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Efficient green solvent-free CO_2/epoxide cycloaddition catalyzed by a β-cyclodextrin-imidazolium-based ionic liquid

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ABSTRACT

The rising atmospheric carbon dioxide (CO_2) levels significantly contribute to climate change. Converting CO_2 into valuable products offers an attractive strategy to mitigate its environmental impact. Here, we present a highly efficient, solvent-free method for CO_2 fixation into cyclic carbonates using a novel green catalyst, β-cyclodextrin, linked to an imidazolium-based ionic liquid (β-CD-Im^+Br^-). This catalyst facilitates the conversion of various terminal and internal epoxides into cyclic carbonates with exceptional performance. Notably, β-CD-Im^+Br^- achieves up to 98 % conversion of styrene oxide to its corresponding carbonate within 24 h at 120 °C, demonstrating significant activity without needing a co-catalyst. Operating under solvent-free conditions, this method avoids environmentally harmful synthetic pathways by utilizing the hydroxyl groups of cyclodextrins as hydrogen bond donors and employing the bromine counterion to facilitate epoxide ring opening. Mechanistic studies reveal that β-CD-Im^+Br^- enhances catalytic performance by lowering the activation energy of the rate-limiting step through its hydrogen bond acceptor properties. Importantly, the catalyst is both recyclable and reusable, highlighting its cost-effectiveness and environmental benefits. This approach represents a significant advancement in sustainable chemistry, offering a green alternative for CO_2 fixation.

Introduction

Carbon dioxide (CO_2) is a significant greenhouse gas, and its excessive levels in the Earth's atmosphere contribute to climate change [1,2]. However, the chemical conversion of CO_2 has generated considerable interest among chemists globally, as CO_2 is a widely available, harmless, and cost-effective carbon resource [3,4]. Notably, in industrial applications, CO_2 is a raw material for synthesizing urea, methanol, polycarbonate, and cyclic carbonate [5]. Among these, the highly efficient cycloaddition reaction of CO_2 with epoxide, which achieves 100 % atom economy and yields cyclic carbonate, holds great promise for applications in lithium batteries, polymer materials, fuel, and other emerging energy sectors [6–8]. Currently, various homogeneous and heterogeneous catalysts have been identified to enhance this cycloaddition reaction, including quaternary ammonium salts, metal complexes, ionic liquids, quaternary phosphonium salts, amines, metal oxides, and metalloporphyrins [9–17]. While many of these catalysts exhibit high efficiency in converting CO_2, they often face significant drawbacks that constrain their effectiveness. These drawbacks include difficulty in product separation, susceptibility to air or water, and a lack of recyclability [6]. Additionally, many catalysts are associated with costly initial materials, metal dependency, or expensive synthetic pathways with environmental implications. Often, demanding reaction conditions, such as the involvement of co-catalyst additives, are necessary [18].

The inherent challenges of corrosion, toxicity, and environmental ramifications associated with metallic cations further complicate the development of effective catalysts. Therefore, designing efficient and

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environmentally benign catalysts for the coupling reaction of CO_2 and epoxide remains a formidable task.

Currently, β-cyclodextrin (β-CD), a cost-effective and stable biopolymer with abundant hydroxyl groups, has gained significant attention as a catalyst component in various reactions [19–23]. Since 2008, it has been employed as an excellent catalyst for the coupling reaction of CO_2 with epoxides in a dual system involving tetrabutylammonium chloride (TBAC), tetrabutylammonium bromine (TBAB), or tetrabutylammonium iodide (TBAI), thus expanding β-CD's application to a novel area [24–26]. Given the ease of modifying cyclodextrins (CDs), we contemplated enhancing the catalytic activity by introducing an ionic liquid as a second component [27–30]. Ionic liquids are well-established as crucial in facilitating CO_2 cycloaddition to epoxide reactions, presenting a forward-thinking and environmentally conscious approach. Typically, a successful catalyst for this type of reaction requires a Lewis acid to activate the epoxide and a nucleophile to open the ring. In this paper, we designed, synthesized, and studied catalyst **1**, based on a β-CD moiety linked to 3-(3-hydroxypropyl)-1*H*-imidazol-3-ium bromide (Fig. 1). The hydroxy groups of β-CD act as hydrogen bond donors, replacing the Lewis acidic metal center, while the bromide counterion facilitates the epoxide ring opening. Linking cyclodextrin to imidazole likely combines the beneficial properties of both molecules. Cyclodextrin provides a unique microenvironment and stability, acting as a hydrogen bond donor thanks to its hydroxy groups. Meanwhile, imidazole contributes to catalytic activity by delivering a bromine counterion, which is crucial for the epoxide ring opening. This combination could result in a highly effective catalyst that leverages the strengths of both components. The strength of this catalyst lies in its exceptional activity, demonstrated by high conversion rates in the CO_2/epoxide cycloaddition reaction in solvent-free conditions and, importantly, its excellent reusability.

Experimental section

Materials

The starting materials β-cyclodextrin, 1-methylimidazole, 3-bromo-1-propanol, styrene epoxide, cyclohexene epoxide, 1,2-epoxy-3-phenoxypropane, 4-vinyl-1-cyclohexene 1,2-epoxide, 1-adamantanol, epichlorohydrine, 2,2-dimethyloxirane, 1,2-epoxyhexane, dimethylformamide, absolute ethanol (EtOH), deuterated chloroform ($CDCl_3$) were purchased from Sigma-Aldrich. Thin-layer chromatographic separations were performed on Merck silica gel 60-F254 precoated aluminum plates. Flash chromatography was accomplished on Merck silica gel (200–400 mesh). Dowex 1X8 (200–400 mesh) analytical grade was purchased from VWR. A Milli-Q water purification system produced deionized water. ^{1}H NMR, ^{13}C NMR, and HSQC spectra were recorded using Bruker AvanceTM 400 MHz and on Varian UNITY Inova 500 MHz.

Synthesis of the catalyst

*Synthesis of 3-(1H-imidazol-1-yl)propan-1-ol (**4**)*

Synthesis of compound **4** was carried out by mixing imidazole **2** (300.0 mg, 4.41 mmol) and 3-bromopropanol **3** (590 mg, 4.41 mmol) at 40 °C in solvent-free conditions. After 24 h, the reaction mixture was cooled to room temperature. The product was purified by flash chromatography using DCM/MeOH (8:2) as eluent. After solvent evaporation, compound **4** was isolated as bromide salt. Yield: 65 %.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H, Im), 7.10 (t, 1H, $J = 1.2$ Hz, Im), 6.97 (t, $J = 1$H, 1.4 Hz, Im), 4.17 (t, 2H, $J = 7.1$ Hz, CH_2), 3.62 (t, 2H, $J = 6.1$ Hz, CH_2O), 2.01 (q, 2H, $J = 6.5$ Hz, CH_2).

Thereafter, compound **4** was eluted from Dowex 66 ion exchange resin using water/methanol (1:1) to obtain the free base. The collected fractions were evaporated under vacuum to obtain a transparent oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H, Im), 7.04 (t, 1H, $J = 1.1$ Hz, Im), 6.93 (t, 1H, $J = 1.3$ Hz, Im), 4.11 (t, 2H, $J = 7.6$ Hz, CH_2), (t, 2H, $J = 5.9$ Hz, CH_2O), 1.99 (q, 2H, $J = 6.5$ Hz, CH_2). HMRS (ESI): *m/z* calcd. for $C_6H_{11}N_2O$ ($M + H^+$): 126.0871, found: 127.0850.

*Synthesis of Mono-6-O-p-toluenesulfonyl-β-cyclodextrin (**6**)*

Compound **6** was synthesized as reported in the literature with minor modifications [31]. To a suspension of β-CD (1.2 g, 1.05 mmol) in 0.4 M NaOH (15 mL) at 0 °C, tosyl chloride (**5**) (0.804 g, 4.22 mmol) was slowly added, and the resulting mixture was stirred at 0 °C for 50 min. The resulting precipitate was removed by filtration, and the pH was adjusted to 8.5 by adding 0.1 M HCl. The reaction was allowed to stir at r.t. for 1 h, and then, the white precipitate was recovered by filtration, washed 3 times with water, and dried in vacuum for 48 h. Yield: 33 %.

*Synthesis of β-cyclodextrin-6-(3-(3-hydroxypropyl)-1H-imidazol-3-ium tosilate (**7**)*

Compound **7** was prepared according to published procedures with minor modifications [32]. Briefly, a mixture of compounds **6** (232 mg, 0.2 mmol) and **4** (252 mg, 2 mmol) were allowed to react in DMF (1 mL) at 90 °C for 48 h under N_2 atmosphere. Then, cold acetone was added, and the precipitate was collected by filtration and washed with acetone. The obtained powder was purified by flash chromatography using a mixture of propanol/ethyl acetate/H_2O/NH_3 (4:2:3:2), $R_f = 0.12$, to afford the final product as a white solid. Yield: 45 %.

^{1}H NMR (400 MHz, D_2O): δ = 8.4 (s, 1H, Im), 7.56 (s, 1H, Im), 5.07–4.95 (m, 1H, H1), 4.33–4.21 (t, 2H, CH_2), 4.00–3.31 (m, 8H, H2–6 and CH_2), 2.11–2.02 (m, 2H, CH_2). MALDI-MS: *m/z* calcd. for $C_{48}H_{79}N_2O_{35}^+$ (M^+): 1243.450, found: 1243.484.

*Synthesis of β-cyclodextrin-6-(3-(3-hydroxypropyl)-1H-imidazol-3-ium bromide (**1**)*

Solid product **7** (35.0 mg, 0.025 mmol) was eluted from Dowex 1X8 ion exchange resin, bromide using water/methanol (1:1). The collected fractions were evaporated under vacuum to give compound **1** as a white solid.

^{1}H NMR (400 MHz, $DMSO_{d6}$): δ = 9.13 (s, 1H, Im), 7.79 (s, 1H, Im), 7.74 (s, 1H, Im), 5.93–5.72 (m, 2H, OH-2 and OH-3), 4.85–4.82 (m, 1H, H1), 4.59–4.51(m, 1H, OH-6), 4.26–4.24 (t, 2H, CH_2), 3.74–3.48 (m, 3H, H3, H4, H5), 3.43–3.23 (m, 3H, H2 and H4, CH_2), 1.97–1.94 (m, 2H, CH_2). MALDI-MS: *m/z* calcd. for $C_{48}H_{79}N_2O_{35}^+$ (M^+): 1243.450, found: 1243.491.

Synthesis of cyclic carbonates

150 mg of CO_2 (dry ice) were added to a high-pressure stainless-steel reactor containing 0.4 mmol of selected epoxide and the catalyst (1.8 % mol). The reaction underwent specific time and temperature conditions and was cooled to room temperature. The optimized conditions were identified as 14 h for the time and 120 °C for the temperature. A fraction of the crude product was immediately transferred into an NMR tube and diluted with $CDCl_3$ for subsequent analysis by NMR spectroscopy.

Reusability

Recyclability was assessed by washing the catalyst with acetone.

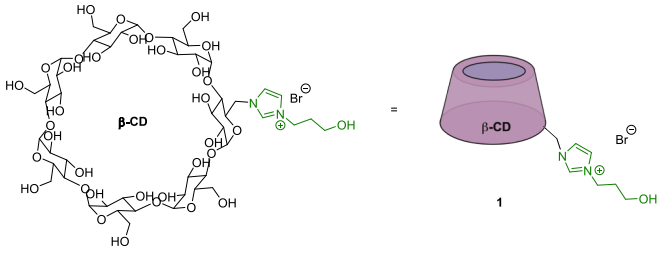


Fig. 1. Designed catalyst **1**.

After centrifugation, the compound was recovered and reused for further reactions involving styrene epoxide and CO_2 as a reference reaction, carried out at optimized conditions.

Computational details

To determine the activation energy barrier of each step and the reaction energy profile, the reactant complex, transition state, and product complex structures were fully optimized. All transition structures were characterized by only one imaginary frequency in normal mode analysis and further supported by Intrinsic Reaction Coordinate (IRC) calculations. Other stationary points (reactant complex, intermediates, and product complex) were characterized by all real frequencies and IRC calculations.

Conformational analyses were conducted using the Conformer-Rotamer Ensemble Sampling Tool (CREST) combined with the xTB at the GFN-2 level of theory. CREST employs an iterative conformational search workflow that generates conformer/rotamer ensembles by extensive metadynamic sampling, with an additional genetic z-matrix crossing step at the end. The most stable structure has been utilized as the starting point for the GFN-2 xTB refinement.

Results and discussion

Synthesis and characterization of catalyst

Catalyst **1** was synthesized through a carefully designed procedure involving the interaction between β-CD and a selected ionic liquid (Scheme 1). Monotosylated β-CD **6** was prepared by reaction of β-CD with tosyl chloride (**5**) in water (Scheme 1). Successively, compound **6** was reacted with 3-(1*H*-imidazol-1-yl)propan-1-ol (**4**), obtained by nucleophilic substitution of imidazole (**2**) with 3-bromopropanol (**3**), to generate the ionic liquid **7**. Therefore, the purified compound **7** underwent anionic exchange with LiBr to obtain the desired catalyst **1**. Compound **7** was characterized by MALDI-TOF MS and ^{1}H NMR (Figs. S1,2), whereas the obtained ionic liquid **1** was characterized by MALDI-TOF MS, ^{1}H, and 2D-COSY NMR (Figs. S5–7). Moreover, thermogravimetric analysis (TGA) was conducted on **1** to assess its thermal stability (Fig. S8).

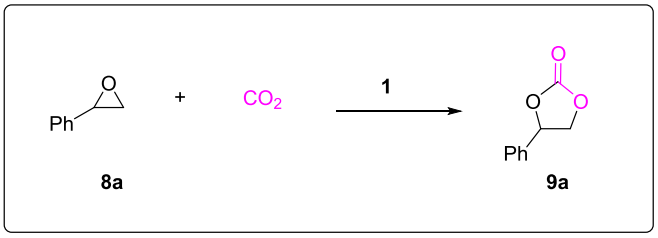
The TGA curve showed that the degradation of **1** starts at 212 °C, a lower temperature compared to β-CD alone, which begins degradation at 314 °C [33]. This disparity may be attributed to the imidazolium moiety, which induces structural distortion in the β-CD [34].

Catalytic activity

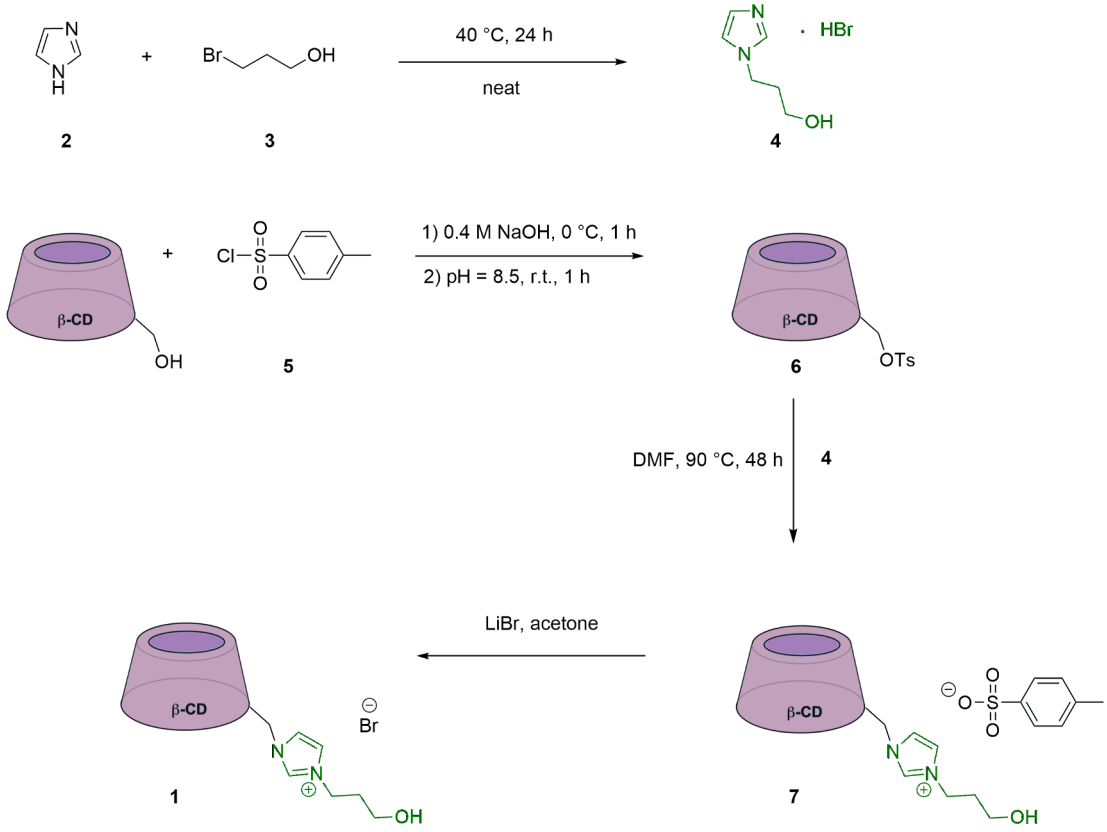
The catalytic activity of newly synthesized **1** was evaluated by a model reaction involving styrene oxide (**8a**) and CO_2 as reactants to produce the corresponding cyclic carbonate **9a** (Scheme 2).

The studies demonstrated that temperature and reaction time strongly influence the catalyst's impact on the reaction (Table 1).

When the reaction was carried out at 40 °C, no product formation was detected (Table 1, entry 1); at 60 °C, the yield was low (Table 1, entry 2). The best conversion (98 %) was obtained by maintaining the



Scheme 2. Model reaction to test the catalyst **1**.



Scheme 1. Synthesis of the catalyst **1**.

Table 1
Optimization of the reaction conditions for the cycloaddition of **8a** with CO_2 using catalyst **1**.

Entry	Temperature (°C)[a]	Conversion (%)[b]
1	40	0
2	60	15
3	80	44
4	100	68
5	120	98
	Time (h)[c]	
6	1	45
7	3	48
8	6	73

[a] Reaction conditions: epoxide **8a** (52.5 mg, 50.0 mL, 0.43 mmol), catalyst **1** (3.0 mg, 1.8 % mol), and CO_2 (150 mg, 3.40 mmol), time = 12 h.
[b] The conversion was determined by ^{1}H NMR spectroscopy.
[c] As in [a] but with a fixed temperature of 120 °C and changing the time.

temperature at 120 °C for 12 h (Table 1, entry 5) under solvent-free conditions, thus employing an environmentally friendly approach and achieving almost a complete conversion of the epoxy group to carbonate.

The progression of the reaction was followed by ^{1}H NMR spectroscopy, looking at the H_2 and H_3 protons of the epoxy ring and the corresponding H_4 and H_5 ones in the carbonate ring (Fig. 2). NMR analysis confirmed the formation of the corresponding carbonate, evidenced by the disappearance of the epoxy group signals at 2.81, 3.16, and 3.87 ppm and the appearance of peaks at 4.35, 4.82, and 5.69 ppm relative to the product. After 1 h, the conversion is 45 % (Table 1, entry 6), and at 3 h, there was no discernible change (48 %, Table 1, entry 7), indicating that the conversion rate remains relatively constant. However, the reaction accelerated after 6 h, ultimately achieving a conversion of 98 % after 12 h. It's crucial to emphasize that no by-products are detectable throughout NMR, then the reaction also proceeds with a selectivity ≥ 99 %. Only the desired product and/or starting reagents are detected in the NMR spectra.

To comprehend the effectiveness of catalyst **1**, control experiments with the starting reagents and intermediates and comparative studies with other catalysts were conducted on the model reaction employing the optimized conditions, and the results are reported in Table 2. The β-CD and bromoalchool **3** were not efficient as a catalyst; no reaction occurred (Table 2, entries 1 and 3), whereas the imidazole (**2**) gave a 36 % conversion (Table 2, entry 2) since **2** functions as both acid and base, we ascribed to this the observed results. When we substitute the imidazole with the *N*-methylimidazole, the conversion percentage increases

Table 2
Screening of different catalysts for the reaction between **8a** and CO_2 under optimized conditions.

Entry	Compound	Conversion (%)
1	β-CD	0
2	**2**	36
3	**3**	0
4	**4**	96
5	**7**	52
6	*N*-methylimidazole	82
7	*N*-hexyl-*N*-methyl imidazolium iodide	93
8	**1** + 1-adamantanol	98

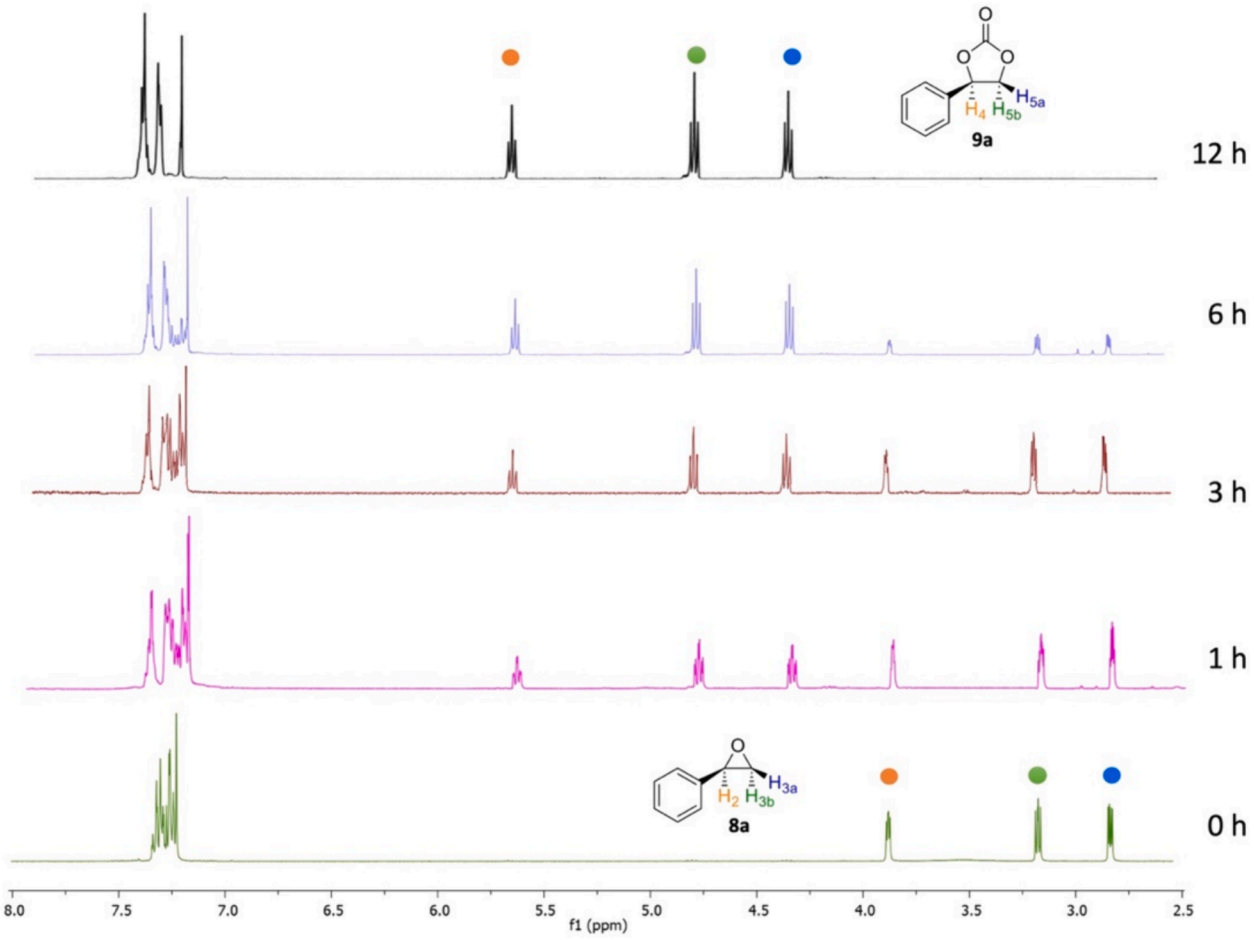


Fig. 2. ^{1}H NMR spectra (400 MHz) in $CDCl_3$ of CO_2 fixation into styrene oxide catalyzed by **1** at optimized reaction conditions.

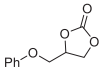
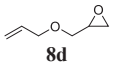
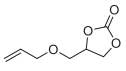
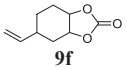
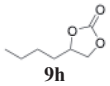
to 82 %, demonstrating that, despite losing the acid function, the reaction not only proceeded but also speeded up.

Furthermore, we employed Compound **4** in both its salt form and as a free base to catalyze the reaction between **8a** and CO_2. It was observed that only compound **4** with HBr achieved a high conversion rate of 96 % (Table 2, entry 4). This conversion is attributed to the Br^- anion, which functions similarly to ionic liquids enhancing reaction rates. This observation is supported by both the literature [35] and our findings, as demonstrated by our testing of the ionic liquid *N*-hexyl-*N*-methyl imidazolium iodide, which yielded a 93 % conversion (Table 2, entry 7).

Although we discovered that only imidazole could be a suitable catalyst for the cycloaddition reaction, its use is limited, considering the difficulty of recycling the material. Moreover, the catalytic activity is not as good as that of catalyst **1**. This can be attributed to the capacity of cyclodextrin for hydrogen bond formation, which can better activate the epoxide toward the nucleophilic attack [36].

Finally, an investigation was conducted to determine if the hydrophobic cavity of β-CD plays a role in the reaction. So, catalyst **1** was mixed with 1-adamantanol (a β-CD cavity competitive guest [37,38]) in a 1:1 M ratio with respect to the β-CD, and the cycloaddition reaction was conducted at optimized conditions (Table 1, entry 5). After 12 h, we obtained compound **9a** with the same conversion percentage as when only catalyst **1** was used (Table 2, entry 8 *vs* Table 1, entry 5), indicating that the cavity of β-CD is not implicated in the reaction. The catalytic activity of **1** was also evaluated by performing the cycloaddition reaction of CO_2 with other structurally different epoxides (**8b–h**). The results, reported in Table 3, showed that catalyst **1** exhibited high conversion toward forming cyclic carbonates for substrates **8b**,**d**,**g**, **h**. Conversely, epoxides **8e**,**f** exhibited lower reactivity, yielding only 49 and 51 % of the corresponding carbonate. This was not surprising, considering that the reactivity of internal epoxides is usually lower than that of terminal ones [39]. However, the conversion percentage is comparable with those reported in the literature [40]. All the obtained carbonates are identified through comparison through NMR matching to what is reported in the NIST database.

Table 3
Reaction of epoxides **8b–f** with CO_2 using catalyst **1** under optimized conditions.

Epoxide	Carbonate	Conversion (%)	Selectivity	TON	TOF (h^{-1})
		98	99	55	2.3
8b	**9b**	87	99	48	2.0
8c	 **9c**	99	99	55	2.3
 **8d**	 **9d**	95	98	52	2.2
8e	**9e**	47	97	26	1.1
8f	 **9f**	51	98	28	1.2
8g	**9g**	93	99	51.6	2.1
8h	 **9h**	86	98	48	2.0

The turnover number (TON) for SC was calculated as mole of SC produced per mole of catalyst. The reaction time of frequency (TOF) was calculated considering the yield obtained in the presence of **1** (P_A), the reaction time in hours (t), and the mol% of **1** (A_0) (Eq. (1) [41]:

$$TOF \approx \frac{P_A}{t \bullet A_0} \quad (1)$$

The obtained values are reported in Table 3.

To highlight the excellent catalytic ability of **1** in CO_2 fixation, its ability to convert styrene oxide in cyclic carbonate was compared with other Lewis-type catalysts (Table 4). The comparison clearly shows that compound **1** offers an excellent compromise in terms of reaction conditions (temperature and time), operating without the need for metals and co-catalysts, which are required in most cases.

Reusability test

Reusability studies have been performed to highlight the advantage of using catalyst **1** for CO_2 cycloaddition reactions. After the first catalysis, **1** was recovered through a straightforward filtration process, washed, dried under vacuum, and reused for the succeeding cycle. As depicted in Fig. 3, the catalyst can be reused for at least four cycles. Only a slight decrease in activity was observed during the fourth cycle, with a conversion rate of 91 %, while maintaining a selectivity of 99 %.

Mechanism of action of the catalyst 1

The many atoms involved in the inquiry led to a high computational cost; therefore, we decided to perform an *in-silico* study utilizing a semiempirical quantum mechanical methods GFN2-xTB as implemented in the xtb (extended tight binding) program package. We have well-validated semiempirical methodologies in calculating activation energies and transition state structures for similar reactions involving several atoms [50,51].

Based on the experimental evidence indicating that catalyst **1** can still catalyze the reaction even when its hydrophobic cavity is occupied, we designed a model to explain such behavior. The literature suggests that the formation of the C-Br bond and the opening of the epoxide ring are the rate-determining steps during the reaction of CO_2 with epoxides [52,53]. Initially, we investigated the energy profile and activation energy for the reaction between isolated epoxide and Br^- in the absence of the catalyst in the gas phase, which showed a ΔG value of 25.78 kcal/mol. Subsequently, we examined the effect of interactions, such as hydrogen bonding between epoxide and the catalyst, on the activation energy of the reaction. Considering that the reaction does not occur inside the cyclodextrin cavity, the proper site for anchoring the imidazole substituent to the cyclodextrin was also investigated. A conformational analysis was conducted to determine the optimal position for anchoring the imidazole substituent, and the optimized structure of this position is reported in Fig. 4.

In this low energy conformation, the N–CH–N proton points inside the cyclodextrin cavity, while the N–CH–CH–N protons point outside the ring. Although the N–CH–N proton of the imidazole has been shown to play a relevant role in the catalytic activity, its position inside the ring suggests it has a minor role in our catalysis. The OH group of the alkyl chain attached to the imidazole forms a network of hydrogen bonds with the bromine ion and the OH group of the small cyclodextrin rim.

A secondary analysis was performed considering the epoxide, aiming to identify the molecular complex before forming the C-Br bond and the

Table 4
Comparison of catalytic activity with Lewis-type catalysts on styrene oxide conversion to cyclic carbonate.

Catalyst	Temperature and time	Co-Catalyst	Metal	Conversion (%)	References
β-CD-Im^{+}Br^{-}	120 °C, 12 h	No	No	98	This work
Im-CD1-Br	130 °C, 5 h	No	No	91	[18]
[DBUH][PFPhO]/β-CD	130 °C, 5 h	No	No	95	[42]
Amino-functional bis-β-CD	110 °C, 4 h	No	No	99	[26]
5B–SiO_2–NH_2–3–I	110 °C, 6 h	No	No	47	[43]
$In_2(OH)(btc)(Hbtc)_{0.4}(L)_{0.6}\cdot 3H_2O$	80 °C, 4 h	Yes	Yes	73	[44]
Mg-MOF-74	100 °C, 4 h	No	Yes	95	[45]
Co-MOF-74	100 °C, 4 h	No	Yes	96	[46]
Hf-NU-1000	r.t., 56 h	Yes	Yes	100	[47]
$[Cd_2(Ni\text{-}L)_2(H_2O)_4]\cdot 3DMF$	80 °C, 4 h	Yes	No	81	[48]
Ni-TCPE2	100 °C, 12 h	Yes	Yes	86	[49]

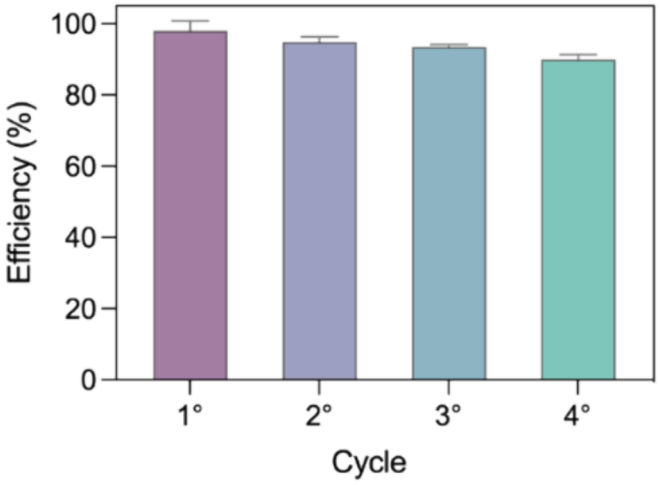


Fig. 3. Reusability of catalyst **1**.

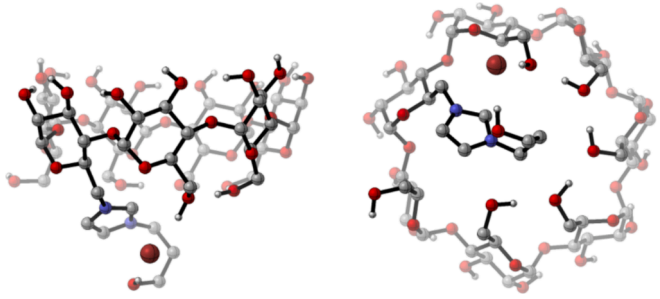


Fig. 4. Optimized structure after conformational analysis of the catalyst **1**. Figures generated with CYLview20 [54].

opening of the epoxide ring in the rate-determining step. The analysis showed that the oxygen of the epoxide ring engages in a hydrogen bond with the OH group of the alkyl chain of the imidazole.

The entire reaction was then studied in the presence of catalyst **1**. Fig. 5 illustrates the free-energy profiles, intercepted minima, and transition states. The analysis revealed that in the molecular complex, the oxygen of the epoxide ring forms a hydrogen bond with the OH group of the functionalized alkyl chain of the derivatization moiety of the catalyst **1**, with an initial bond length of 1.74 Å (Fig. 5, MC). After the activation of the epoxide by coordination to catalyst **1**, the reaction proceeds via a nucleophilic attack by the bromide ion on the methylene carbon, resulting in the ring-opening and subsequent formation of the anion I1 (Fig. 5). The calculated energy barrier, i.e., the activation energy of the rate-limiting step, relative to I1 is 23.95 kcal/mol. It involves a transition state referred to as TS1. In TS1, the oxygen of the epoxide ring also deprotonates the OH group of the derivatization moiety of catalyst **1**, shortening the initial H-bond interaction from 1.74 Å to 1.54 Å. Additionally, the bromine ion is 2.23 Å away from the C2 of the epoxide ring (Fig. 5, TS1) [55].

The activation of the CO_2 molecule for the reaction is indicated by the slight deviation of the O-C-O angle from its linearity to 175.9° [56]. Due to this activation, the insertion into the alkoxide becomes a straightforward step, requiring an activation energy of 4.61 kcal/mol (Fig. 5, TS2). In the optimized TS2 structure, the calculated distance between the epoxide oxygen O1 and the carbon of the CO_2 is 2.00 Å, while the calculated O–C–O angle of the CO_2 is 153.6°. The formed carbonate anion I2 is 19.28 kcal/mol more stable than TS2. In this intermediate, the delocalized negative charge of the carbonate anion is stabilized by hydrogen bonding with the catalyst **1**. In the final step of the reaction, the cyclic carbonate product is formed by releasing the bromide and creating a new C–C bond. The product **9a** intermediate is highly exergonic, lying 22.45 and 29.85 kcal/mol below the MC reactants and TS3, respectively.

While the geometry calculation suggested a network of hydrogen interactions during the TS, they also indicated that the N-CH-N proton of the imidazole is not involved in the catalysis, which differs from the previously reported mechanism [57]. The activation energy involved in the TS was calculated to be 1.83 kcal/mol lower than the activation energy of the reaction without a catalyst. This reduction in activation energy is due to the hydrogen bond acceptor properties of the catalyst, which lower the activation energy of the rate-limiting step, thereby explaining the catalytic behavior of catalyst **1**.

Conclusions

To address the pressing issue of global warming, it is imperative to develop an efficient, cost-effective, and environmentally sustainable system for capturing or converting CO_2. In this context, we have developed a low-cost and reusable catalyst based on β-CD linked to an ionic liquid, free of metallic cations, capable of converting epoxides into cyclic carbonates, a valuable product for industries, with high efficiency. Comparative studies and control experiments have highlighted the superior performance of the cyclodextrin-ionic liquid catalyst in promoting the CO_2 cycloaddition reaction. This catalyst facilitates the transformation of various epoxides into cyclic carbonates with high conversion rates, including challenging substrates such as internal epoxides. Mechanistic insights further elucidate the role of hydrogen bond donors and acceptors in enhancing catalytic performance.

Overall, this method demonstrates high efficiency and selectivity, operating under environmentally friendly, solvent-free conditions, thus mitigating the adverse impacts of conventional synthetic pathways.

Beyond its immediate impact on chemical transformations, this catalyst holds promise for applications in diverse fields, including lithium batteries, polymer materials, and emerging energy sectors. The integration of this catalyst addresses current environmental concerns

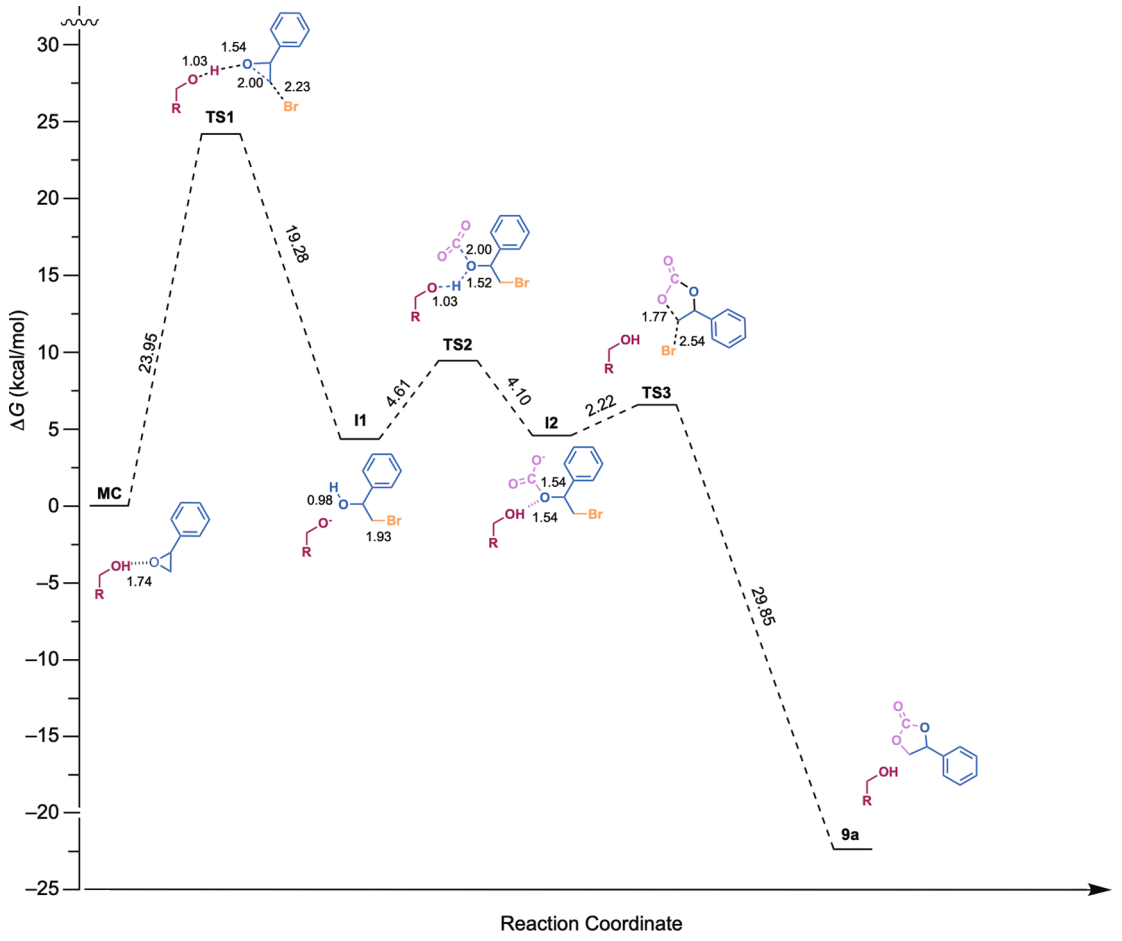


Fig. 5. Gibbs free energy profiles for the studied reaction mechanism to produce **9a**. All the distances are measured in Å. Catalyst **1** has been simplified for clarity.

and contributes to the development of cleaner and more sustainable technologies for the future.

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CRediT authorship contribution statement

Elisabetta Grazia Tomarchio: Visualization, Validation, Methodology, Investigation. **Chiara Zagni:** Writing – review & editing, Writing – original draft, Data curation, Conceptualization. **Rita Turnaturi:** Methodology, Investigation, Conceptualization. **Sandro Dattilo:** Writing – original draft, Validation, Investigation. **Vincenzo Patamia:** Methodology, Formal analysis. **Giuseppe Floresta:** Writing – original draft, Methodology, Formal analysis. **Sabrina Carola Carroccio:** Writing – review & editing, Resources. **Tommaso Mecca:** Methodology, Investigation. **Antonio Rescifina:** Writing – review & editing, Validation, Supervision, 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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jiec.2024.08.024.

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