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Organocatalyzed aza-Payne-type rearrangement of epoxy amines and carbon dioxide for efficient construction of oxazolidinones†

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The aza-Payne-type rearrangement reaction, employing epoxy amines and carbon dioxide (CO_2), offers an atom economical method for synthesizing 5-hydroxymethyl oxazolidinones. Traditionally, alkaline catalysts are primarily utilized for this transformation. In this work, a halide-free pyridinolate based binary organocatalyst was developed for this transformation under atmospheric pressure. The ion pair organocatalyst consists of a positively charged hydrogen-bond donor (HBD^+) and a negatively charged hydrogen bond acceptor (HBA^-). These HBD^+/HBA^- ion pair catalysts were generated through the deprotonation of weakly acidic 2-, 3-, and 4-hydroxy pyridine (4-HOP) using super strong nitrogen bases (*i.e.* TBD, MTBD, DBU, TMG, and DMAP). The reaction achieved high selectivity for oxazolidinones, with minimal cyclic carbonate formation. Seven ion pair catalysts were evaluated for catalyzing the aza-Payne-type rearrangement reaction of epoxy amine **1a** and carbon dioxide at 80 °C, using a 5 mol% catalyst loading and a carbon dioxide pressure of 0.1 MPa. Among them, the $TBDH^+/4\text{-}OP^-$ ion pair catalyst exhibited the best performance, achieving a high yield of oxazolidinones (84%) in 1 hour. A total of 14 oxazolidinones were synthesized with yields ranging from 72% to 97% under mild conditions (0.1 MPa CO_2, 60–80 °C). The dual activation mechanism of the catalyst was confirmed through NMR titration and control experiments. As a bifunctional catalyst, the ion pair polarized the oxygen atom of epoxy amines *via* H-bonding with $N^+–H$, while the phenolate anion activated the N–H bonding of epoxy amines simultaneously, facilitating the subsequent insertion of carbon dioxide. This approach offers a new method for synthesizing oxazolidinones using organic ion pair catalysts, with promising potential for broader applications.

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Sustainability spotlight

(1) The significant increase in the concentration of carbon dioxide (CO_2) in the atmosphere can lead to various environmental pollution issues. The use of environmentally friendly catalysts to convert CO_2 into valuable chemicals is becoming increasingly important for carbon neutrality and the carbon cycle. (2) No metal or halogen-containing catalysts were used in this work, distinguishing it from the alkaline catalysts previously employed for this type of reaction. The conversion of CO_2 and epoxy amines into drug precursor oxazolidinone helps mitigate climate change pressures and contributes to a sustainable economy. (3) Our work emphasizes the importance of the following UN sustainable development goals: Affordable and Clean Energy (SDG 7), Industry, Innovation and Infrastructure (SDG 9), and Climate Action (SDG 13).

1. Introduction

The five-membered heterocyclic compound 2-oxazolidinone, featuring nitrogen and oxygen atoms, is a crucial structural unit used in medicinal chemistry and organic synthesis. The 2-oxazolidinone nucleus has been utilized in the synthesis of various active pharmaceutical agents, including toloxatone (antidepressant), rivaroxaban (blood clot treatment), delpazolid and linezolid (antibiotic agents),[1–4] which have been developed for clinical use (Fig. 1). Therefore, the synthesis of these high-value heterocyclic compounds has garnered significant attention from researchers. Numerous novel strategies for the synthesis of 2-oxazolidinone derivatives have been developed,[5] including the multi-component coupling of amino derivatives with carbonylating agents,[6,7] cycloaddition reactions using epoxides or aziridines as starting materials,[8–13] and intramolecular cyclization of carbamates.[14,15] However, these starting

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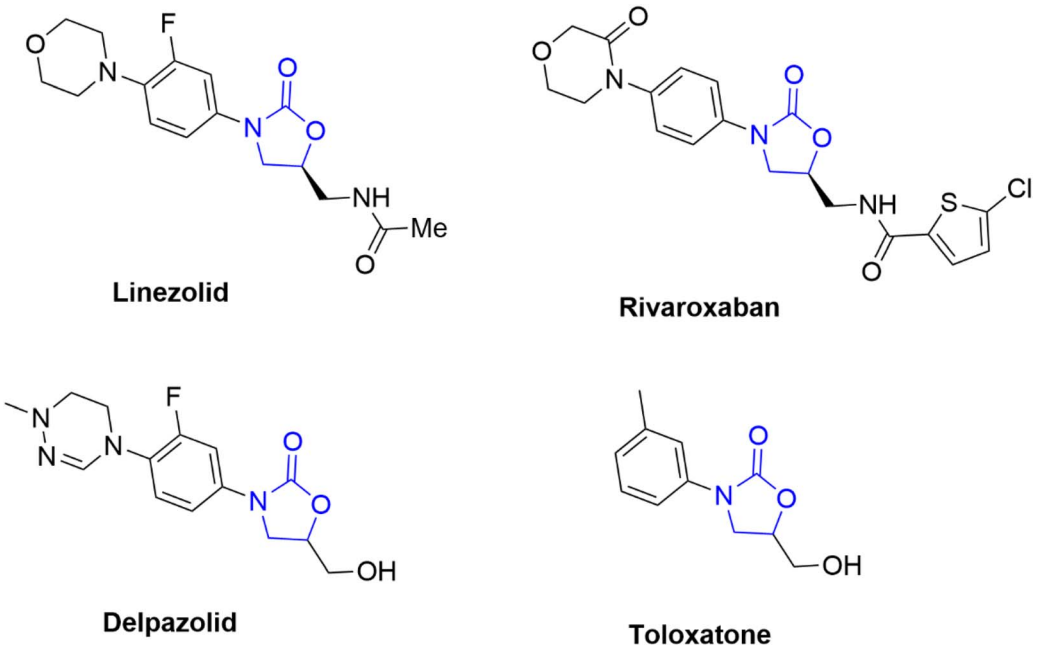


Fig. 1 Examples of oxazolidinone-based medicines.

materials, such as isocyanates, which are toxic, or aziridines, which are difficult to synthesize, often require complex catalysts and/or harsh reaction conditions.[16] Among these preparation methods, the chemical conversion of carbon dioxide into oxazolidinones has become a prominent research focus.[9] The utilization of carbon dioxide as a chemical feedstock is currently attracting significant interest from both industry and academia due to its low cost and abundance as a C1 resource. Thus, converting this non-toxic, renewable resource into high-value-added chemicals represents one of the most promising strategies for CO_2 fixation.[17,18] However, due to the thermodynamic stability and chemical inertness of carbon dioxide as a linear molecule,[19] developing an effective conversion strategy is vital for the successful synthesis of oxazolidinones from carbon dioxide.

The Payne-type rearrangement reaction of epoxy amine and carbon dioxide enables the efficient synthesis of 5-hydroxymethyl oxazolidinones with high atom economy. The Payne rearrangement, first discovered in 1962, refers to the isomerization of 2,3-epoxy alcohols to 1,2-epoxy alcohols under alkaline conditions.[20] The epoxy alcohol anion, formed after deprotonation of the epoxy alcohol by a base, can be captured by an electrophilic reagent E^+ to yield Payne-type derivatives (Fig. 2a). When the electrophilic reagent (E) is a reactive group such as urethane, carbonate, or carbamate, the catalytic rearrangement or ring-opening at the C-2 position of the epoxide results in the formation of a heterocyclic compound with a hydroxyl side chain (Fig. 2b).[21–23] Here, we envision that the secondary amine of the epoxidized aniline was activated and nucleophilically attacked carbon dioxide, forming carbamic acid. This intermediate then catalytically opened the three-membered epoxy ring and rearranged to produce 5-hydroxymethyl oxazolidinone (Fig. 2c).

Most catalytic processes for the cyclization of epoxy amine and carbon dioxide rely on alkaline catalysts to drive the reaction. The base catalyst abstracts the N–H proton of the epoxy amine, to form $B–H^+$, followed by the activation of carbon dioxide by the nitrogen anion (Scheme 1A).[16,24,25] The monofunctional Lewis acid (LA) catalyzed cycloaddition reaction of epoxy amine and carbon dioxide was first proposed by Kleij, where a metal–aluminum complex activates the epoxide through coordination and then converts it to the target oxazolidinone under pressurized carbon dioxide.[21] In their subsequent work, aluminum triphenolate complexes were utilized to catalyze the conversion of epoxy alcohols into glycerol carbonate through the coupling reaction with carbon dioxide.[26] It has been observed that the selectivity between cyclic carbonates and oxazolidinones can be controlled by adjusting the loading of the co-catalyst TBAI. In previous studies, many heterogeneous catalysts have been reported for the synthesis of oxazolidinones,[27] including several metal–organic framework (MOF) catalysts.[28–30] In Kleij's recent work, an organic hydrogen-bonded solid-supported catalyst, a single-component polystyrene-supported 1,5,7-triazabicyclodec5-ene (**TBD@PS**), was developed and applied to facilitate a continuous flow reaction of epoxidized amines and carbon dioxide (Scheme 1B).[31] In their earlier work, they were the first to report the use of an immobilized organocatalyst (TBD@Merrifield) for the preparation of glycerol carbonate by coupling glycidol with CO_2 in a continuous flow reaction.[32] Kim's group proposed a binary Lewis acid/base catalytic system, where the aluminum metal complex activates the epoxide, and the secondary amine, after deprotonation by the base catalyst, attacks the carbon dioxide, functioning as a synergistic catalyst (Scheme 1C). The selectivity of the reaction can be further tuned by adding different co-catalysts, such as TBAI or DMAP.[25] Since the reported

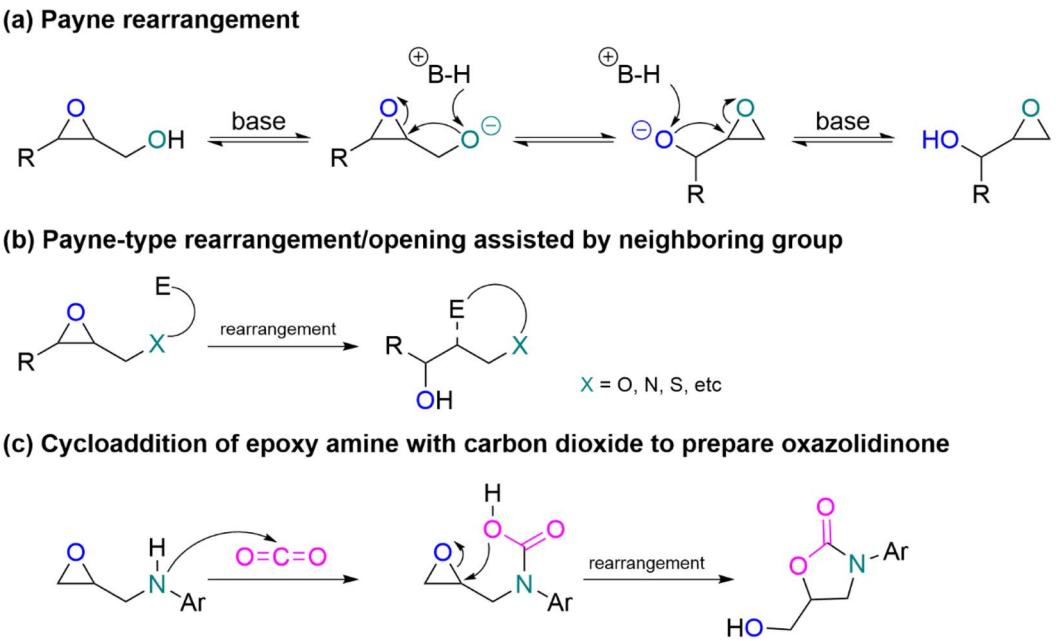
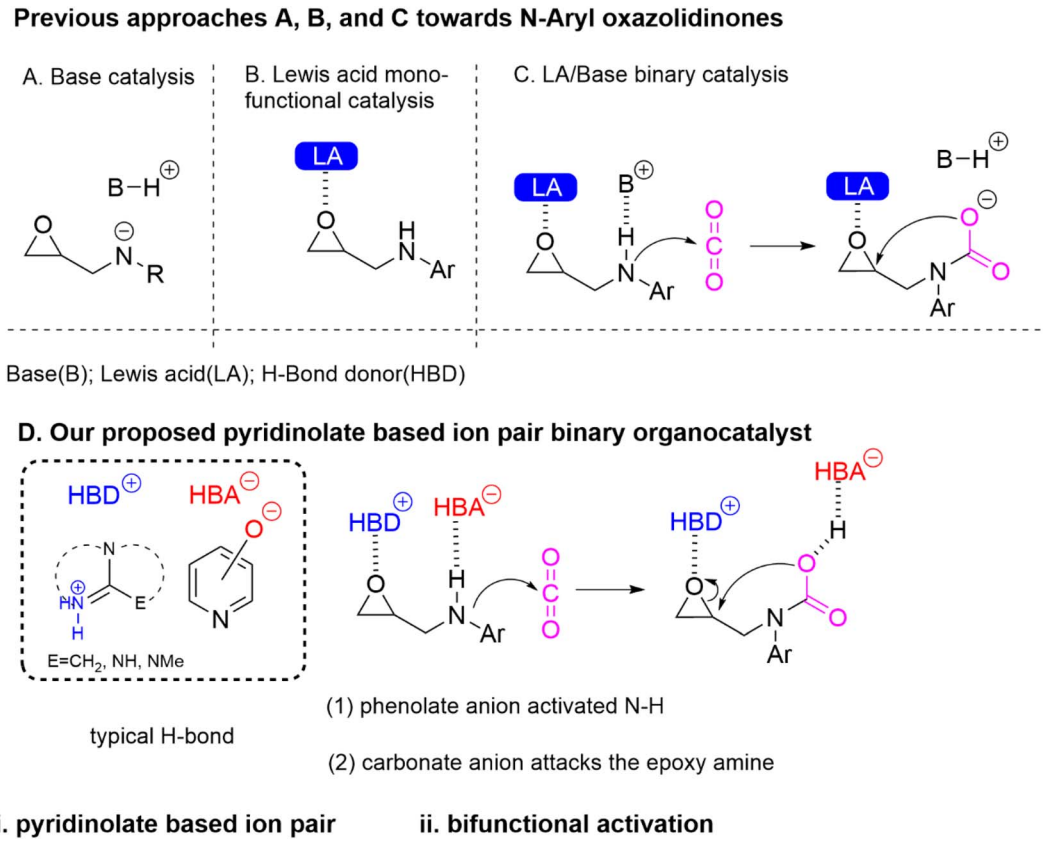


Fig. 2 (a) Classical Payne rearrangement catalyzed by base; (b) C-2 Payne-type rearrangement/opening assisted by the neighboring group; (c) cycloaddition reaction of epoxy amine with carbon dioxide to prepare oxazolidinones.



Scheme 1 Design of a halide-free catalysis platform for organocatalytic aza-Payne-type rearrangement reactions involving epoxy amines and carbon dioxide. (A) Base-catalyzed activation of epoxy amines; (B) the catalytic model for the monofunctional activation of epoxy amines using Lewis acid (LA); (C) LA/base binary catalysis; (D) our proposed pyridinolate based ion pair, (i) consisting of organic base cations and pyridine-containing anions; (ii) the typical ion pair cocatalyst provided both HBD/HBA synergistically activated epoxy amines.

examples all require metal catalysts, developing non-metal catalysts for the site-selective reaction of epoxy amines with CO_2 is highly desirable. D'Elia and Poater *et al.* reported the 3,4-diaminopyridine-catalyzed reaction of epoxy amines with CO_2, which required high pressure (10 bar) and was demonstrated in only two instances.[33] In the past decade, significant progress has been made in developing organocatalysts, allowing for the preparation of oxazolidinones without the use of expensive and/or toxic metals. Among these strategies for synthesizing oxazolidinones was the generation of *N*-aryl-substituted oxazolidinones *via* the [3 + 2] coupling reaction of isocyanates and epoxides catalyzed by tetraarylphosphonium salts[8] and the synthesis of 5-aryl-2-oxazolidinones using carbon dioxide and aziridines catalyzed by protic onium salts under mild conditions.[34] These reported catalysts are halogen-containing, but halogens can corrode metal reactors and contribute to environmental pollution.[35] Therefore, there is a need to develop organic halide-free catalysts. Suga *et al.* demonstrated that the base-promoted reaction of carbon dioxide with 1-amino-3-chloropropan-2-ol derivatives at atmospheric pressure could be employed for the transformative synthesis of five- and six-membered cyclic carbamates. By simply adjusting the base and solvent, the selectivity of products could be effectively controlled.[24] In 2018, Kleij *et al.* successfully achieved a domino [3 + 2] cycloaddition/Payne-type rearrangement of epoxy alcohols with carbon dioxide, catalyzed by a simple and inexpensive superorganic base under mild conditions.[22] Subsequently, in 2022, Yao *et al.* achieved the stereo-selective coupling of carbon dioxide with epoxy amines for the preparation of oxazolidinones under atmospheric pressure using various tertiary amines. This work provided a simple and convenient method for the organocatalytic synthesis of oxazolidinones.[16] Although these novel catalytic strategies effectively facilitate the reaction, there remains potential for further optimization. Alkaline catalysts are not perfectly compatible with this system. On one hand, bases may induce epoxy ring opening, leading to competitive polymerization reactions.[36,37] On the other hand, bases might nucleophilically attack carbon dioxide, forming adducts that result in catalyst deactivation.[38] Such reactions typically require harsh conditions and may necessitate the use of carbon dioxide at elevated pressures. Therefore, the rational design of a halide-free organocatalyst capable of converting epoxidized amines into the pharmaceutically active intermediate 5-hydroxymethyl oxazolidinone under atmospheric carbon dioxide conditions is highly promising.

In previous work, we have designed an organic halide-free ionic liquid catalyst, which has previously been shown to be effective in catalyzing cycloaddition reactions between epoxides and carbon dioxide.[39] In this work, we report the development of a halide-free pyridinolate based binary organocatalyst for the coupling of epoxy amines with carbon dioxide, yielding 5-hydroxymethyl oxazolidinone without the need for a co-catalyst under ambient pressure. The range of epoxy amine substrates explored in this study includes fourteen different compounds. Additionally, gram-scale experiments were conducted to assess the feasibility of scaling up this reaction for potential industrial production.

2. Results and discussion

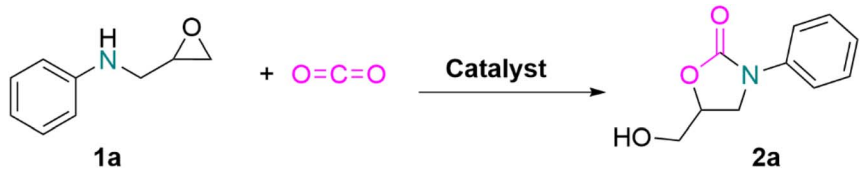
2.1 Preparation of pyridinolate based catalysts and evaluation of their catalytic performance in aza-Payne-type rearrangement utilizing epoxy amines and carbon dioxide

All seven catalysts evaluated in this work were synthesized based on the binary cocatalyst from our previous work. The purity of these catalysts was confirmed through ^1H and ^{13}C NMR spectroscopy. The initial experiments were carried out under mild conditions, specifically at 80 °C and 0.1 MPa CO_2 pressure, using a catalyst loading of 5 mol%. Seven different binary cocatalysts were tested using *N*-(oxiran-2-ylmethyl) aniline (**1a**) as the benchmark substrate under reaction conditions with DMF as the solvent. All catalysts successfully catalyzed the aza-Payne-type rearrangement reaction, producing oxazolidinone **2a** with yields ranging from 44% to 84% (Table 1). Although a solvent is typically unnecessary for the cycloaddition reaction of epoxides with carbon dioxide, the epoxy amine **1a** is a solid, necessitating the use of a solvent. DMF was ultimately selected due to its high boiling point and its ability to activate carbon dioxide during the reaction.[40,41] As shown in Fig. 3, the optimal balance between the conversion of starting epoxy amine **1a** and the selectivity towards oxazolidinone **2a** was achieved when **TBDH$^+$/4-OP$^-$** was used as the catalyst (Table 1, entry 1). The pK_a value of the hydroxyl group significantly influences the catalytic effect. If the acidity is too strong or too weak, it will negatively affect the reaction.[39,42,43] This result holds significant importance for us, as the feedstock used in the synthesis of **TBDH$^+$/4-OP$^-$** is relatively inexpensive. Moreover, it aligns with previous findings from catalyzed epoxide–carbon dioxide cycloaddition reactions. On the other hand, **TBDH$^+$/2-OP$^-$** and **TBDH$^+$/3-OP$^-$** yield nearly identical results and demonstrate a high level of selectivity (see entries 2 and 3, Table 1 for comparison). Hydroxypyridine exhibited better selectivity under relatively weak acidic conditions, while 4-OP$^-$ was milder and had no isomerization compared to 2-OP$^-$.[42] Therefore, taking all factors into account, **TBDH$^+$/4-OP$^-$** was selected as the final optimization target. Notably, no conversion of **1a** was detected in the absence of any catalyst (Table 1, entry 8).

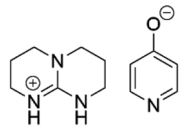
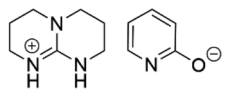
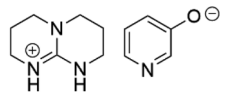
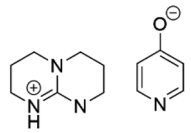
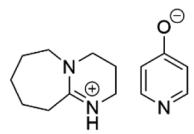
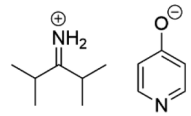
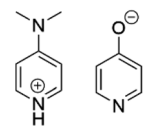
2.2 Optimization of the conditions of the aza-Payne-type rearrangement reaction of epoxy amine under the catalysis of TBDH+/4-OP−

The conditions for the **TBDH$^+$/4-OP$^-$** catalyzed aza-Payne-type rearrangement reaction involving the oxidation of epoxy amine and carbon dioxide were thoroughly investigated. With the optimal catalyst in hand, the screening of reaction conditions was performed with epoxy amine **1a** as the benchmark substrate (Table 2). Initially, **1a** could not be converted at 25 °C and CO_2 atmospheric pressure (Table 2, entry 1). The conversion of **1a** increased with increasing temperature, while the selectivity remained unaffected (Table 2, entries 2–4). When the reaction temperature was raised to 100 °C, a significant drop in yield was observed, decreasing to 61% (Table 2, entry 4). Considering the conversion and selectivity, 80 °C was chosen as the optimal reaction temperature. Investigations into catalyst

Table 1 Evaluation of the catalytic effect of catalysts **1–7** [a]



1a **2a**

Entry	Catalyst	Conv.[b]/[%]	Sel.[b]/[%]	Yield[b]/[%]	TON[c]	TOF[d]/[h^{-1}]
1	 **1. TBDH$^+$/4-OP$^-$**	84	>99	84	16.80	16.80
2	 **2. TBDH$^+$/2-OP$^-$**	77	90	70	13.86	13.86
3	 **3. TBDH$^+$/3-OP$^-$**	81	91	74	14.74	14.74
4	 **4. MTBDH$^+$/4-OP$^-$**	81	90	73	14.58	14.58
5	 **5. DBUH$^+$/4-OP$^-$**	50	88	44	8.80	8.80
6	 **6. TMGH$^+$/4-OP$^-$**	58	>99	58	11.60	11.60
7	 **7. DMAPH$^+$/4-OP$^-$**	46	>99	46	9.20	9.20
8	None	—	—	—	—	—

[a] Reaction conditions: epoxy amine **1a** (0.5 mmol), CO_2 (0.1 MPa), catalyst (5 mol%), DMF (0.5 mL), 80 °C, 1 h. [b] Determined by ^{1}H NMR spectroscopy ($CDCl_3$) using tetraethylsilane as an internal standard. [c] Turnover number (TON) = moles of product/moles of catalyst. [d] Turnover frequency (TOF) = moles of product/(moles of catalyst × time).

loading revealed that reducing the catalyst loading to 1 mol% led to a significant decrease in the conversion of **1a**. Optimal performance was achieved with a catalyst loading of 5 mol% (Table 2, entry 3). Shortening the reaction time to 0.5 hours caused a 38% decrease in conversion (Table 2, entries 3, and 7). In contrast, extending the reaction time to 2 hours led to the nearly complete conversion of **1a** and quantification of oxazolidinone **2a** (Table 2, entry 8). Increasing the CO_2 pressure to

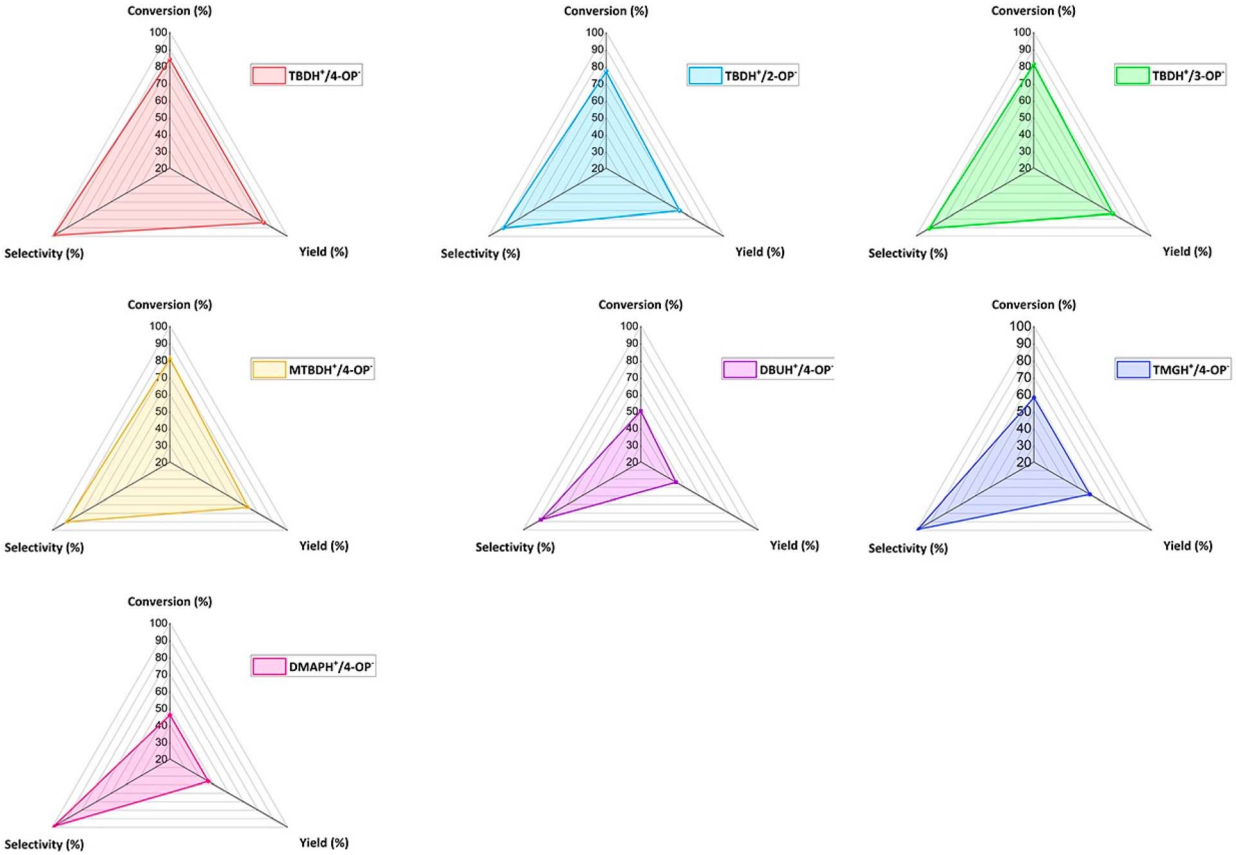
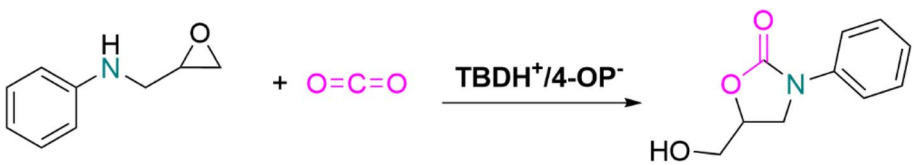


Fig. 3 Graphic representation of conversion, yield and selectivity for all 7 tested catalysts under the reaction conditions reported in Table 1 in the aza-Payne-type rearrangement reactions.

Table 2 Screening the optimal conditions for cycloaddition of epoxy amine and carbon dioxide[a]



1a 2a

Entry	Catalyst loading/[mol%]	Pressure/[MPa]	Solvent	Temperature/[°C]	Time/[h]	Conv.[b]/[%]	Sel.[b]/[%]
1	5	0.1	DMF	25	1	—	—
2	5	0.1	DMF	60	1	76	>99
3	5	0.1	DMF	80	1	84	>99
4	5	0.1	DMF	100	1	61	>99
5	2.5	0.1	DMF	80	1	64	>99
6	1	0.1	DMF	80	1	36	>99
7	5	0.1	DMF	80	0.5	46	>99
8	5	0.1	DMF	80	2	>99	>99
9	5	0.5	DMF	80	1	85	>99
10	5	1	DMF	80	1	87	>99
11	5	0.1	Acetonitrile	80	1	35	70
12	5	0.1	Chlorobenzene	80	1	29	60
13	5	0.1	1,4-Dioxane	80	1	44	62

[a] Reaction conditions: epoxy amine **1a** (0.5 mmol), catalyst **TBDH⁺/4-OP⁻**. [b] Determined by ^{1}H NMR spectroscopy ($CDCl_3$) using tetraethylsilane as an internal standard.

either 0.5 MPa or 1 MPa results in only a minimal improvement in the conversion rate of **1a** (Table 2, entries 9 and 10). This phenomenon indicated that CO_2 pressure does not play a crucial role in promoting this reaction, further suggesting that the reaction mechanism differs significantly from that of the typical epoxides and carbon dioxide cycloaddition reaction. Common organic solvents such as acetonitrile, chlorobenzene and 1,4-dioxane were screened and DMF proved to be the best choice (Table 2, entries 3 and 11–13). Overall, a catalyst loading of 5 mol%, 2 h, 0.1 MPa of CO_2 and 80 °C were considered the optimal reaction conditions. In comparison to existing catalysts for catalyzing such reactions, our designed halide-free bifunctional ion pair catalysts offer distinct advantages and have some limitations. Unlike conventional alkaline catalysts, our catalysts achieve quantitative conversion in just 2 hours, whereas alkaline catalysts in previous studies require 18–20 hours.[16,22] Moreover, in contrast to metal catalysts, our catalysts are both metal-free and halide-free, allowing for the efficient preparation of oxazolidinones under mild conditions, without the need for co-catalysts.[21,25] However, the catalysts we designed also have some limitations. Due to their homogeneous catalyst characteristics, their recycling and reuse need to be improved compared to heterogeneous catalysts.[31]

2.3 The substrate scope of the cycloaddition reaction of various epoxy amines with CO_2 catalyzed by catalyst TBDH+/4-OP−

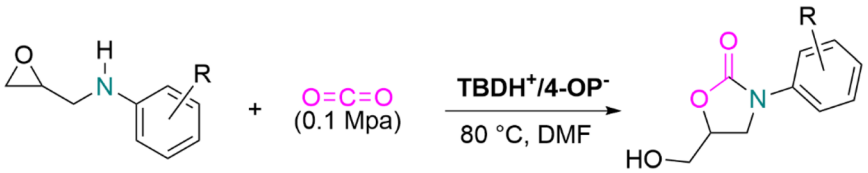
To facilitate a more intuitive comparison of the reaction properties of different substrates, the reaction of CO_2 with various substituted epoxy amines was investigated under optimal conditions, with the reaction time reduced to 1 hour (Table 3). The general procedure for synthesizing the epoxy amine substrate was adapted from previously reported methods,[16,44] incorporating modifications outlined in the experimental section. The methyl-substituted epoxy amine substrates were all successfully converted to the corresponding oxazolidinones (**2b–2d**) within one hour. The results indicate a slight variation in reactivity, which may be attributed to steric hindrance caused by site-blocking effects. Among these, the *m*-tolyl-substituted oxazolidinone **2c** is particularly notable, as it serves as the active compound in the pharmaceutical drug toloxanone. In addition, epoxy amines with electron-withdrawing substituents were investigated, and the corresponding oxazolidinones (**2e–2j**) were successfully synthesized under the optimized conditions. From the results of **2e–2g**, it can be concluded that for electron-withdrawing group substituents, steric hindrance plays a significant role in influencing the reaction yield. The *p*-chloro-substituted substrate **1g** gave the highest yield, reaching 89%. The catalyst exhibited optimal activity towards the bromo-substituted substrate **1i**, achieving nearly complete conversion of the epoxy amine to oxazolidinone with an impressive yield of 97%. Among the polyhalogen-substituted substrates, the 3,5-dichlorophenyl epoxy amine also produced the target oxazolidinone in high yield, with the yield of **2h** reaching 80%. The 2,6-diisopropylphenyl-substituted epoxy amine substrate **1k** was similarly converted to the target oxazolidinone product under optimized conditions, achieving an 80% yield. The same strategy was successfully applied to substrates containing ester bonds, yielding 72% of the corresponding oxazolidinone product **2l**. When the substituent is a 2-naphthyl group with significant steric hindrance, the oxazolidinone **2n** was still obtained in an impressive 87% yield. The polysubstituted compound 3-fluoro-4-morpholino-*N*-(oxiran-2-ylmethyl)aniline was converted to oxazolidinone **2m** in 86% yield, a key precursor of the active drug linezolid. A gram-scale synthesis of **2a** was conducted, and the conversion of **2a** was monitored over two hours (Table S1†), producing 4.8 grams of **2a** with a yield of over 99% from **1a** in 1.5 hours. This indicates that the catalytic system can efficiently convert various epoxy arylamines into the corresponding oxazolidinones in a short period while achieving high yields, highlighting its great potential for broader applications.

2.4 Proposed and validated mechanism for the cycloaddition reaction of epoxy amine with CO_2 catalyzed by TBDH+/4-OP−

To validate the ionic liquid as an HBD/HBA bifunctional catalyst promoting the aza-Payne-type rearrangement reaction mechanism in the reaction between epoxy amine and carbon dioxide, ^{1}H NMR titration experiments were conducted using substrate **1a** and catalyst **TBDH$^+$/4-OP$^-$**. The ratios of catalyst **TBDH$^+$/4-OP$^-$** to epoxy amine **1a** were progressively increased from 0.2 : 1 to 1 : 1 (labeled as 2 to 6, Fig. 4). The pure epoxy amine **1a** served as a benchmark substrate. The chemical shift of the N–H in the secondary amine portion of epoxy amine **1a** shifted from 5.7806 ppm to 5.8304 ppm (Fig. 4, red circle) as the concentration of the catalyst **TBDH$^+$/4-OP$^-$** increased. This suggests that the 4-pyridinolate (**4-OP$^-$**) in the catalyst, acting as a hydrogen bond acceptor, interacts with the N–H, leading to a notable change in the chemical environment around the N–H proton. Meanwhile, as the ratio of the substrate to the catalyst decreases, the methylene hydrogen protons in the epoxide portion of the substrate upfield slightly from 2.7306 ppm to 2.7287 ppm toward the high field (Fig. 4, blue square). Additionally, the hydrogen proton of the TBD$^+$–H cation shows a more significant shift from 4.4335 ppm to 6.0158 ppm (Fig. 4, green circle). The chemical perturbation of the hydrogen protons on the epoxide and the displacement of the catalytic hydrogen protons indicate the TBD$^+$–H coordinating with the substrate **1a** *via* H-bonding, corroborating the hypothesis that the cation serves as a dual-function hydrogen bond donor for epoxide activation. ^{1}H NMR titration experiments support the bifunctional HBD$^+$/HBA$^-$ co-catalytic mechanism of the catalyst.

To provide additional evidence for the proposed mechanism in which **TBDH$^+$/4-OP$^-$** acts as HBD/HBA bifunctional catalyst for the aza-Payne-type rearrangement reaction of epoxy amine with carbon dioxide, catalyst analogs **8–11** were designed and utilized as control catalysts for a benchmark reaction (Fig. 5). The detailed synthesis of catalysts 8–11 can be found in our previous work.[39] TBD$^+$–H onium (catalyst **8**), which lacks a nucleophilic counter anion, was initially tested as a catalyst in

Table 3 Cycloaddition reaction of various epoxy amines with CO_2[a]



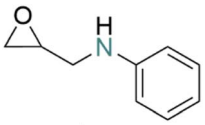
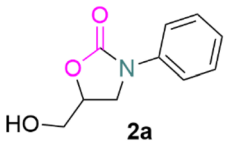
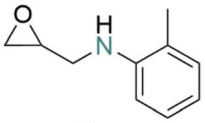
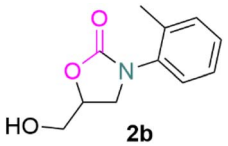
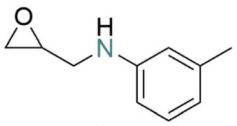
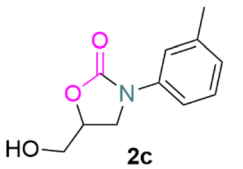
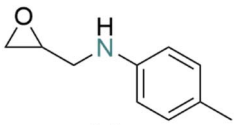
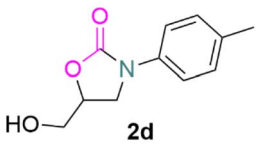
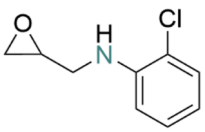
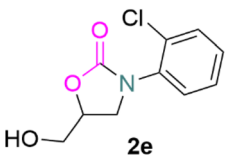
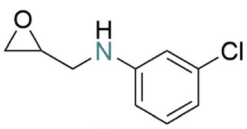
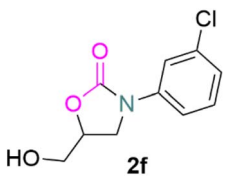
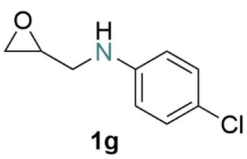
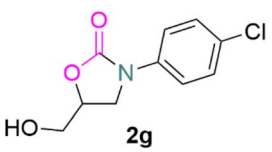
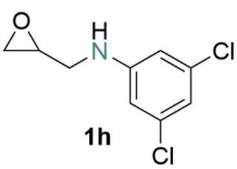
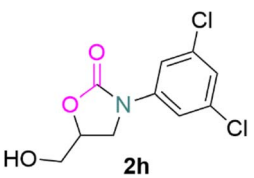
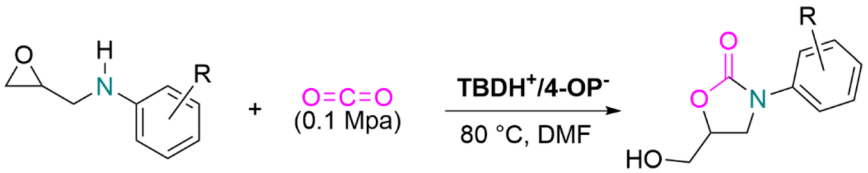
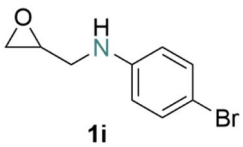
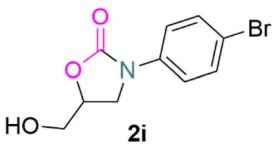
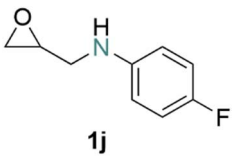
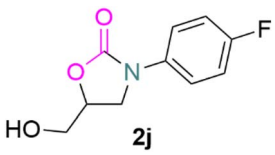
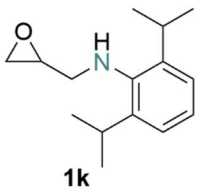
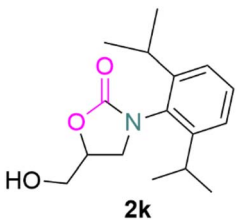
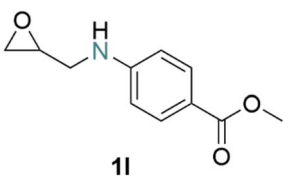
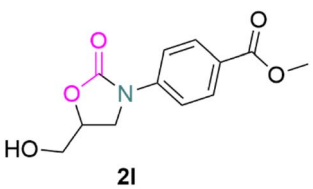
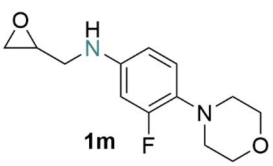
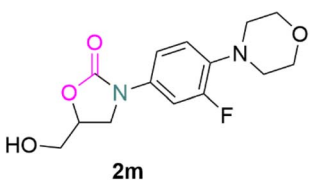
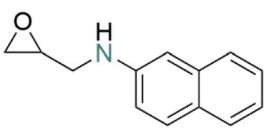
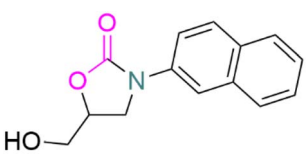
Entry	Substrate 1	Product 2	Conv.[b]/[%]	Sel.[b]/[%]	Yield.[b]/[%]	TON[c]	TOF[d]/[h^{-1}]
1	 1a	 2a	84	>99	84	16.80	16.80
2	 1b	 2b	80	>99	80	16.00	16.00
3	 1c	 2c	86	>99	86	17.20	17.20
4	 1d	 2d	81	>99	81	16.20	16.20
5	 1e	 2e	82	71	58	11.64	11.64
6	 1f	 2f	87	>99	87	17.40	17.40
7	 1g	 2g	89	>99	89	17.80	17.80
8	 1h	 2h	80	>99	80	16.00	16.00

Table 3 (*Contd.*)



Entry	Substrate **1**	Product **2**	Conv.[b]/[%]	Sel.[b]/[%]	Yield.[b]/[%]	TON[c]	TOF[d]/[h^{-1}]
9	 **1i**	 **2i**	97	>99	97	19.40	19.40
10	 **1j**	 **2j**	83	>99	83	16.60	16.60
11	 **1k**	 **2k**	80	>99	80	16.00	16.00
12	 **1l**	 **2l**	72	>99	72	14.40	14.40
13	 **1m**	 **2m**	86	>99	86	17.20	17.20
14	 **1n**	 **2n**	87	>99	87	17.40	17.40

[a] Reaction conditions: CO_2 (0.1 MPa), 5 mol% of catalyst **TBDH$^+$/4-OP$^-$**, 80 °C, 1 h. [b] Determined by ^{1}H NMR spectroscopy ($CDCl_3$) using tetraethylsilane as an internal standard. [c] Turnover number (TON) = moles of product/moles of catalyst. [d] Turnover frequency (TOF) = moles of product/(moles of catalyst × time).

control experiments under optimal reaction conditions, resulting in only 23% product yield. The catalytic performance of catalyst **10** (TBD$^+$–Me/4-OP$^-$) without TBD$^+$–H was also found to be unsatisfactory in terms of conversion (conv. 38%). To verify the activation of the substrate N–H by the pyridine-containing anion (4-OP$^-$) as a hydrogen bond acceptor (HBA), the anion

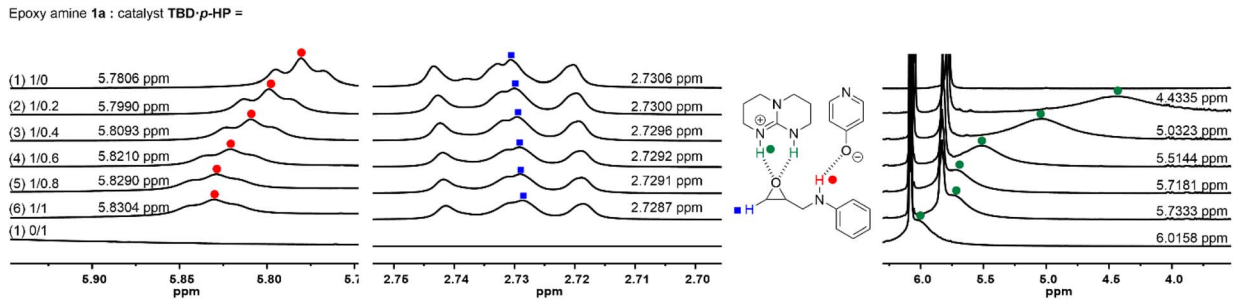


Fig. 4 The chemical shift of the N–H* onium proton in catalyst **TBDH$^+$/4-OP$^-$** in the ^{1}H NMR spectra (DMSO-d_6) (green circle), N–H in the secondary amine portion (red circle) and the methylene hydrogen protons in the epoxide portion of the substrate **1a** (blue circle) observed by titration of catalyst **TBDH$^+$/4-OP$^-$** with epoxy amine **1a**: epoxy amine **1a**/catalyst **TBDH$^+$/4-OP$^-$** ratios: (1) 1/0, (2) 1/0.2, (3) 1/0.4, (4) 1/0.6, (5) 1/0.8, (6) 1/1, and (7) 0/1.

was substituted with tetrafluoroborate (**9**, TBD$^+$–H·BF$_4^-$). Under the same reaction conditions, no product formation was observed. *N*-Methyl TBD was substituted for TBD$^+$–H in catalyst **11** (TBD$^+$–Me·BF$_4^-$), and no product was generated (conv. 0%). Subsequently, to confirm the critical step of carbamate formation through the attack of carbon dioxide following the activation of the secondary amine N–H, *N*-methyl-*N*-(ethylene oxide-2-methyl)aniline was synthesized.[44,45] It was hypothesized that the epoxy amines, after substituting hydrogen protons with a methyl group, would lack nucleophilicity and be incapable of undergoing the rearrangement reaction. Experiments conducted with *N*-methyl-*N*-(ethylene oxide-2-methyl)aniline under the same conditions showed that the substrate was completely unreactive. Overall, the control experiments demonstrated that the ion pair played a vital role in catalyzing the cycloaddition reaction of epoxy amine with CO_2.

Based on the above experimental results and previous studies,[39] a plausible bifunctional synergistic catalytic mechanism has been proposed, wherein TBD$^+$–H acted as a hydrogen-bond donor and the pyridine-containing anion served as a hydrogen-bond acceptor.[16] Scheme 2 outlines a systematic catalytic cycle comprising four distinct steps. In step I, catalyst **1** (**TBDH$^+$/4-OP$^-$**) adopted its ion-pair configuration (TBD$^+$–H/4-OP$^-$), which increased the nucleophilicity of the nitrogen atom through hydrogen bonding between the pyridine-containing anion and the N–H proton. This interaction subsequently facilitated the activation of carbon dioxide, leading to the formation of the epoxy aminocarboxylic acid intermediate; step II, the HBD$^+$ provided a dual hydrogen bond interaction to activate the epoxide group. At this point, the pyridine-containing anion formed an O–H-4-OP$^-$ hydrogen bond with the terminal hydroxyl group of the carbamic acid intermediate, stabilizing the epoxide and facilitating the formation of the

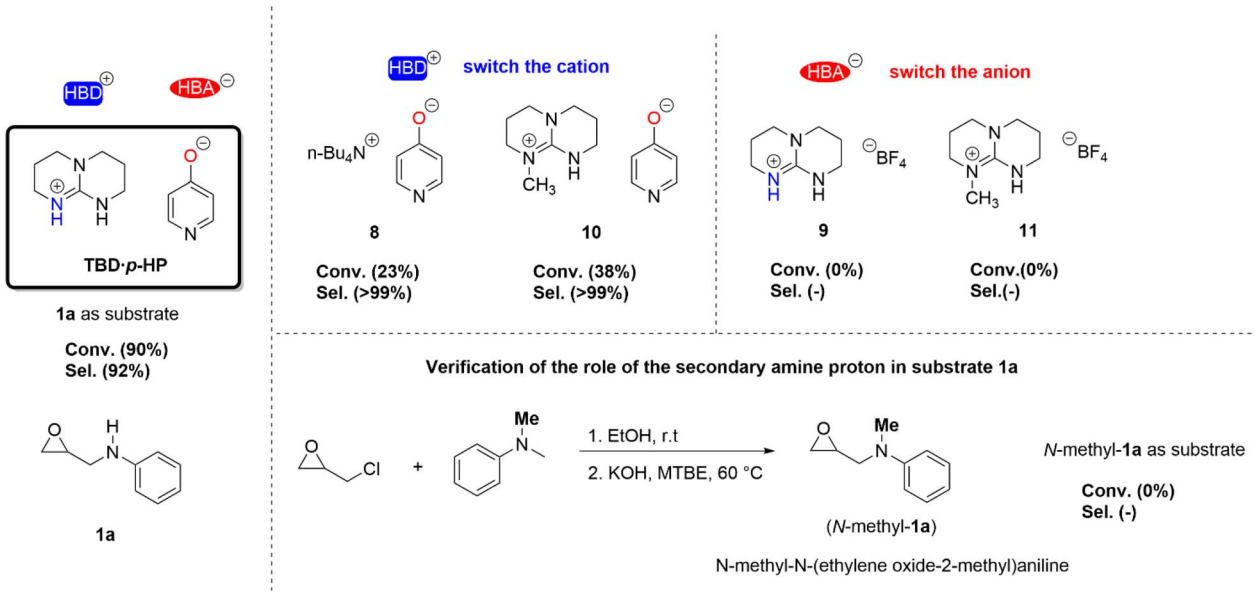
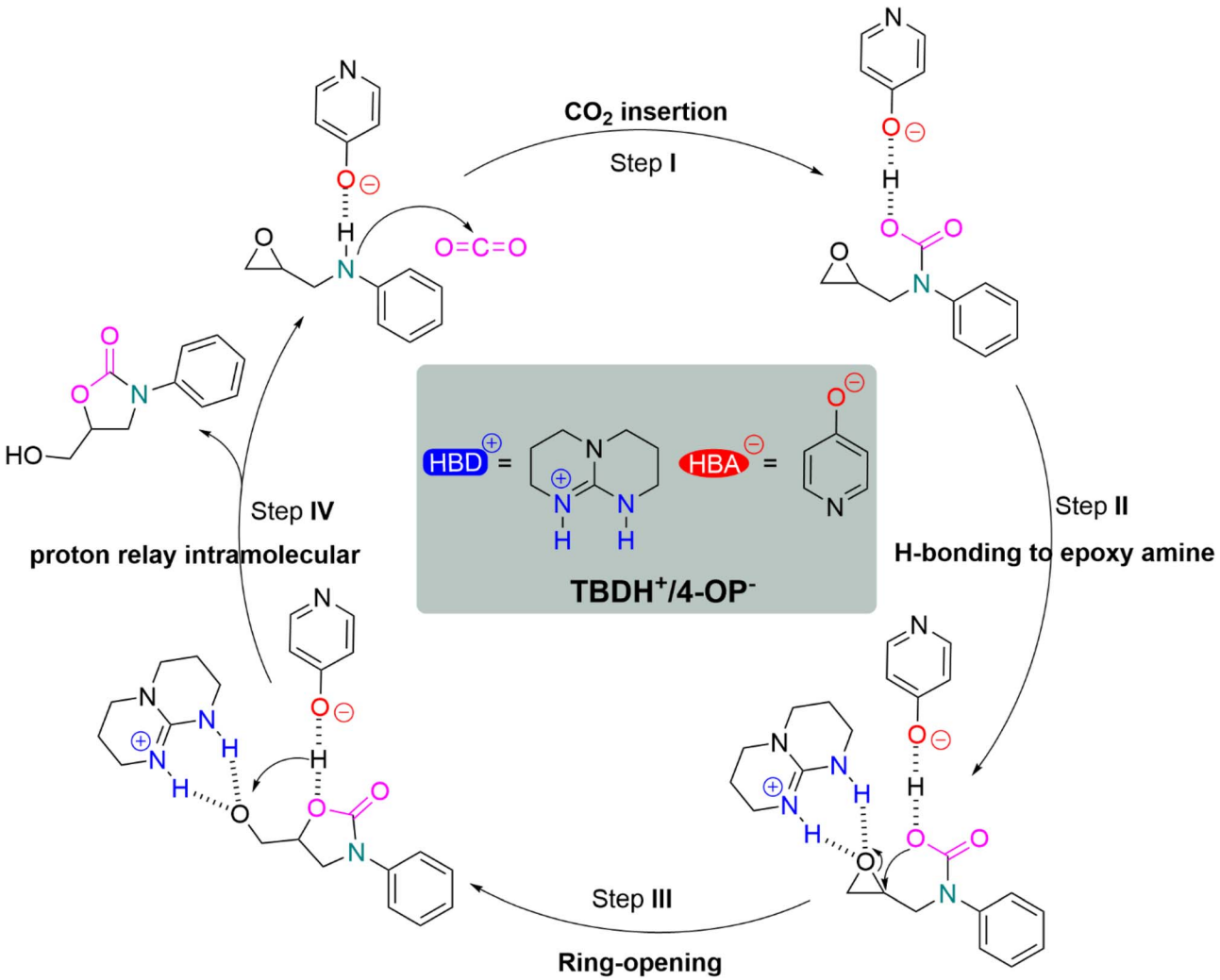


Fig. 5 Catalysts analogs **8**–**11** were designed to validate the cooperative catalysis of cation HBD$^+$ and anion A$^-$; benchmark reaction conditions: CO_2 (0.1 MPa), 5 mol% of catalyst loading, 80 °C, 1 h; conversions and selectivity were determined by ^{1}H NMR spectroscopy with $CDCl_3$ as the solvent mixture using tetraethylsilane as the internal standard. No product formation was observed when the secondary amine proton of substrate **1a** was substituted with a methyl group.



Scheme 2 Proposed mechanism of the cocatalysis by catalyst TBDH$^+$/4-OP$^-$ in aza-Payne-type rearrangement reactions. The catalytic cycle is composed of four steps: step I, the establishment of hydrogen bonds between the 4-OP$^-$ anion and the N–H proton facilitated the activation of carbon dioxide, resulting in the formation of epoxidized carbamate intermediates; step II, HBD$^+$ activated the epoxide group, while the 4-OP$^-$ anion formed an O–H-4-OP$^-$ hydrogen bond with the terminal hydroxyl group of the carbamate intermediate, thereby promoting the formation of the activated epoxide–carbamate intermediate; step III, formic acid attacked the epoxidized hypomethyl carbon, initiating an intramolecular cyclization reaction; step IV, after the intramolecular cyclization, 5-hydroxymethyl oxazolidinone was formed and the catalyst TBDH$^+$/4-OP$^-$ was regenerated.

activated epoxide–carbamic acid intermediate; step III, formic acid attacked the epoxidized hypomethyl carbon, initiating an intramolecular cyclization reaction. This leads to the opening of the epoxide ring, resulting in the formation of a cyclic intermediate. The nucleophilic attack and ring closure proceed in a concerted manner, with increased stability facilitated by the hydrogen bonding of TBD$^+$–H; step IV, the generation of 5-hydroxymethyl oxazolidinone occurred as the final step in the catalytic cycle. After the intramolecular cyclization, 5-hydroxymethyl oxazolidinone was formed and the catalyst (TBD-H$^+$/4-OP$^-$) was regenerated. The catalyst was then released, allowing it to enter a new catalytic cycle, ready to facilitate another round of reaction between the epoxidized amine and carbon dioxide. This efficient turnover of the catalyst ensures the continuity of the catalytic process.

3. Conclusions

In conclusion, a pyridinolate based binary organocatalyst was developed to facilitate the aza-Payne-type rearrangement of epoxy amines and carbon dioxide for the synthesis of 5-hydroxy-2-oxazolidinones under mild conditions. Among the seven ion pair catalysts assessed, **TBDH$^+$/4-OP$^-$** demonstrated the best performance, nearly achieving complete conversion of the epoxy amines to oxazolidinones within 2 hours at 80 °C, under atmospheric carbon dioxide pressure, with a catalyst loading of 5 mol%. To intuitively compare the activities of various epoxy amine substrates, we employed **TBDH$^+$/4-OP$^-$** as the catalyst. Under optimal reaction conditions and a reduced timeframe of one hour, a series of aryl-substituted epoxide amines were successfully converted to oxazolidinones, achieving yields

between 58% and 97%. This study demonstrates a non-metallic catalyst for the conversion of epoxy amines to oxazolidinones at atmospheric pressure for the synthesis of precursor compounds of the active drugs linezolid and toloxatone, a method that has a wide range of applications. TBD^+–H functioned as a bifunctional catalyst by providing dual hydrogen bond donors to activate the epoxide portion of the substrate, while the pyridine anion served as a hydrogen bond acceptor, coordinating with the secondary amine. This coordination enhanced the nucleophilicity of the nitrogen atom, facilitating the formation of an epoxy carbamic acid intermediate *via* addition to carbon dioxide. Simultaneously, the anion activated the hydroxyl hydrogen of formic acid, allowing the oxygen atom to attack the hypomethyl carbon of the epoxide, leading to intramolecular cycloaddition and yielding the target oxazolidinone product. The mechanism of cooperative catalysis involving hydrogen bonding of TBD^+–H was validated through ^{1}H NMR titrations and controlled experiments. The halide-free nature of the pyridinolate based binary catalyst made it highly suitable for commercial applications, as it reduced the risk of reactor corrosion. This binary organocatalyst served as a prime example of a halide-free HBD anion catalyst, offering new approaches for synthesizing oxazolidinones under mild conditions. This organic ion-pair catalyst will be further applied in a broader range of organic transformation reactions, showing significant promise as a novel class of organocatalytic platforms for future developments.

4. Experimental section

4.1 Materials

CO_2 was supplied by Nanjing Shangyuan Industrial Gas Factory with a purity of 99.99%. Epoxides were purchased from Energy Chemical. Organic base and hydroxyproline were provided by Sinopharm Chemical Reagent Co. All the other reagents were purchased from Aldrich and used without further purification.

4.2 Characterization

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 and 101 MHz NMR spectrometer in $CDCl_3$ or DMSO-d_6 as stated deuterated solvents. Chemical shifts δ are reported in parts per million (ppm) relative to a residual undeuterated solvent as an internal reference (^{1}H δ 7.26 for $CDCl_3$, δ 2.50 for DMSO-d_6, ^{13}C δ 77.16 for $CDCl_3$, and δ 39.52 for DMSO-d_6). Conversions and selectivity of epoxy amines were determined by ^{1}H NMR spectroscopy.

4.3 General procedure for the aza-Payne-type rearrangement utilizing epoxy amines and carbon dioxide

The synthesis of catalysts **1–11** was carried out following previously reported protocols.[33] All operations were performed under an argon atmosphere following standard Schlenk techniques, including pre-dewatering and deoxygenation. Epoxy amine (0.5 mmol, 1.0 equiv.) and the catalyst (0.05 equiv.) were dissolved in anhydrous DMF (0.5 mL, 1.0 M). A 10 mL Schlenk reaction tube was thoroughly heated to displace residual gases, followed by vacuum evacuation. The reaction tube was then purged with carbon dioxide for one minute. This gas exchange process was repeated twice, ensuring a full CO_2 atmosphere inside the reaction tube. The prepared solution of epoxy amine and catalyst dissolved in DMF was added to the reaction tube, and a carbon dioxide-filled gas bag was attached. The reaction mixture was heated in a preheated stirrer at 80 °C for 1–2 hours. After the reaction was complete, the tube was cooled to room temperature and the reaction mixture was purified by column chromatography (PE/EA = 1 : 1) to isolate the corresponding oxazolidinones (**2a–2n**).

Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its ESI.† Further information concerning this study is available upon request from the corresponding authors.

Author contributions

Xin Yuan: investigation, methodology, writing – original draft, writing – review & editing. Jiahui Ma: investigation, methodology, validation. Zhenjiang Li: conceptualization, resources, supervision, funding acquisition, project administration, writing – review & editing. Ziqi Liu: investigation, validation. Yanqi Shi: investigation, validation. Ming Zhang: investigation, validation. Yujia Wang: investigation, validation. Xin Zou: investigation, validation. Sha Li: resources, investigation. Kai Guo: resources, funding acquisition, supervision, project administration.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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