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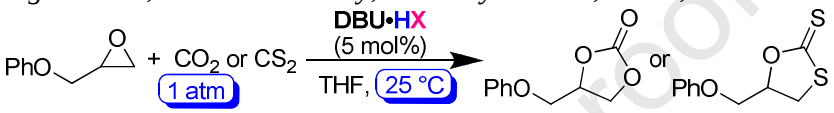

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ABSTRACT

Hydroiodides of amidines can catalyze the reaction of carbon dioxide and epoxides under mild conditions such as ordinary pressure and ambient temperature, and the corresponding five-membered cyclic carbonates were obtained in high yields. The reaction of epoxide with carbon disulfide was also examined under the same conditions. Detailed investigation showed that the catalytic activity was highly affected by the counter anions of the amidine salts; the iodides were effective catalysts for both of the reaction of epoxide with carbon dioxide and carbon disulfide, whereas the bromide, chloride and fluoride counterparts exhibited almost no catalysis.

1. Introduction

The increasing concentration of carbon dioxide (CO_2) in the atmosphere is partly responsible for the climate changes, while CO_2 is also regarded as a cheap, green C1 resource.[1] CO_2 is an environmentally friendly chemical reagent and is especially useful as a phosgene substitute.[2] One of the most important processes is incorporation of CO_2 into epoxides to give five-membered cyclic carbonates,[3] which are widely used as chemical feedstocks for polycarbonate derivatives,[4] aprotic polar solvents,[5] electrolytes,[6] and lithium ion batteries.[7] Additionally, polyaddition of bifunctional cyclic carbonates and α,ω-diamines gives poly(hydroxyurethane)s, which have recently attracted much attention.[8] For example, poly(hydroxyurethane)s can be crosslinked by utilizing their hydroxyl functionalities to give networked polymers.[9] Judicious choice of the crosslinkers can adjust the polarity of the networked polymers, leading to control over the affinity of the networked polymers toward solvents with different polarities. A wide range of CO_2-incorporation catalysts for the synthesis of cyclic carbonates have been developed, including alkali metal salts,[10] onium salts,[11] metal complexes,[12] ionic liquids,[13] and so on. However, most of these catalytic systems require high pressure and/or high temperature for achieving high efficiency with the exception of several expensive metal catalysts.

We have previously reported that the LiBr-catalyzed reaction of CO_2 and epoxides is highly accelerated in the presence of *N*-methyltetrahydropyrimidine (MTHP) as a CO_2 carrier, and the corresponding cyclic carbonates are obtained in moderate to high yields under mild conditions (1 atm, r.t. to 45 °C).[14] However, this system requires large amounts of LiBr as well as MTHP for obtaining the carbonates in reasonable yields. Over the course of our program to develop CO_2-capturing materials based on amidines such as MTHP,[15] we have found that hydroiodides of amidines efficiently catalyze the cyclic carbonate-forming reactions from CO_2 and epoxides.[16] Herein, we report the full details of the optimum structure of amidine salts which catalyze the reaction of epoxides with CO_2 under mild conditions such as ordinary pressure and ambient temperature (Figure 1). The reaction of epoxide with carbon disulfide (CS_2) was also examined under the same conditions using the same catalysts (Scheme 1).

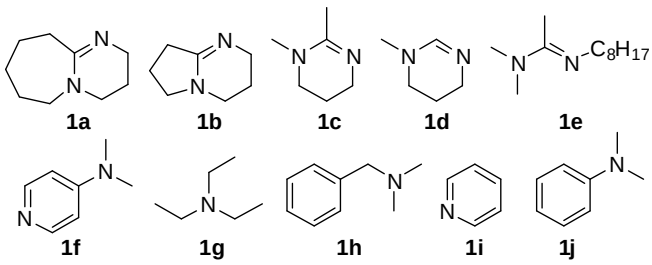

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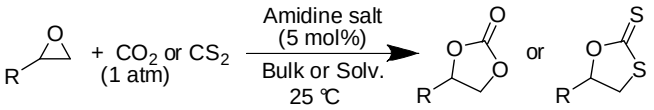
Figure 1. Amidines and amines used in this study.

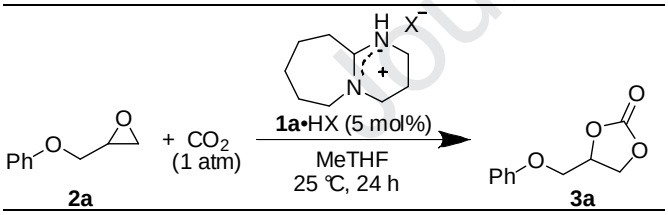
Scheme 1. Synthesis of cyclic carbonates and cyclic dithiocarbonates.



2. Results and discussion

First, we investigated the effect of the anion moietiy of the salts of **1a** (DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene) on the carbonate formation from phenyl glycidyl ether (**2a**) and CO_2 in MeTHF (2-methytetrahydrofuran) at 1 atm and ambient temperature (Table 1). The salts of **1a** were synthesized according to the literature procedures.[13d] It has recently been reported that the acetate (**1a**•HOAc) catalyzes the reaction of propylene oxide and CO_2 under relatively severe conditions such as 10 atm and 140 °C.[13d] However, neither **1a**•HOAc nor other oxyanion salts (**1a**•$HOCOCF_3$ and **1a**•$HOSO_2CF_3$) gave the cyclic carbonate (**3a**) at 1 atm and 25 °C for 24 h (entries 1–3). The halide salts such as the fluoride (**1a**•HF) and the chloride (**1a**•HCl) also gave no product under the same conditions (entries 4 and 5). In contrast, the use of the bromide (**1a**•HBr) resulted in an increased yield of 33%, and the yield was remarkably increased up to 95% when the iodide (**1a**•HI) was used as the catalyst (entries 6 and 7). The use of **1a** alone showed no catalytic activity (entry 8). It has been proposed that mechanism of the cycloaddition reaction involves leaving of the anion moiety from a ring-opened intermediate formed by nucleophilic attack of the anion on the epoxide.[3] The catalysis is thus highly affected by the leaving ability of the counter anion moiety of the amidine salt. Therefore, the leaving of iodide anion at the ring-closure step is most likely to be the rate-determining step for the reaction.

Table 1. Effect of anion moiety of catalyst for the synthesis of cyclic carbonate under ambient conditions.[a]



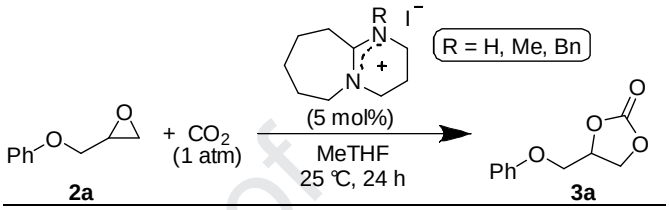
Entry	Catalyst	Yield/ %[b]
1	**1a**•HOAc	<1
2	**1a**•$HOCOCF_3$	Not detected
3	**1a**•$HOSO_2CF_3$	Not detected
4	**1a**•HF	Not detected
5	**1a**•HCl	4
6	**1a**•HBr	33
7	**1a**•HI	95
8	**1a**	<1

[a]Reaction conditions: 1 mmol of **2a**, 0.05 mmol of **1a**•HX, 0.2 mL of MeTHF, 25 °C under 1 atm of CO_2 for 24 h.

[b]Determined by ^{1}H NMR.

Next, we synthesized *N*-methyl- and *N*-benzyl-1,8-diazabicyclo[5.4.0]undec-7-en-8-ium iodide (*N*-Me-**1a**•I and *N*-Bn-**1a**•I) to study effects of the cation moiety on the carbonate formation at ordinary temperatures and pressures. As shown in Table 2, quaternary amidinium salts (*N*-Me-**1a**•I and *N*-Bn-**1a**•I) gave much lower yields of **3a** than that obtained by using tertiary amidinium salt (**1a**•HI) as carbonate-forming catalyst (entries 1-3). Quaternary ammonium salts (*n*-Bu_4N•I) had also less activity than that of the tertiary amidinium salt (**1a**•HI) (entry 4). The oxonium cation was not suitable for the catalyst of the synthesis of carbonate, because the aqueous hydrogen iodide gave no cyclic carbonate (entry 5). The order of catalytic activity was tertiary amidinium iodide > quaternary amidinium (ammonium) iodide >> oxonium iodide, indicating that the proton on the amidinium nitrogen atoms played an important role in the synthesis of carbonate (**3a**) under mild conditions.

Table 2. Effect of cation moiety of catalyst for the synthesis of cyclic carbonate under ambient conditions.[a]



Entry	Catalyst	Yield/ %[b]
1	**1a**•HI	95
2	*N*-Me-**1a**•I	33
3	*N*-Bn-**1a**•I	45
4	*n*-Bu_4N•I[c]	37
5	H_3O•I[d]	Not detected

[a]Reaction conditions: 1 mmol of **2a**, 0.05 mmol of **1a**•HX, 0.2 mL of MeTHF, 25 °C under 1 atm of CO_2 for 24 h.

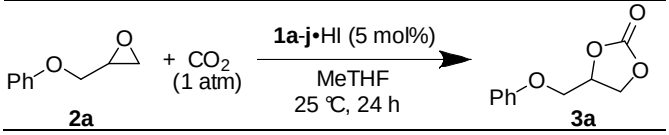
[b]Determined by ^{1}H NMR.

[c]NMP (1-Methyl-2-pyrrolidinone) was used as solvent.

[d]0.05 mmol of 55% aqueous hydroiodic acid.

Furthermore, we examined various hydroiodides of tertiary amidines and amines (**1a-i**) in the carbonate formation from **2a** and CO_2 in MeTHF at 1 atm and ambient temperature (Table 3). For the amidinium iodides with bicyclic structure (**1a**•HI and **1b**•HI), the yields of the carbonate **3a** surpassed 90% (entries 1 and 2). The use of the monocyclic amidinium iodides (**1c**•HI and **1d**•HI) or linear amidinium iodide (**1e**•HI) resulted in moderate to high yields (entries 3-5). In contrast, the use of hydroiodides obtained from moderately basic amines (**1f-h**•HI) gave low yields of **3a** (entries 6-8), and yields were greatly decreased below 9% when hydroiodides obtained from weakly basic amines (**1i**•HI and **1j**•HI) were used as the catalyst (entries 9 and 10). As a result, it is indicated that the high basicity of the amidine moiety is prerequisite for the efficient catalysis, and the DBU hydroiodide (**1a**•HI) was the best catalyst among the tertiary amidinium and ammonium salts investigated here (**1a-j**•HI).

Table 3. Effect of structure of catalyst for the synthesis of cyclic carbonate under ambient conditions.[a]



Entry	Catalyst	Yield/ %[b]
1	**1a**•HI	95
2	**1b**•HI	91
3	**1c**•HI	87
4	**1d**•HI	76

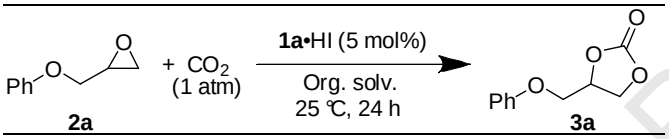
5	**1e**•HI	76
6	**1f**•HI	51
7	**1g**•HI	29
8	**1h**•HI	42
9	**1i**•HI	9
10	**1j**•HI	<1

[a]Reaction conditions: 1 mmol of **2a**, 0.05 mmol of **1a-j**•HI, 0.2 mL of MeTHF, 25 °C under 1 atm of CO_2 for 24 h.

[b]Determined by ^{1}H NMR.

Next, the carbonate formation of **2a** with CO_2 was carried out in various solvents using **1a**•HI (Table 4). Cyclic carbonate (**3a**) was obtained in high yields in non polar and moderately polar solvents such as hexane, toluene, tetrahydrofuran (THF), ethyl acetate (EtOAc) and acetone (entries 1–5). In contrast, aprotic polar solvents such as 1-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) gave moderate to low yields (entries 6-9). Thus, the catalysis is more efficient in nonpolar and moderately polar solvents than in highly aprotic polar solvents. These results can be explained by the polarity of the solvents, which affects activation of the epoxide by cationic moiety of the catalyst through hydrogen bonds.[17]

Table 4. Effect of solvent for the synthesis of cyclic carbonate under ambient conditions.[a]



2a **3a**

Entry	Solvent (D_N)[b]	Yield/ %[c]
1	Hexane (0)	88
2	Toluene (0.1)	93
3	THF (20)	97
4	EtOAc (17.1)	95
5	Acetone (17)	87
6	NMP (27.3)	64
7	DMAc (27.8)	59
8	DMAc (27.8)	32
9	DMSO (29.8)	12

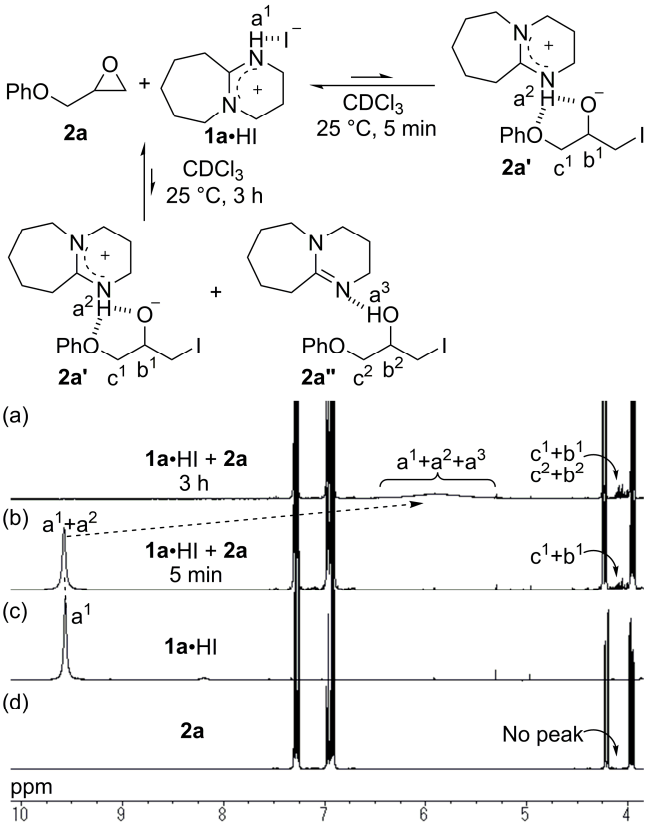
[a]Reaction conditions: 1 mmol of **2a**, 0.05 mmol of **1a**•HI, 0.2 mL of solvent, 25 °C under 1 atm of CO_2 for 24 h.

[b]ref. 17.

[c]Determined by ^{1}H NMR.

The ^{1}H NMR spectrum of an equimolar mixture of **1a**•HI and **2a** in deuterated chloroform ($CDCl_3$) in the absence of CO_2 was measured in order to observe the activation of the epoxide by the amidinium ion moiety of the catalyst through hydrogen-bonding interaction (Figure 2). It was found that the NH proton of **1a**•HI and one proton of the methylene of **2a** showed downfield shifts from 9.57 to 9.59 and 4.22 to 4.24, respectively, while another proton of the methylene of **2a** gave an upfield shift from 3.97 to 3.96 (Supporting Information, Figure S1). Moreover, the ^{1}H NMR spectrum quickly changed in the absence of CO_2 and showed a new set of signals at 3.40-3.52 and 3.98-4.12 ppm within 5 min, which were assignable to the methine and methylene protons of the ring-opened intermediate **2a'**. Then, after 3 h, the time-averaged signal of the active protons of **2a'**, **2a''** and unreacted **1a**•HI appeared at *ca*. 6 ppm as a broad singlet due to their chemical exchange faster than on the ^{1}H NMR time scale. On the other hand, **2a** does not form ring-opened intermediate with **1a**•HI in highly polar aprotic solvent such as DMSO, because the ^{1}H NMR spectrum of **2a** with **1a**•HI in DMSO-d_6 did not show peaks of ring-opened structure even after 3 h (Supporting Information, Figure S2). This absence of the activation of the epoxide by **1a**•HI can be attributed to the strong hydrogen accepting ability of DMSO, of which the donor number is 29.8.[17] Then the carbonate formation of **2a** with CO_2 was carried out using **1a**•HI in $CDCl_3$ and DMSO-d_6 at 1 atm and ambient temperature. The reaction in DMSO-d_6 gave much lower yield of **3a** (17%) than that obtained by using $CDCl_3$ as reaction solvent (70% yield) (Supporting Information, Figure S3). The **1a**•HI does not catalyze the reversible ring-opening reaction of **3a** with iodide anion, because the ^{1}H NMR spectrum of **3a** with **1a**•HI in $CDCl_3$ did not show peaks of ring-opening products even after 3 h (Supporting Information, Figure S4).

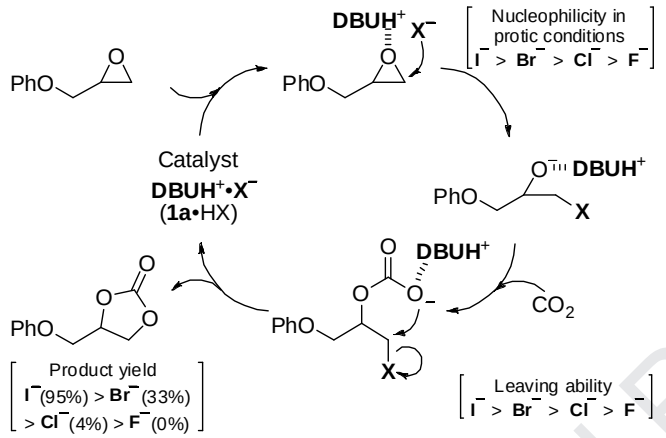
Figure 2. Partial ^{1}H NMR spectra (400MHz, 25 °C) of a solution



of **2a** (55 µmol) with **1a**•HI (55 µmol) in $CDCl_3$ (550 µL) 3 h (a) and 5 min (b) after mixing, and $CDCl_3$ solutions of **1a**·HI (c) and **2a** (d).

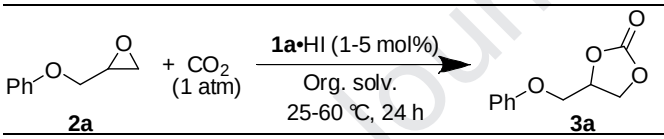
A plausible mechanism for the catalytic synthesis of carbonate is shown in scheme 2. Initially, tertiary amidine hydroiodide such as **1a**•HI activates the epoxide through hydrogen bonds. Then, the ring-opened intermediate is formed by the nucleophilic attack of the halide anion on the activated epoxy group, and subsequent nucleophilic attack on CO_2 leads to the alkylcarbonate anion.[18] Finally, the ring-closure through the elimination of the halide anion gives the cyclic carbonate. The counter anion of the catalysts is important factor of the catalytic activity, which was in the order of iodide > bromide > chloride > fluoride. This could be accounted for by the nucleophilicity of halide anions at the ring-opening step as well as the leaving ability at the ring-closing step, both in the order of $I^- > Br^- > Cl^- > F^-$.

Table 5 shows the effect of temperature on the carbonate formation of **2a** with 1-5 mol% **1a**•HI in the temperature range 25-60 °C at 1 atm of CO_2 for 24 h. Although the **3a** yield decreased with decreasing catalyst loading from 5 mol% to 2.5 mol% at 25 °C in THF, the yield of **3a** increased when the reaction temperature was raised from 25 to 45 °C in the presence of 2.5 mol% **1a**•HI (entries 1-3). In the case of using 1 mol% **1a**•HI, the yield of **3a** increased from 78% to 96% when the reaction temperature was raised from 45 to 60 °C (entries 4 and 5). By using toluene as reaction solvent, the effect of temperature was observed, as in the case of using THF (entries 6-10). Under the ambient conditions (25 °C, 1 atm CO_2), the reaction progress in the presence of 5 mol% **1a**•HI was monitored by ^{1}H NMR (Figure 3). The conversion of **2a** increased gradually with the reaction time from the initial stage and nearly all the **2a** was converted to the corresponding cyclic carbonate after 24 h.



Scheme 2. A plausible mechanism for cyclic amidine salt-catalyzed synthesis of cyclic carbonates from epoxides and CO_2.

Table 5. Effect of reaction temperature for the synthesis of cyclic carbonate under 1 atm of CO_2.[a]



Entry	Solvent	**1a**•HI/mol %	Temp./°C	Yield/ %[b]
1	THF	5.0	25	97
2	THF	2.5	25	74
3	THF	2.5	45	96
4	THF	1.0	45	81
5	THF	1.0	60	96
6	Toluene	5.0	25	95
7	Toluene	2.5	25	78
8	Toluene	2.5	45	98
9	Toluene	1.0	45	75
10	Toluene	1.0	60	86

[a]Reaction conditions: 1 mmol of **2a**, 0.01-0.05 mmol of **1a**•HI, 0.2 mL of solvent, 25-60 °C under 1 atm of CO_2 for 24 h.

[b]Determined by ^{1}H NMR.

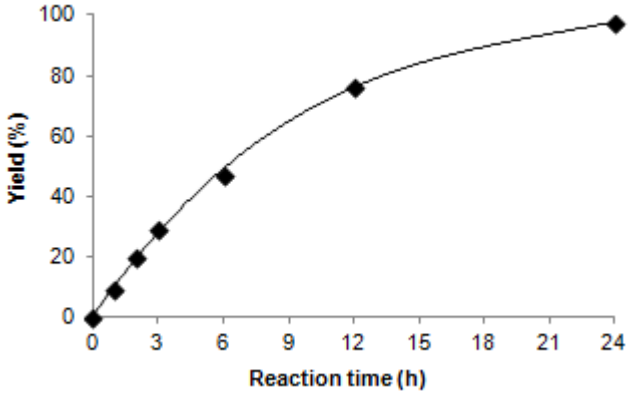
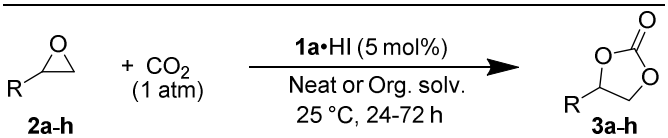


Figure 3. Time-conversion plots for the carbonate formation of **2a**. Reaction conditions: 1 mmol of **2a**, 0.05 mmol of **1a**•HI, 0.2 mL of THF, 25 °C under 1 atm of CO_2.

Furthermore, we examined the carbonate-forming reactions of various epoxides with **1a**•HI at 25 °C (Table 6). The carbonate (**3a**) was isolated almost quantitatively by simple precipitation from water (entry 1). Epichlorohydrin (**2b**) and glycidyl methacrylate (**2c**) containing electron-withdrawing groups, and other glycidyl ethers such as *n*-butyl glycidyl ether (**2d**) and allyl glycidyl ether (**2e**), gave the corresponding carbonates (**3b-e**) in lower yields than that for the reaction of **2a** at 25 °C (entries 1-5). 4-Phenyl-1,3-dioxolan-2-one (**3f**) was obtained in a low yield, which could be attributed to the low reactivity of styrene oxide (**2f**) due to steric hindrance around the epoxy group (entry 6). The aliphatic hydrocarbon-substituted epoxides such as propylene oxide (**2g**) and 1,2-epoxyhexane (**2h**) had much lower reactivity than those of other epoxides (entries 7 and 8). Although the yields of aromatic- and hetero-functional carbonates (**3b-f**) increased when the reactions carried out without solvent (entries 9-18), the hydrocarbon-substituted epoxides with low reactivity (**2g** and **2h**) gave almost no cyclic carbonate under the same conditions (entries 19 and 20). When 2-propanol (IPA) was used as the solvent, the yields of **3g** and **3h** were remarkably increased (entries 21-24). The protic solvent such as IPA can activate the epoxides via hydrogen bonds formed between the hydroxy and epoxy groups, which were suggested by the ^{1}H NMR spectra of **2g** with IPA in $CDCl_3$ (Figure 4).[19] On the other hand, the reactivity of **2a** in IPA was slightly decreased in comparison with that in THF (entry 25). The reactivity of **2f** was more decreased in IPA compared to neat conditions (entry 26). These results could be explained in terms of the solvation of the alkylcarbonate anion. Especially in the case of bulky epoxide such as **2f**, the reactivity of the ring-closing reaction is diminished by IPA. Effect of protic solvents on the synthesis of cyclic carbonate was also described previously.[19] The carbonates (**3b-h**) were isolated in high yields after purification by partitioning between ethyl acetate and water.

Table 6. Synthesis of various cyclic carbonates by using **1a**•HI under ambient conditions.[a]



Entry	**2**	R	Solvent	Time/h	Yield/ %[b]
1	**2a**	$PhOCH_2$	THF	24	97 (96)[c]
2	**2b**	$ClCH_2$	THF	24	85
3	**2c**	CH_2=C(Me)CO_2CH_2	THF	24	78

4	**2d**	*n*-BuOCH$_2$	THF	24	67
5	**2e**	CH$_2$=CHCH$_2$OCH$_2$	THF	24	64
6	**2f**	Ph	THF	24	38
7	**2g**	Me	THF	24	8
8	**2h**	*n*-Bu	THF	24	3
9	**2b**	ClCH$_2$	Neat	24	95
10	**2b**	ClCH$_2$	Neat	36	>99 (97)[c]
11	**2c**	CH$_2$=C(Me)CO$_2$CH$_2$	Neat	24	95
12	**2c**	CH$_2$=C(Me)CO$_2$CH$_2$	Neat	36	>99 (98)[c]
13	**2d**	*n*-BuOCH$_2$	Neat	24	86
14	**2d**	*n*-BuOCH$_2$	Neat	48	99 (97)[c]
15	**2e**	CH$_2$=CHCH$_2$OCH$_2$	Neat	24	82
16	**2e**	CH$_2$=CHCH$_2$OCH$_2$	Neat	48	>99 (99)[c]
17	**2f**	Ph	Neat	24	64
18	**2f**	Ph	Neat	72	>99 (99)[c]
19	**2g**	Me	Neat	24	3
20	**2h**	*n*-Bu	Neat	24	2
21	**2g**	Me	IPA	24	77
22	**2g**	Me	IPA	48	96 (91)[c]
23	**2h**	*n*-Bu	IPA	24	63
24	**2h**	*n*-Bu	IPA	72	95 (92)[c]
25	**2a**	PhOCH$_2$	IPA	24	92
26	**2f**	Ph	IPA	24	32

[a] Reaction conditions: 1 mmol of **2a**-**h**, 0.05 mmol of **1a**•HI, 0.2 mL of solvent or bulk, 25 °C under 1 atm of CO_2 for 24-72 h.

[b]Determined by ^{1}H NMR.

[c] Isolated yields are in parentheses.

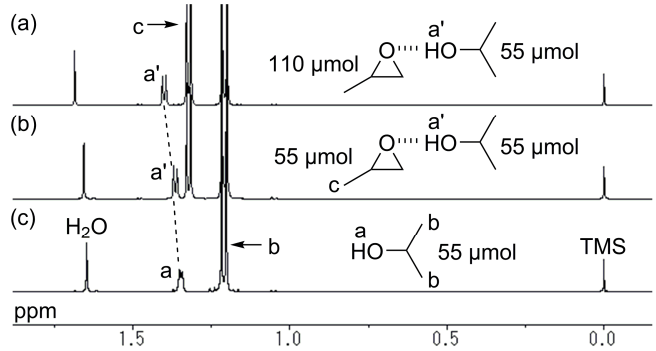
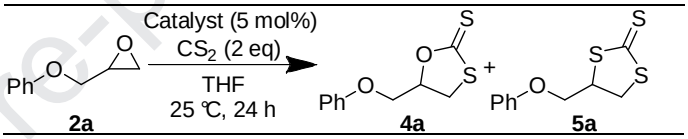


Figure 4. Partial ^{1}H NMR spectra (400MHz, 25 °C) of solutions of (c) 2-propanol (55 μmol) in $CDCl_3$ (550 μL), (b) **2g** (55 μmol) and 2-propanol (55 μmol) in $CDCl_3$ (550 μL), and (a) **2g** (110 μmol) and 2-propanol (55 μmol) in $CDCl_3$ (550 μL).

Finally, we investigated the reaction between epoxide (**2a**) and CS_2 in the presence of DBU salts (**1a**•HX) to compare with the carbonate formation of **2a** with CO_2 under mild conditions. The direct incorporation of CS_2 into **2a** gives five-membered cyclic dithiocarbonate (**4a**) which is possible to use as starting compound for the synthesis of rare-metal absorbing polymer.[20] Other dithiocarbonates can also give thiocarbamate functionalized polymers for the application of adhesive curing and modification of wool fiber.[21] The reaction of epoxides with CS_2 can be carried out at room temperature in the presence of 5 mol% of LiBr in THF,[22] 10 mol% of DMAP in H_2O,[23] 10 mol% of Et_3N in $MeNO_2$[24] and 5 mol% of LiO^tBu in neat.[25] As shown in Table 7, the fluoride (**1a**•HF) and the chloride (**1a**•HCl) gave cyclic dithiocarbonate (**4a**) in low yields (entries 1 and 2). In contrast, the use of the bromide (**1a**•HBr) resulted in an increased yield of 61%, and the yield was remarkably increased up to 89% when the iodide (**1a**•HI) was used as the catalyst (entries 3 and 4). Both **1a**•HI and **1a**•HBr also gave a small amount of trithiocarbonate (**5a**) during formation of the **4a** as main product, and similar reactions of epoxides with CS_2 have been reported previously.[26] The products (**4a** and **5a**) were separated by silica gel column chromatography using *n*-hexane-ethyl acetate (entry 4). As with the case of carbonate-forming reaction, the counter anion of the catalysts is an important factor of the catalytic activity, which was in the order of iodide > bromide > chloride > fluoride. Furthermore, the active proton on the amidinium nitrogen atoms of catalyst played an important role because quaternary amidinium salt (*N*-Me-**1a**•I) gave a much lower yield of **4a** than that obtained by using tertiary amidinium salt (**1a**•HI) as dithiocarbonate-forming catalyst (entry 5). In addition, the ^{13}C NMR signal of CS_2 in $CDCl_3$ (192.5 ppm) did not change after addition of **1a**•HI (Supporting Information, Figure S5), suggesting that **1a**•HI does not directly activate CS_2 before ring opening of **2a**. Therefore, a plausible mechanism for the catalytic synthesis of dithiocarbonate from CS_2 and epoxide is suggested to be similar to that of cyclic carbonate-forming reaction from CO_2 and epoxide (scheme 2).

Table 7. Effect of anion moiety of catalyst for the synthesis of cyclic dithiocarbonate under ambient conditions.[a]



Entry	Catalyst	Yield/ %[b]	
		4a	**5a**
1	**1a**•HF	13	Not detected
2	**1a**•HCl	34	Not detected
3	**1a**•HBr	61	2
4	**1a**•HI	89 (88)[c]	3 (3)[c]
5	*N*-Me-**1a**•I	13	1

[a] Reaction conditions: 1 mmol of **2a**, 2 mmol of CS_2, 0.05 mmol of **1a**•HX or *N*-Me-**1a**•I, 0.2 mL of THF, 25 °C for 24 h.

[b]Determined by ^{1}H NMR.

[c] Isolated yields are in parentheses.

3. Conclusion

We have demonstrated that the hydroiodides of the amidines catalyze effectively the reactions of various epoxides with CO_2 and the corresponding five-membered cyclic carbonates are obtained in high yields under mild conditions such as ordinary pressure and ambient temperature. The catalytic activity is highly affected by the counter anions of the amidinium catalysts; the iodides catalyze efficiently the carbonate-forming reactions, in contrast to the bromide, chloride and fluoride counterparts that show low reactivity or almost no catalysis. The choice of the amine (including amidine) moiety is also important in terms of the following two factors. First, the proton on the amidinium nitrogen atoms played an important role in the synthesis of carbonate. Second, strongly basic amine moieties such as DBU and DBN are more effective than moderately and weakly basic amine moieties such as triethylamine and pyridine. By using DBU hydroiodide as a catalyst, various epoxides were converted in excellent yields to the corresponding cyclic carbonates. The carbonates were isolated in high yields after simple purification by precipitation from water or partitioning between ethyl acetate

and water. Furthermore, DBU hydroiodide also catalyzed effectively the reaction of epoxide with CS_2 as well as with CO_2, which provides the corresponding five-membered cyclic dithiocarbonate under mild, ambient conditions. We believe that the above results obtained in this study would serve as a basis for creating more efficient and green catalysts for CO_2- and CS_2-fixation reactions with epoxy-functional organic compounds.

4. Experimental section

4.1. Materials and instruments

CO_2 (>99.99%) was obtained from Fukuho Teisan (Iizuka, Japan). 1,8-Diazabicyclo[5.4.0]-7-undecene (**1a**) and 1,5-diazabicyclo[4.3.0]-5-nonene (**1b**) were purchased from Tokyo Kasei Kogyo (Tokyo, Japan), and were dried over CaH_2 and then distilled prior to use. 1,2-Dimethyl-1,4,5,6-tetrahydropyrimidine (**1c**), 1-methyl-1,4,5,6-tetrahydropyrimidine (**1d**) and *N*,*N*-dimethyl-*N*'-octylacetamidine (**1e**) were synthesized according to the previous publication.[15d] All other starting materials and solvents were purchased from Aldrich, Wako Pure Chemical Industries (Osaka, Japan), Tokyo Kasei Kogyo (Tokyo, Japan) and Kanto Chemical (Tokyo, Japan), and were used as received without further purification. ^{1}H (400 MHz), ^{13}C (100 MHz) and ^{19}F (376 MHz) nuclear magnetic resonance (NMR) spectroscopy measurements were performed on a JEOL ECS-400/SS instrument at 25 °C. The ^{1}H NMR spectra were referenced to tetramethylsilane (TMS: 0 ppm) as an internal standard or to the residual protons of the deuterated solvents (CD_3OD: 2.05 ppm, DMSO-d_6: 2.50 ppm). The ^{13}C NMR spectra were referenced to the ^{13}C signals of the deuterated solvents ($CDCl_3$: 77.0 ppm, CD_3OD: 49.0 ppm, DMSO-d_6: 39.5 ppm). The ^{19}F NMR spectra were referenced to hexafluorobenzene (C_6F_6: -164.0 ppm) as an internal standard. The IR spectra were recorded as KBr discs or pellets on a JASCO FT/IR-460 Plus spectrometer. Mass spectroscopy was performed on a Shimadzu GCMS-QP5050A in electron ionization (EI) mode.

4.2. Synthesis of 1.8-diazabicyclo[5.4.0]undec-7-ene hydrohalides (1a•HI, 1a•HBr and 1a•HCl)

To a stirred mixture of DBU (1.52 g, 10 mmol) in anhydrous MeOH (10 mL) was added of ammonium halide (NH_4I, NH_4Br or NH_4Cl, 10 mmol) at room temperature. After the mixture was stirred at room temperature for 6 h, the mixture was evaporated *in vacuo*. The residue was washed with ether, and the precipitate was dried *in vacuo* for 12 h at 50 °C to give **1a**•HI, **1a**•HBr or **1a**•HCl.

*4.2.1. 1.8-Diazabicyclo[5.4.0]undec-7-ene hydroiodide (**1a**•HI):* Pale yellow solid (2.81 g, 100%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 1.73-1.86 (m, 6 H), 2.12 (quin, J = 6.0 Hz, 2 H), 2.98-3.04 (m, 2 H), 3.46-3.52 (m, 2 H), 3.58-3.64 (m, 4 H), 9.58 (brs, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 19.3, 23.7, 26.6, 28.8, 32.7, 37.7, 48.9, 54.8, 166.1.

*4.2.2. 1.8-Diazabicyclo[5.4.0]undec-7-ene hydrobromide (**1a**•HBr):* White solid (2.34 g, 100%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 1.70-1.84 (m, 6 H), 2.08 (quin, J = 6.0 Hz, 2 H), 2.99-3.06 (m, 2 H), 3.45-3.50 (m, 2 H), 3.54-3.60 (m, 4 H), 10.58 (brs, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 19.4, 23.9, 26.7, 28.9, 32.3, 37.8, 48.8, 54.6, 166.2.

*4.2.3. 1.8-Diazabicyclo[5.4.0]undec-7-ene hydrochloride (**1a**•HCl):* White solid (1.89 g, 100%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 1.69-1.84 (m, 6 H), 2.07 (quin, J = 6.0 Hz, 2 H), 2.96-3.02 (m, 2 H), 3.41-3.47 (m, 2 H), 3.57-3.64 (m, 4 H), 11.2 (brs, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 19.1, 23.6, 26.4, 28.6, 31.8, 37.5, 48.4, 54.1, 165.7.

4.3. Synthesis of 1.8-diazabicyclo[5.4.0]undec-7-ene hydrofluoride (1a•HF)

To a stirred mixture of DBU (1.52 g, 10 mmol) in anhydrous MeOH (20 mL) was added of NH_4F (741 mg, 20 mmol) at room temperature. After the mixture was stirred at room temperature for 24 h, the mixture was evaporated *in vacuo*. The residue was extracted with acetone (10 mL × 3), and the combined organic extracts were evaporated *in vacuo*. The residue was washed with ether/dioxane (1:1, 10 mL × 5), and the precipitate was dried *in vacuo* for 48 h at 40 °C to give **1a**•HF (1.42 g, 83%) as a pale yellow solid. ^{1}H NMR (400 MHz, CD_3OD, 25 °C) δ (ppm): 1.63-1.78 (m, 6 H), 1.98 (quin, J = 5.8 Hz, 2 H), 2.77-2.84 (m, 2 H), 3.27 (t, J = 5.8 Hz, 2 H), 3.56 (t, J = 6.0 Hz, 2 H), 3.59-3.64 (m, 2 H), 13.4 (brs, 1 H). ^{13}C NMR (100 MHz, CD_3OD, 25 °C) δ (ppm): 20.4, 24.9, 27.5, 29.9, 33.6, 39.3, 49.5, 55.3, 167.4. ^{19}F (376 MHz , CD_3OD, 25 °C) δ (ppm): -164.7 (brs).

4-4. Synthesis of 1.8-diazabicyclo[5.4.0]undec-7-enium acetates (1a•HOAc and 1a•HOCOCF$_3$)

A mixture of carboxylic acid (AcOH or trifluoroacetic acid, 4.2 mmol) in anhydrous CH_2Cl_2 (2 mL) was added dropwise over 5 min to a stirred mixture of DBU (609 mg, 4 mmol) in anhydrous CH_2Cl_2 (18 mL) at room temperature. After the mixture was stirred at room temperature for 6 h, the mixture was evaporated *in vacuo*. The residue was washed with ether, and the precipitate was dried *in vacuo* for 12 h at 50 °C to give **1a**•HOAc or **1a**•$HOCOCF_3$.

*4-4-1. 1.8-Diazabicyclo[5.4.0]undec-7-enium acetate (**1a**•HOAc):* Colorless syrup (851 mg, 100%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 1.67-1.83 (m, 6 H), 1.98 (s, 3 H), 2.04 (quin, J = 6.0 Hz, 2 H), 2.83-2.88 (m, 2 H), 3.43 (t, J = 5.6 Hz, 2 H), 3.49-3.57 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 19.0, 23.4, 23.5, 26.3, 28.4, 31.3, 37.4, 47.9, 53.5, 165.3, 176.4.

*4-4-2. 1.8-Diazabicyclo[5.4.0]undec-7-enium trifluoroacetate (**1a**•HO COCF$_3$):* Colorless syrup (1.06 g, >99%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 1.59-1.83 (m, 6 H), 2.05 (quin, J = 6.0 Hz, 2 H), 2.77-2.87 (m, 2 H), 3.40-3.57 (m, 6 H), 11.4 (brs, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 19.4, 23.9, 26.7, 28.9, 32.2, 38.0, 48.5, 54.3, 116.9 (q, J_{CF} = 293.4 Hz), 161.5 (q, J_{CF} = 33.6 Hz), 166.2.

4-5. Synthesis of 1.8-diazabicyclo[5.4.0]undec-7-enium triflate (1a•HOSO$_2$CF$_3$)

A mixture of triflic acid (600 mg, 4 mmol) in anhydrous CH_2Cl_2 (12 mL) was added dropwise over 10 min to a stirred mixture of DBU (609 mg, 4 mmol) in anhydrous CH_2Cl_2 (8 mL) at room temperature. After the mixture was stirred at room temperature for 6 h, the mixture was evaporated *in vacuo*. The residue was washed with ether, and the precipitate was dried *in vacuo* for 12 h at 50 °C to give **1a**•$HOSO_2CF_3$ (1.12 g, 92%) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 1.65-1.92 (m, 6 H), 2.06 (quin, J = 5.8 Hz, 2 H), 2.65-2.77 (m, 2 H), 3.39 (t, J = 5.8 Hz, 2 H), 3.51-3.65 (m, 4 H), 7.39 (brs, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 19.2, 23.6, 26.3, 28.7, 32.7, 38.2, 48.5, 54.4, 120.4 (q, J_{CF} = 318.1 Hz), 166.0.

4-6. Synthesis of 8-methyl-1.8-diazabicyclo[5.4.0]undec-7-ene-8-ium iodide (*N*-Me-1a•I)

A mixture of methyl iodide (625 mg, 4.4 mmol) in anhydrous CH_2Cl_2 (4 mL) was added to a stirred mixture of DBU (609 mg, 4 mmol) in anhydrous CH_2Cl_2 (4 mL) at room temperature. After the mixture was stirred at room temperature for 12 h, the mixture was evaporated *in vacuo*. The residue was washed with ether, and

the precipitate was dried *in vacuo* for 12 h at 40 °C to give *N*-Me-**1a•**I (1.18 g, 100%) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 1.81-1.91 (m, 6 H), 2.25 (quin, *J* = 6.0 Hz, 2 H), 2.93-2.98 (m, 2 H), 3.38 (s, 3 H), 3.65-3.76 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 20.0, 22.3, 26.1, 28.5, 29.5, 42.0, 49.1, 49.3, 55.7, 166.8.

4-7. Synthesis of 8-benzyl-1.8-diazabicyclo[5.4.0]undec-7-ene-8-ium iodide (*N*-Bn-1a•I)

A mixture of benzyl iodide (872 mg, 4 mmol) in anhydrous CH_2Cl_2 (4 mL) was added to a stirred mixture of DBU (609 mg, 4 mmol) in anhydrous CH_2Cl_2 (4 mL) at room temperature. After the mixture was stirred at room temperature for 12 h, the mixture was evaporated *in vacuo*. The residue was washed with ether/THF (1:1), and the precipitate was dried *in vacuo* for 12 h at 40 °C to give *N*-Bn-**1a•**I (1.49 g, 100%) as a pale yellow syrup. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 1.71-1.91 (m, 6 H), 2.27 (quin, *J* = 5.8 Hz, 2 H), 2.91-2.97 (m, 2 H), 3.74 (t, *J* = 5.8 Hz, 2 H), 3.78-3.83 (m, 4 H), 4.86 (s, 2 H), 7.23 (d, *J* = 6.8 Hz, 2 H), 7.32-7.37 (m, 1 H), 7.38-7.44 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 20.2, 22.5, 25.9, 28.4, 29.6, 47.7, 49.7, 56.0, 57.2, 126.2, 128.4, 129.3, 133.9, 167.4.

4-8. Synthesis of amine and amidine hydrohalides (1a-j•HI)

A solution of 55% aqueous hydroiodic acid (1 mL, ca. 7.3 mmol) was added dropwise over 1 min to a stirred mixture of amidine (**1a-e**, 4 mmol) or amine (**1f-j**, 4 mmol) in dioxane (8 mL) at 0 °C. After the mixture was stirred at room temperature for 12 h, the mixture was evaporated *in vacuo*. The residue was washed with ether/THF (1:1 or 1:0), and the precipitate was dried *in vacuo* for 12 h at 50 °C (**1i•**HI and **1j•**HI were dried for 6h at 30 °C) to give corresponding hydroiodides (**1a-j•**HI).

*4-8-1. 1.8-Diazabicyclo[5.4.0]undec-7-ene hydroiodide (**1a•**HI):* Pale yellow solid (1.10 g, 98%). Spectroscopic data and catalytic activity are the same as product made from **1a** with NH_4I.

*4-8-2. 1.5-Diazabicyclo[4.3.0]-5-nonene hydroiodide (**1b•**HI):* Pale yellow powder (1.01 g, 100%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 2.16 (quin, *J* = 6.0 Hz, 2 H), 2.24 (quin, *J* = 7.7 Hz, 2 H), 3.19 (t, *J* = 8.0 Hz, 2 H), 3.51-3.59 (m, 4 H), 3.79 (t, *J* = 7.4 Hz, 2 H), 9.45 (brs, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 18.6, 18.8, 30.7, 37.8, 42.8, 53.7, 164.4.

*4-8-3. 1,2-Dimethyl-1,4,5,6-tetrahydropyrimidine hydroiodide (**1c•**HI):* Paleorange solid (962 mg, 100%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 2.16 (quin, *J* = 6.0 Hz, 2 H), 2.54 (s, 3 H), 3.25 (s, 3 H), 3.47-3.52 (m, 2 H), 3.56 (t, *J* = 6.0 Hz, 2 H), 9.40 (brs, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 18.9, 19.4, 38.0, 39.9, 48.4, 161.0.

*4-8-4. 1-Methyl-1,4,5,6-tetrahydropyrimidine hydroiodide (**1d•**HI):* Red brown oil (901 mg, >99%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 2.17 (quin, *J* = 6.0 Hz, 2 H), 3.02 (s, 3 H), 3.49-3.57 (m, 4 H), 8.35 (d, *J* = 6.0 Hz, 1 H), 9.22 (brs, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 18.4, 36.8, 42.7, 46.2, 152.0.

*4-8-5. N,N-Dimethyl-N'-octylacetamidine hydroiodide (**1e•**HI):* Pale brown solid (1.28 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 0.88 (t, *J* = 6.8 Hz, 3 H),1.21-1.40 (m, 10 H), 1.70 (quin, *J* = 7.4 Hz, 2 H), 2.39 (s, 3 H), 3.36 (s, 3 H), 3.46 (s, 3 H), 3.48-3.56 (m, 2 H), 8.43 (brs, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 13.9, 15.8, 22.4, 26.5, 29.0, 30.2, 31.6, 42.2, 42.8, 44.7, 163.0.

*4-8-6. N,N-Dimethylaminopyridine hydroiodide (**1f•**HI):* Dark brown solid (1.04 g, 100%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 3.33 (s, 6 H), 6.91 (d, *J* = 7.2 Hz, 2 H), 8.17 (d, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 40.8, 107.1, 138.1, 157.5.

*4-8-7. Triethylamine hydroiodide (**1g•**HI):* pale yellow solid (890 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 1.49 (t, *J* = 7.4 Hz, 9 H), 3.21 (d, *J* = 7.4 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.61, 46.3.

*4-8-8. N,N-Dimethylbenzylamine hydroiodide (**1h•**HI):* Pale orange solid (1.05 g, 100%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 2.89 (s, 6 H), 4.45 (s, 2 H), 7.41-7.49 (m, 3 H), 7.70-7.75 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 42.2, 60.7, 128.0, 129.1, 130.1, 131.3.

*4-8-9. Pyridine hydroiodide (**1i•**HI):* White solid (828 mg, 100%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ (ppm): 7.25 (br, 1 H), 8.11 (dd, *J* = 7.6, 6,4 Hz, 2 H), 8.65 (tt, *J* = 7.8, 1.4 Hz, 1 H), 8.97 (dd, *J* = 6.6, 1.4 Hz, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ (ppm): 127.3, 142.1, 146.5.

*4-8-10. N,N-Dimethylaniline hydroiodide (**1j•**HI):* Pale yellow solid (983 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 3.24 (s, 6 H), 7.52-7.60 (m, 3 H), 7.87-7.92 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 46.9, 120.6, 130.6, 142.0.

4-9. General procedure in aprotic solvent for five-membered cyclic carbonate

The catalyst **1a•**HI (14.0 mg, 0.05 mmol) was added to a solution of **2a** (150 mg, 1 mmol) in THF (0.2 mL) at room temperature. The atmosphere inside the flask was replaced with CO_2 (balloon, *ca.* 1 atm), and the reaction mixture was stirred at 25 °C. After 24 h, the heterogeneous mixture was diluted with THF (1 mL), and dropped into water (20 mL). The precipitation was filtered off and washed with water. The residue was dried *in vacuo* for 12 h at 50 °C to give (phenoxymethyl)ethylene carbonate (**3a**) (187 mg, 96%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 4.15 (dd, *J* = 10.4, 3.6 Hz, 1 H), 4.24 (dd, *J* = 10.4, 4.4 Hz, 1 H), 4.53 (dd, *J* = 8.4, 6.0 Hz, 1 H), 4.61 (dd, *J* = 8.4, 8.4 Hz, 1 H), 4.99-5.06 (m, 1 H), 6.89-6.93 (m, 2 H), 6.99-7.04 (m, 1 H), 7.31 (dd, *J* = 8.8, 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 66.2, 66.8, 74.1, 114.6, 122.0, 129.7, 154.6, 157.7. IR (KBr): ṽ = 2926, 1803, 1250, 1166, 1092 cm^{-1}. MS (EI): *m/z* = 194 $[M]^+$.

4-10. General procedure without solvent for five-membered cyclic carbonate

The catalyst **1a•**HI (14.0 mg, 0.05 mmol) was added to fluid epoxide (**2b-f**, 1 mmol) at room temperature. The atmosphere inside the flask was replaced with CO_2 (balloon, *ca.* 1 atm), and the reaction mixture was stirred at 25 °C. After 36-72 h, the mixture was diluted with ethyl acetate, and washed with water. The aqueous phase was extracted with twice ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and evaporated *in vacuo*. The residue was dried *in vacuo* for 12 h at 40 °C to give corresponding cyclic carbonate (**3b-f**).

*4-10-1. (Chloromethyl)ethylene carbonate (**3b**):* Colorless oil (133 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 3.74 (dd, *J* = 12.0, 4.0 Hz, 1 H), 3.79 (dd, *J* = 11.8, 5.4 Hz, 1 H), 4.42 (dd, *J* = 9.0, 5.8 Hz, 1 H), 4.60 (dd, *J* = 8.6, 8.6 Hz, 1 H), 4.94-5.01 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 43.6, 66.9, 74.2, 154.1. IR (neat): ṽ = 2987, 2970, 2925, 1797, 1166, 1071, 768 cm^{-1}. MS (EI): *m/z* = 136, 138 $[M]^+$.

*4-10-2. (2-Oxo-1,3-dioxolane-4-yl)methyl methacrylate (**3c**):* Pale yellow oil (183 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$, 25

°C) δ (ppm): 1.96 (t, *J* = 1.6 Hz, 3 H), 4.31-4.38 (m, 2 H), 4.44 (dd, *J* = 13.2, 3.2 Hz, 1 H), 4.59 (dd, *J* = 8.4, 8.4 Hz, 1 H), 4.95-5.02 (m, 1 H), 5.67 (quin, *J* = 1.4 Hz, 1 H)), 6.14-6.19 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 18.1, 63.4, 66.0, 73.8, 127.3, 135.1, 154.4, 166.6. IR (neat): ṽ = 2986, 2960, 2930, 1798, 1724, 1637, 1162, 1052 cm^{-1}. MS (EI): *m/z* = 186 $[M]^+$.

*4-10-3. (n-Butoxymethyl)ethylene carbonate (**3d**):* Colorless oil (169 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 0.92 (t, *J* = 7.4 Hz, 3 H), 1.36 (sext, *J* = 7.4 Hz, 2 H), 1.56 (quin, *J* = 7.1 Hz, 2 H), 3.51 (t, *J* = 6.6 Hz, 2 H), 3.60 (dd, *J* = 11.0, 3.8 Hz, 1 H), 3.67 (dd, *J* = 10.8, 4.0 Hz, 1 H), 4.39 (dd, *J* = 8.0, 6.0 Hz, 1 H), 4.50 (t, *J* = 8.2 Hz, 1 H), 4.78-4.85 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 13.7, 19.1, 31.4, 66.2, 69.6, 71.8, 75.1, 155.0. IR (neat): ṽ = 2959, 2934, 2871, 1793, 1171, 1053 cm^{-1}. MS (EI): *m/z* = 174 $[M]^+$.

*4-10-4. (Allyloxymethyl)ethylene carbonate (**3e**):* Colorless oil (157 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 3.63 (dd, *J* = 11.0, 3.8 Hz, 1 H), 3.70 (dd, *J* = 11.0, 4.2 Hz, 1 H), 4.01-4.12 (m, 2 H), 4.41 (dd, *J* = 8.2, 5.8 Hz, 1 H), 4.51 (dd, *J* = 8.2, 8.2 Hz, 1 H), 4.79-4.86 (m, 1 H), 5.24 (dd, *J* = 10.2, 1.4 Hz, 1 H), 5.29 (dq, *J* = 17.4, 1.4 Hz, 1 H), 5.82-5.93 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 66.3, 68.8, 72.6, 74.9, 118.0, 133.6, 154.9. IR (neat): ṽ = 2924, 2863, 1782, 1166, 1042 cm^{-1}. MS (EI): *m/z* = 158 $[M]^+$.

*4-10-5. Styrene carbonate (**3f**):* Pale yellow solid (163 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 4.34 (dd, *J* = 8.0, 8.0 Hz, 1 H), 4.80 (dd, *J* = 8.4, 8.4 Hz, 1 H), 5.68 (t, *J* = 8.2 Hz, 1 H), 7.33-7.48 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 71.1, 77.9, 125.8, 129.2, 129.7, 135.7, 154.8. IR (KBr): ṽ = 3036, 2982, 2921, 1790, 1168, 1068 cm^{-1}. MS (EI): *m/z* = 164 $[M]^+$.

4-11. General procedure in protic solvent for five-membered cyclic carbonate

The catalyst **1a**•HI (14.0 mg, 0.05 mmol) was added to a solution of epoxide (**2g** or **2h**, 1 mmol) in 2-propanol (0.2 mL) at room temperature. The atmosphere inside the flask was replaced with CO_2 (balloon, *ca.* 1 atm), and the reaction mixture was stirred at 25 °C. After 48-72 h, the mixture was diluted with ethyl acetate, and washed with water. The aqueous phase was extracted twice with ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and evaporated *in vacuo*. The residue was dried *in vacuo* for 6 h at 30 °C to give corresponding cyclic carbonate (**3g** or **3h**).

*4-11-1. Propyrene carbonate (**3g**):* Pale yellow oil (93 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 1.43 (d, *J* = 6.4 Hz, 3 H), 3.97 (dd, *J* = 8.0, 7.2 Hz, 1 H), 4.50 (dd, *J* = 8.8, 7.6 Hz, 1 H), 4.75-4.85 (m, 1 H. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 19.3, 70.6, 73.5, 155.0. IR (neat): ṽ = 2989, 2937, 1790, 1183, 1052 cm^{-1}. MS (EI): *m/z* = 102 $[M]^+$.

*4-11-2. 1,2-Hexylene carbonate (**3h**):* Colorless oil (133 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 0.86 (t, *J* = 6.8 Hz, 3 H), 1.22-1.45 (m, 4 H), 1.57-1.81 (m, 2 H), 4.01 (dd, *J* = 8.2, 7.4 Hz, 1 H), 4.47 (dd, *J* = 8.0, 8.0 Hz, 1 H), 4.60-4.69 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 13.7, 22.1, 26.3, 33.4, 69.3, 77.0, 155.0. IR (neat): ṽ = 2959, 2934, 2872, 1797, 1174, 1066 cm^{-1}. MS (EI): *m/z* = 144 $[M]^+$.

4-12. General procedure for five-membered cyclic dithiocarbonate

The catalyst **1a**•HI (14.0 mg, 0.05 mmol) was added to a solution of **2a** (150 mg, 1 mmol) and CS_2 (152 mg, 2 mmol) in THF (0.2 mL) at room temperature. After the mixture was stirred at 25 °C for 24 h, to the reaction mixture was added water. The heterogeneous mixture was extracted thrice with ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and evaporated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 5:1) to give dithiocarbonate **4a** (2nd fraction, main product) and trithiocarbonate **5a** (1st fraction, minor product).

*4-12-1. 5-(Phenoxymethyl)-1,3-oxathiolane-2-thione (**4a**):* Colorless oil (199 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 3.70 (dd, *J* = 11.2, 7.2 Hz, 1 H), 3.77 (dd, *J* = 11.2, 8.0 Hz, 1 H), 4.25 (dd, *J* = 10.2, 4.6 Hz, 1 H), 4.30 (dd, *J* = 10.4, 5.6 Hz, 1 H), 5.37-5.45 (m, 1H), 6.91 (dd, *J* = 8.8, 0.8 Hz, 2 H), 7.00 (t, *J* = 7.6 Hz, 1 H), 7.30 (dd, *J* = 8.8, 7.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 36.1, 66.2, 87.8, 114.4, 121.7, 129.6, 157.6, 211.4. IR (neat): ṽ = 2926, 2870, 1597, 1495, 1185, 1045 cm^{-1}. MS (EI): *m/z* = 226 $[M]^+$.

*4-12-2. 4-(Phenoxymethyl)-1,3-dithiolane-2-thione (**5a**):* Yellow solid (8.1 mg, 3.3%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 4.07 (dd, *J* = 12.2, 3.8 Hz, 1 H), 4.19 (dd, *J* = 10.2, 5.4 Hz, 1 H), 4.22 (dd, *J* = 12.2, 5.4 Hz, 1 H), 4.37 (dd, *J* = 9.6, 9.6 Hz, 1 H), 4.60-4.67 (m, 1 H), 6.92 (dd, *J* = 8.6, 1.0 Hz, 2 H), 7.01 (t, *J* = 7.2 Hz, 1 H), 7.28-7.34 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 44.9, 57.2, 66.5, 114.6, 121.9, 129.7, 157.7, 226.4. IR (neat): ṽ = 2923, 1597, 1487, 1459, 1236, 1036 cm^{-1}. MS (EI): *m/z* = 242 $[M]^+$

A mixture of benzyl ether **22** (61.4 mg, 0.145 mmol) and 10% palladium on charcoal (0.12 g) in dry ethanol (2 mL) was stirred under a hydrogen atmosphere at room temperature for 6 h. The reaction mixture was filtered through celite and the solvent evaporated *in vacuo* to give the crude product, which was purified by flash chromatography (30% Et_2O/CH_2Cl_2) to give the *title compound* **23** (44.0 mg, 91%) as a colourless oil; [Found: C, 64.6; H, 12.2. $C_{18}H_{41}O_3Si$ requires C, 64.81; H, 12.39%]; R_f (30% Et_2O/CH_2Cl_2) 0.43; $[a]_D^{20}$-1.9 (*c* 2.1, $CHCl_3$); n_{max} (liquid film) 3600–3100 (br), 1470, 1390, 1255, 1105 cm^{-1}; d_H (400 MHz $CDC1_3$) 3.79–3.56 (2H, m, C<u>H</u>$_2$OSi), 3.79–3.56 (2H, m, C<u>H</u>$_2$OH), 3.46 (3H, s, OMe), 2.95 (1H, dd, *J* 7.0, 4.0 Hz, C<u>H</u>OMe), 2.00–1.91 (1H, m, C<u>H</u>$_a$H$_b$CH$_2$OSi), 1.91–1.83 (1H, m, C<u>H</u>$_a$H$_b$CH$_2$OSi), 1.81–1.73 (1H, m, C<u>H</u>Me), 1.35–1.27 (1H, m, C<u>H</u>Me), 1.06–1.01 (3H, buried m, Me$_2$C<u>H</u>Si), 1.04 (18H, br d, *J* 4.5 Hz, <u>Me</u>$_2$CHSi), 0.97 (3H, d, *J* 7.0 Hz, CH<u>Me</u>), 0.93 (3H, d, *J* 7.0 Hz, CH<u>Me</u>); d_C (100.6 MHz, $CDCl_3$) 92.3, 66.7, 61.5, 60.9, 37.0, 34.4, 32.0, 18.0, 16.9, 15.3, 11.9; *m/z* (CI, NH_3) 333 (30, MH^+), 257 (25), 159 (100), 141 (50), 109 (37%); HRMS (CI, NH_3): MH^+, found 333.2825. $C_{18}H_{41}O_3Si$ requires 333.2825.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2019.xxxxxx.

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Highlights

- Efficient synthesis of cyclic carbonates from epoxides with CO_2.
- Efficient synthesis of cyclic dithiocarbonate from epoxides with CS_2.
- Cyclic amidine hydroiodides had high catalytic activity.
- Cyclic carbonates and dithiocarbonate were obtained in high yields under mild conditions.

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