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Aminocyclopropenium as a novel hydrogen bonding organocatalyst for cycloaddition of carbon disulfide and epoxide to prepare cyclic dithiocarbonate†

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The smallest Hückel aromatic ring cyclopropenium substituted by electron-donating C-amino groups produced a aminocyclopropenium electron-rich cation. A bifunctional aminocyclopropenium halide catalyst installed with bis-(hydroxyethyl) functions on the amino group was then designed. A typical (diethanolamino)cyclopropenium halide catalyst **C5·I** was screened optimally for the cycloaddition of carbon disulfide into an epoxide to produce cyclic dithiocarbonate with an excellent conversion (95%) and high selectivity (92%). The electrostatic enhancement of alkyl C–H HBD capability was implemented *via* vicinal positive charges on the cyclopropenium core, and the acidity of the terminal O–**H** hydrogen proton increased by intramolecular H-bonding between the two hydroxy groups on the diethanolamino group (O–H···O–**H**). Then, a hybrid H-bond donor comprising enhanced alkyl C–H and hydroxy O–**H** was formed. The hybrid HBD offered by aminocyclopropenium was vital in activating the epoxide and stabilizing the intermediate, resulting in reduced O/S scrambling. Moreover, weakly coordinated iodide anion served as a nucleophilic reagent to open the ring of the epoxide. The cooperative catalytic mechanism of the HBD cation and halide anion was supported by NMR titrations and control experiments. Eleven epoxides with various substituents were converted into the corresponding cyclic thiocarbonate with high conversion and selectivity under mild conditions (25 °C, 6 h) without a solvent. The cycloaddition of carbon disulfide with epoxides catalyzed by aminocyclopropenium developed a new working model for hydrogen bonding organocatalysis.

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1 Introduction

Epoxides are not only easily prepared but also react with numerous reagents and are versatile intermediates for organic synthesis.[1] The cycloaddition reaction of epoxide and heterocumulene is a convenient, efficient, and atom-economical approach to synthesizing high-value-added five-membered heterocyclic compounds.[2–5] In recent years, the cycloaddition of epoxide with carbon dioxide (CO_2) to produce cyclic carbonate has been well studied and is quite promising for industrial applications.[6–12] Cyclic dithiocarbonates are sulfur-containing analogs of cyclic carbonates, which can also be produced by coupling epoxides with carbon disulfide (CS_2).[13] Despite potential applications in monomers for sulfur-containing polymers[14–18] and radiation protection material,[19] relatively few studies have been published. CS_2 is an isoelectronic analogue of CO_2,[20] which occurs naturally in gases released from the surface and produced by microbial metabolism;[21] this bulk chemical can also be considered an inexpensive C1 building block.[13] Studies on the cycloaddition of carbon disulfide with epoxides were first published in 1960.[22,23] In contrast to carbon dioxide, the cycloaddition of carbon disulfide and epoxide often yielded complex by-products at high temperatures or long reaction times (Scheme 1). This is primarily due to the frequent scrambling of oxygen and sulfur atoms, leading to a decrease in the selectivity of the reaction, which was first documented by Endo *et al.*[24]

For the insertion of CS_2 in epoxides, base catalysts were most frequently used. The nucleophilic base-activated carbon disulfide forms an adduct intermediate, and then the sulfur anion attacks the epoxide causing the ring-opening[20,23,25–31] (Scheme 2a). The monofunctional metal halide offered a nucleophilic halide anion to open the three-membered ring of the epoxide[24,32–34] (Scheme 2b). Another catalytic mode was a metal complex (ML_n) and a halogen anion binary co-catalysis

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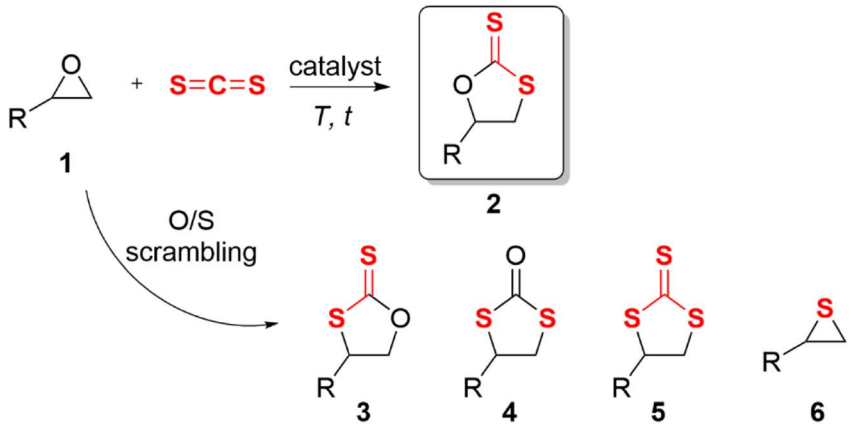
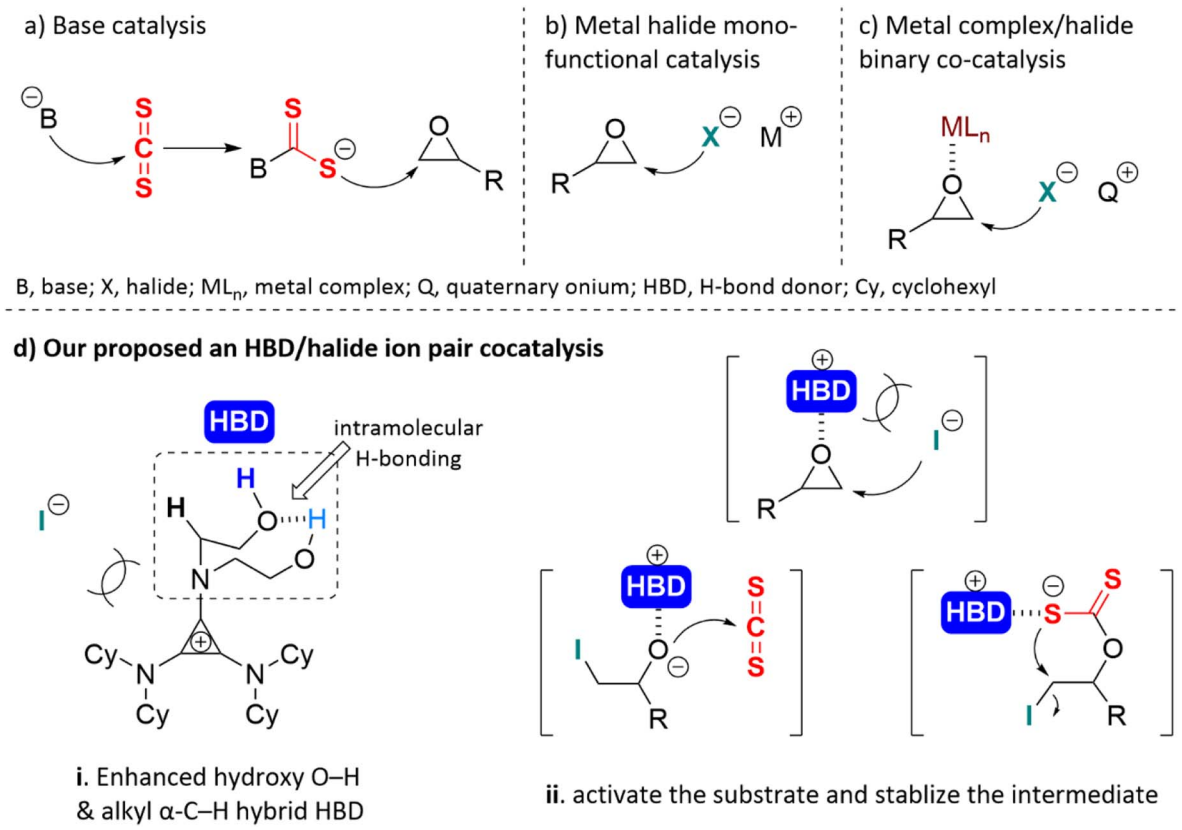


Scheme 1 Cycloaddition of epoxides with carbon disulfide and other side reactions.

system.[2,5,35–38] The metal complex served as Lewis acid to activate the epoxide, and the halogen anion nucleophilically attacked the methylene carbon of the epoxide to open the ring (Scheme 2c). Most of them require co-catalysts, high catalyst loading, toxic solvents, or harsh reaction conditions. The prolonged time and high temperature sharply increased the risk of generating unwanted by-products, such as cyclic trithiocarbonate 5 or sulfur-containing polycarbonate.[38] Moreover, the base may lead to ring opening or self-polymerization of the epoxide.[39] There is little information available in the literature about bifunctional hydrogen bonding catalysis for this reaction.[33,40,41] Noncovalent H-bonding interactions between charge-deficient hydrogen protons and electrophilic species can activate substrates and/or stabilize intermediates,[42] which has



Scheme 2 (a) Base activated carbon disulfide first, then the sulfur anion opened the ring of the epoxide; (b) the monofunctional metal halide offered a halide anion to attack the methylene carbon of the epoxide; (c) the metal complex (ML$_n$) activated the epoxide, and the halide anion opened the ring of the epoxide; (d) a novel H-bonding catalyst was proposed to facilitate the cycloaddition of the epoxide and carbon disulfide. (i) Intramolecular H-bonding between the hydroxy group enhanced O–H, formed a hybrid HBD system with α-C–H. (ii) The HBD system could activate the epoxide and stabilize the anion intermediate.

emerged as a key strategy for organic transformations.[43] We predicted that the O/S scrambling during the coupling of CS_2 with epoxide can be well controlled through H-bonding. Herein, a neutral H-bonding bifunctional organocatalyst was proposed to facilitate its gentle conversion.

Cyclopropenium is the smallest aromatic compound that satisfies the Hückel's rule and was first synthesized in 1957 by Breslow *et al.*[44] When it was substituted with amino groups, the aromatic cation electrostatically enhanced the acidity of the side chain α-C–H,[45] which can be regarded as a nonclassical H-bond donor. The orbital repulsion between the electron-excess ion pair would offset some of the coulombic force.[46,47] This phenomenon gave rise to what is known as "ion pair strain", characterized by the weakened coordination of the halide anion with cyclopropenium, and it was predicted that the catalytic activity of these anions was very high.[48] Aminocyclopropenium as an H-bonding catalyst has been utilized in many organic reactions,[49–52] such as ring-opening polymerization,[53] cycloaddition of CO_2 into epoxide,[54] pyranylation of alcohols,[55] and Payne-type rearrangement of glycidol.[56] Based on previous studies, a novel HBD aminocyclopropenium ion pair catalyst was designed to efficiently convert epoxide and carbon disulfide to cyclic carbonate under solvent-free and mild conditions. The intramolecular H-bonding between two hydroxyl groups improved the acidity of the hydrogen proton of the terminal hydroxyl group (O–H···O–**H***).[57] The enhanced O–H and α-C–H formed a hybrid H-bond donor system (Scheme 2d(i)). The hybrid HBD polarized the epoxide and stabilized the anion intermediate *via* H-bonding (Scheme 2d(ii)).

2 Experimental section

2.1 General procedure for the cycloaddition reaction of carbon sulfide and epoxides

All operations were performed using standard Schlenk techniques with a nitrogen atmosphere to reduce exposure to water and oxygen. A flame-dried 10 mL Schlenk tube containing a magnetic stirring bar was charged with carbon sulfide (0.14 mL, 2.4 mmol, 1.2 equiv.), epoxide **1** (2 mmol, 1 equiv.), and 1-diethanolamino-2,3-bis(dicyclohexylamino)cyclopropenium iodide (**C5·I**) (63 mg, 0.1 mmol, 0.05 equiv.) under an argon atmosphere. The reaction mixture was stirred at 25 °C for 6 h. After that, the mixture was purified by silica gel flash column chromatography (PE : EA = 5 : 1) to give the corresponding products **2a–2k**.

3 Results and discussion

3.1 Design of aminocyclopropenium catalysts and evaluation of the catalytic performances

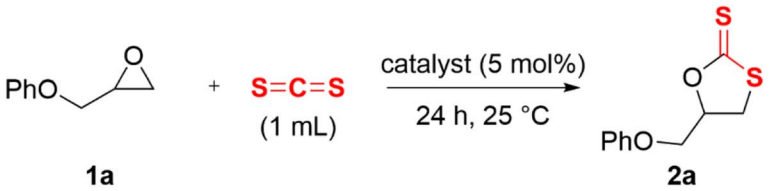
Aminocyclopropenium acted as a hydrogen bond donor (HBD) by rationally designing the amino substituents. Typical HBDs were O–H and N–H, and C–H was too weak to serve as an H-bond donor from a common perception. However, the electron-donating π-conjugative effect of amino group was stronger than the electron-withdrawing σ-inductive effect in the cyclopropenium system. The α-C–H of the substituted alkylamino group on the cyclopropenium cation was weakly acidic and exhibited a capacity of HBD.[54,56] On the basis of the above theoretical foundations and previous research work, three types of HBD cyclopropenium cations were designed and synthesized, in which alkylaminocyclopropenium **C1–C3** was nonclassical C–H HBD. Anilino-cyclopropenium **C4** synthesized according to the literature procedure[58] had a bidentate N–H HBD, and the diethanolamino on **C5** provided two hydroxyl groups. To investigate the effect of the amount of O–H on the catalytic behavior, morpholino- and *N*-aniline-*N*-ethanolamino-substituted cyclopropenium **C6** and **C7** were synthesized. With the purpose of verifying the promotion of the cyclopropenium moiety, the catalyst **C8** was prepared through Hofmann alkylation of *N*-methyl-*N*-diethanolamine.[59] Carbon disulfide (CS_2, 1 mL) and phenyl glycidyl ether **2a** (PGE, 2 mmol) were reacted at 25 °C for 24 h as a template reaction to evaluate the catalytic effect of the catalysts mentioned above (Table 1).

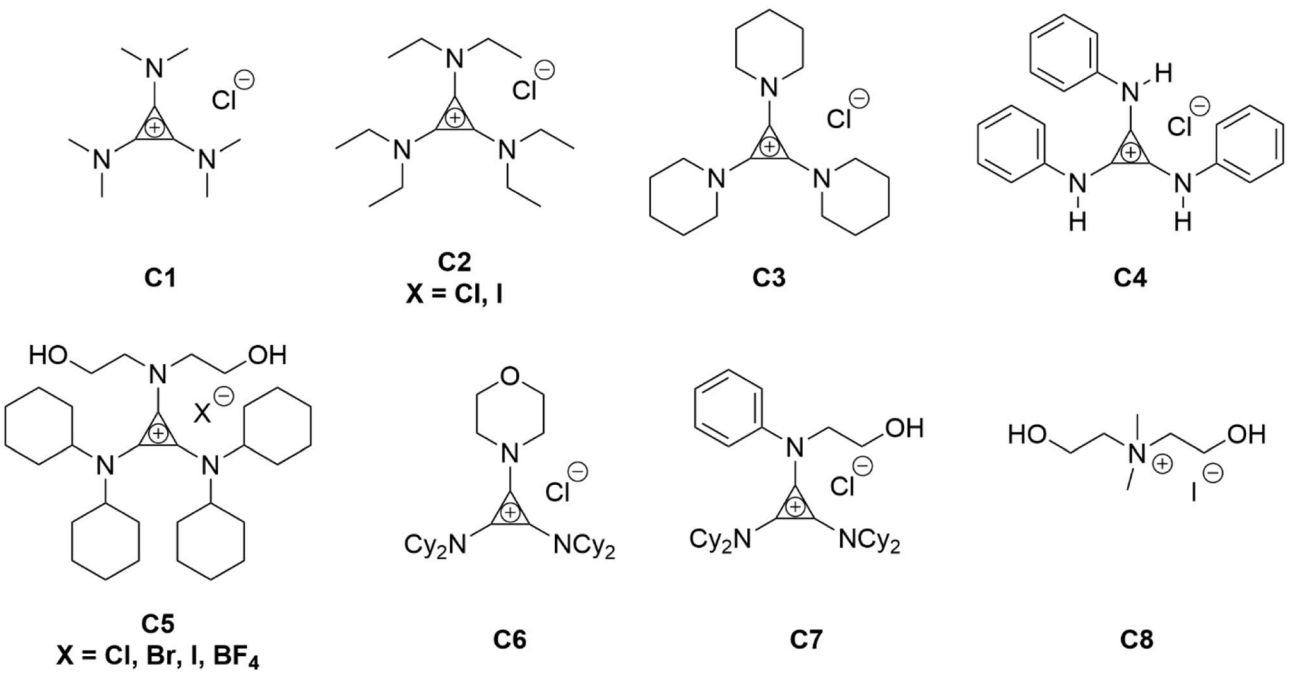
Initially, 2-(phenoxymethyl)oxirane (**1a**) was selected as a model substrate for the screening of the optimal catalysts. The evaluation results of aminocyclopropenium catalysts are shown in Table 1. With the increase of the alkylamino chain length on the cyclopropenium, the conversion and selectivity of the substrate improved (Table 1, entries 1–3, the detailed analytical method of conversion and selectivity, see ESI†). Tetrabutylammonium chloride (TBAC) was used as a control catalyst without the H-bond donor and exhibited a weak catalytic ability (Table 1, entry 4), which indicated that the aromatic cyclopropenium cation did enhance the acidity of C–H by electrostatic interaction. While the anion was switched to iodide, the conversion improved significantly but was still unsatisfactory at 46% (Table 1, entry 5). The reaction could not proceed when the N–H hydrogen bond donor catalyst **C4** was applied (Table 1, entry 6). Diethanolamino-cyclopropenium chloride (**C5·Cl**) catalyzed the cycloaddition of the epoxide and carbon disulfide with 51% conversion and 90% selectivity (Table 1, entry 7). Surprisingly, the anions of **C5** were replaced with bromine and iodine with improved conversion and the same selectivity (Table 1, entries 8 and 9, **C5·Br**: Conv. 76%, Selec. 91%; **C5·I**: Conv. 88%, Selec. 92%). A similar experimental result has been reported in a previous work.[33] The morpholino-substituted catalyst **C6** showed comparable activity to **C3** (Table 1, entry 11), probably due to both playing the role of C–H HBD. Catalysts with only a single hydroxyl group were less effective and less selective (Table 1, entry 12). The cycloaddition reaction did not occur if the catalyst was omitted (Table 1, entry 15). In fact, N–H HBD could not convert the epoxide and C–H HBD catalysts were poor to fair in the catalytic performance. However, the O–H HBD-containing cyclopropenium iodide was able to promote the cycloaddition of epoxide and carbon disulfide, and the number of hydroxyl groups was also important to the success of the reaction. Moreover, we believed that the anion influenced the conversion of the epoxide and the steric hindrance of the cyclopropenium substituent affected the selectivity of cyclic dithiocarbonate.

3.2 Optimization of the cycloaddition reaction conditions

Reaction conditions were then optimized with **C5·I** as the catalyst. The initial experiment was performed with **1a** and CS_2

Table 1 Evaluation of the effect of the catalyst[a]





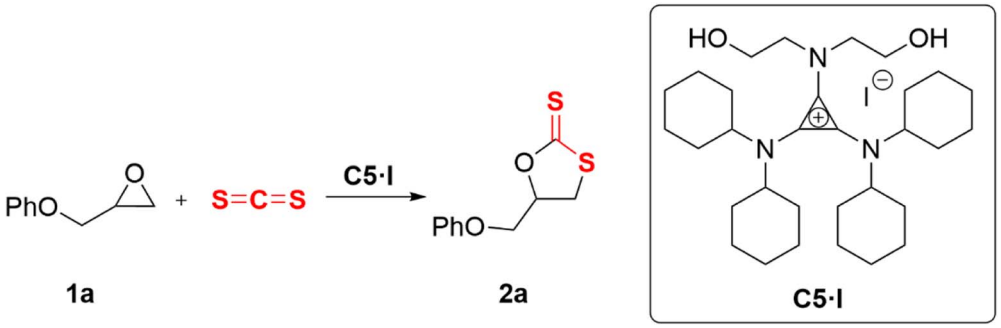
Entry	Catalyst	Conv.[b] (%)	Selec.[b] (%)
1	**C1**	22	83
2	**C2·Cl**	23	85
3	**C3**	33	90
4	**TBAC**	12	n.d.
5	**C2·I**	46	87
6	**C4**	n.d.	n.d.
7	**C5·Cl**	51	90
8	**C5·Br**	76	91
9	**C5·I**	88	92
10	**C5·BF_4**	8	n.d.
11	**C6**	33	90
12	**C7**	25	85
13	**C8**	19	n.d.
14	**NaI**	n.d.	n.d.
15	—	n.d.	n.d.

[a] All reactions were performed with 2 mmol of 2-(phenoxymethyl)oxirane (**1a**) and carbon disulfide (1 mL) catalyzed by **C5·I** (5 mol%) for 24 hours at 25 °C under Ar; n.d. = not determined; Conv. = conversion; Selec. = selectivity; **TBAC** in entry 13 was tetrabutylammonium chloride. [b] Conversions (of **1a**) and selectivity (to **2a**) were determined by ^{1}H NMR with dodecane as an internal standard.

in the presence of **C5·I**. Catalyst loading, solvent, reaction temperature, reaction time, and the equivalent amount of carbon disulfide were the five factors related to optimization.

With increase in catalyst loading, the conversion improved and selectivity deteriorated (Table 2, entries 1–5). The conversion of **2a** only showed a minor increase when the reaction temperature was raised from 25 °C to 80 °C (Table 2, entries 3, 6 and 7). Elevated temperatures harmed the formation of cyclic dithiocarbonates, resulting in increased occurrence of oxygen/sulfur scrambling in the reaction intermediates, leading to a reduction in selectivity.[24] By extending the reaction time to 24 h, a significant improvement in the conversion was observed

Table 2 Optimization of cycloaddition reaction conditions[a]



Entry	Catalyst loading (mol%)	Solvent	Temperature (°C)	Time (h)	Conv.[b]	Selec.[b]
1	1	Neat	80	24	6%	n.d.
2	2	Neat	25	24	37%	88%
3	5	Neat	25	24	88%	92%
4	8	Neat	25	24	95%	86%
5	10	Neat	25	24	96%	65%
6	5	Neat	40	24	90%	88%
7	5	Neat	80	24	92%	86%
8	5	Neat	25	4	35%	90%
9	5	Neat	25	8	56%	91%
10	5	Neat	25	16	70%	91%
11[c]	5	Chloroform	25	6 (24)	31% (57%)	90%
12[d]	5	Neat	25	6 (24)	84% (95%)	89%
13[e]	5	Neat	25	6	75%	90%

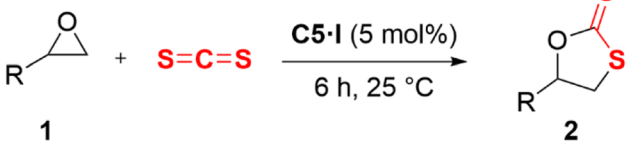
[a] All reactions were performed with 2 mmol of 2-(phenoxymethyl)oxirane (**1a**) and carbon disulfide (1 mL) catalyzed by **C5·I** (5 mol%) under Ar; n.d. = not determined; Conv. = conversion; Selec. = selectivity. [b] Conversions (of **1a**) and selectivity (to **2a**) were determined by ^{1}H NMR with dodecane as an internal standard. [c] 1.5 mL solvent was added; prolonging the reaction time to 24 h, the conversion was 57%. [d] CS_2 (0.14 mL, 2.4 mmol, 1.2 equiv.); prolonging the reaction time to 24 h, the conversion was 95%. [e] CS_2 (0.24 mL, 4 mmol, 2 equiv.).

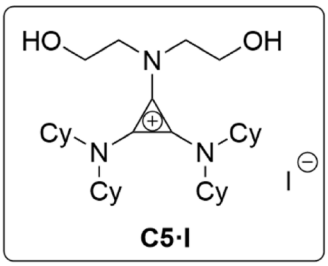
(Table 2, entries 3 and 8–10). Considering that the catalyst was soluble in chloroform and methanol only, the experiment was conducted utilizing chloroform as the solvent to avoid interference caused by methanol protons. It was observed that the addition of the solvent did not contribute to an increase in the reaction rate (Table 2, entry 11). The desired conversion rate was not obtained even when the reaction time was prolonged to 24 h (Table 2, entry 11, parentheses). Finally, the equivalent of carbon disulfide was also screened. Carbon disulfide served as both the solvent and reactant in the initial experiments. Surprisingly, as the amount of carbon disulfide was gradually reduced to 1.2 equivalents, compound **2a** could be rapidly obtained at room temperature with excellent conversion and selectivity (Table 2, entries 12 and 13). Prolonging the reaction time to 24 h did not significantly improve the conversion and selectivity (Table 2, entry 12, parentheses). To summarize, the optimal conditions were established as catalyst **C5·I** (5 mol%), CS_2 (1.2 equiv.), solvent-free, 25 °C, and 6 h.

3.3 Substrate scope studies for cycloaddition of epoxides into CS_2 catalyzed by C5·I

With the advent of this efficient cooperative catalytic system, a variety of substituted epoxides were tested to probe the versatility of this catalytic system (Table 3). Aryl glycidyl ethers were generally suitable for this protocol, with 84% of phenyl glycidyl ethers converted to **2a** within 6 h. Prolonging the reaction time to 24 h increased the conversion to 95% with 89% selectivity. The reactivity of *o*-tolyl glycidyl ether was relatively low and afforded **2b** in 88% conversion in 12 h. It is noteworthy that not only cyclic trithiocarbonate **5c** but also a mixture of the regional isomers of dithiocarbonate **3c** was determined through thin-layer chromatography and ^{1}H NMR (Table 3, entry 3, Conv. 92%; Selec. 82%). The cycloaddition reaction of styrene oxide and carbon disulfide generated preferentially the regioisomer **3c** because of the accelerated α-cleavage by the phenyl substituent; this phenomenon was supported by previously reported studies.[1,24,26] The trifluoromethyl-substituted epoxide **1d** was well tolerated with 94% conversion, indicating that the electron-withdrawing substituted substrate was also suitable for this protocol. The lower reaction selectivity of epichlorohydrin may suffer from the generation of cyclic trithiocarbonate (Table 3, entry 5, Conv. 86%; Selec. 80%). Epoxides with electron-donating substituents were utilized to study the influence of the electronic effect of the substrate on the reaction. The methyl- and *t*-butyl-substituted glycidyl ethers yielded the corresponding products **2h** and **2j** in 75% and 82% conversions, respectively. Olefin-containing

Table 3 Epoxides scope in [3 + 2] cycloaddition reaction[a]





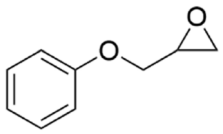
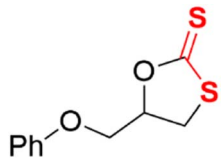
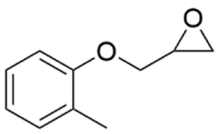
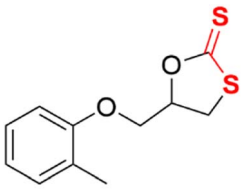
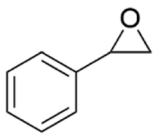
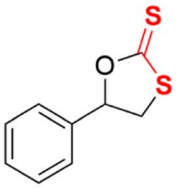
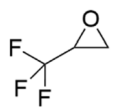
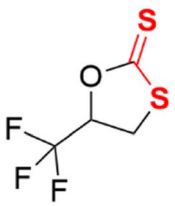
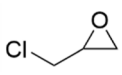
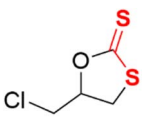
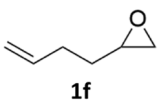
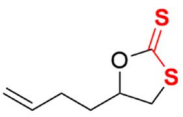
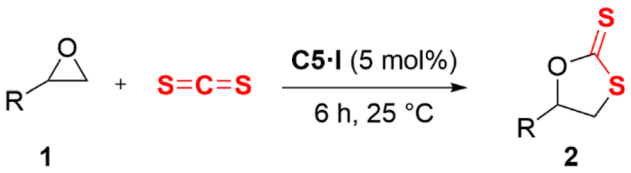
Entry	Epoxide 1	Product 2	Conv.[b]	Selec.[b]
1	 1a	 2a	84% (95% for 24 h)	89%
2[c]	 1b	 2b	88%	91%
3	 1c	 2c	92%	82%
4	 1d	 2d	94%	91%
5[c]	 1e	 2e	86%	80%
6	 1f	 2f	85%	91%

Table 3 (*Contd.*)



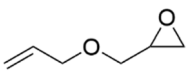
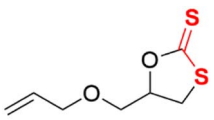
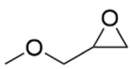
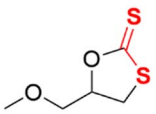
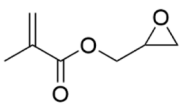
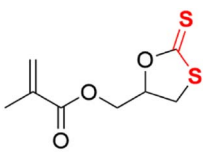
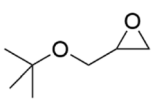
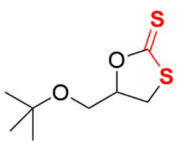
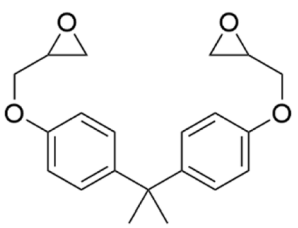
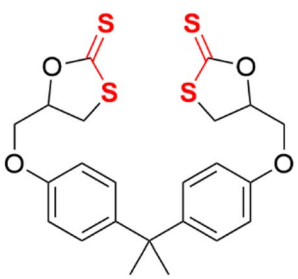
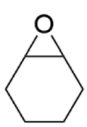
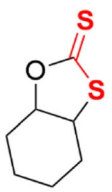
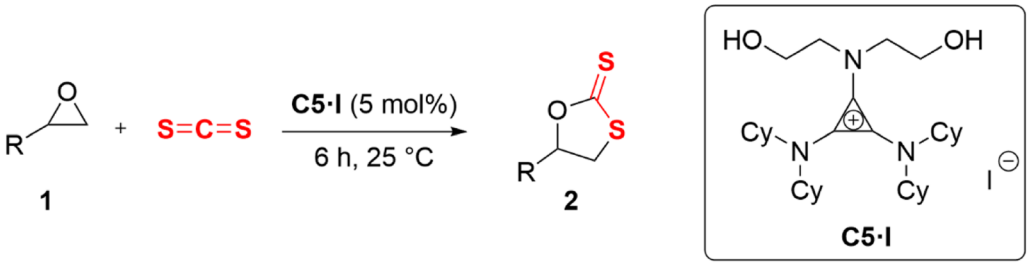
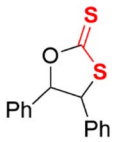
Entry	Epoxide 1	Product 2	Conv.[b]	Selec.[b]
7[c]	 1g	 2g	92%	91%
8	 1h	 2h	75%	91%
9	 1i	 2i	92%	91%
10	 1j	 2j	82%	89%
11[d]	 1k	 2k	85%	89%
12	 1l	 2l	n.d.	n.d.

Table 3 (*Contd.*)



Entry	Epoxide 1	Product 2	Conv.[b]	Selec.[b]
13	 **1m**	 **2m**	n.d.	n.d.

[a] All reactions were performed with epoxides (2 mmol, 1 equiv.) and carbon disulfide (0.14 mL, 2.4 mmol, 1.2 equiv.) catalyzed by **C5·I** (5 mol%) for 6 h under Ar; n.d. = not determined; Conv. = conversion; Selec. = selectivity. [b] Conversions (of substrate **1**) and selectivity (to product **2**) were determined by ^{1}H NMR with dodecane as an internal standard. [c] Reaction time was 12 hours. [d] CS_2 (0.48 mL, 8 mmol, 4 equiv.) was used. DMF (0.5 mL) was added as a solvent to dissolve the substrate.

epoxides were able to facilitate the cycloaddition with carbon disulfide with excellent conversions and selectivity (Conv. **2f**: 85%; **2g**: 92%; **2i**: 92%). Besides, the conversion of bisepoxide BPA **1k** was 85%, and the selectivity of **2k** was 89%, which was the monomer for the sulfur-containing polymers.[60,61] Note that 0.5 mL DMF was added as a solvent to promote solid substrate **1k** dissolution. However, internal epoxides such as **1l** and **1m** were not observed to produce the products even after 48 h of reaction, probably the excessive substituent hindering the ring-opening process.

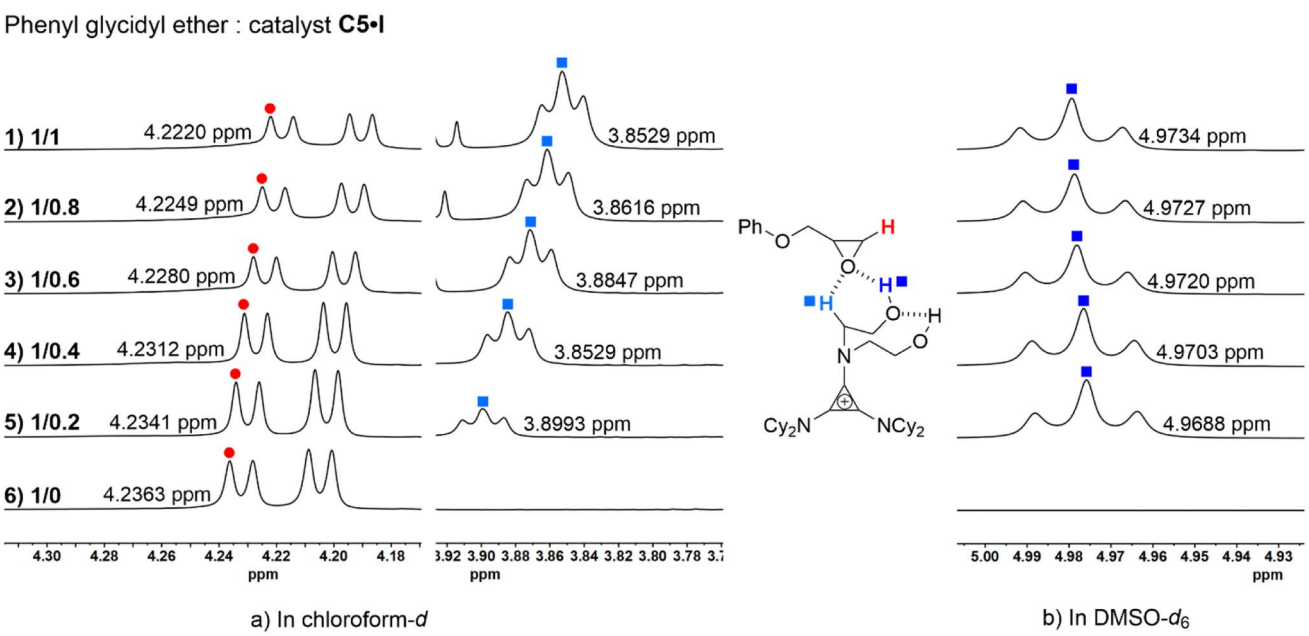
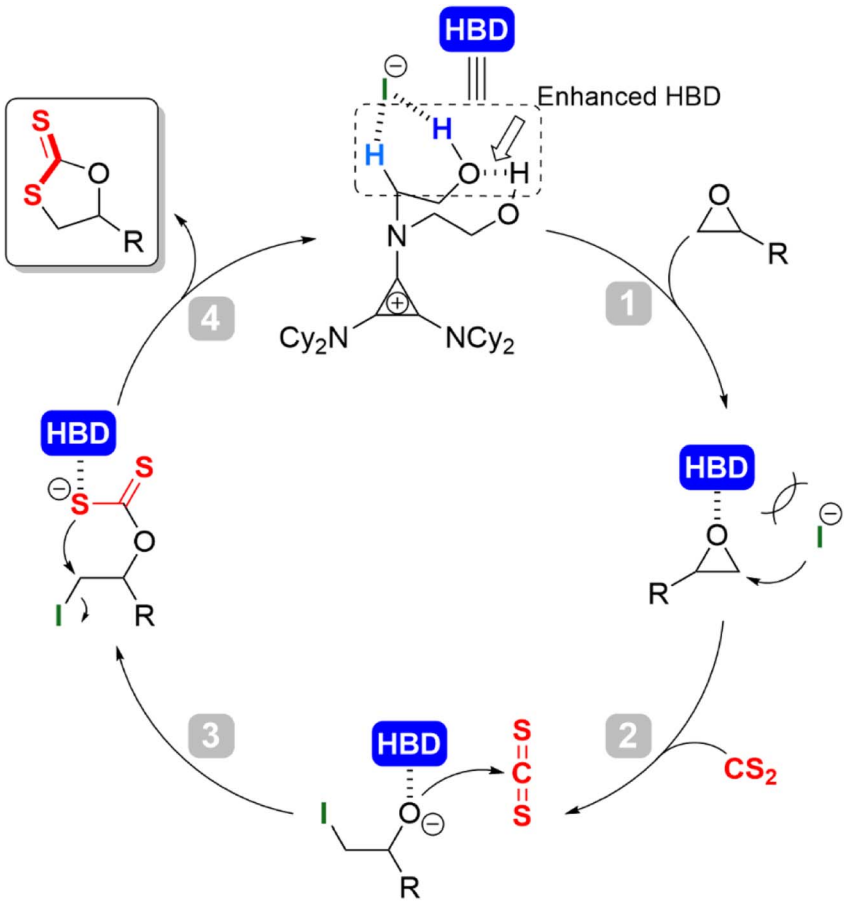


Fig. 1 Phenyl glycidyl ether **1a** and catalyst **C5·I** were mixed in the ratio of 1 : 1, 1 : 0.8, 1 : 0.6, 1 : 0.4, 1 : 0.2, and 1 : 0; (a) the chemical shift of the methine proton of **2a** (left, red) and α-C–H of **C5·I** (right, light blue) in the ^{1}H NMR spectra (in $CDCl_3$); and (b) the chemical shift of the hydrogen proton of the O–H (deep blue) of C5·I (DMSO-d_6).

3.4 Proposition and validation of the mechanism of the cycloaddition reaction catalyzed by C5·I

To validate the role of the catalyst in both its cationic and anionic species in the reaction cycle, analog catalysts **C5·BF$_4$** and **C8** were synthesized to perform the control experiments. The key step in the cycloaddition reaction was the opening of the epoxide ring by the nucleophilic reagent. Switching the counterion of **C5** to non-nucleophilic tetrafluoroborate anion BF_4^- (**C5·BF$_4$**) and performing the benchmark reaction under the same conditions. Only a negligible amount of product was generated as per NMR analysis (Table 2, entry 9); the probable explanation for this is that the ion exchange process was unable to reach 100%, and the residual iodide ions led to the formation of the product. Therefore, sodium iodide (Table 1, entry 14) was applied to attempt the benchmark reaction with only a 5% conversion of **1a**. The results of the control experiments demonstrated that the halide anion of the strained ion pair played a critical role as the nucleophilic reagent in the catalytic cycle. The catalyst **C8** (*N*,*N*-dimethyl-dihydroxyethylammonium iodide), which could provide a pair of O–H hydrogen bond donors and an iodide anion, has also been used for the benchmark reaction. Only 19% of **2a** was generated *via* ^{1}H NMR analysis (Table 1, entry 12), which indicated that the H-bond donor aminocyclopropenium was indispensable in catalyzing this reaction.

NMR titration experiments were carried out to further support the importance of hydrogen bond donors in activating the substrate (Fig. 1). The phenyl glycidyl ether **1a** and catalyst **C5·I** were mixed in ratios of 1 : 1, 1 : 0.8, 1 : 0.6, 1 : 0.4, 1 : 0.2, and 1 : 0, and $CDCl_3$ and DMSO-d_6 were used as solvents for ^{1}H NMR analysis (for the full NMR spectra see ESI†). As the ratio of the substrate to the catalyst increased, the chemical shift of the C–H proton on the methylene carbon of the **1a** was observed to downshift from 4.2220 ppm to 4.2363 ppm (Fig. 1a, left, red). Moreover, the chemical shift of α-C–H on **C5·I** distinctly moved from 3.8529 ppm to 3.8993 ppm (Fig. 1a, right, light blue). Hydrogen protons of the hydroxyl group could not be monitored in $CDCl_3$ due to proton exchange. To verify the activation of O–H HBD, NMR titration experiments were performed in DMSO-d_6 at the same ratio (Fig. 1b, deep blue). With a gradually decreasing ratio of **1a** and **C5·I**, the chemical shift of the O–H proton was upshifted from 4.9734 to 4.9688 ppm. These experimental results suggested a strong coordination between the epoxide and the O–H/α-C–H hybrid HBD of the catalyst. Combined with the fact that catalyst **C8** had almost no catalytic effect, we suggested that the hybrid H-bond donor system on the cationic part of **C5·I** played a vital role in activating the substrate.



Scheme 3 Plausible mechanism for synthesis of cyclic dithiocarbonate.

Combining previous works[5,36] and the results of mechanistic experiments, a plausible H-bond donor/halide anion catalytic cycle was probed (Scheme 3). At the initial stage of the reaction, the intramolecular H-bonding (O–H···O–**H**) between the two hydroxyls enhanced the acidity of the terminal O–**H** hydrogen proton. The enhanced hydroxyl O–H and alkyl α-C–H formed a hybrid hydrogen bond donor (HBD) system. The iodine anion was in dynamic equilibrium with the cation at a larger distance due to ion pair strain. Upon addition of the epoxide, the HBD coordinated with the oxygen atom of the epoxide to activate it (Scheme 3, step **1**); the iodine anion as a nucleophile attacked the methylene carbon of the epoxide for the ring-opening to afford the alkoxide anion intermediate (Scheme 3, step **2**); the facile attack of the resulting alkoxide anion attacks at the electrophilic carbon center of the CS_2 formed the intermediate alkoxide anion, leading to the incorporation of CS_2. The generated dithiocarbonate anion intermediate was subsequently stabilized by the HBD cyclopropenium (Scheme 3, step **3**); intramolecular cyclization occurred along with the leaving of iodide to give the target product cyclic dithiocarbonate (Scheme 3, step **4**). In this step, the oxygen/sulfur scrambling was reduced by the stabilization of H-bonding, which inhibited the formation of thiirane and other by-products, and improved the selectivity of the reaction.

4 Conclusions

Aminocyclopropenium was first utilized as an H-bonding organocatalyst to facilitate the cycloaddition of epoxide and carbon disulfide under mild conditions for the efficient preparation of cyclic dithiocarbonate. The side chain of cyclopropenium was substituted by the functional amino groups with an H-bond donor (HBD), which could promote activating the substrate and stabilizing the intermediate. The hybrid HBD/nucleophile catalyst **C5·I** was selected as the optimal catalyst for the cycloaddition reaction. All terminal epoxides were converted to the corresponding cyclic dithiocarbonates at 5 mol% catalyst loading, 25 °C, and solvent-free in 6 h with excellent conversion and selectivity. Based on the NMR titrations and control experiments, a plausible mechanism was proposed. The aromatic cation electronically enhanced the acidity of alkyl α-C–H. Two hydroxy groups of diethanolamino substituted on a cation formed O–H···O–**H** type intramolecular H-bonding. This enhanced alkyl α-C–H and hydroxy O–**H** constituted a hybrid HBD system that served to activate epoxide substrates and stabilize anion intermediates, suppressing the O/S scrambling and the generation of by-products. The reactivity of the halide anion was increased dramatically due to the repulsion between this type of electron-excess system. The aminocyclopropenium halide cooperative catalysis for the potential application will be further explored.

Author contributions

Xinru Du: methodology, investigation. Ziqi Liu: methodology, investigation. Zhenjiang Li: conceptualization, funding acquisition, project administration, resources, supervision, writing – review and editing. Xin Yuan: methodology, investigation. Chunyu Li: methodology, investigation. Min Zhang: methodology, investigation. Zhihao Zhang: investigation, methodology, writing – original draft, writing – review and editing. Xin Hu: funding acquisition, resources, supervision. Kai Guo: conceptualization, funding acquisition, project administration, resources, supervision.

Conflicts of interest

The authors declare no competing financial interest.

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