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Resorcinarene bearing carbanion ion pair as organocatalyst for carbon dioxide fixation

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ABSTRACT

The development of efficient and environmentally friendly catalysts for carbon dioxide (CO_2) cycloaddition remains a significant challenge due to the corrosion, pollution, and purity issues caused by conventional halide-containing systems. Herein, we present a halide-free tetra-1,3-diketone resorcinarene ion pair organocatalyst that facilitates CO_2 fixation under mild conditions (120 °C, 0.1 MPa) through a dual activation mechanism—CO_2 activation by the resorcinarene carbanion and epoxide activation via H-bonding. This catalytic system has been shown to achieve high conversion (83–99 %) for terminal epoxides, retain notable activity for internal epoxides, and demonstrate exceptional thermal stability (>230 °C) and recyclability (five cycles without significant loss of activity). This system offers a sustainable alternative to traditional halide catalysts, combining environmental advantages with practical industrial feasibility.

1. Introduction

Carbon dioxide (CO_2), a greenhouse gas, is employed as an economical and sustainable C1 building block to produce high-value industrial commodities, contributing to the mitigation of fossil fuel dependence while simultaneously addressing carbon emission reduction [1]. Substantial progress in this domain has facilitated the utilization of CO_2 as a molecular synthon, enabling the synthesis of diverse organic structures [2]. Among these derivatives, cyclic carbonates occupy a prominent position due to their extensive applicability, such as chemical intermediate [3], polar aprotic solvent [4], electrolyte for lithium-ion batteries [5], and monomers of polycarbonate [6] and non-isocyanate polyurethane [7]. However, the inherent thermodynamic stability and kinetic inertness of CO_2 necessitate catalytic activation to overcome its high energy barrier [8]. A notable advancement in this field involves the widespread adoption of organocatalysts, which offer distinct advantages over conventional metal-based systems, including cost-effectiveness, ready availability, non-toxicity, and exceptional stability [9–12]. Consequently, these catalysts are increasingly supplanting metallic alternatives in industrial applications.

Catalytic systems composed of hydrogen bond donors (HBDs) and halides have been demonstrated to exhibit exceptional catalytic activity for the cycloaddition of CO_2 to epoxides (CCE) reaction (Scheme 1, a) [13–15]. Significant progress has been made in the development of catalytic systems, including binary catalytic systems, which combine HBDs such as phenolic derivatives [13], fluorinated alcohols [16], boronic acids [17], and even water [18] are combined with halides, as well as one-component catalytic systems, which include ammonium salts [19–21], phosphonium salts [22–24] and imidazolium-based ionic liquids [25–27] with –OH, –NH, or –COOH functional groups. Despite the outstanding performance of some of these catalysts, most halide-containing systems suffer from inherent drawbacks, including equipment corrosion, environmental concerns, and reduced product purity caused by halide residues [28–31]. Consequently, the development of novel, highly efficient, and halide-free catalytic systems for this cycloaddition reaction has become imperative.

In recent years, considerable attention has been devoted to the design of halide-free catalysts, particularly those based on amines [32, 33], ion pairs [34,35], a series of binary catalytic system [36–40], and supported catalysts [41]. One of the earliest examples of halide-free catalytic system of cyclic carbonate synthesis was reported by Shi et al., employed a binary catalytic system consisting of 4-dimethylaminopyridine (DMAP) and phenol under harsh conditions (120 °C, 3.6 MPa CO_2) to successfully convert various terminal epoxides into cyclic

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carbonates [36]. Our research group has recently developed several halide-free HBD/Lewis base (LB) catalytic systems, with CO_2 activation confirmed by ^{13}C NMR and FT-IR spectra, while H-bonding interactions between the catalyst and epoxides were verified via ^1H NMR titration experiments (Scheme 1, b) [42,43]. However, nearly all halide-free catalytic systems exhibit limitations, including insufficient activity, narrow substrate scope, lack of recyclability, and typically requiring elevated temperatures and pressures to achieve efficient epoxide conversion.

Calixarenes are an important class of macrocyclic compounds that serve as third-generation supramolecular hosts after crown ethers and cyclodextrins [44]. These compounds are distinguished by structurally tunable 3D-shaped cavities and exhibit versatile molecular recognition properties [45]. Resorcinarene, a special subset of calixarene, synthesised via the acid-catalyzed condensation of resorcinol with aliphatic or aromatic aldehydes, allow precise functionalization at well-defined positions, including the upper rim phenolic hydroxyl groups, the *C*-5 positions of aromatic rings and the lower rim bridging methylene units [46]. These modifications result in the attainment of well-defined functionalities, thereby rendering resorcinarenes highly adaptable for a variety of applications. Recent reports have demonstrated the catalytic potential of certain resorcinarene derivatives in organic transformations [47,48]. However, the application of halide-free resorcinarene-based ion pair catalysts in CCE reactions remains unreported to date. Consequently, the development of novel and highly efficient resorcinarene-derived ion pair catalysts, along with the exploration of their catalytic performance in organic synthesis, represents a research area of significant scientific importance.

1,3-Diketone is a class of robust and non-toxic compounds widely used in organic synthesis [49]. These compounds readily undergo deprotonation to form stable carbanion intermediates after treated by Brønsted base. High-resolution mass spectrometric analyses have confirmed that 1,3-diketone-derived carbanions efficiently trap CO_2 at the α-carbon position to yield carboxylate intermediates [50]. This observation highlights their potential as effective Lewis base catalysts for cycloaddition reactions. When incorporated into a macrocyclic framework, the enol tautomer of 1,3-diketones is sterically constrained due to the proximity of methylene-bridged substituents, and were applied as versatile ligands for metal complexes and nanoparticles [51,52]. Treatment of the resorcinarene scaffold with an organic base in a 1:4 stoichiometry produces a predominantly carbanionic ion pair species (Scheme 1, c).

We have developed a new resorcinarene bearing carbanion ion pair as halide-free organocatalyst for the cycloaddition of epoxides with CO_2 to cyclic carbonates. A systematic evaluation of resorcinarene structural variants and organic base combinations was conducted to identify the optimal ion pair configuration. Extensive reaction parameter optimization and mechanistic studies enabled the development of a highly efficient CO_2 fixation system under mild conditions.

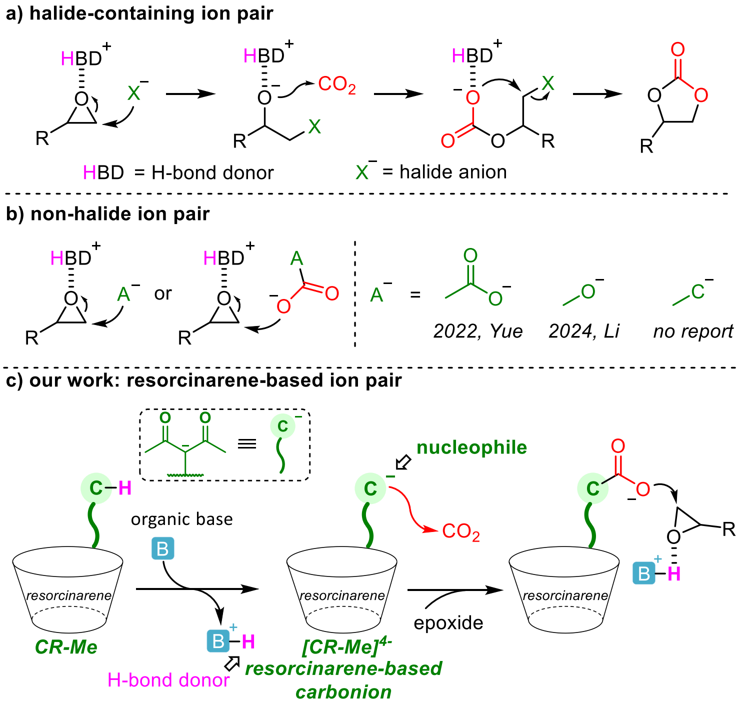
2. Experimental section

2.1. Materials

Epoxides were purchased from Energy Chemical. CO_2 with a purity of 99.999 % was commercially available from Nanjing Shangyuan Co. 2-methylresorcinol, hexanal, bromochloromethane, N-bromosuccinimide, 2,2′-azobis(2-methylpropionitrile), acetylacetone, dibenzoylmethane, 2,2,6,6-tetramethyl-3,5-heptanedione, sodium hydroxide and reaction solvents were purchased from Titan. 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU, purity >99 %, Macklin), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, purity >99 %, Adamas), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, purity >99 %, Adamas) were purchased commercially. 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-*d6* as the solvent. Chemical shifts *δ* are reported in parts per million (ppm)



Scheme 1. Ion pair organocatalysts for CCE reactions. a) Halide containing ion pairs catalytic system for CCE reaction; b) non-halide ion pairs, such as carboxyl anion [35], oxyanion [42,43], or carbanion; c) Carbanion containing resorcinarene-based ion pair as halide-free organocatalyst.

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*).

2.3. General procedure for the pre-organocatalysts

The compounds tetramethyloctol **3**, tetramethylcavitand **4**, and tetrakis(bromomethyl)cavitand **5** were obtained according to previous literature (Scheme 2) [53–55]. Characterization data match those reported in the literature.

Tetramethyloctol **3** [53]. 2-Methylresorcinol (5.0 g, 40.3 mmol) was dissolved in a solution of ethanol (50 mL) and concentrated hydrochloric acid (6.7 mL). To this stirring, solution was added dropwise hexanal (4.7 mL, 40.3 mmol) over a period of 30 min at 0 °C. The reaction mixture was warmed to room temperature before transferring to a preheated oil bath and was kept at 70 °C for 24 h. After completion of the reaction, the reaction mixture was poured into distilled water, the residue was obtained and filtered. The solid was triturated with water, filtered, and recrystallized from ethanol-water to give resorcinarene **3**, yield 6.5 g (91 %). ^{1}H NMR (400 MHz, DMSO-*d6*) δ 8.65 (s, 8H), 7.24 (s, 4H), 4.20 (t, $J = 7.8$ Hz, 4H), 2.21 (q, $J = 7.7$ Hz, 8H), 1.94 (s, 12H), 1.36–1.15 (m, 24H), 0.85 (t, $J = 7.0$ Hz, 12H). ^{13}C NMR (100 MHz, DMSO-*d6*) δ 149.0, 124.8, 121.1, 111.6, 56.1, 34.3, 33.1, 31.5, 27.7, 22.3, 18.6, 14.0, 10.1.

Tetramethylcavitand **4** [54]. To a solution of 6.2 g tetramethyloctol **3** (7.5 mmol, 1.0 equiv.) in 400 mL dry DMF was added 25.2 g K_2CO_3 (0.16 mol, 24.0 equiv.) in a 1000 mL three-necked flask. To this mixture was added 7.9 mL bromochloromethane (0.12 mol, 16.0 equiv.) at room temperature and stirred for 30 min before transferring to a preheated oil bath, and the reaction mixture was stirred at 70 °C for 12 h. After completion of the reaction, the reaction mixture was poured into ice-cold water. The organic layer was extracted with 200 mL dichloromethane and washed with water (twice) and brine. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The residue was passed through column chromatography afford tetramethylcavitand **4** as white solid, yield 5.8 g (88 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.99 (s, 4H), 5.90 (d, $J = 6.9$ Hz, 4H), 4.78 (t, $J = 8.1$ Hz, 4H), 4.27 (d, $J = 6.9$ Hz, 4H), 2.24–2.15 (m, 8H), 1.99 (s, 12H), 1.47–1.31 (m, 24H), 0.92 (t, $J = 7.1$ Hz, 12H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.4, 138.1, 123.7, 117.7, 98.6, 37.1, 32.2, 30.2, 27.8, 22.8, 14.2, 10.5.

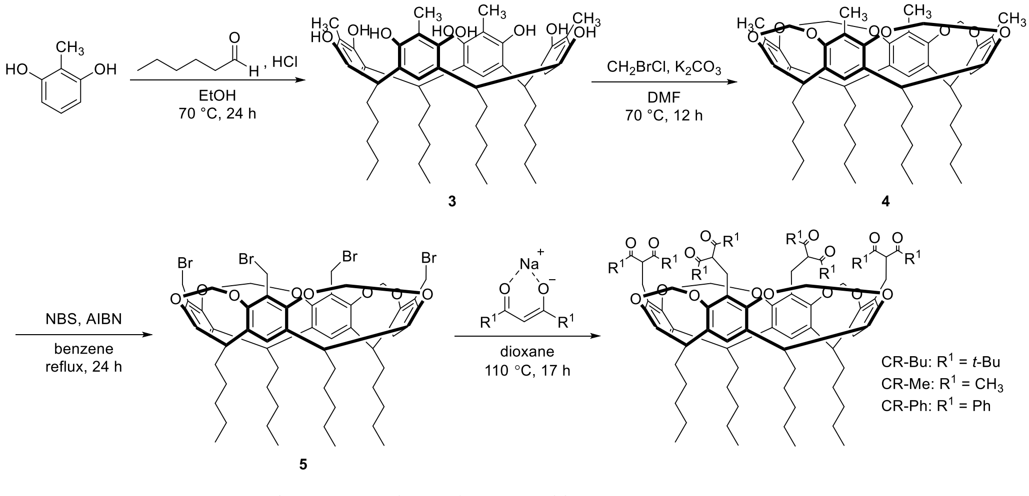
Tetrakis(bromomethyl)cavitand **5** [55]. A solution of tetramethylcavitand **4** (5.5 g, 6.3 mmol, 1.0 equiv.), AIBN (0.6 mmol, 0.1 equiv.), and recrystallized NBS (25.2 mmol, 4.0 equiv.) in benzene (200 mL) were stirred at room temperature for 30 min. Subsequently, the reaction mixture was transferred to a preheated oil bath (80 °C) and stirred vigorously for 24 h. After completion of the reaction, the precipitated succinimide was removed by filtration, and the benzene was evaporated under reduced pressure. Finally, the crude product was purified by column chromatography to afford tetrakis(bromomethyl) cavitand **5** as a white crystalline solid, yield 6.0 g (80 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (s, 4H), 6.02 (d, $J = 6.9$ Hz, 4H), 4.78 (t, $J = 8.0$ Hz, 4H), 4.56 (d, $J = 7.3$ Hz, 4H), 4.42 (s, 8H), 2.20 (q, $J = 7.9$ Hz, 8H), 1.47–1.28 (m, 24H), 0.91 (t, $J = 7.0$ Hz, 12H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.7, 138.2, 124.7, 121.1, 99.3, 37.0, 32.1, 30.2, 27.7, 23.1 22.8, 14.2.

General Procedure for Synthesizing Cavitand CR [51]: A mixture of sodium salt of diketone (5.1 mmol, 6.0 equiv.) and 1.0 g tetrakis(bromomethyl)cavitand 5 (0.84 mmol, 1.0 equiv.) in 20 mL anhydrous dioxane was placed in a 100 mL pressure vessel and stirred at 110 °C for 17 h in oil bath. After the mixture was cooled to room temperature and filtered to remove insoluble residues. The filtrate was concentrated under reduced pressure. The residue was acidified with aqueous HCl (20 mL, 1 M), followed by the addition of dichloromethane (20 mL). The organic layer was separated, washed with water (3 × 20 mL), and dried over anhydrous $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated under reduced pressure to obtain the crude product. Finally, purification by flash column chromatography separation (PE: EA = 50: 1–20: 1, v/v) afford white powder cavitand CR, the product was further dried under vacuum at 40 °C for 24 h, yield 71–83 %.

Cavitand CR-Bu. Yield 5.8 g (71 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.97 (d, $J = 13.8$ Hz, 4H), 5.76 (dd, $J = 12.7$, 7.0 Hz, 4H), 4.72–4.59 (m, 4H), 4.17 (t, $J = 7.2$ Hz, 4H), 3.86 (t, $J = 6.4$ Hz, 3H), 2.80 (d, $J = 6.3$ Hz, 8H), 2.13 (s, 31H), 1.48–1.22 (m, 24H), 0.91 (t, $J = 6.9$ Hz, 12H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.0, 153.2, 153.2, 138.3, 138.3, 125.0, 119.2, 98.8, 67.6, 37.0, 32.0, 30.1, 29.5, 27.6, 23.6, 22.8, 14.2. HRMS-TOF (*m/z*): calcd for $C_{100}H_{145}O_{16}$ $[M + H]^{+}$ 1602.0533, found: 1602.0529.

Cavitand CR-Me. Yield 5.4 g (83 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.97 (s, 4H), 5.89 (d, $J = 7.1$ Hz, 4H), 4.97 (t, $J = 6.5$ Hz, 4H), 4.72 (t, $J = 8.1$ Hz, 4H), 4.08 (d, $J = 7.2$ Hz, 4H), 2.79 (d, $J = 6.5$ Hz, 8H), 2.11 (q, $J = 7.8$ Hz, 8H), 1.40–1.25 (m, 24H), 1.05 (s, 72H), 0.90 (t, $J = 7.1$ Hz, 12H). ^{13}C NMR (100 MHz, Chloroform-*d*)δ 208.9, 153.5, 137.8, 124.9, 118.8, 98.8, 52.8, 44.8, 36.8, 31.8, 30.2, 27.5, 27.0, 26.9, 22.7, 13.9. FT-IR (cm^{-1}) 2924, 2861, 1632, 1453, 1389, 1344, 1301, 1237, 1144, 1083, 1010, 967, 936, 883. HRMS-TOF (*m/z*): calcd for $C_{76}H_{97}O_{16}$ $[M + H]^{+}$ 1265.6777, found: 1265.6771.

Cavitand CR-Ph. Yield 7.0 g (78 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, $J = 7.2$ Hz, 16H), 7.45 (t, $J = 7.4$ Hz, 8H), 7.29 (t, $J = 7.7$ Hz, 16H), 6.67 (s, 4H), 5.70 (d, $J = 6.9$ Hz, 4H), 5.46 (t, $J = 6.9$ Hz, 4H), 4.37 (t, $J = 8.0$ Hz, 4H), 4.15 (d, $J = 7.0$ Hz, 4H), 3.04 (d, $J = 6.9$ Hz,



Scheme 2. Synthesis of tetra-1,3-diketone resorcinarene CR.

8H), 1.90–1.86 (q, $J = 8.0$ Hz, 8H), 1.40–1.35 (m, 16H), 1.01–0.95 (m, 12H). ^{13}C NMR (100 MHz, Chloroform-*d*)δ 156.7, 135.3, 128.3, 122.0, 31.1, 23.4, 10.5. FT-IR (cm^{-1}) 2929, 2861, 1635, 1448, 1394, 1303, 1235, 1147, 1083, 1010, 967, 931, 685. HRMS-TOF (*m/z*): calcd for $C_{114}H_{117}O_{16}$ $[M + H]^+$ 1764.8239, found: 1764.8232.

Analog molecular M-Me. The preparation method is analogous to that of CR. A mixture of sodium salt of the sodium salt of acetylacetone (0.46 g, 3.7 mmol, 1.5 equiv.) and 2,6-dimethylbenzyl bromide (0.5 g, 2.5 mmol, 1.0 equiv.) in 8 mL anhydrous dioxane was placed in a 25 mL pressure vessel and stirred at 110 °C for 17 h in oil bath. After the mixture was cooled to room temperature and filtered to remove insoluble residues. The filtrate was concentrated under reduced pressure. The residue was acidified with aqueous HCl (8 mL, 1 M), followed by the addition of dichloromethane (10 mL). The organic layer was separated, washed with water (3 × 10 mL), and dried over anhydrous $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated under reduced pressure to obtain the crude product. Finally, purification by flash column chromatography separation (PE: EA = 80: 1, v/v) afford pale-yellow liquid, the product was further dried under vacuum at 40 °C for 24 h, yield 4.1 g (87 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.06–6.97 (m, 3H), 3.93 (t, $J = 7.2$ Hz, 1H), 3.21 (d, $J = 7.2$ Hz, 2H), 2.28 (s, 6H), 2.07 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.4, 136.6, 135.2, 128.8, 126.8, 66.9, 30.4, 28.5, 20.3. HRMS-TOF (*m/z*): calcd for $C_{12}H_{15}O_2$ $[M+H]^+$ 191.1072, found: 191.1071.

2.4. General procedure for the cycloaddition of epoxides and CO_2

In a 2.0 mL glass vial, styrene oxide (0.57 mL, 5.0 mmol), cavitand CR (0.005 mmol, 0.1 mol%), and organic base (0.02 mmol, 0.4 mol%) were combined, and the mixture was stirred at room temperature for 10 min. The resulting solution was transferred to a 25 mL stainless steel autoclave reactor. The reactor was sealed and subjected to three consecutive purge cycles with CO_2 through alternating vacuum and gas-fill sequences. Following the purge procedure, the system was pressurized to 0.5 MPa with CO_2 and immersed in a preheated oil bath maintained at 120 °C, where it was stirred for 12 h to facilitate the reaction. The reactor was immediately cooled to 0 °C in an ice-water bath. The pressure was carefully released to atmospheric conditions by gradual valve opening. A sample of the crude reaction mixture was dissolved in chloroform-*d* containing 1,3,5-trimethoxybenzene as an internal standard [56]. Conversion of epoxide **1** and selectivity of cyclic carbonate **2** were determined by ^{1}H NMR. For reaction under atmospheric pressure (0.1 MPa), a 25 mL Schlenk reaction tube equipped with a CO_2-filled balloon was employed instead of the reactor. Cyclic carbonate products were obtained by flash chromatography on silica gel (SiO_2) with hexane: ethyl acetate = 10: 1–3: 1.

3. Results and discussion

3.1. Design of resorcinarene ion pair catalysts and evaluation of the catalytic performances in CCE reactions

Among the various functional building blocks that exist, 1,3-diketones have emerged as pivotal reagents, extensively employed in the design of diverse fine chemical and pharmaceutical agents [49]. The presence of two strongly electron-withdrawing carbonyl groups in 1, 3-diketones facilitates the formation of stabilized carbanions through α-proton abstraction upon treatment with Brønsted bases. The resulting carbanion exhibits significant electron delocalization towards both carbonyl groups, thereby enhancing charge distribution and thermodynamic stability. We propose to utilize these stabilized carbanions as Lewis basic sites for CO_2 activation, generating carboxylate anions that may serve as alternative nucleophiles for epoxide ring-opening reactions, potentially replacing conventional halide anions. The 1,3-diketone moiety has been incorporated into the upper rim structure of rigid, bowl-shaped resorcinarene scaffolds, three functionalized derivatives bearing *tert*-butyl (CR-Bu), methyl (CR-Me) and phenyl (CR-Ph) substituents were obtained (Fig. 1). The resulting compounds were comprehensively characterized using NMR, IR, and thermogravimetric analysis (TGA).

Notably, the keto-enol transformation was found to be significantly restricted due to steric hindrance induced by cavitand. The use of ^{1}H NMR studies in $CDCl_3$ revealed minimal enol content (≤5–10 %) in solution. These observations were further corroborated by X-ray crystallographic analysis conducted by Zairov's group, which confirmed that CR-Me derivative adopts a "cone" conformation. In this configuration, the pendant aryl rings exhibit nearly identical spatial orientations relative to the reference plane defined by the four bridging carbon atoms [57].

Homogeneous solution was prepared by dissolving CR and TBD in styrene in a stoichiometric ratio of 1: 4, and the catalytic performance was evaluated at 120 °C with a CO_2 pressure of 0.5 MPa. The obtained results revealed that the methyl-substituted CR-Me/TBD system exhibited superior activity (Table 1, entries 1–3). This observation can be rationalized by considering the delicate balance between carbanions stability and basicity: while the strongly electron-donating *tert*-butyl group enhanced the nucleophilicity of carbanions, it concomitantly reduced its thermodynamic stability. Conversely, the electron-withdrawing phenyl group not only diminished carbanion's basicity but also introduced substantial steric hindrance, thereby significantly compromising catalytic performance.

The catalytic performance was further evaluated by other organic bases, and a trend of CR-Me/TBD (75 %) > CR-Me/MTBD (64 %) > CR-Me/DBU (50 %) activity was found (Table 1, entries 2, 4, and 5). This result seems to be due to the alkalinity, but we believe that it was a coincidental result due to the combined influence of a complex of factors, including: i) Carbon ion concentration. ^{1}H NMR analysis of a mixture of CR and base according to a 1:4 stoichiometric ratio was conducted, revealing that the more strongly basic TBD (p*K*a = 15 0.3) and MTBD (p*K*a = 14.8) completely deprotonated the CR-Me, thereby generating stable carbanions and a minor amount of allylic alcohol anion. In contrast, the relatively weak base DBU (p*K*a = 13.9) achieved only partial deprotonation (~50 %, Fig. 2). (ii) Mechanistic differences. In contrast to the CR-Me/TBD and CR-Me/MTBD catalytic systems, free DBU in the CR-Me/DBU system may participate in the reaction through an alternative pathway of competitive activation of CO_2. (iii), there is the complex host-guest behavior of resorcinarene. The deprotonation of the upper rim of carbanions results in the formation of local electron-rich centers where the cations ($[TBDH]^+$, $[MTBDH]^+$, or $[DBUH]^+$) are more likely to be enriched, and the binding strength is also affected by the structural smallness of the; (iv), the H-bonding ability of the cations is a contributing factor. In comparison to $[MTBDH]^+$, $[TBDH]^+$

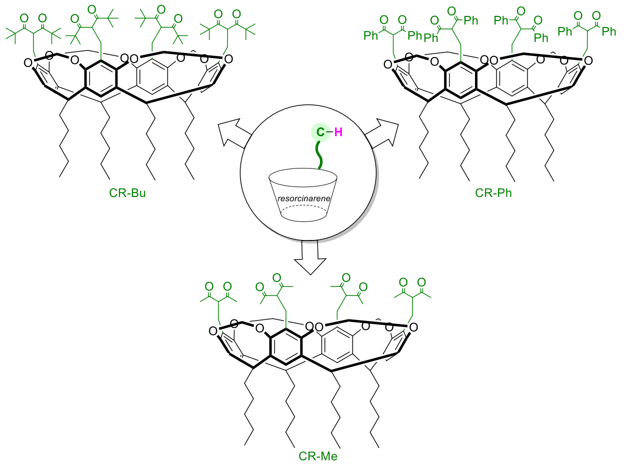
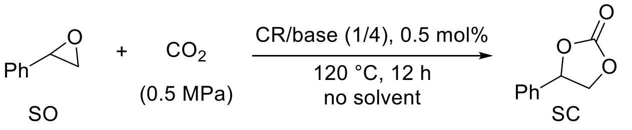


Fig. 1. The structure of various tetra-1,3-diketone resorcinarene **CR**.

Table 1

The cycloadditions of CO_2 to SO promoted by different resorcinarene ion pair catalysts.



Entry	Catalyst	Conv.[a] [%]	Yield[a] [%]	Sel.[a] [%]	TON[b]	TOF[b] [h^{-1}]
1	CR-Bu/TBD	69	69	>99	34.56	2.88
2	CR-Me/TBD	75	74	98	36.96	3.08
3	CR-Ph/TBD	63	60	95	30.00	2.50
4	CR-Me/MTBD	64	61	95	30.48	2.54
5	CR-Me/DBU	50	50	>99	25.00	2.08
6	CR-Me/-	0	0	–	–	–
7[c]	-/TBD	45	39	87	4.88	0.41
8[c]	M-Me/TBD (1/1)	52	42	80	5.25	0.44

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.

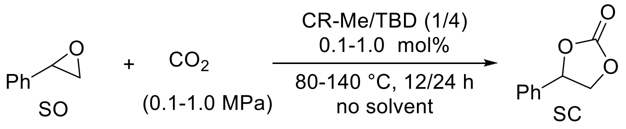
[a] Conversion and selectivity were determined via ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

[b] Turnover number (TON) = moles of product/(moles of 1,3-diketone unit in catalysts). Turnover frequency (TOF) = moles of product/(moles of 1,3-diketone unit in catalysts × time).

[c] catalyst loading (2.0 mol% = 4 × 0.5 mol%).

Table 2

Optimization of reaction conditions for the cycloaddition of CO_2 to epoxides.



Entry	Catalyst Loading [mol%]	Temp. [°C]	Time [h]	P(CO_2) [MPa]	Conv.[a] [%]	Sel.[a] [%]	TOF[b]
1	0.1	120	12	0.1	68	95	13.46
2	0.1	120	12	0.5	75	98	15.31
3	0.1	120	12	1.0	81	>99	16.71
4	0.1	120	24	0.1	93	95	9.20
5	0.1	80	24	0.1	42	77	3.37
6	0.1	100	24	0.1	64	87	5.80
7	0.1	140	12	0.1	97	84	16.98
8	0.3	120	12	0.1	77	92	4.92
9	0.5	120	12	0.1	90	92	3.45
10	1.0	120	12	0.1	98	88	1.80

Reaction conditions unless specified otherwise: SO (5.0 mmol, 0.57 mL), no solvent.

[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 1,3-diketone in catalysts × time).

exhibits a greater abundance of N–H groups and demonstrates more robust HBD capability.

In addition, the non-ionic CR-Me precursor showed negligible catalytic activity, while TBD alone afforded merely 45 % conversion with 87 % selectivity (Table 1, entries 6–7). Notably, when employing a 1: 1 ion pair formed between the CR-Me monomer analog M-Me and TBD, both conversion (52 %) and selectivity (80 %) were substantially reduced (Table 1, entry 8). This diminished performance may be attributed to either dilution effects or unfavorable keto–enol transformation of the monomers. These findings conclusively demonstrate that the rigid resorcinarene scaffold plays a dual role in the cycloaddition reaction: it not only enhances catalytic activity but also improves reaction selectivity.

To evaluate the catalytic performance of resorcinarene ion pairs under mild conditions, we examined the CR-Me/TBD catalyzed cycloaddition of CO_2 with epoxides was examined under different reaction parameters. Initial experiments were conducted with 0.1 mol% catalyst loading at 120 °C for 12 h while varying CO_2 pressure (0.1, 0.5, and 1.0 MPa). The results demonstrated a positive correlation between CO_2 pressure and conversion rate, increasing from 68 % to 81 % (Table 2, entries 1–3). To achieve satisfactory conversion under atmospheric pressure (P (CO_2) = 0.1 MPa), it was prolonged to 24 h with a conversion of 93 % (Table 2, entry 4). Subsequent temperature optimization revealed that reducing the temperature to 100 °C and 80 °C significantly decreased conversions to 64 % and 42 %, respectively, while elevating to 140 °C improved conversion at the expense of slightly reduced selectivity (Table 2, entries 5–7). Notably, increasing the catalyst loading to 1 mol% under ambient pressure conditions afforded 98 % conversion, albeit with decreased selectivity (88 %) (Table 2, entries 8–10). Comprehensive analysis identified the optimal reaction conditions as:

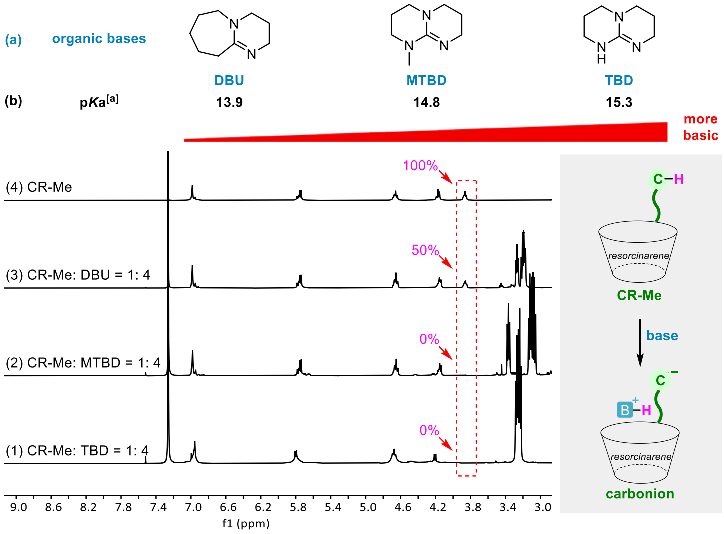
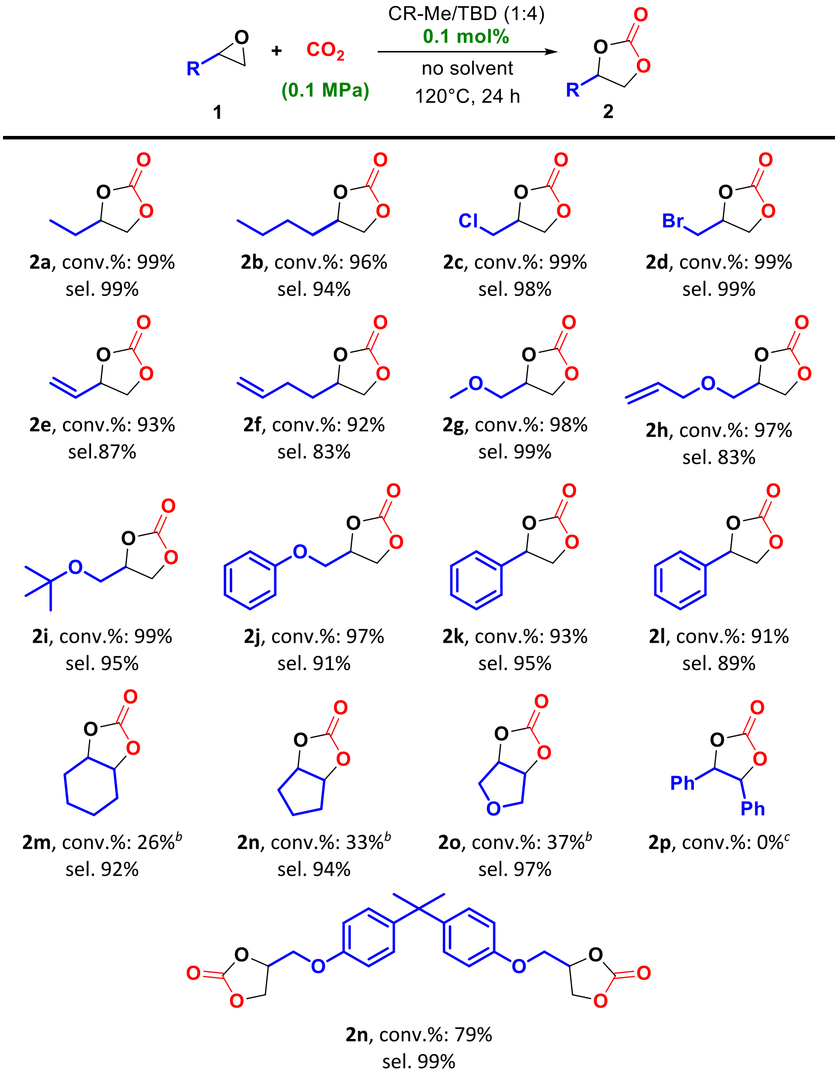


Fig. 2. (a) The p*K*a values of conjugated acids of organic bases in DMSO [58]; (b) ^{1}H NMR (400 MHz, Chloroform-*d*) spectra of 1,3-diketone resorcinarene CR-Me mixed with organic base at ratio of 1: 4.

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



2a, conv.%: 99%
sel. 99%

2b, conv.%: 96%
sel. 94%

2c, conv.%: 99%
sel. 98%

2d, conv.%: 99%
sel. 99%

2e, conv.%: 93%
sel.87%

2f, conv.%: 92%
sel. 83%

2g, conv.%: 98%
sel. 99%

2h, conv.%: 97%
sel. 83%

2i, conv.%: 99%
sel. 95%

2j, conv.%: 97%
sel. 91%

2k, conv.%: 93%
sel. 95%

2l, conv.%: 91%
sel. 89%

2m, conv.%: 26%[b]
sel. 92%

2n, conv.%: 33%[b]
sel. 94%

2o, conv.%: 37%[b]
sel. 97%

2p, conv.%: 0%[c]

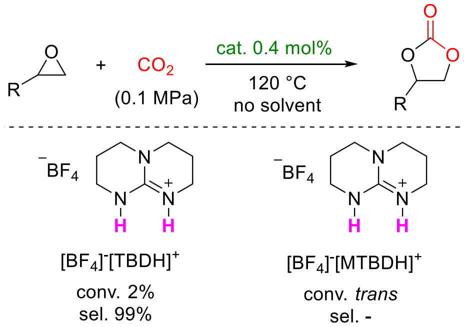
2n, conv.%: 79%
sel. 99%

[a] Reaction conditions: 0.1 mol% CR-Me/TBD, 120 °C, 0.1 MPa CO_2 (use a balloon), 24 h, no solvent. [b] 0.4 mol% CR-Me/TBD, 120 °C, 1.0 MPa, 48 h [c] *n*-Butanol was employed as a solvent, 1.0 M **1p**, 120 °C, 1.0 MPa CO_2, 48 h.

120 °C, 0.1 mol% catalyst loading, 0.1 MPa CO_2 pressure, and 24 h, which balanced both conversion efficiency and selectivity.

3.2. Substrate scope studies for cycloaddition of epoxides into CO_2 catalyzed by CR-Me/TBD

With optimized reaction conditions (120 °C, 0.1 MPa CO_2, 24 h), we further investigated the substrate scope of the CR-Me/TBD catalyzed cycloaddition reaction using various epoxides (Table 3). Remarkably, terminal epoxides, including aliphatic (**1a**–**1f**), glycidyl (**1g**–**1j**) and aromatic (**1k**–**1l**) derivatives, all exhibited excellent conversions (>90 %) under atmospheric CO_2 pressure, with exceptional selectivity (83–99 %) towards the corresponding cyclic carbonates. However, sterically hindered internal epoxides showed markedly different reactivity behavior. Cyclohexene oxide showed no detectable conversion under optimized conditions. By applying more stricter conditions (1.0 MPa CO_2, 0.4 mol% catalyst loading, 48 h) moderate conversions were obtained for the internal epoxides: cyclohexene oxide (16 %), **1n** (23 %) and **1o** (37 %). Notably, the highly hindered diphenyl-substituted epoxide **1p** remained unreactive even under these improved conditions.



Scheme 3. The catalytic performance of catalyst analogs ion pairs were compared under optimized conditions.

3.3. Proposition of the mechanism of the CCE reaction by halide organocatalyst CR-Me/TBD

The activation mechanism was further elucidated through control

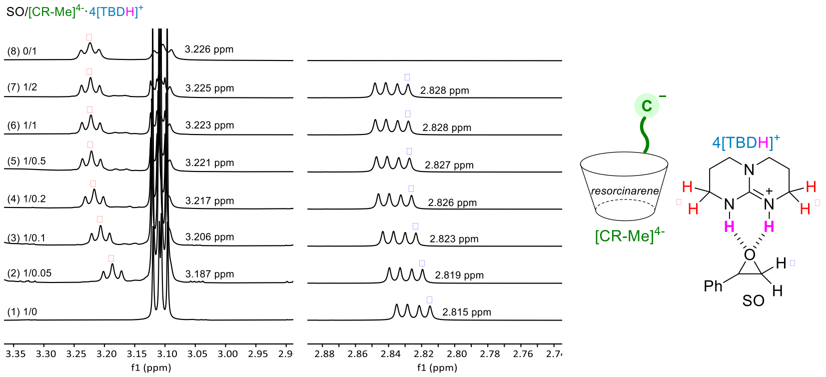


Fig. 3. Chemical shifts of the C–H proton of the [TBDH]$^{+}$ (pink circle) and methylene protons (blue squares) of the substrate SO in the titration in the ^{1}H NMR spectra (DMSO-*d*6), the series ratios of SO/[CR-Me]$^{4-}$·4[TBDH]$^{+}$ in (1) 1/0, (2) 1/0.05, (3) 1/0.1, (4) 1/0.2, (5)1/0.5, (6) 1/1, (7) 1/2, and (8) 0/1.

experiments, which verified the essential role of the resorcinarene carbanion [CR-Me]$^{4-}$, we prepared analog catalysts [TBDH]$^{+}$·[BF$_4$]$^{-}$ and [MTBDH]$^{+}$·[BF$_4$]$^{-}$ by replacing the reactive [CR-Me]$^{4-}$ with inert [BF$_4$]$^{-}$ anions [42]. When evaluated under optimized cycloaddition conditions, these modified catalysts showed negligible activity (Scheme 3), clearly demonstrating that the 1,3-diketone-functionalized resorcinarene scaffold is essential for catalytic activity. The proposed activation involves Brønsted base abstraction of the CR-Me methylene proton by TBD, generating the conjugate acid [TBDH]$^{+}$. Comparative studies revealed the superior performance of the CR-Me/TBD system (75 % conversion) over CR-Me/MTBD (64 % conversion) in Table 1, suggesting the critical role of the N–H groups in [TBDH]$^{+}$ as HBDs.

The resorcinarene-based ion pair [CR-Me]$^{4-}$·4[TBDH]$^{+}$ was prepared by mixing the resorcinarene CR-Me with the organic base TBD in dichloromethane in a ratio of 1: 4 for 10 min at room temperature, with direct removal of the solvent. To experimentally verify these interactions, we performed ^{1}H NMR titration studies (Fig. 3). The chemical shift changes of the methylene protons in the adjacent region were recorded, while the labile N–H protons were not directly observable. Progressive addition of [CR-Me]$^{4-}$·4[TBDH]$^{+}$ to SO (molar ratio 1: 0.05 to 1: 2) induced characteristic upfield shifts: The methylene protons of [TBDH]$^{+}$ (pink circles) shifted from 3.187 ppm to 3.224 ppm, while the methyl protons of SO (blue squares) shifted from 2.815 ppm to 2.828 ppm. These systematic chemical shift perturbations provide indirect evidence for H-bonding interactions between the catalyst and the epoxide substrate, and support the proposed activation mechanism.

Based on the experimental evidence and supported by previous mechanism studies [50,56,59], a plausible catalytic cycle for this transformation is proposed (Scheme 4). The reaction mechanism involves four distinct steps: Step I, the nucleophilic addition of the [CR-Me]$^{4-}$ carbanion to CO$_2$ generates the reversible carboxylate intermediate **A**. Step II, the [TBDH]$^{+}$ cation activates the epoxide **1** through H-bond formation. Step III, the activated carboxylate species then undergoes nucleophilic attack on the less hindered methylene carbon of the epoxide to yield the alkoxide intermediate **C**. Step IV, the end of alkoxides **C** initiates an SN2 nucleophilic attack within the molecule, and the ring closes to produce the cyclic carbonate **2**.

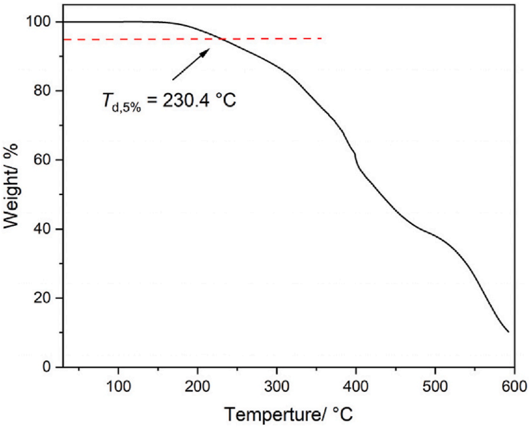


Fig. 4. TGA thermogram of resorcinarene ion pair catalyst [CR-Me]$^{4-}$·4 [TBDH]$^{+}$. Determined by TGA at a heat in grate under N$_2$ atmosphere, operation procedure: heat from room temperature to 600 °C at 10 °C/min.

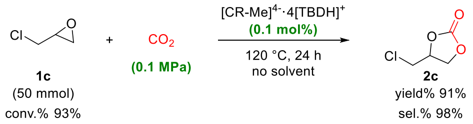
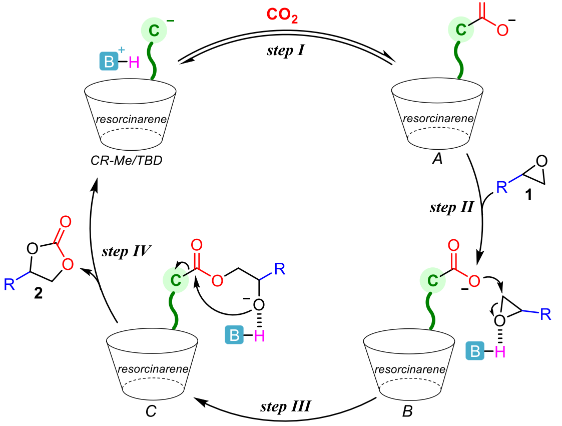


Fig. 5. Larger-scale synthesis.



Scheme 4. Proposed mechanism for the formation of cyclic carbonates from epoxides and CO$_2$ promoted by resorcinarene ion pair catalyst CR-Me/TBD.

3.4. *Catalyst recycling of CCE reaction catalyzed by CR-Me/TBD*

Thermogravimetric analysis (TGA) was performed under a N$_2$ atmosphere with a heating rate of 10 °C/min from 30 to 600 °C. The results revealed negligible mass loss below 150 °C, confirming the high thermal stability of the ion pair catalyst [CR-Me]$^{4-}$·4[TBDH]$^{+}$ under optimized reaction conditions. A 5 wt% mass loss was observed at 230.4 °C (Fig. 4), further supporting the robustness of the catalyst structure. To assess recyclability, the reaction was scaled up 10-fold

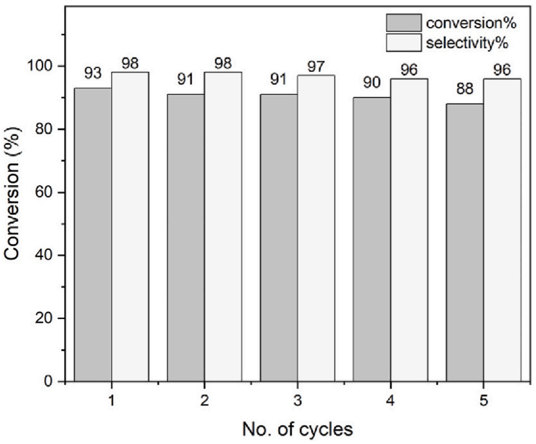


Fig. 6. Recyclability study of resorcinarene ion pair catalyst $[\text{CR-Me}]^{4-}\cdot 4[\text{TBDH}]^{+}$. Reaction conditions: ECH (50.0 mmol, 3.9 mL), $[\text{CR-Me}]^{4-}\cdot 4[\text{TBDH}]^{+}$ (0.05 mmol, 0.1mol %), 120 °C, 0.1 MPa CO_2, 24 h, solvent-free.

using epichlorohydrin (ECH) as a model substrate under optimized conditions (0.1 MPa CO_2, 0.1 mol% catalyst loading, 24 h), achieving 93 % conversion (Fig. 5). Since the ion pair catalyst is insoluble in diethyl ether, the cyclic carbonate products and unreacted epichlorohydrin (ECH) are removed via ether extraction after each reaction cycle. Following solvent evaporation and drying, the recovered catalyst is reactivated through the addition of fresh ECH for subsequent reaction cycles. The catalyst maintained high activity over five consecutive cycles, with only a slight decrease in conversion from 93 % to 88 % (Fig. 6), ^{1}H NMR analysis indicated that the slight deactivation might result from partial catalyst decomposition upon repeated use (Fig. S17).

4. Conclusions

In conclusion, this study successfully developed a highly efficient and reusable resorcinarene-based ion pair catalytic system (CR-Me/TBD) for the cycloaddition of CO_2 to epoxides under mild conditions. The optimal catalyst exhibited outstanding performance, achieving 93 % conversion of styrene oxide at ambient CO_2 pressure (0.1 MPa) and 120 °C, while demonstrating broad substrate scope with >91 % conversion for 12 terminal epoxides and good activity for sterically hindered internal epoxides under elevated pressure. Detailed mechanistic investigations revealed a synergistic dual-activation mechanism, where the $[\text{TBDH}]^{+}$ cation activates epoxides through H-bonding while the $[\text{CR-Me}]^{4-}$ carbanion facilitates CO_2 activation, with NMR studies providing evidence for these interactions. The catalyst showed excellent thermal stability ($T_{d,5\,\%} > 230\,^{\circ}C$) and maintained high activity over five consecutive cycles (93 %–88 % conversion). This work not only presents a practical solution for CO_2 utilization but also provides fundamental insights into the design of cooperative ion pair catalysts, offering a promising strategy for developing advanced catalytic systems for sustainable chemical transformations.

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. **Yujia Wang:** Methodology. **Min Zhang:** Methodology. **Xin Yuan:** Methodology. **Xin Zou:** Methodology. **Chunyu Li:** Methodology. **Tianyu Zhu:** 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2025.134897.

Data availability

Data will be made available on request.

References

[1] A.J. Hunt, E.H.K. Sin, R. Marriott, J.H. Clark, Generation, capture, and utilization of industrial carbon dioxide, ChemSusChem 3 (3) (2010) 306–322.
[2] Q. Liu, L. Wu, R. Jackstell, M. Beller, Using carbon dioxide as a building block in organic synthesis, Nat. Commun. 6 (1) (2015) 5933.
[3] J.H. Clements, Reactive applications of cyclic alkylene carbonates, Ind. Eng. Chem. Res. 42 (4) (2003) 663–674.
[4] B. Schäffner, F. Schäffner, S.P. Verevkin, A. Börner, Organic carbonates as solvents in synthesis and catalysis, Chem. Rev. 110 (8) (2010) 4554–4581.
[5] J.P. Vivek, N. Berry, G. Papageorgiou, R.J. Nichols, L.J. Hardwick, 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) (2016) 3745–3751.
[6] W. Yu, E. Maynard, V. Chiaradia, M.C. Arno, A.P. Dove, Aliphatic polycarbonates from cyclic carbonate monomers and their application as biomaterials, Chem. Rev. 121 (18) (2021) 10865–10907.
[7] G. Rokicki, P.G. Parzuchowski, M. Mazurek, Non-isocyanate polyurethanes: synthesis, properties, and applications, Polym. Adv. Technol. 26 (7) (2015) 707–761.
[8] M. Cokoja, C. Bruckmeier, B. Rieger, W.A. Herrmann, F.E. Kühn, Transformation of carbon dioxide with homogeneous transition-metal catalysts: a molecular solution to a global challenge? Angew. Chem. Int. Ed. 50 (37) (2011) 8510–8537.
[9] M. Cokoja, M.E. Wilhelm, M.H. Anthofer, W.A. Herrmann, F.E. Kuhn, Synthesis of cyclic carbonates from epoxides and carbon dioxide by using organocatalysts, ChemSusChem 8 (15) (2015) 2436–2454.
[10] G. Fiorani, W. Guo, A.W. Kleij, Sustainable conversion of carbon dioxide: the advent of organocatalysis, Green Chem. 17 (3) (2015) 1375–1389.
[11] M. Alves, B. Grignard, R. Mereau, C. Jerome, T. Tassaing, C. Detrembleur, Organocatalyzed coupling of carbon dioxide with epoxides for the synthesis of cyclic carbonates: catalyst design and mechanistic studies, Catal. Sci. Technol. 7 (13) (2017) 2651–2684.
[12] L. Guo, K.J. Lamb, M. North, Recent developments in organocatalysed transformations of epoxides and carbon dioxide into cyclic carbonates, Green Chem. 23 (1) (2021) 77–118.
[13] C.J. Whiteoak, A. Nova, F. Maseras, A.W. Kleij, Merging sustainability with organocatalysis in the formation of organic carbonates by using CO(2) as a feedstock, ChemSusChem 5 (10) (2012) 2032–2038.
[14] S. Sopeña, E. Martin, E.C. Escudero-Adán, A.W. Kleij, Pushing the limits with squaramide-based organocatalysts in cyclic carbonate synthesis, ACS Catal. 7 (5) (2017) 3532–3539.
[15] H. Büttner, L. Longwitz, J. Steinbauer, C. Wulf, T. Werner, Recent developments in the synthesis of cyclic carbonates from epoxides and CO_2, Top. Curr. Chem. 375 (3) (2017) 50.
[16] S. Gennen, M. Alves, R. Mereau, T. Tassaing, B. Gilbert, C. Detrembleur, C. Jerome, B. Grignard, Fluorinated alcohols as activators for the solvent-free chemical fixation of carbon dioxide into epoxides, ChemSusChem 8 (11) (2015) 1845–1849.
[17] J. Wang, Y. Zhang, Boronic acids as hydrogen bond donor catalysts for efficient conversion of CO_2 into organic carbonate in water, ACS Catal. 6 (8) (2016) 4871–4876.

[18] Y.A. Alassmy, P.P. Pescarmona, The role of water revisited and enhanced: a sustainable catalytic system for the conversion of CO(2) into cyclic carbonates under mild conditions, ChemSusChem 12 (16) (2019) 3856–3863.

[19] H. Büttner, K. Lau, A. Spannenberg, T. Werner, Bifunctional one-component catalysts for the addition of carbon dioxide to epoxides, ChemCatChem 7 (3) (2014) 459–467.

[20] M. Hong, Y. Kim, H. Kim, H.J. Cho, M.-H. Baik, Y. Kim, Scorpionate catalysts for coupling CO_2 and epoxides to cyclic carbonates: a rational design approach for organocatalysts, J. Org. Chem. 83 (16) (2018) 9370–9380.

[21] Y. Hu, X. Du, Z. Li, J. He, T. Chang, N. Shi, N. Li, X. Zou, J. Sun, K. Guo, Monodentate h-bond donor bifunctional catalyst in fixation of atmospheric pressure carbon dioxide into cyclic carbonates, Mol. Catal. 553 (2024) 113765.

[22] Y. Toda, Y. Komiyama, A. Kikuchi, H. Suga, Tetraarylphosphonium salt-catalyzed carbon dioxide fixation at atmospheric pressure for the synthesis of cyclic carbonates, ACS Catal. 6 (10) (2016) 6906–6910.

[23] S. Liu, N. Suematsu, K. Maruoka, S. Shirakawa, Design of bifunctional quaternary phosphonium salt catalysts for CO_2 fixation reaction with epoxides under mild conditions, Green Chem. 18 (17) (2016) 4611–4615.

[24] J. Steinbauer, C. Kubis, R. Ludwig, T. Werner, Mechanistic study on the addition of CO_2 to epoxides catalyzed by ammonium and phosphonium salts: a combined spectroscopic and kinetic approach, ACS Sustain. Chem. Eng. 6 (8) (2018) 10778–10788.

[25] Y. Xie, Z. Zhang, T. Jiang, J. He, B. Han, T. Wu, K. Ding, CO_2 cycloaddition reactions catalyzed by an ionic liquid grafted onto a highly cross-linked polymer matrix, Angew. Chem. Int. Ed. 46 (38) (2007) 7255–7258.

[26] J. Sun, W. Cheng, W. Fan, Y. Wang, Z. Meng, S. Zhang, Reusable and efficient polymer-supported task-specific ionic liquid catalyst for cycloaddition of epoxide with CO_2, Catal. Today 148 (3) (2009) 361–367.

[27] S. Wu, B. Wang, Y. Zhang, E.H.M. Elageed, H. Wu, G. Gao, Phenolic hydroxyl-functionalized imidazolium ionic liquids: highly efficient catalysts for the fixation of CO_2 to cyclic carbonates, J. Mol. Catal. A: Chem. 418–419 (2016) 1–8.

[28] A.W. Kleij, Advancing halide-free catalytic synthesis of CO_2-based heterocycles, Curr. Opin. Green Sustainable Chem. 24 (2020) 72–81.

[29] F. Zhang, Y. Wang, X. Zhang, X. Zhang, H. Liu, B. Han, Recent advances in the coupling of CO_2 and epoxides into cyclic carbonates under halogen-free condition, Green Chem. Eng. 1 (2) (2020) 82–93.

[30] J. Li, C. Yue, W. Ji, B. Feng, M.-Y. Wang, X. Ma, Recent advances in cycloaddition of CO_2 with epoxides: halogen-free catalysis and mechanistic insights, Front. Chem. Sci. Eng. 17 (12) (2023) 1879–1894.

[31] H. Yasuda, L.-N. He, T. Sakakura, C. Hu, Efficient synthesis of cyclic carbonate from carbon dioxide catalyzed by polyoxometalate: the remarkable effects of metal substitution, J. Catal. 233 (1) (2005) 119–122.

[32] H.-G. Kim, C.-S. Lim, D.-W. Kim, D.-H. Cho, D.-K. Lee, J.S. Chung, Multifunctional alkanolamine as a catalyst for CO_2 and propylene oxide cycloaddition, Mol. Catal. 438 (2017) 121–129.

[33] X. Wu, C. Chen, Z. Guo, M. North, A.C. Whitwood, Metal- and halide-free catalyst for the synthesis of cyclic carbonates from epoxides and carbon dioxide, ACS Catal. 9 (3) (2019) 1895–1906.

[34] P. Goodrich, H.Q.N. Gunaratne, J. Jacquemin, L. Jin, Y. Lei, K.R. Seddon, Sustainable cyclic carbonate production, utilizing carbon dioxide and azolate ionic liquids, ACS Sustain. Chem. Eng. 5 (7) (2017) 5635–5641.

[35] S. Yue, H.-L. Qu, X.-X. Song, X.-N. Feng, 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) (2022) 5881–5888.

[36] Y.-M. Shen, W.-L. Duan, M. Shi, Phenol and organic bases co-catalyzed chemical fixation of carbon dioxide with terminal epoxides to form cyclic carbonates, Adv. Synth. Catal. 345 (3) (2003) 337–340.

[37] Y.-M. Shen, W.-L. Duan, M. Shi, Chemical fixation of carbon dioxide co-catalyzed by a combination of schiff bases or phenols and organic bases, Eur. J. Org. Chem. 2004 (14) (2004) 3080–3089.

[38] Y. Qi, W. Cheng, F. Xu, S. Chen, S. Zhang, Amino acids/superbases as eco-friendly catalyst system for the synthesis of cyclic carbonates under metal-free and halide-free conditions, Synth. Commun. 48 (8) (2018) 876–886.

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

[40] R. Ma, L.-N. He, X.-F. Liu, X. Liu, M.-Y. Wang, DBU as activator for the n -iodosuccinimide promoted chemical fixation of carbon dioxide with epoxides, J. CO2 Util. 19 (2017) 28–32.

[41] M. Sankar, T.G. Ajithkumar, G. Sankar, P. Manikandan, Supported imidazole as heterogeneous catalyst for the synthesis of cyclic carbonates from epoxides and CO_2, Catal. Commun. 59 (2015) 201–205.

[42] H. Tong, Y. Qu, Z. Li, J. He, X. Zou, Y. Zhou, T. Duan, B. Liu, J. Sun, K. Guo, Halide-free pyridinium saccharinate binary organocatalyst for the cycloaddition of CO_2 into epoxides, Chem. Eng. J. 444 (2022).

[43] B. Liu, T. Duan, Z. Li, J. He, W. Huang, J. Li, T. Zhu, C. Ma, J. Sun, K. Guo, Rigid tertiary amine/saccharin adduct as halide-free organocatalyst for the cycloaddition of CO_2 into epoxides, Fuel 348 (2023) 128478.

[44] V. Böhmer, Calixarenes, macrocycles with (almost) unlimited possibilities, Angew Chem. Int. Ed. Engl. 34 (7) (1995) 713–745.

[45] A. Ikeda, S. Shinkai, Novel cavity design using calix[n]arene skeletons: toward molecular recognition and metal binding, Chem. Rev. 97 (5) (1997) 1713–1734.

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

[47] M. Wang, T. Li, J. Shi, X. Sun, K. Yang, Z.Y. Li, Recent advances in calix[4]arene-catalyzed synthesis of five- and six-membered oxa- and azacycles, Eur. J. Org. Chem. 28 (15) (2025).

[48] N. Li, R.G. Harrison, J.D. Lamb, Application of resorcinarene derivatives in chemical separations, J. Inclusion Phenom. Macrocycl. Chem. 78 (1–4) (2013) 39–60.

[49] E.A. Shokova, J.K. Kim, V.V. Kovalev, 1,3-diketones. Synthesis and properties, Russ. J. Org. Chem. 51 (6) (2015) 755–830.

[50] P. Basuri, S. Mukhopadhyay, K.S.S.V.P. Reddy, K. Unni, B.K. Spoorthi, J. Shantha Kumar, S.S.R.K.C. Yamijala, T. Pradeep, Spontaneous α-c−h carboxylation of ketones by gaseous CO_2 at the air-water interface of aqueous microdroplets, Angew. Chem. Int. Ed. 63 (27) (2024) e202403229.

[51] N.A. Shamsutdinova, S.N. Podyachev, S.N. Sudakova, A.R. Mustafina, R.R. Zairov, V.A. Burilov, I.R. Nizameev, I.K. Rizvanov, V.V. Syakaev, B.M. Gabidullin, et al., A facile synthetic route to convert Tb(iii) complexes of novel tetra-1,3-diketone calix[4]resorcinarene into hydrophilic luminescent colloids, New J. Chem. 38 (9) (2014) 4130–4140.

[52] S.N. Podyachev, R.R. Zairov, A.R. Mustafina, 1,3-diketone calix[4]arene derivatives—a new type of versatile ligands for metal complexes and nanoparticles, Molecules 26 (5) (2021).

[53] H. Boerrigter, W. Verboom, G.J. van Hummel, S. Harkema, D.N. Reinhoudt, Selective functionalization of resorcinarene cavitands; single crystal x-ray structure of a distally functionalized cavitand, Tetrahedron Lett. 37 (29) (1996) 5167–5170.

[54] H. Boerrigter, W. Verboom, D.N. Reinhoudt, Novel resorcinarene cavitand-based CMP(O) cation ligands: synthesis and extraction properties, J. Org. Chem. 62 (21) (1997) 7148–7155.

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

[56] B. Liu, H. Yu, Z. Li, J. He, Y. Hu, X. Zou, L. Lu, S. Cao, C. Ma, K. Guo, Halide-free squaramide–phenolate organocatalyst for the cycloaddition of CO_2 into epoxides, J. Environ. Chem. Eng. 11 (5) (2023) 110886–110897.

[57] S.N. Podyachev, R.R. Zairov, A.R. Mustafina, 1,3-diketone calix[4]arene derivatives—a new type of versatile ligands for metal complexes and nanoparticles, Molecules 26 (5) (2021) 1214.

[58] S. Tshepelevitsh, A. Kütt, M. Lõkov, I. Kaljurand, J. Saame, A. Heering, P. G. Plieger, R. Vianello, I. Leito, On the basicity of organic bases in different media, Eur. J. Org. Chem. 2019 (40) (2019) 6735–6748.

[59] H. Zhou, X. Lu, Lewis base-CO_2 adducts as organocatalysts for CO_2 transformation, Sci. China Chem. 60 (7) (2017) 904–911.