016), and monomers for non-isocyanate polyurethane (Guan et al., 2011) and polycarbonates (Yu et al., 2021). In terms of the reaction process, epoxides can be used as high-energy reactants to compensate for the high energy input of the cycloaddition reaction process, and the addition of well-designed catalysts can overcome the very high thermodynamic energy barriers to CO_2 fixation (Etacheri et al., 2011). Researchers have developed a variety of

---

[*] Corresponding author.
E-mail address: zjli@njtech.edu.cn (Z. Li).

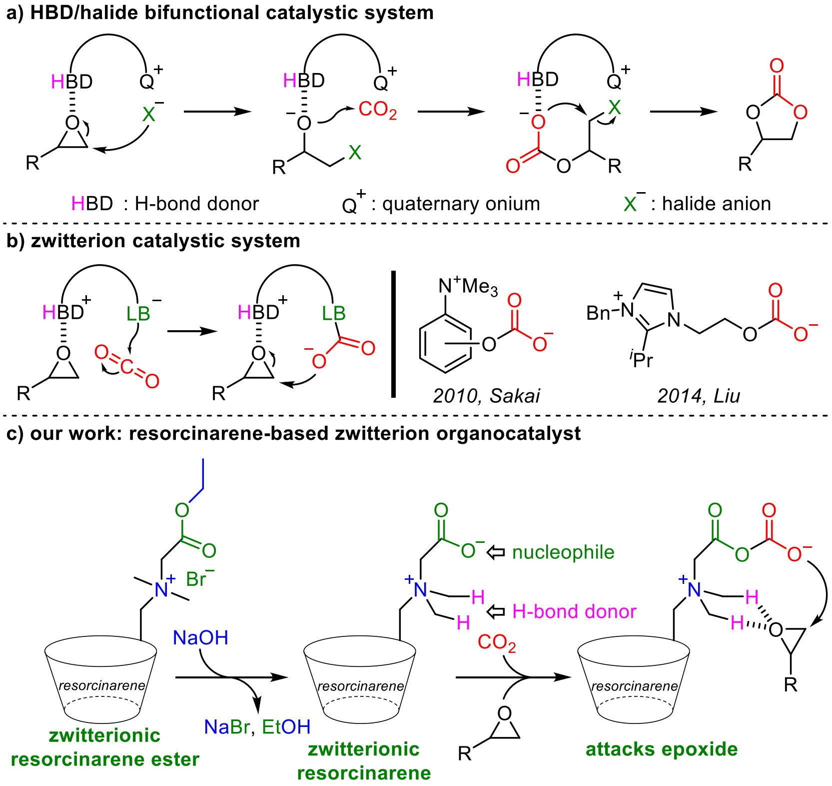
https://doi.org/10.1016/j.scp.2025.102102
Received 7 May 2025; Received in revised form 21 June 2025; Accepted 1 July 2025

catalytic systems to facilitate this reaction. These catalytic systems include metal complexes (Comerford et al., 2015; Cokoja et al., 2011b), organocatalysts (Fiorani et al., 2015; Alves et al., 2017; Büttner et al., 2017; Aytar et al., 2024; Kilic et al., 2024, 2025a, 2025b), and functional polymers. Compared to metal-based catalysts, organocatalysts are more attractive because they are inexpensive, readily available, low-toxicity, and sustainable.

In popular binary catalyst systems commonly utilized for cycloaddition reactions, pronounced synergistic catalytic effects have been consistently observed between hydrogen bond donor (HBD) and nucleophilic co-catalysts (Alves et al., 2017). Extensive literature reported numerous highly efficient bifunctional catalyst systems, particularly those incorporating ammonium salt (Kumatabara et al., 2017), phosphonium salt (Wei-Li et al., 2014), pyridinium salt (Rostami et al., 2018), or imidazolium-based ion liquid (Peng and Deng, 2001) functionalized with –OH, –NH, or –COOH groups. A common feature of most HBD/nucleophile systems, regardless of their configuration as one-component or binary catalysts, is their fundamental reliance on halide anions as indispensable catalytic components (Scheme 1, a). However, the practical application exists limitations of such catalytic systems, due to equipment corrosion, environmental concerns, and reduced product purity resulting from halide residues (Kleij, 2020; Li et al., 2023; Ma et al., 2014). Consequently, significant research efforts have been directed toward the development of halide-free organocatalysts, which have emerged as a pivotal focus within the field of cyclic carbonate synthesis. This strategic shift not only addresses pressing environmental and safety concerns but also fulfills practical application requirements while preserving catalytic performance.

In the context of catalytic reaction mechanisms, the catalytic activity of halide containing system is attributed to the pronounced nucleophilicity and dissociative capacity of halide ion, which facilitate the cleavage of C–O bonds in epoxides and subsequent ring-closure processes (Zhang et al., 2020). As previous studies have reported, certain nucleophile have been shown to possess the capacity to competitively displace halide ions and directly interact with epoxides through cooperative H-bonding interactions (Shen et al., 2003; Tong et al., 2022; Yue et al., 2022). Furthermore, a series of Lewis bases (LB) systems with CO_2 activation ability have been successfully applied to cycloaddition reactions, including organic bases (Sun et al., 2014), carbenes (Kayaki et al., 2009; Kilic et al., 2020), N-heterocyclic olefins (Wang et al., 2013), zwitterions (Scheme 1, b) (Tsutsumi et al., 2010; Wang et al., 2014), phosphorus-ylide (Buβ et al., 2016; Zhou et al., 2015), and ion pairs (Liu et al., 2023; Zhu et al., 2024; Yuan et al., 2024).

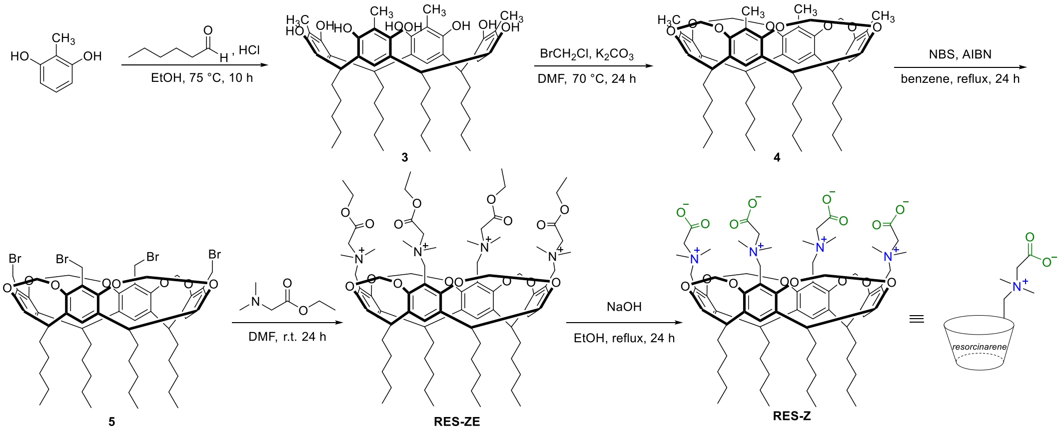
Resorcinarene, a cyclic tetramer synthesized by the acid-catalyzed the condensation of resorcinol and aldehydes, has been demonstrates easy to synthesize and functionalize (Neri et al., 2016). It exhibits distinctive structural features, including conformational flexibility, and variable cavity size. The structural versatility of resorcinarenes has been demonstrated to result in remarkable performance in the domain of supramolecular self-assembly (Gajjar et al., 2020). This ability enables the construction of multicomponent architectures via directed H-bonding or metal coordination. The properties outlined above have led to the widespread applications of


a) HBD/halide bifunctional catalytic system

b) zwitterion catalytic system

c) our work: resorcinarene-based zwitterion organocatalyst

Scheme 1. Organocatalysts for CCE reactions. a) HBD/halide bifunctional catalytic system; b) zwitterion as halide-free catalyst (Tsutsumi et al., 2010; Wang et al., 2014); c) resorcinarene-based zwitterion as halide-free organocatalyst.



Scheme 2. Preparation of zwitterionic resorcinarene **RES-Z**.

resorcinarenes in nanomaterial fabrication (Podyachev et al., 2021), fluorescent sensor (Makwana et al., 2015), molecular recognition (Murayama and Aoki, 1997), and catalysis (Liu et al., 2022). It is of particular interest that they exhibit exceptional self-assembly capability, which provides an innovative platform for designing multifunctional catalytic systems. Several prominent research groups including Dufaud (Mirabaud et al., 2015, 2017, 2018), Kleij (Martínez-Rodríguez et al., 2016; Jose et al., 2017), Patra (Giri et al., 2019), and Ma (Lu et al., 2017a, 2017b) et al. have developed various functionalized resorcinarene derivatives for CCE reactions. However, metal- and halide-free resorcinarene-based organocatalytic systems have not been reported. Thus, the development of organocatalysts derived from resorcinarene scaffolds that are environmentally benign for this transformation is of significant scientific value.

Based on the above inspiration, we designed and synthesized a halide-free, zwitterionic resorcinarene as a one-component bifunctional catalyst for the cycloaddition reaction of epoxide with CO_2 (Scheme 1, c). In contrast to conventional HBD/nucleophile systems that rely on halide anions, this system combines (1) a rigid macrocyclic cavity for substrate binding and (2) zwitterionic sites that enable synergistic CO_2 activation and epoxide ring-opening, thereby eliminating the requirement for metals or co-catalysts. The tetracarboxylic resorcinarene derivatives were successfully constructed through a series of radical substitution, alkylation, and saponification reactions (Morozova et al., 2022); the effects of catalyst loading, reaction temperature, CO_2 pressure, and reaction time on the catalytic performance were systematically investigated, substrate universality and catalyst cyclic stability experiments were carried out.

2. Experimental section

2.1. Materials

Epoxides were purchased from Energy Chemical. Carbon dioxide with a purity of 99.999 % was commercially available from Nanjing Shangyuan Co. 2-Methylresorcinol, hexanal, bromochloromethane, 2,2′-azobis(2-methylpropionitrile), *N*-bromosuccinimide, *N*,*N*-dimethylglycine ethyl ester, sodium hydroxide, and reaction solvents were purchased from Titan. All reagents were used without any further purification.

2.2. Characterizations

^1H 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-d_6 as the solvent. Chemical shifts δ are reported in parts per million (ppm) relative to a residual undeuterated solvent as an internal reference (^1H δ 7.26 for Chloroform-*d*, δ 2.50 for DMSO-d_6; δ 3.31 for CD_3OD-*d*4; and ^{13}C δ 77.16 for Chloroform-*d*, δ 39.52 for DMSO-d_6, and δ 48.00 for CD_3OD-*d*4). Melting points were measured on a Jingke melting point apparatus (uncorrected). FT-IR spectra were recorded on a Thermo Fisher Nicolet iS5 Fourier transform infrared spectrometer. High resolution mass spectra (HRMS) were conducted using an Ionspec 7.0 T spectrometer. Thermal gravimetric analysis (TGA) was conducted using TGA550 instrument model.

*2.3. Synthesis of zwitterionic resorcinarene **RES-Z***

The compound tetramethyloctol **3**, tetramethylcavitand **4**, and tetrakis(bromomethyl)cavitand **5** were synthesis according literature procedures (Boerrigter et al., 1996, 1997; Wu et al., 2014).

Zwitterionic resorcinarene esters **RES-ZE** (Morozova et al., 2022). A 100 mL round-bottom flask was charged sequentially with tetrakis(bromomethyl)cavitand **5** (5.0 g, 4.2 mmol, 1.0 equiv.), anhydrous acetonitrile (50 mL), and N,N-dimethylaminoacetate ethyl ester (2.4 mL, 17.2 mmol, 4.1 equiv.). The reaction mixture was stirred at room temperature for 30 min, followed by heating at 60 °C in an oil bath with continuous stirring for 24 h. Upon completion of the reaction, the system was allowed to cool to ambient temperature. The resulting suspension was filtered, and the collected solid was washed thoroughly with acetonitrile (3 × 15 mL). Subsequent vacuum drying at 40 °C for 24 h afforded zwitterionic resorcinarene esters **RES-ZE** as a white powder in 94 % yield. m.p. 152–153 °C. ^{1}H NMR (400 MHz, CD_3OD-*d4*) δ 8.04 (s, 4H), 6.16 (d, $J = 7.5$ Hz, 4H), 5.50 (s, 4H), 4.80 (d, $J = 8.3$ Hz, 4H), 4.63 (s, 8H), 4.44–4.32 (m, 20H), 3.29 (s, 24H), 2.62 (q, $J = 8.3$ Hz, 8H), 1.53–1.32 (m, 36H), 0.93 (t, $J = 7.3$ Hz, 12H). ^{13}C NMR (100 MHz, CD_3OD-*d4*) δ 166.5, 156.7, 140.0, 128.4, 115.9, 101.2, 63.5, 62.0, 59.0, 52.3, 39.1, 32.8, 31.4, 28.9, 23.9, 14.6, 14.5. FT-IR (cm^{-1}) 3671, 2974, 2899, 1741, 1453, 1405, 1232, 1065, 969, 893, 934. HRMS (ESI-ToF) *m/z* calcd for $[M - 4Br]^{4+}$ $C_{80}H_{120}Br_4N_4O_{16}$ 1392.8699, found: 1392.8653.

Zwitterionic resorcinarene **RES-Z** (Morozova et al., 2022). A 100 mL round-bottom flask was charged with zwitterionic resorcinarene esters **RES-ZE** (4.0 g, 2.3 mmol, 1.0 equiv.) in ethanol (40 mL). To solution was added an aqueous NaOH solution (2 mL, containing 1.2 g NaOH, 28.1 mmol, 12.0 equiv.). The reaction mixture was heated to 60 °C with vigorous stirring for 24 h under a nitrogen atmosphere. Upon completion, the system was cooled to room temperature, and the resulting precipitate was collected by vacuum filtration. The solid product was washed extensively with cold ethanol (3 × 15 mL) to remove residual salts and byproducts. The crude product was then dissolved in distilled water (10 mL), and the PH was adjusted to 7–8 by the addition of 0.1 M HCl solution. The aqueous solution was subjected to dialysis (MWCO 1000 Da) against distilled water for 72 h, with water changes every 4 h. The purified product solution was concentrated under reduced pressure, followed by final drying in a vacuum oven at 40 °C for 48 h to obtain the RES-Z as a white powder in 90 % yield. m.p. 227–229 °C. ^{1}H NMR (400 MHz, CD_3OD-*d4*) δ 7.64 (s, 4H), 6.10 (d, $J = 7.4$ Hz, 4H), 4.82 (t, $J = 8.1$ Hz, 4H), 4.71 (s, 8H), 4.22 (d, $J = 7.5$ Hz, 4H), 3.85 (s, 8H), 3.16 (s, 24H), 2.43–2.38 (m, 8H), 1.52–1.31 (m, 24H), 0.93 (t, $J = 7.1$ Hz, 12H). ^{13}C NMR (100 MHz, CD_3OD-d_4) δ 169.1, 156.8, 139.7, 126.1, 117.3, 100.9, 65.6, 56.7, 51.6, 38.7, 33.0, 31.1, 28.8, 23.8, 14.5. FT-IR (cm^{-1}) 2926, 2961, 1630, 1455, 1387, 1344, 1320, 1237, 1145, 1084, 1010, 967, 929, 883, 711. HRMS (ESI-ToF) *m/z* calcd for $[M+H]^{+}$ $C_{72}H_{101}N_4O_{16}$ 1277.7213, found: 1277.7187.

2.4. General procedure for the cycloaddition of epoxides and CO_2

The epoxide (5.0 mmol) and **RES-Z** (31.9 mg, 0.025 mmol, 0.5 mol%) were placed in a dry 25 mL stainless steel reactor containing a magnetic stir bar. The reactor was constantly purged with 0.3 MPa CO_2 to remove air and finally maintain the pressure at 1.0 MPa. The reactor was put into the oil bath at 120 °C and stirred for 12 h. After the reaction, the reactor was placed in an ice water bath and cooled to 0 °C. Then the reactor was slowly depressurized to atmospheric pressure. The 1,3,5-trimethoxybenzene was added as an internal standard to determine the conversion of epoxide **1** and the selectivity for the product cyclic carbonate **2** using ^{1}H NMR internal standard method with reference to our previous work (Liu et al., 2023). Cyclic carbonate products were obtained by flash chromatography on silica gel (SiO_2) with hexane: ethyl acetate = 10: 1–3: 1.

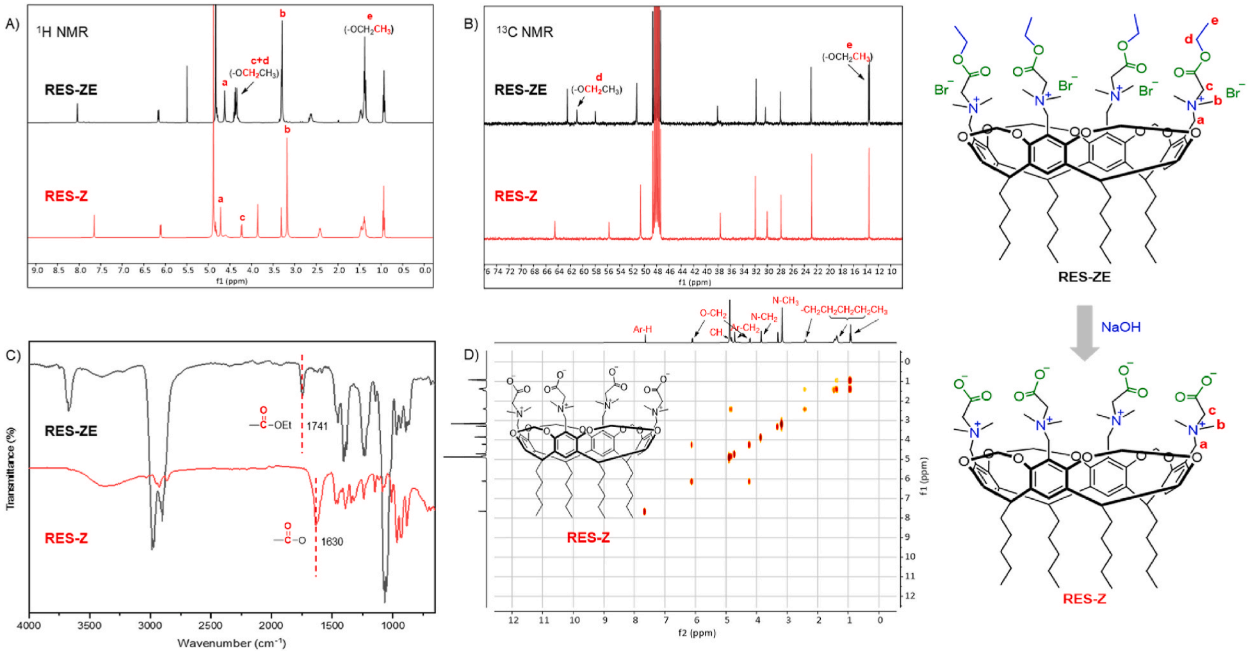


Fig. 1. (A) ^{1}H NMR spectrum of **RES-ZE** and **RES-Z**; (B) ^{13}C NMR spectrum of **RES-ZE** and **RES-Z**; (C) FT-IR spectrum of **RES-ZE** and **RES-Z**. D) 2D COSY spectrum of **RES-Z**.

3. Results and discussion

3.1. *Preparation of zwitterionic resorcinarene organocatalyst and evaluation of the catalytic performances in CCE reactions*

The macrocyclic compound tetramethyloctol **3** was synthesized via acid-catalyzed condensation of 2-methylresorcinol and *n*-hexanal. Subsequent treatment with CH_2BrCl facilitated the regioselective introduction of methylene bridges between adjacent resorcinol units, thereby resulting in the formation of a bowl-shaped tetramethylcavitand **4**. Further structural modification of the upper rim through sequential bromination and alkylation afforded the zwitterionic resorcinarene esters **RES-ZE**. The zwitterionic resorcinarene **RES-Z** was synthesized through alkaline saponification, purified via sequential PH adjustment and dialysis (see Scheme 2), and comprehensively characterized by ^{1}H NMR, ^{13}C NMR, COSY, HMBC, FT-IR, MS, TGA, and melting point determination.

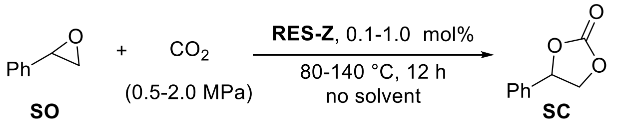
The NMR spectrum demonstrated the complete saponification of zwitterionic resorcinarene esters **RES-ZE**, as evidenced by the disappearance of the characteristic ester proton signals at δ 1.3–1.4 ppm (d) and δ 4.3–4.4 ppm (e) in the ^{1}H NMR spectrum (Fig. 1, A), and the disappearance of the carbon signals at δ 62.0 ppm (d) and δ 14.6 ppm (e) in the ^{13}C NMR spectrum (Fig. 1, B). The attribution of protons can be clearly determined by COSY spectra (Fig. 1, D), and. A substantial discrepancy in the FT-IR spectra (Fig. 1, C) is observed at 1741 cm^{-1} and 1630 cm^{-1} (stretching vibrations of C=O groups of **RES-ZE** and **RES-Z**, respectively). The observed differences in structural characterization, particularly the complete disappearance of ester signals, provide definitive spectroscopic evidence of successful conversion to the zwitterion. These results clearly confirm both the structural integrity and the high purity of the product **RES-Z**.

The catalytic performance of zwitterionic resorcinarene catalyst **RES-Z** was evaluated using styrene oxide (SO) as the benchmark substrate for the reaction with CO_2. Styrene oxide, a substrate with moderate ring-opening difficulty, has been selected as a template substrate in the majority of studies. Cyclic carbonate SC was prepared under solvent-free conditions at 120 °C under 0.5 MPa of CO_2 pressure. The zwitterionic resorcinarene **RES-Z** catalyst was loaded at 0.1 mol%, and the conversion was recorded at 36 % (Table 1, entry 1). Increasing the CO_2 pressure while maintaining a low catalyst loading resulted in a significant increase in the conversions to 54 % and 78 % (Table 1, entry 2–3), respectively. Subsequent examination of the catalyst loading effect, employing 1.0 MPa as the optimal pressure, indicated that a conversion of 97 % was attained with a catalyst loading of 0.5 mol% (Table 1, entry 6). While employing an excess catalyst of 1.0 mol% does give near-complete conversion of the epoxide, this approach is considered inefficient. A more economical alternative is determined to be 0.5 mol% of the catalyst. By elevating the temperature to 140 °C, the conversion efficiency can surpass 90 % within a reduced time (Table 1, entry 7). A decline in temperature to 100 °C or 80 °C led to a substantial reduction in catalyst activity (Table 1, entry 8–9). A more detailed scatter plot representation of these data is provided in Fig. 2. In summary, the optimal reaction conditions were ascertained to be 120 °C, 1.0 MPa, 0.5 mol% catalyst loading, and 12 h.

The scope of substrate suitability for the CCE reaction was investigated based on the optimized conditions obtained, using zwitterionic resorcinarene as an organocatalyst. A series of terminal epoxides bearing distinct substituents was selected for evaluation at 120 °C, 0.5 mol% catalyst loading of **RES-Z**, a CO_2 pressure of 1.0 MPa, and a reaction time of 12 h. The results are presented in Table 2. It was demonstrated that the aliphatic, glycidyl, and aromatic substituted terminal epoxides all demonstrated more than 91 % conversion and 99 % selectivity. The internal epoxide with a large site resistance cyclohexene oxide was not converted, and the commercially valuable epoxide bisphenol A diglycidyl ether resins **1n** achieved a conversion of 73 %.

Zwitterionic resorcinarene **RES-Z** is a stable, externally neutral compound that possesses a partially positively charged nitrogen atom and a partially negatively charged carboxyl oxygen atom as Lewis base sites in its molecular structure. This was demonstrated in several studies that Lewis bases and CO_2 can form reversible adducts as epoxides when attacked by nucleophiles, thereby promoting ring opening (Tsutsumi et al., 2010; Wang et al., 2014; Zhou and Lu, 2017). To demonstrate the existence of CO_2 adduction

Table 1
The cycloadditions of CO_2 to SO promoted by zwitterionic resorcinarene catalysts under different reaction conditions[a].



Entry	Catalyst Loading [mol%]	Temp. [°C]	Time [h]	P (CO_2) [MPa]	Conv.[b] [%]	Sel.[b] [%]	TOF[c]
1	0.1	120	12	0.5	36	>99	7.50
2	0.1	120	12	1.0	54	>99	11.25
3	0.1	120	12	2.0	78	>99	16.25
4	0.3	120	12	1.0	77	>99	4.93
5	0.5	120	12	1.0	97	>99	4.04
6	1.0	120	12	1.0	99	>99	2.06
7	0.5	140	10	1.0	93	>99	4.65
8	0.5	100	12	1.0	75	>99	3.13
9	0.5	80	12	1.0	59	>99	2.46

[a] Reaction conditions unless specified otherwise: SO (5.0 mmol, 0.57 mL), no solvent. [b] Conversion and selectivity were determined via1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard (Liu et al., 2023). [c] Turnover frequency (TOF) = moles of product/(moles of zwitterion unit in **RES-Z** × time).

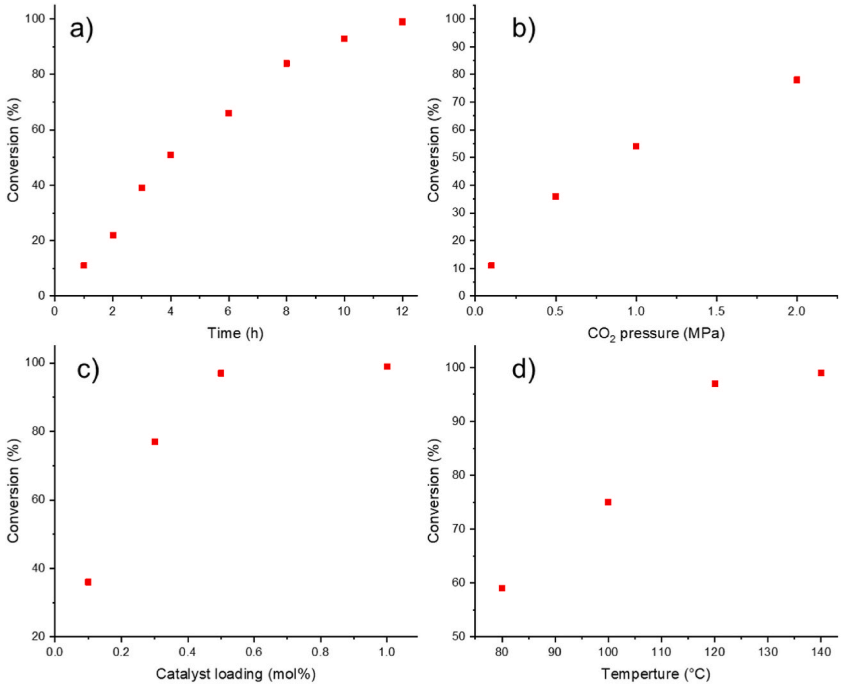


Fig. 2. Influence of different conditions of a) Reaction time (120 °C, 0.5 MPa CO_2, 0.5 mol% **RES-Z**, 0–12 h), b) CO_2 pressure (120 °C, 0.5 mol% **RES-Z**, 0.1–2.0 MPa CO_2, 12 h), c) Catalyst loading (120 °C, 0.5 MPa CO_2, 0.1–1.0 mol%, 12 h), and d) Reaction temperature (80–140 °C, 0.5 MPa CO_2, 0.5 mol% **RES-Z**, 12 h) on SO conversion.

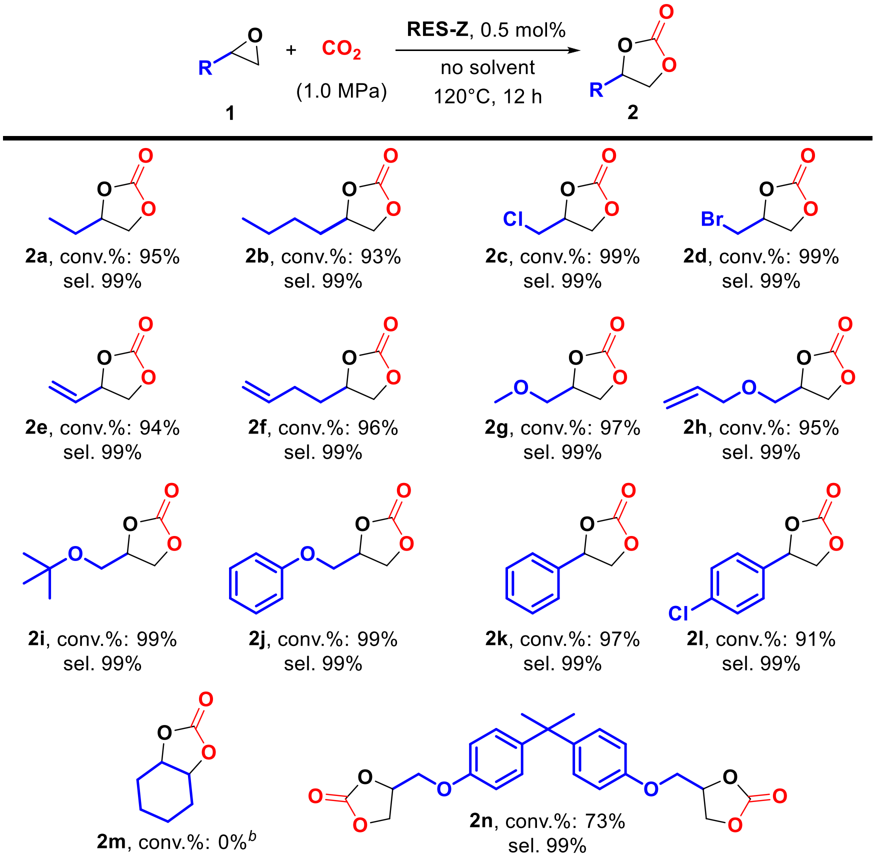
intermediates, zwitterionic resorcinarene was maintained in contact with CO_2 under conditions that were optimized to ensure the efficacy of the reaction. These conditions included a temperature of 120 °C and a CO_2 pressure of 1.0 MPa for 12 h. The carbon atom signal peaks on the carboxyl group were found to be significantly weakened by the ^{13}C NMR spectrum (Fig. S1), and the carbon spectral peaks of CO_2 appeared. These results may be related to the CO_2 adduct instability, possibly due to the reversible release of free CO_2 and the catalyst by decarboxylation occurring during the detection process.

Zwitterion is a naturally occurring substance derived from plants that has exhibited remarkable efficacy as a HBD organocatalyst in ring-opening polymerization reactions (Saito et al., 2019; Xu et al., 2024). To verify the catalytic mechanism of zwitterionic resorcinarene **RES-Z** in CCE reactions. As demonstrated in Fig. 3, a ^{1}H NMR titration experiment was conducted using **RES-Z** in conjunction with the substrate SO in CD_3OD-*d*4. In the absence of a catalyst, the chemical shifts of the methylene protons in the epoxide were 3.096 ppm (orange rhombus) and 2.766 ppm (blue square), respectively. As the ratio of the substrate SO to **RES-Z** gradually changed from 1: 0.05 to 1: 2, the chemical shifts (blue squares and orange rhombuses) of the methylene protons of the substrate SO shifted from 2.735 ppm to 3.063 ppm–2.770 ppm and 3.101 ppm, respectively, as the catalyst concentration increased. Concurrently, the chemical shift of the methyl proton at the upper edge of the calixarene (pink circle) exhibited a shift from 3.125 ppm to 3.175 ppm. The experimental results demonstrate the occurrence of a hydrogen bond interaction between the calixarene catalyst and the epoxide.

The mechanism of zwitterionic resorcinarene-catalyzed CCE reaction is proposed based on previous literature reports (Li et al., 2023; Tsutsumi et al., 2010; Liu et al., 2023) and the validation experiments described above. As demonstrated in Scheme 3, under the stipulated experimental conditions, the reaction of carboxyl ions and CO_2 leads to the formation of the adduct **A**. The methyl group adjacent to the quaternary ammonium cation functions as HBD, thereby forming interactions with the oxygen atom of the epoxide **1**. The methylene group, which demonstrates reduced resistance to nucleophilic attack, exhibits heightened susceptibility to such attacks. Consequently, epoxide **1** undergoes ring-opening, resulting in the formation of intermediate **C** due to the occurrence of SN2 nucleophilic substitutions within the epoxide. After the ring closure, the generation of cyclic carbonate **2** occurs, concomitant with the release of the catalyst **RES-Z**.

Thermogravimetric analysis (TGA) was performed to evaluate the thermal stability of catalyst **RES-Z** under a nitrogen atmosphere, with the temperature being raised from 30 °C to 600 °C at a heating rate of 10 °C/min (Fig. S2). The observation of a mere 5 wt% mass loss at 228.1 °C confirmed the exceptional thermal stability of **RES-Z**, thereby demonstrating its robustness during the reaction process. The recyclability of **RES-Z** was systematically investigated under optimized reaction conditions (120 °C, 1.0 MPa CO_2 pressure, 0.5 mol % catalyst loading, 6 h). The recycling procedure of the catalyst is outlined as follows: (1) the employment of anhydrous zwitterionic resorcinarene **RES-Z** as the initial catalyst for the cycloaddition reaction of epichlorohydrin (ECH) and CO_2; (2) the periodic sampling of the reaction mixture for the purpose of conversion monitoring by means of ^{1}H NMR spectra; (3) the separation of the insoluble **RES-Z** from the reaction products via ether extraction; and (4) the recovery of the catalyst through vacuum drying for subsequent reuse. Remarkably, the catalytic performance demonstrated consistent excellence across five successive cycles, the conversion of ECH to the

Table 2
Synthesis of different cyclic carbonates under optimal conditions^a.



2a, conv.%: 95% sel. 99%
2b, conv.%: 93% sel. 99%
2c, conv.%: 99% sel. 99%
2d, conv.%: 99% sel. 99%
2e, conv.%: 94% sel. 99%
2f, conv.%: 96% sel. 99%
2g, conv.%: 97% sel. 99%
2h, conv.%: 95% sel. 99%
2i, conv.%: 99% sel. 99%
2j, conv.%: 99% sel. 99%
2k, conv.%: 97% sel. 99%
2l, conv.%: 91% sel. 99%
2m, conv.%: 0%^{b}
2n, conv.%: 73% sel. 99%

[a]Reaction conditions: 0.5 mol%, 120 °C, 1.0 MPa, 12 h, solvent-free. [b] 48 h.

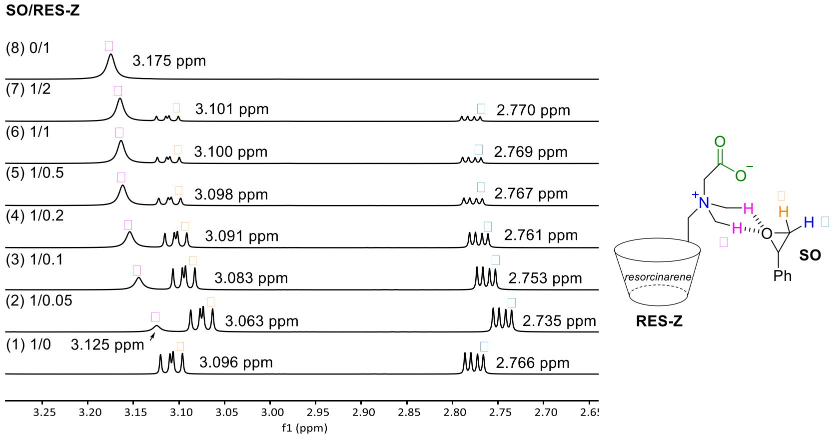
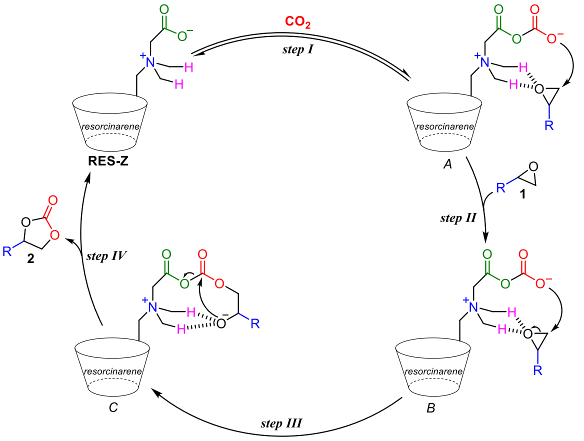


Fig. 3. Chemical shifts of the O–H proton of the catalyst **RES-Z** (pink circle) and methylene protons (blue squares and orange rhombus) of the substrate SO in the titration in the ^{1}H NMR spectra (CD_3OD-*d*4), the series ratios of SO/**RES-Z** in (1) 1/0, (2) 1/0.05, (3) 1/0.1, (4) 1/0.2, (5)1/0.5, (6) 1/1, (7) 1/2, and (8) 0/1.

corresponding cyclic carbonate **2c** decreased from 77.3 % to 73.6 %, the activity did not decline significantly (Fig. 4). The notable recyclability of the catalyst, in conjunction with its thermal stability, underscores the practical potential of **RES-Z** for sustainable catalytic applications.



Scheme 3. Proposed mechanism for the formation of cyclic carbonates from epoxides and CO_2 promoted by zwitterionic resorcinarene catalyst.

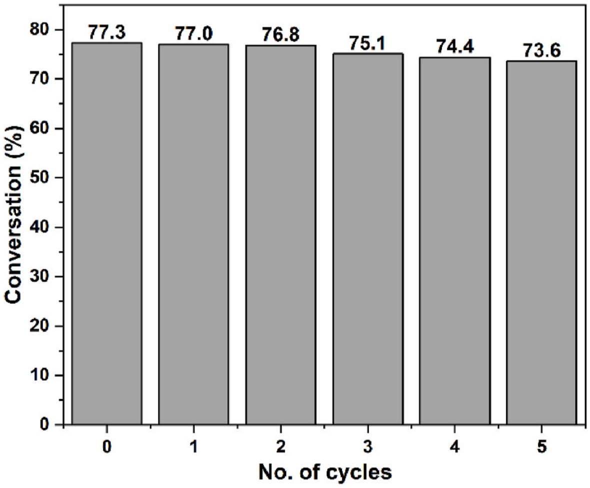


Fig. 4. Recyclability study of halide-free catalyst **RES-Z** Reaction conditions: ECH **1c** (10.0 mmol, 0.78 mL), **RES-Z** (0.05 mmol, 0.5 mol%), 120 °C, 1.0 MPa of CO_2, 12 h, neat. Selectivity for cyclic carbonate **2c** was all >99 %.

4. Conclusions

In summary, we proposed a novel, halide-free, and highly stable resorcinarene-based organocatalyst, thereby preventing the detrimental corrosion of halide anions on steel reactors and reducing the environmental impact of halide waste. Zwitterionic resorcinarene was successfully prepared by a series of substitution, alkylation, and saponification reactions, with its structure confirmed by NMR, FT-IR, and MS. Key mechanistic insights were obtained through NMR titration experiments, which revealed that the methyl group on the quaternary ammonium moiety of RES-Z forms H-bonding interactions with the epoxide. Simultaneously, the carboxyl groups serve as Lewis base sites, generating reversible adducts with CO_2. The resulting carboxylate-CO_2 adduct then attacks the activated epoxide, leading to ring opening and subsequent cyclization into the cyclic carbonate via a synergistic mechanism. Optimization studies demonstrated that the reaction conditions—including temperature, catalyst loading, reaction time, and CO_2 pressure—played crucial roles in catalytic efficiency. Under optimized conditions (120 °C, 0.5 mol% catalyst loading, 1.0 MPa CO_2, 12 h), 13 terminal epoxides were converted into their corresponding cyclic carbonates with 91–99 % conversion and 99 % selectivity. Notably, the catalyst exhibited broad substrate compatibility, accommodating both electron-rich and electron-deficient epoxides with high efficiency. The successful development of this zwitterionic resorcinarene catalyst system establishes a valuable paradigm for the rational design of halide-free organocatalysts.

CRediT authorship contribution statement

Yongzhu Hu: Writing – review & editing, Writing – original draft, Methodology, Investigation. **Haoyu Wang:** Writing – review & editing, Writing – original draft. **Zhenjiang Li:** Writing – review & editing, Supervision, Resources, Project administration, Funding

acquisition, Conceptualization. **Jiahui Ma:** Methodology. **Yue Xu:** Methodology. **Ziqi Liu:** Methodology. **Yanqi Shi:** Methodology. **Xiaolong Huang:** Methodology. **Hui Zhao:** Methodology. **Kai Guo:** Supervision, Resources, Project administration, Funding acquisition.

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.

Acknowledgments

This work was supported by the National Key Research and Development Program of China (2022YFC2105603), 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. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scp.2025.102102.

Data availability

Data will be made available on request.

References

Alves, M., Grignard, B., Mereau, R., Jerome, C., Tassaing, T., Detrembleur, C., 2017. Organocatalyzed coupling of carbon dioxide with epoxides for the synthesis of cyclic carbonates: catalyst design and mechanistic studies. Catal. Sci. Technol. 7 (13), 2651–2684. https://doi.org/10.1039/c7cy00438a.

Artz, J., Müller, T.E., Thenert, K., Kleinekorte, J., Meys, R., Sternberg, A., Bardow, A., Leitner, W., 2018. Sustainable conversion of carbon dioxide: an integrated review of catalysis and life cycle assessment. Chem. Rev. 118 (2), 434–504. https://doi.org/10.1021/acs.chemrev.7b00435.

Aytar, E., Yasar, E., Kilic, A., 2024. The efficient and reusable imidazolium-organoboron catalysts for green CO_2 insertion reactions in solvent-free under atmospheric and high-pressure conditions. Fuel 378, 132867. https://doi.org/10.1016/j.fuel.2024.132867.

Boerrigter, H., Verboom, W., van Hummel, G.J., Harkema, S., Reinhoudt, D.N., 1996. Selective functionalization of resorcinarene cavitands; single crystal X-ray structure of a distally functionalized cavitand. Tetrahedron Lett. 37 (29), 5167–5170. https://doi.org/10.1016/0040-4039(96)01027-1.

Boerrigter, H., Verboom, W., Reinhoudt, D.N., 1997. Novel resorcinarene cavitand-based CMP(O) cation ligands: synthesis and extraction properties. J. Org. Chem. 62 (21), 7148–7155. https://doi.org/10.1021/jo9703414.

Büttner, H., Longwitz, L., Steinbauer, J., Wulf, C., Werner, T., 2017. Recent developments in the synthesis of cyclic carbonates from epoxides and CO_2. Top. Curr. Chem. 375 (3), 50. https://doi.org/10.1007/s41061-017-0136-5.

Buß, F., Mehlmann, P., Mück-Lichtenfeld, C., Bergander, K., Dielmann, F., 2016. Reversible carbon dioxide binding by simple lewis base adducts with electron-rich phosphines. J. Am. Chem. Soc. 138 (6), 1840–1843. https://doi.org/10.1021/jacs.5b13116.

Cokoja, M., Bruckmeier, C., Rieger, B., Herrmann, W.A., Kuhn, F.E., 2011a. Transformation of carbon dioxide with homogeneous transition-metal catalysts: a molecular solution to a global challenge? Angew Chem. Int. Ed. Engl. 50 (37), 8510–8537. https://doi.org/10.1002/anie.201102010.

Cokoja, M., Bruckmeier, C., Rieger, B., Herrmann, W.A., Kühn, F.E., 2011b. Transformation of carbon dioxide with homogeneous transition-metal catalysts: a molecular solution to a global challenge? Angew. Chem. Int. Ed. 50 (37), 8510–8537. https://doi.org/10.1002/anie.201102010.

Cokoja, M., Wilhelm, M.E., Anthofer, M.H., Herrmann, W.A., Kuhn, F.E., 2015. Synthesis of cyclic carbonates from epoxides and carbon dioxide by using organocatalysts. ChemSusChem 8 (15), 2436–2454. https://doi.org/10.1002/cssc.201500161.

Comerford, J.W., Ingram, I.D.V., North, M., Wu, X., 2015. Sustainable metal-based catalysts for the synthesis of cyclic carbonates containing five-membered rings. Green Chem. 17 (4), 1966–1987. https://doi.org/10.1039/C4GC01719F.

Etacheri, V., Marom, R., Elazari, R., Salitra, G., Aurbach, D., 2011. Challenges in the development of advanced Li-ion batteries: a review. Energy Environ. Sci. 4 (9), 3243–3262. https://doi.org/10.1039/c1ee01598b.

Fiorani, G., Guo, W., Kleij, A.W., 2015. Sustainable conversion of carbon dioxide: the advent of organocatalysis. Green Chem. 17 (3), 1375–1389. https://doi.org/10.1039/c4gc01959h.

Gajjar, J.A., Vekariya, R.H., Parekh, H.M., 2020. Recent advances in upper rim functionalization of resorcin[4]arene derivatives: synthesis and applications. Synth. Commun. 50 (17), 2545–2571. https://doi.org/10.1080/00397911.2020.1766080.

Giri, A., Hussain, M.D.W., Sk, B., Patra, A., 2019. Connecting the dots: knitting C-Phenylresorcin[4]arenes with aromatic linkers for task-specific porous organic polymers. Chem. Mater. 31 (20), 8440–8450. https://doi.org/10.1021/acs.chemmater.9b02563.

Guan, J., Song, Y., Lin, Y., Yin, X., Zuo, M., Zhao, Y., Tao, X., Zheng, Q., 2011. Progress in study of non-isocyanate polyurethane. Ind. Eng. Chem. Res. 50 (11), 6517–6527. https://doi.org/10.1021/ie101995j.

Jose, T., Cañellas, S., Pericàs, M.A., Kleij, A.W., 2017. Polystyrene-supported bifunctional resorcinarenes as cheap, metal-free and recyclable catalysts for epoxide/CO_2 coupling reactions. Green Chem. 19 (22), 5488–5493. https://doi.org/10.1039/c7gc02856c.

Kayaki, Y., Yamamoto, M., Ikariya, T.N.-, 2009. Heterocyclic carbenes as efficient organocatalysts for CO_2 fixation reactions. Angew Chem. Int. Ed. Engl. 48 (23), 4194–4197. https://doi.org/10.1002/anie.200901399.

Kilic, A., Sobay, B., Aytar, E., Söylemez, R., 2020. Synthesis and effective catalytic performance in cycloaddition reactions with CO_2 of boronate esters versus N-heterocyclic carbene (NHC)-stabilized boronate esters. Sustain. Energy Fuels 4 (11), 5682–5696. https://doi.org/10.1039/D0SE01189D.

Kilic, A., Aytar, E., Okcu, C., Durgun, M., 2024. An improved boron-catalyzed cycloaddition of CO2 to epoxides for the production of five-membered cyclic carbonates under atmospheric versus high-pressure conditions. Sustain. Chem. Pharm. 39, 101620. https://doi.org/10.1016/j.scp.2024.101620.

Kilic, A., Aytar, E., Kleij, A.W., 2025a. Boron catalysis to expedite the synthesis of organic carbonates from carbon dioxide. ChemCatChem 17 (7), e202500002. https://doi.org/10.1002/cctc.202500002.

Kilic, A., D'Elia, V., Aytar, E., Phungpanya, C., Aslanli, F., 2025b. Synthesis of cyclic carbonates from CO2 and epoxides by novel metal and halide-free chiral boron compounds. Tetrahedron 174, 134485. https://doi.org/10.1016/j.tet.2025.134485.

Kleij, A.W., 2020. Advancing halide-free catalytic synthesis of CO_2-based heterocycles. Curr. Opin. Green Sustainable Chem. 24, 72–81. https://doi.org/10.1016/j.cogsc.2020.04.002.

Kumatabara, Y., Okada, M., Shirakawa, S., 2017. Triethylamine hydroiodide as a simple yet effective bifunctional catalyst for CO_2 fixation reactions with epoxides under mild conditions. ACS Sustain. Chem. Eng. 5 (8), 7295–7301. https://doi.org/10.1021/acssuschemeng.7b01535.

Li, J., Yue, C., Ji, W., Feng, B., Wang, M.-Y., Ma, X., 2023. Recent advances in cycloaddition of CO_2 with epoxides: halogen-free catalysis and mechanistic insights. Front. Chem. Sci. Eng. 17 (12), 1879–1894. https://doi.org/10.1007/s11705-023-2354-4.

Liu, J.-L., Sun, M., Shi, Y.-H., Zhou, X.-M., Zhang, P.-Z., Jia, A.-Q., Zhang, Q.-F., 2022. Functional modification, self-assembly and application of calix[4] resorcinarenes. J. Inclusion Phenom. Macrocycl. Chem. 102 (3–4), 201–233. https://doi.org/10.1007/s10847-021-01119-w.

Liu, B., Yu, H., Li, Z., He, J., Hu, Y., Zou, X., Lu, L., Cao, S., Ma, C., Guo, K., 2023. Halide-free squaramide–phenolate organocatalyst for the cycloaddition of CO_2 into epoxides. J. Environ. Chem. Eng. 11 (5), 110886–110897. https://doi.org/10.1016/j.jece.2023.110886.

Lu, B.-B., Yang, J., Liu, Y.-Y., Ma, J.-F., 2017a. A Polyoxovanadate–Resorcin[4]arene-Based porous metal–organic framework as an efficient multifunctional catalyst for the cycloaddition of CO_2 with epoxides and the selective oxidation of sulfides. Inorg. Chem. 56 (19), 11710–11720. https://doi.org/10.1021/acs.inorgchem.7b01685.

Lu, B.-B., Jiang, W., Yang, J., Liu, Y.-Y., Ma, J.-F., 2017b. 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 9 (45), 39441–39449. https://doi.org/10.1021/acsami.7b14179.

Ma, X., Zou, B., Cao, M., Chen, S.-L., Hu, C., 2014. Nitrogen-doped porous carbon monolith as a highly efficient catalyst for CO_2 conversion. J. Mater. Chem. A 2 (43), 18360–18366. https://doi.org/10.1039/C4TA02734E.

Makwana, B.A., Vyas, D.J., Bhatt, K.D., Jain, V.K., Agrawal, Y.K., 2015. Highly stable antibacterial silver nanoparticles as selective fluorescent sensor for Fe3+ ions. Spectrochim. Acta Mol. Biomol. Spectrosc. 134, 73–80. https://doi.org/10.1016/j.saa.2014.05.044.

Martínez-Rodríguez, L., Otalora Garmilla, J., Kleij, A.W., 2016. Cavitand-based polyphenols as highly reactive organocatalysts for the coupling of carbon dioxide and oxiranes. ChemSusChem 9 (7), 749–755. https://doi.org/10.1002/cssc.201501463.

Mirabaud, A., Mulatier, J.-C., Martinez, A., Dutasta, J.-P., Dufaud, V., 2015. Investigating host–guest complexes in the catalytic synthesis of cyclic carbonates from styrene oxide and CO_2. ACS Catal. 5 (11), 6748–6752. https://doi.org/10.1021/acscatal.5b01545.

Mirabaud, A., Mulatier, J.-C., Martinez, A., Dutasta, J.-P., Dufaud, V., 2017. Merging host-guest chemistry and organocatalysis for the chemical valorization of CO_2. Catal. Today 281, 387–391. https://doi.org/10.1016/j.cattod.2016.03.050.

Mirabaud, A., Martinez, A., Bayard, F., Dutasta, J.-P., Dufaud, V., 2018. A new heterogeneous host–guest catalytic system as an eco-friendly approach for the synthesis of cyclic carbonates from CO_2 and epoxides. New J. Chem. 42 (20), 16863–16874. https://doi.org/10.1039/c8nj03065k.

Morozova, J.E., Gilmullina, Z.R., Voloshina, A.D., Lyubina, A.P., Amerhanova, S.K., Syakaev, V.V., Babaeva, O.B., Ziganshina, A.Y., Mukhametzyanov, T.A., Samorodov, A.V., et al., 2022. Calix[4]Resorcinarene carboxybetaines and carboxybetaine esters: synthesis, investigation of In vitro toxicity, anti-platelet effects, anticoagulant activity, and BSA binding affinities. Int. J. Mol. Sci. 23 (23). https://doi.org/10.3390/ijms232315298.

Murayama, K., Aoki, K., 1997. Molecular recognition involving multiple cation–π interactions: the inclusion of the acetylcholine trimethylammonium moiety in resorcin[4]arene. Chem. Commun. (1), 119–120. https://doi.org/10.1039/A607131G.

Neri, P., Sessler, J.L., Wang, M.-X., 2016. Calixarenes and Beyond. https://doi.org/10.1007/978-3-319-31867-7.

Peng, J., Deng, Y., 2001. Cycloaddition of carbon dioxide to propylene oxide catalyzed by ionic liquids. New J. Chem. 25 (4), 639–641. https://doi.org/10.1039/B008923K.

Podyachev, S.N., Zairov, R.R., Mustafina, A.R., 2021. 1,3-Diketone Calix[4]arene derivatives—A new type of versatile ligands for metal complexes and nanoparticles. Molecules 26 (5), 1214. https://doi.org/10.3390/molecules26051214.

Rostami, A., Mahmoodabadi, M., Hossein Ebrahimi, A., Khosravi, H., Al-Harrasi, A., 2018. An electrostatically enhanced phenol as a simple and efficient bifunctional organocatalyst for carbon dioxide fixation. ChemSusChem 11 (24), 4262–4268. https://doi.org/10.1002/cssc.201802028.

Saito, T., Takojima, K., Oyama, T., Hatanaka, S., Konno, T., Yamamoto, T., Tajima, K., Isono, T., Satoh, T., 2019. Trimethyl glycine as an environmentally benign and biocompatible organocatalyst for ring-opening polymerization of cyclic carbonate. ACS Sustain. Chem. Eng. 7 (9), 8868–8875. https://doi.org/10.1021/acssuschemeng.9b00884.

Schäffner, B., Schäffner, F., Verevkin, S.P., Börner, A., 2010. Organic carbonates as solvents in synthesis and catalysis. Chem. Rev. 110 (8), 4554–4581. https://doi.org/10.1021/cr900393d.

Shen, Y.-M., Duan, W.-L., Shi, M., 2003. Phenol and organic bases Co-Catalyzed chemical fixation of carbon dioxide with terminal epoxides to form cyclic carbonates. Adv. Synth. Catal. 345 (3), 337–340. https://doi.org/10.1002/adsc.200390035.

Sun, J., Cheng, W., Yang, Z., Wang, J., Xu, T., Xin, J., Zhang, S., 2014. Superbase/cellulose: an environmentally benign catalyst for chemical fixation of carbon dioxide into cyclic carbonates. Green Chem. 16 (6). https://doi.org/10.1039/c3gc41850b.

Tong, H., Qu, Y., Li, Z., He, J., Zou, X., Zhou, Y., Duan, T., Liu, B., Sun, J., Guo, K., 2022. Halide-free pyridinium saccharinate binary organocatalyst for the cycloaddition of CO_2 into epoxides. Chem. Eng. J. 444. https://doi.org/10.1016/j.cej.2022.135478.

Tsutsumi, Y., Yamakawa, K., Yoshida, M., Ema, T., Sakai, T., 2010. Bifunctional organocatalyst for activation of carbon dioxide and epoxide to produce cyclic carbonate: Betaine as a new catalytic motif. Org. Lett. 12 (24), 5728–5731. https://doi.org/10.1021/ol102539x.

Vivek, J.P., Berry, N., Papageorgiou, G., Nichols, R.J., Hardwick, L.J., 2016. Mechanistic insight into the superoxide induced ring opening in propylene carbonate based electrolytes using in situ surface-enhanced infrared spectroscopy. J. Am. Chem. Soc. 138 (11), 3745–3751. https://doi.org/10.1021/jacs.5b12494.

Wang, Y.-B., Wang, Y.-M., Zhang, W.-Z., Lu, X.-B., 2013. Fast CO_2 sequestration, activation, and catalytic transformation using N-Heterocyclic olefins. J. Am. Chem. Soc. 135 (32), 11996–12003. https://doi.org/10.1021/ja405114e.

Wang, Y.-B., Sun, D.-S., Zhou, H., Zhang, W.-Z., Lu, X.-B., 2014. Alkoxide-functionalized imidazolium betaines for CO_2 activation and catalytic transformation. Green Chem. 16 (4), 2266–2272. https://doi.org/10.1039/C3GC42346H.

Wei-Li, D., Bi, J., Sheng-Lian, L., Xu-Biao, L., Xin-Man, T., Chak-Tong, A., 2014. Functionalized phosphonium-based ionic liquids as efficient catalysts for the synthesis of cyclic carbonate from expoxides and carbon dioxide. Appl. Catal. Gen. 470, 183–188. https://doi.org/10.1016/j.apcata.2013.10.060.

Wu, R., Al-Azemi, T.F., Bisht, K.S., 2014. Influence of a resorcin[4]arene core structure on the spatial directionality of multi-arm poly(ε-caprolactone)s. RSC Adv. 4 (32), 16864–16870. https://doi.org/10.1039/c3ra47678b.

Xu, Y., Guo, P., Li, Z., Liu, Z., Zhu, T., Wang, Y., Zhang, H., He, W., Lyu, M., Guo, K., 2024. Zwitterionic organocatalysis for ring-opening polymerization of cyclic esters. Green Chem. 26 (13), 7825–7836. https://doi.org/10.1039/d4gc01171f.

Yu, W., Maynard, E., Chiaradia, V., Arno, M.C., Dove, A.P., 2021. Aliphatic polycarbonates from cyclic carbonate monomers and their application as biomaterials. Chem. Rev. 121 (18), 10865–10907. https://doi.org/10.1021/acs.chemrev.0c00883.

Yuan, X., Liu, Z., Li, Z., Shi, Y., Yang, B., Zou, X., Hu, Y., Li, C., Li, S., Guo, K., 2024. Halide-free pyridinium base binary organocatalyst for the cycloaddition of carbon dioxide to epoxides. New J. Chem. 48 (25), 11435–11446. https://doi.org/10.1039/d4nj01686f.

Yue, S., Qu, H.-L., Song, X.-X., Feng, X.-N., 2022. Novel hydroxyl-functionalized ionic liquids as efficient catalysts for the conversion of CO_2 into cyclic carbonates under metal/halogen/cocatalyst/solvent-free conditions. New J. Chem. 46 (12), 5881–5888. https://doi.org/10.1039/D2NJ00257D.

Zhang, F., Wang, Y., Zhang, X., Zhang, X., Liu, H., Han, B., 2020. Recent advances in the coupling of CO_2 and epoxides into cyclic carbonates under halogen-free condition. Green Chem. Eng. 1 (2), 82–93. https://doi.org/10.1016/j.gce.2020.09.008.

Zhou, H., Lu, X., 2017. Lewis base-CO_2 adducts as organocatalysts for CO_2 transformation. Sci. China Chem. 60 (7), 904–911. https://doi.org/10.1007/s11426-016-0442-5.

Zhou, H., Wang, G.-X., Zhang, W.-Z., Lu, X.-B., 2015. CO_2 adducts of phosphorus ylides: highly active organocatalysts for carbon dioxide transformation. ACS Catal. 5 (11), 6773–6779. https://doi.org/10.1021/acscatal.5b01409.

Zhu, T., Xu, Y., Li, Z., He, J., Yuan, X., Qian, D., Chang, T., Lu, L., Chi, B., Guo, K., 2024. Cholinium pyridinolate ionic pair-catalyzed fixation of CO_2 into cyclic carbonates. J. Org. Chem. 89 (11), 7408–7416. https://doi.org/10.1021/acs.joc.3c02609.