Synthesis of Cyclic Organic Carbonates Using Atmospheric Pressure CO_2 and Charge-Containing Thiourea Catalysts

Yang Fan[a], Maximilian Tiffner[b], Johannes Schörgenhumer,[b] Raphaël Robiette,[c]
Mario Waser[b]* and Steven R. Kass[a]*

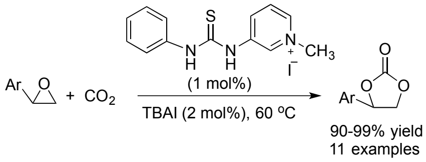
[a]Department of Chemistry, University of Minnesota, 207 Pleasant Street, SE, Minneapolis, Minnesota 55455, United States

[b]Institute of Organic Chemistry, Johannes Kepler University Linz, Altenbergerstraße 69, 4040 Linz, Austria

[c]Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Place Louis Pasteur 1, box L4.01.02, 1348 Louvain-la-Neuve, Belgium

E-mail: Mario.waser@jku.at, kass@umn.edu

Table of Content Graphic



ABSTRACT

Cycloadditions of epoxides with CO_2 to synthesize cyclic five-membered ring organic carbonates are of broad interest from a synthetic, environmental and green chemistry perspective, and the development of effective catalysts for these transformations is an ongoing challenge. A series of eight charge-containing thiourea salts that catalyze these reactions under mild conditions (i.e., 60 ˚C and atmospheric CO_2 pressure) are reported. Substrate scope and mechanistic studies were also carried out, isotope effects were measured, and a reactive intermediate was isolated revealing a surprising pathway in which a thiourea catalyst serves as a nucleophile in the cleavage of the epoxide ring.

INTRODUCTION

Carbon dioxide (CO_2) is a problematic greenhouse gas of great concern in the Earth's atmosphere. Its atmospheric concentration has been rapidly rising over the past fifty years in large part due to human activities such as fuel combustion, and this is a major cause of global warming.[1] Reduction of unwanted CO_2 emissions and atmospheric levels, consequently is a subject of the utmost importance in the development of a modern sustainable society.[2] Carbon dioxide is also a non-toxic and renewable potential C1 feedstock in organic synthesis that could be of enormous utility in industrial and pharmaceutical applications.[3] Sustainable and efficient methods of chemical fixation of CO_2 are urgently needed, and are the focus of current research in the management strategy of this greenhouse gas.[4] One alternative approach is the incorporation of CO_2 into epoxides to afford cyclic five-membered ring organic carbonates because this chemical transformation is 100% atom economical and the resulting compounds are of broad utility. For example, they are used as aprotic polar solvents in the development of batteries and ionic liquids, and as precursors and intermediates in organic and polymer syntheses.[5,6]

Despite the global desire to readily and sustainably make use of CO_2 in chemical reactions, this has proven to be difficult due to its kinetic and thermodynamic stability. Elevated temperatures and pressures are typically required to overcome energy barriers and make use of this abundant potential C1 feedstock. The development of catalysts to exploit this reagent under milder conditions has received considerable attention in recent years. A wide range of species have been studied for carrying out cycloadditions of epoxides with CO_2 to afford cyclic carbonates with a focus on metal complexes,[7] ionic liquids[8] and combinations of the two. Halide salt additives have proven useful in these systems but the resulting processes suffer from air and/or water sensitivity, poor reactivity necessitating harsh reaction conditions, and the need for organic solvents.[9] In this context, the development of organocatalysts has emerged as an attractive new research direction.

Hydrogen bond catalysts such as alcohols,[10] polyphenols,[11] carboxylic acids,[12] silanediols[13] and squaramides[14] have been reported recently and show promising results for the preparation of cyclic carbonates. Electrophilic activation of the epoxide via a hydrogen bonded complex is generally considered to facilitate its ring-opening in the presence of a halide anion in the rate determining step.[15] When compared to metal-based catalysts and ionic liquids, organic hydrogen bond donors are considered to be advantageous with respect to toxicity, sustainability, and the use of milder conditions.[16]

Thioureas are the most extensively studied hydrogen bond catalysts and of these, Schreiner's thiourea (**1**, $(3,5\text{-}(CF_3)_2C_6H_3NH)_2CS$) is commonly viewed as the most active species. We recently reported on a series of novel charge-enhanced derivatives bearing one or two *N*-alkylpyridinium ion centers and a weakly coordinating counteranion.[17] These solid salts proved to be more active than Schreiner's thiourea by orders of magnitude in several organic transformations carried out in non-polar media. Inspired by these results, we decided to examine their ability to catalyze the cycloadditions of epoxides with CO_2. The catalytic performance of eight such derivatives (**T1-T8**, Figure 1) is reported herein.

RESULTS AND DISCUSSION

To initiate our study upon the chemical fixation of CO_2 into epoxides using charged thiourea salts as catalysts, we first examined the reaction of 2-phenyloxirane (**2**) with CO_2 to afford the phenyl-substituted carbonate **3** (eq. 1). Under mild solvent free conditions at 60 ˚C with an

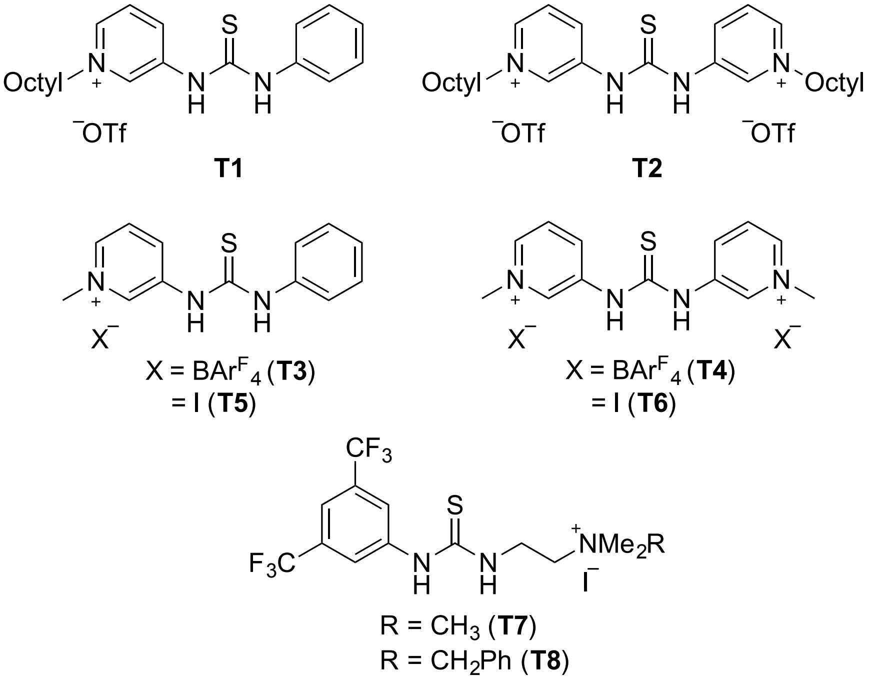
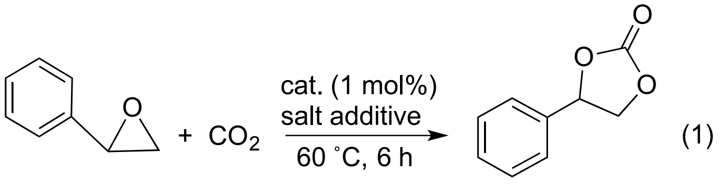


Figure 1. Charge-containing thiourea salts examined in this work.



2 **3** (1)

atmospheric pressure of CO$_2$, 1 mol% of **T1** and a halide salt, the cyclic carbonate was formed with moderate conversions after 6 h (Table 1). When tetrabutylammonium iodide (TBAI) was employed, 57% of the 2-phenyloxirane was converted to **3** (entry 1) whereas progressively smaller amounts were obtained in going to the bromide and chloride salts (entries 2-3). This order is the reverse of the gas-phase proton affinities of these halide anions and their nucleophilicities in aprotic media. Use of bis(triphenylphosphine)iminium chloride (PPNCl) had little, if any, impact (entry 4) even though this salt is known to dissociate to a larger extent than

Table 1. Catalytic Performance of T1 with Various Halide Salt Co-catalysts in the Fixation of CO_2 into 2-Phenyloxirane.[a]

entry	additive	(mol%)	conversion (%)[b]
1	$(Bu)_4NI$	1	57
2	$(Bu)_4NBr$	1	41
3	$(Bu)_4NCl$	1	20
4	$(Ph_3P)_2NCl$	1	19
5	none		0
6[c]	$(Bu)_4NI$	1	29
7[c]	$(Bu)_4NI$	2	56
8	$(Bu)_4NI$	2	74
9	$(Bu)_4NI$	3	65
10	$(Bu)_4NI$	5	66
11	$(Bu)_4NI$	10	53
12[d]	$(Bu)_4NI$	2	16

[a]Unless otherwise indicated, this reaction was carried out at 60 ˚C with 1 mol% of catalyst **T1** and the indicated additive under an atmospheric pressure (0.1 MPa) of CO_2. [b]Reaction conversions were obtained after 6 h by ^1H NMR. [c]No thiourea catalyst was used. [d]The reaction was carried out under 4.0 MPa of CO_2 and analyzed after 1.5 h.

TBACl in nonpolar media.[18] Omission of the halide salt led to no observed product (entry 5) whereas when the catalyst (**T1**) was excluded but 1 mol% of TBAI was employed about half the amount of product was formed (entry 6). These results indicate that a nucleophilic anion is required for product formation and the presence of thiourea **T1** improves the efficiency of this process.

Further optimization of this transformation was carried out by varying the amount of the TBAI additive. When 2 mol% of this salt was used, a higher conversion of 74% was achieved (entry 8) and this exceeds the 56% that is obtained when **T1** was omitted from the reaction (entry 7). Further increases of TBAI were explored (3-10 mol%), but this led to smaller amounts of product (entries 9-11). We speculate that this is due to aggregation and/or a medium effect resulting in a decrease in the nucleophilicty of I^-. A reaction was also carried out at an elevated pressure of CO_2 (4.0 MPa) with 1 mol% **T1** and 2 mol% TBAI, but this did not appear to accelerate the transformation.[19] These results suggest that CO_2 is not involved in the rate-determining step, but that both the nucleophile and the hydrogen bond catalyst play an important role in this process.

Based upon these preliminary results with catalyst **T1**, a variety of catalyst structures (**T2-T8**) were examined with varying amounts of TBAI (Table 2). Incorporation of a second positively charged center into the thiourea (**T2**) leads to a less efficient catalyst than **T1** (entries 1-2). The

Table 2. Catalyst and Additive Screening for the Reaction of 2-Phenyloxirane with CO_2.[a]

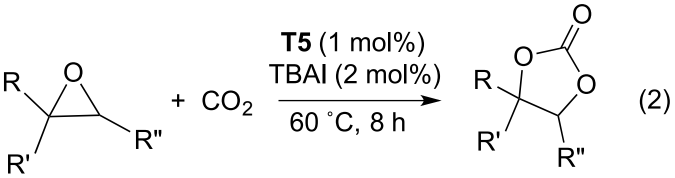
entry	catalyst	TBAI (mol%)	conversion (%)[b]
1	**T1**	2	74
2	**T2**	2	53
3	**T3**	0	0
4	**T3**	1	20
5	**T3**	2	52
6	**T4**	0	0
7	**T4**	2	87
8	**T5**	0	48
9	**T5**	1	61
10	**T5**	2	88
11	**T5**	3	88
12	**T5**	2[c]	79
13[d]	**T5**	2	83
14[e]	**T5**	2	71
15[f]	**T5**	2	82
16	**T6**	0	17
17	**T6**	2	54
18	**T7**	0	28
19	**T8**	0	34
20	$(PhNH)_2CS$	2	48
21	**1**	2	40

[a] These transformations were carried out for 6 h with 1 mol% of the catalyst and atmospheric pressure (0.1 MPa) CO_2 at 60 °C. [b] Product conversions were obtained by ^1H NMR. [c] Tetra-*n*-heptylammonium iodide was used instead of TBAI. [d] 4-Dimethylaminopyridine (DMAP, 2 mol%) was added. [e] Acetic acid (1 mol%) was added. [f] Trifluoroacetic acid (1 mol%) was added.

triflate counteranion is weakly basic but previously was shown to have a deleterious effect on the rate of a Friedel-Crafts alkylation.[20] Consequently, mono- and bis-charged thioureas **T3** and **T4** with weakly coordinating tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anions ($BAr^F{}_4^-$) were explored.[17] In the absence of a nucleophile no carbonate was produced (entries 3 and 6) and the mono-charged catalyst **T3** is not as effective as **T1** (entries 4-5), but the bis-charged derivative **T4** gave an improved result (entry 7). Bifunctional thiourea salts **T5-T8** with iodide counteranions were also examined. Unlike **T1-T4**, these species led to product formation without the need for an external iodide source and the conversions followed the order: **T6** < **T7** < **T8** < **T5** (entries 8, 16 and 18-19). Further optimization of **T5** led to our best result and an 88% conversion to product in a 6 h time period at 60 ˚C (entries 9-11); this was achieved with 2 or 3 mol% TBAI. A larger quaternary ammonium salt, tetra-*n*-heptylammonium iodide was tested too (entry 12), but it led to slightly poorer results.

Previous studies have found that organic bases can facilitate the cycloaddition of epoxides with CO_2 by activating the latter reagent.[21] When we added 2 mol% of 4-dimethylamino-pyridine (DMAP) along with **T5** and TBAI, no improvement was observed (entry 13). This is consistent with our observation that an increase in the CO_2 pressure did not accelerate the reaction. Alternatively, thioureas can be activated by Brønsted acids[22] so 1 mol% of acetic acid and trifluoroacetic acid were tested (entries 14-15). Both of these additives, however, had a small deleterious effect. Finally, reactions were carried out with diphenylthiourea and $(3,5\text{-}(CF_3)_2C_6H_3NH)_2CS$ (**1**), and as suspected the conversions (48 and 40%, respectively) were reduced with respect to our charged analogs (entries 20-21). In fact under the employed conditions both compounds actually function slightly as inhibitors since a 56% conversion was obtained when they were omitted.

Given the excellent performance of the binary **T5**/TBAI catalyst system,[23] the scope of this transformation was explored (eq. 2, Table 3). A series of 11 monosubstituted aromatic and aliphatic epoxides were examined at 60 °C with 1 atmosphere pressure of CO_2, 1 mol% **T5** and 2 mol% TBAI, and isolated yields of ≥ 90% were obtained after 8 h in all cases (entries 1-11); see the supporting information for the application scope of **T7** and **T8**. Disubstituted epoxides (1,1- and 1,2-), however, are not suitable substrates under the employed reaction conditions (entries 12-13). From a mechanistic standpoint, these results suggest that sterics are important.



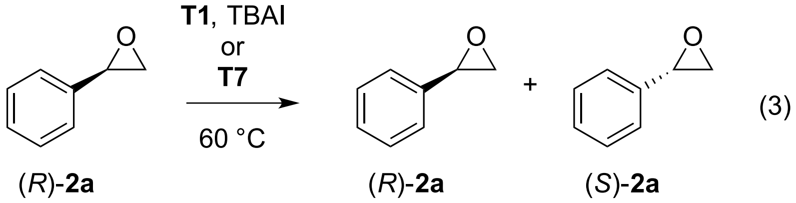
(2)

Table 3. Reaction scope with the use of the T5/TBAI binary catalyst system.

entry	epoxide (and carbonate **3**)	yield (%)
1	R = Ph, R', R" = H (**2a**)	95
2	R = *p*-ClC_6H_4, R', R" = H (**2b**)	95
3	R = *p*-FC_6H_4, R', R" = H (**2c**)	93
4	R = *p*-$MeOC_6H_4$, R', R" = H (**2d**)	98[a]
5	R = *p*-$O_2NC_6H_4$, R', R" = H (**2e**)	98[b]
6	R = $PhOCH_2$, R', R" = H (**2f**)	99
7	R = $ClCH_2$, R', R" = H (**2g**)	98
8	R = $CH_2{=}CHCH_2CH_2$, R', R" = H (**2h**)	90
9	R = $CH_2{=}CH$, R', R" = H (**2i**)	97
10	R = $PhCH_2$, R', R" = H (**2j**)	97
11	R = $BnOCH_2$, R', R" = H (**2k**)	95
12	R,R" = $(CH_2)_4$, R' = H (**2l**)	trace
13	R = Ph, R' = CH_3, R" = H (**2m**)	trace

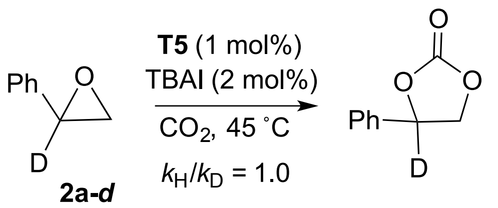
[a] t = 3 h. [b] t = 4 h and T = 90 °C.

To address the mechanism of this transformation further, (*R*)-2-phenyloxirane (**2a**, ≥ 99% ee) and (*R*)-2-(benzyloxymethyl)oxirane (**2k**, ≥ 99% ee) were reacted with **T5** as illustrated in eq. 2 and the isolated products were both obtained in 95% yields with 86% ee for **3a** and ≥ 99% ee for **3k**. The absolute configuration of the major enantiomer in both cases corresponded to retention of configuration (*R*) by comparison to previously reported chiral HPLC data.[24] In accord with these findings, when enantiopure samples of **2a** were heated to 60 ˚C in the absence of CO_2 but in the presence of **T1** and TBAI (1 and 2 mol%, respectively) or **T7** (1 and 3 mol%), racemization was observed to slowly occur (eq. 3). In the former case, the epoxide had an 86% ee after 1 h and was completely racemized within 18 h. In the latter instance with 1 or 3 mol% of **T7**, 86% and 55% ee samples were obtained respectively after 15 h. These results reveal that a slow epimerization takes place when a stabilized benzylic cation can form when starting with **2a**, but not when a secondary alkyl carbenium ion would be produced using epoxide **2k**. These acid-catalyzed processes presumably are catalytically off-cycle events (i.e., they are unrelated to the mechanism for formation of the cyclic carbonate) given that alkyl substituted epoxides are good substrates, 1,1-disubstituted derivative **2l** is unreactive, and a competition study showed that the reaction of 2-(*p*-nitrophenyl)oxirane (**2e**) takes place more rapidly than the parent compound, 2-phenyloxirane (**2a**). That is, a 1:1 mixture of **2e** and **2a** at 60 ˚C with 1 mol% **T5** and 2 mol% TBAI led to 54% and 32% conversions to their respective carbonates after 2 h.

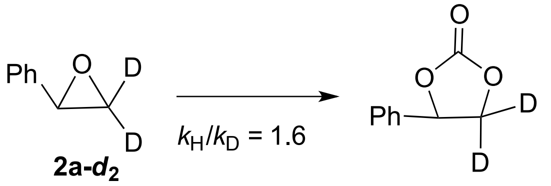


T1 (1 mol%), TBAI (2 mol%): 86% ee (*R*) (1 h), racemic (18 h)
T7: 86% ee (*R*) (1 mol%, 15 h), 55% ee (*R*) (3 mol%, 15 h)

Electrophilic activation of the monosubstituted epoxide by coordination to the thiourea catalyst via hydrogen bond formation might be expected to preferentially activate the internal position due to a larger build-up of positive charge at this site.[17] To probe this latter mechanistic detail, kinetic isotope effects were measured using 2-deuterio-2-phenyloxirane (**2a**-d_1, >99% D) and 3,3-dideuterio-2-phenyloxirane (**2a**-d_2, 85% D_2) at 45 ˚C with 1 mol% **T5** and 2 mol% TBAI (eq. 4). Surprisingly, k_H/k_D = 1.0 for the monodeuterio compound and 1.6 for the dideuterio species were observed (see Table S4 in the supporting information for additional details). The latter secondary kinetic isotope effect is large, and taken together these results indicate that nucleophilic attack occurs at the terminal methylene carbon of 2-phenyloxirane. Additionally, when the reaction of **2a** with **T7** was monitored by ^{1}H NMR, a small amount of an intermediate was observed. This species (**4**) was subsequently isolated and characterized, and is the product resulting from nucleophilic attack of the epoxide by the sulfur atom of the thiourea; a similar observation with 2-methyloxirane to afford **4'** was found. Submission of this compound to the reaction conditions led to the formation of the cyclic carbonate product in a kinetically competent fashion and led us to propose the novel mechanism illustrated in Scheme 1.

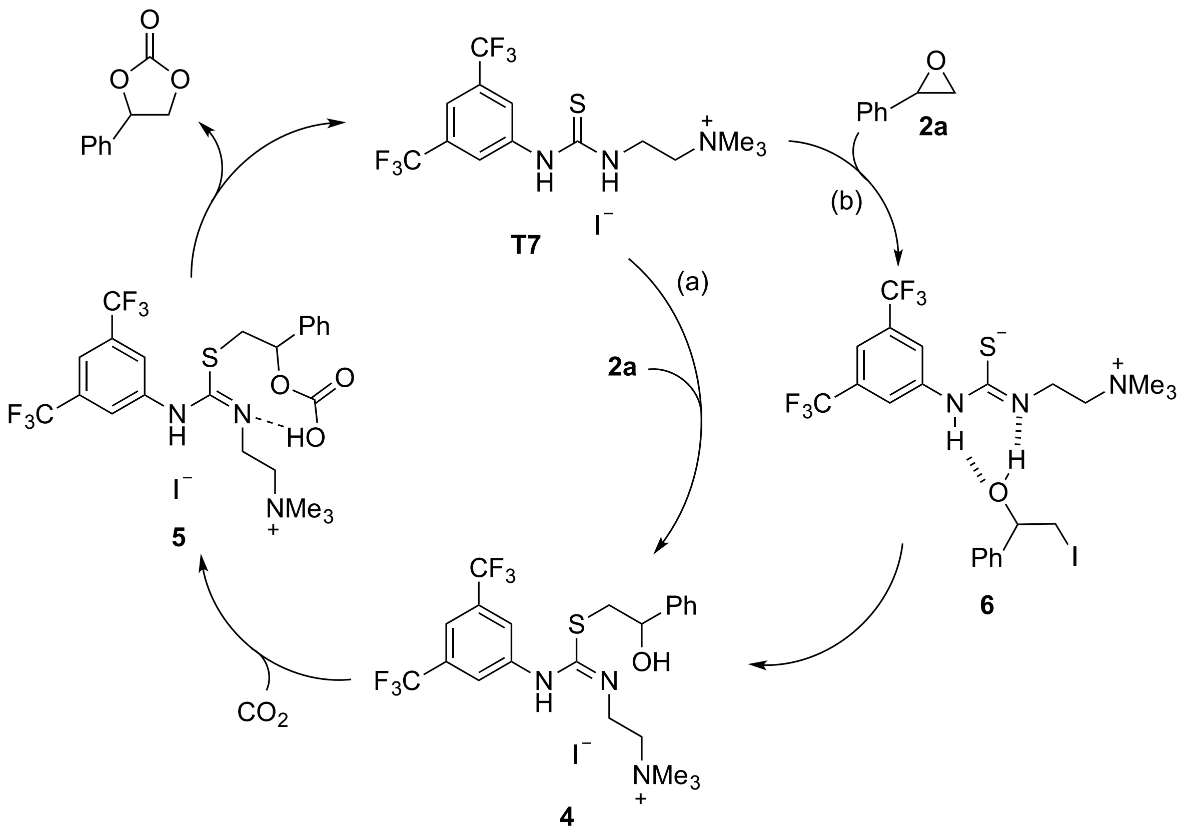


(4a)

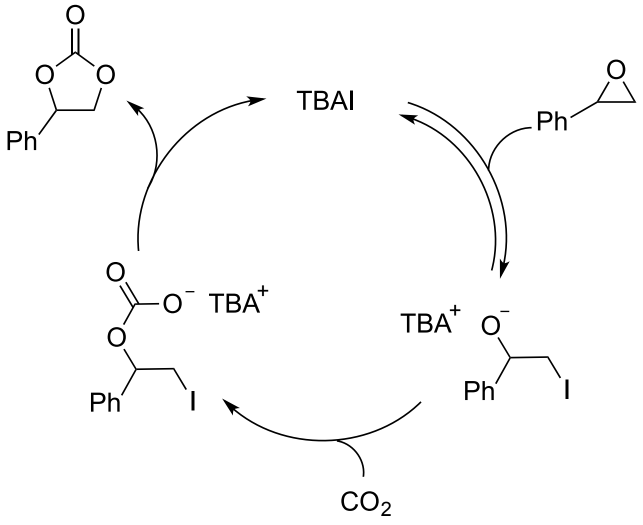


(4b)

Thiourea-catalyed pathways:



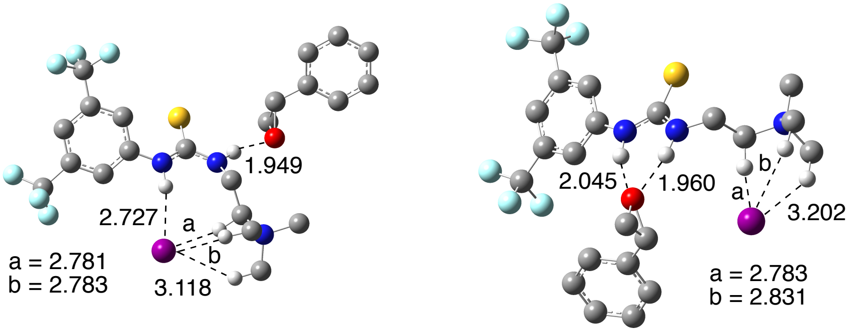
TBAI-catalyed route in the absence of **T7**:



Scheme 1. Proposed mechanism for the cycloaddition of 2-phenyloxirane with CO_2 in the presence of a charge-containing thiourea/TBAI binary catalyst system (top), and an alternative route in the absence of the thiourea (bottom).

In our proposed mechanism, the charge-containing thiourea catalyst acts as a nucleophile in an S_N2 ring opening of the epoxide at the less hindered methylene carbon to yield **4** via pathway a. Alternatively, iodide may serve as the initial nucleophile to afford **6** as shown in route b. An ensuing displacement of I^- by the sulfur atom of the thiourea would lead to **4** by a two step process. Both pathways account for the formation of this intermediate and the observed secondary kinetic isotope effect, and are consistent with 1,1- and 1,2-disubstituted epoxides being poor reaction partners due to increased steric effects. Subsequent trapping of CO_2 to give **5** followed by cyclization via an intramolecular substitution reaction affords the carbonate product and regenerates the thiourea catalyst. Putative intermediate **6** also could react with CO_2 (pathway c, not shown) in a similar manner to the TBAI-catalyzed process that takes place in the absence of a thiourea. If this is the case, then the conversion of **6** to **4** would need to be reversible.

To address these mechanistic alternatives further, B3LYP calculations were carried out on different structural arrangements of hydrogen bonded complexes between **T7** and **2a** (see supporting information for additional details). Low energy structures that are well positioned to use the sulfur or iodine atom as the nucleophile were located (Figure 2, **7** and **8**, respectively).



7 **8**

Figure 2. Fully optimized B3LYP/aug-cc-pVDZ/6-311G(d) structures, where the second all electron basis set was used for iodine. Distances are given in Å and most of the hydrogen atoms attached to carbon are omitted for clarity sake.

The covalently bound complex between the thiourea catalyst and 2-phenyloxirane (i.e., **4**) is more stable than **6** by 13.3 kcal mol^{-1}, but the reaction barrier for formation of the latter is much more favorable than the one for direct formation of **4**. That is, nucleophilic attack of the epoxide by I^{-} has a computed barrier of 25.5 kcal mol^{-1} whereas that for the sulfur atom of the catalyst is 46.8 kcal mol^{-1} (Figure 3).[25] These results suggest that pathway b is the favored process,[26] but given the computational complexity of this system, additional experimental data would be useful for further differentiating the various reaction pathways.

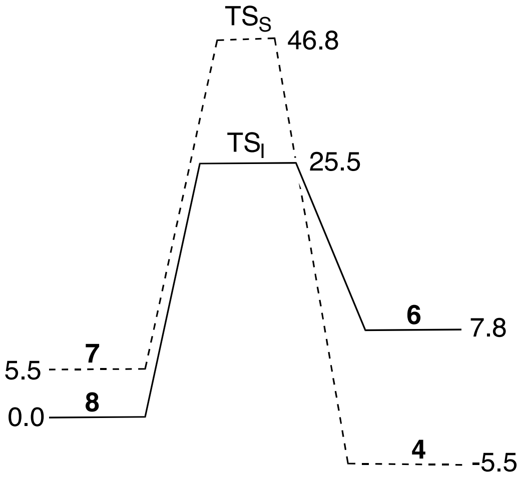


Figure 3. Computed B3LYP/aug-cc-pVDZ/6-311+G(d) single point free energy reaction diagrams for the **T7** catalyzed ring opening of 2-phenyloxirane. Relative free energies are given in kcal mol^{-1} at 298 K.

CONCLUSION

A series of metal-free electrostatically enhanced thiourea catalysts **T1-T8** were explored and found to induce CO_2 fixation at atmospheric pressure into monosubstituted epoxides with low loadings (1 mol%) and the addition of a small amount (2 mol%) of tetrabutylammonium iodide. High yields of ≥ 90% were obtained at modest temperatures for 11 different substrates in 8 h or less. These species are more active than the only other thiourea catalyst previously reported, an ionic liquid containing a remote imidizolium ion,[7g] in that lower temperatures (60 vs 130 ˚C) and pressures (1 vs 15 atm.) were employed in this work. Mechanistic studies suggest that this cycloaddition reaction occurs via a novel pathway in which the thiourea acts as a nucleophile to either open the epoxide directly at the less hindered position or to replace the iodine in 2-iodo-1-phenylethanol. In either case, the resulting covalently bound thiourea **4** was spectroscopically observed, isolated, and found to react with CO_2 in a kinetically competent manner to afford the cyclic carbonate product and regenerate the thiourea catalyst.

Experimental

General. All chemicals and reagents were obtained from Sigma Aldrich and Alfa Aesar except for deuterated solvents which came from Cambridge Isotope Laboratories. Reactions were carried out in oven-dried glassware (i.e., flasks, vials and NMR tubes) under an argon or CO_2 atmosphere. NMR spectra were recorded on 300, 500 and 700 MHz instruments. The ^1H and ^{13}C chemical shifts are given in ppm and were referenced respectively as follows: 7.26 and 77.2 ($CDCl_3$); 2.05 and 29.8 (acetone-d_6). IR spectra were obtained with a FT-IR and an ATR source. High resolution mass spectra were recorded by ESI with a TOF mass analyzer using methanolic solutions containing polyethylene glycol as an internal standard. Enantiomeric ratios were measured with HPLC systems using 25 cm x 4.6 mm (5 μm) RegisPack™ and Chiracel OD-H chiral columns. Synthesis and characterization data for **T1-T6** have been reported in previous work.[17,20]

General Procedure for the Cycloaddition Reactions of 2-Phenyloxirane (2) with CO_2. A 3-dram vial was purged with gaseous CO_2 for 5 min and then charged with 2-phenyloxirane (57 μL, 0.5 mmol), TBAI (3.7 mg, 10 μmol) and **T5** (1.9 mg, 5 μmol). The vial was then sealed with a septum which was connected to a balloon filled with CO_2 and heated at 60 °C for 6 h. Reaction conversions were obtained by ^{1}H NMR in $CDCl_3$ using integrations for the signals of **2** at δ 3.84 and **3** at δ 4.32 ppm.

3,3-Dideuterio-2-phenyloxirane (**2a-*d*$_2$**). A solution of 2-bromoacetophenone (1999 mg, 10 mmol) in 5 mL $CDCl_3$ was cooled to 0 °C. Carefully, *t*-BuOK (842 mg, 7.5 mmol) was added in small portions while the reaction mixture was strongly stirred (**Warning:** chloroform is incompatible with strong caustics). After 1 h of stirring at 0 °C, 3 mL of D_2O was slowly added. A ^{1}H NMR sample of the $CDCl_3$ phase was recorded which showed a degree of deuteration of only 33%. Additional *t*-BuOK (562 mg, 5.0 mmol) was then carefully added to the strongly stirred biphasic mixture, which was stirred for 2 h while allowing it to warm to room temperature. The two phases were separated and the aqueous solution was extracted with $CDCl_3$ (2 x 2 mL). The combined organic material was dried with Na_2SO_4 and the solvent was removed by rotatory evaporation. Purification of the crude product was carried out by column chromatography on silica gel with heptanes/EtOAc (50:1 → 30:1) to afford 1.42 g (62%) of 2-bromoacetophenone-2,2-d_2 as a white orange solid with 90% deuterium incorporation at the acidic α-position. Analytical data are in accord with those reported in the literature.[27] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.65 – 7.56 (m, 1H), 7.54 – 7.45 (m, 2H), 4.47 – 4.42 (m, 0.21 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.3, 133.9, 133.8, 128.8, 128.7, 30.3 (quintet, $J = 22.5$ Hz).

2-Bromoacetophenone-2,2-d_2 (1400 mg, 7 mmol) was put into a Schlenk flask which was then evacuated and refilled three times with argon before adding 15 mL of MeOH. This suspension was cooled to 0 °C using an ice-salt water bath and sodium borohydride (294 mg, 7.7 mmol) was added portionwise. The resulting reaction mixture was stirred for 3 h while letting it slowly warm to room temperature. Subsequently, K_2CO_3 (968 mg, 7 mmol) was added in one portion and stirring was continued for 15 h. Methanol was then removed by rotatory evaporation, 50 mL of H_2O was added and the aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic material was washed with brine (50 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure to afford 720 mg (84%) of **2a-*d*₂** as a colorless liquid. Its analytical data are in accord with those reported in the literature.[28] ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 5H), 3.86 (s, 1H), 3.18 – 3.12 (m, 0.15H), 2.83 – 2.78 (m, 0.15H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137, 128.4, 128.1, 125.4, 52.1, 51.5 (quintet, $J = 26$ Hz).

2-Deuterio-2-phenyloxirane (**2a-*d***). 2-Bromoacetophenone (1000 mg, 5 mmol) was put into a Schlenk flask and then evacuated and refilled with argon (3x) before adding 12 mL of MeOH. The resulting suspension was cooled to 0 ˚C with an ice-salt water bath and sodium borodeuteride (210 mg, 5.5 mmol) was added portionwise with stirring. Over the course of 3 h the reaction mixture was allowed to warm up to room temperature. Potassium carbonate (691 mg, 5 mmol) was then added in one portion and stirring was continued for 20 h. The reaction mixture was then filtered through a plug of Na_2SO_4 and the solvent was removed by rotatory evaporation. Purification of the crude product by column chromatography on silica gel with heptanes/EtOAc (100:1 → 50:1) afforded 545 mg (91%) of **2a-*d*** as a colourless liquid. Its analytical data are in accord with those reported in the literature.[29] ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 5H), 3.17 (d, $J = 5.5$ Hz, 1H), 2.84 (d, $J = 5.5$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 128.4, 128.1, 125.4, 51.9 (t, 27 Hz), 51.0.

Catalyst **T7.** To a suspension of 2-(aminoethyl)trimethylammonium iodide (1 g, 2.81 mmol)[30] in 10 mL of dry CH_2Cl_2 was added triethylamine (392 µL, 2.81 mmol) at room temperature. This mixture turned clear and subsequently 3,5-bis(trifluoromethylphenyl)isothiocyanate (517 µl, 3.09 mmol) was added. Stirring was continued for 15 h before filtering the reaction mixture through a plug of Na_2SO_4. Removal of the solvent by rotatory evaporation afforded the crude product which was purified by column chromatography on silica gel with CH_2Cl_2/MeOH (50:1 → 10:1) to afford 1.35 g (96%) of **T7** as a white solid; analytical data are in accord with the previously reported chloride salt.[31] ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.79 (s, 1H) ppm, 8.49 (t, J = 5.8 Hz, 1H), 8.24 (s, 2H), 7.60 (s, 1H), 4.38 – 4.28 (m, 2H), 3.98 – 3.91 (m, 2H), 3.45 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.7, 140.3, 131.4 (q, J = 34 Hz), 123.1 (q, J = 274 Hz), 123.0, 118.0, 64.9, 54.8, 38.3. ^{19}F NMR (282 MHz, D_2O) δ -64.5. HRMS-ESI: calcd for $C_{14}H_{18}F_6N_3S^+$ $(M)^+$ 374.1120, found: 374.1125.

Catalyst **T8.** To a solution of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (0.336 mL, 1.84 mmol) in toluene (2 mL) was added *N*,*N*-dimethylethylenediamine (0.201 mL, 1.84 mmol). After stirring for 14 h at room temperature the reaction mixture was directly subjected to column chromatography on silica gel with CH_2Cl_2/MeOH (20:1) to afford 625 mg (95%) of the known thiourea intermediate.[32] A mixture of this compound (100 mg, 0.278 mmol) and benzyl bromide (95 mg, 0.556 mmol) was stirred in 2 mL of CH_3CN for 15 h at room temperature. The reaction mixture was directly subjected to column chromatography on silica gel with CH_2Cl_2/MeOH (10:1) to yield 148 mg (92%) of **T8** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.83 (s, 1H), 8.74 (t, J = 5.7 Hz, 1H), 8.24 (s, 2H), 7.42 – 7.60 (m, 6H), 4.83 (s, 2H), 4.37 – 4.48 (m, 2H), 3.99 (t, J = 5.8 Hz, 2H), 3.29 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.8, 140.4, 133.0, 131.4 (q, J = 34 Hz), 131.4, 129.6, 126.0, 123.1 (q, J = 274 Hz), 123.0, 118.0, 68.9, 63.6, 50.7, 38.3. HRMS-ESI: calcd for $C_{20}H_{22}F_6N_3S^+$ $(M)^+$ 450.1433, found 450.1439.

Isolation of 4. This compound can be obtained by heating 0.04 mmol (20 mg) of the ammonium salt **T7** with 48 mg (10 equivalents) of 2-phenyloxirane in a pressure Schlenk vessel until the ammonium salt is dissolved, allowing the organic material to cool to room temperature and then performing a purification by silica gel column chromatography with CH_2Cl_2/MeOH (20:1) as the eluent. This afforded 9 mg (36%) of **4** as a colorless oil. ^{1}H NMR (700 MHz, MeOD) δ 7.51 (s, 1H), 7.39 (s, 2H), 7.37 – 7.34 (m, 2H), 7.34 – 7.30 (m, 2H), 7.28 – 7.25 (m, 1H), 4.83 (dd, J = 8.4 and 3.7 Hz, 1H), 3.88 (t, J = 6.4 Hz, 2H), 3.66 (t, J = 6.6 Hz, 2H), 3.26 (s, 9H), 3.24 – 3.21 (m, 2H), 3.14 (dd, J = 14.4 and 3.4 Hz, 1H). ^{13}C NMR (175 MHz, MeOD) δ 155.6, 152.0, 143.0, 131.7 (q, J = 33 Hz), 128.2, 127.7, 125.8, 123.8 (q, J = 273 Hz), 123.0, 115.2, 73.5, 64.2, 52.9, 39.6, 36.6. HRMS-ESI: calcd for $C_{22}H_{26}F_6N_3OS^+$ $(M)^+$ 494.1695, found: 494.1699.

Isolation of 4'. This compound was obtained when heating 0.04 mmol (20 mg) of the ammonium salt **T7** with 23 mg (10 equivalents) of methyloxirane in a pressure Schlenk vessel until the ammonium salt is dissolved, allowing the organic material to cool to room temperature and then performing a purification by silica gel column chromatography with CH_2Cl_2/MeOH (20:1) as the eluent. This afforded 7 mg (31%) of **4'** as a colorless oil ^{1}H NMR (300 MHz, MeOD) δ 7.53 (s, 1H), 7.45 (s, 2H), 3.96 – 3.89 (m, 3H), 3.72 (t, J = 6.5 Hz, 2H), 3.30 (s, 9H), 3.15 – 2.93 (m, 2H), 1.26 (d, J = 6.2 Hz, 3H). ^{13}C NMR (75 MHz, MeOD) δ 155.7, 151.9, 131.6 (q, J = 33 Hz), 123.5 (q, J = 273 Hz), 122.9, 115.0, 66.9, 64.1, 52.9, 39.2, 36.5, 21.3.[33] HRMS-ESI calcd for $C_{17}H_{24}F_6N_3OS^+$ $(M)^+$ 432.1539, found 432.1539.

Analytical Data for Carbonates 3. *4-Phenyl-1,3-dioxolan-2-one* (**3a**). This material (311 mg) was formed in a 95% yield and the analytical data are in accord with those reported in the literature.[34] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 3H), 7.38 – 7.33 (m, 2H), 5.67 (t, J = 8 Hz, 1H), 4.79 (t, J = 8.4 Hz, 1H), 4.34 (dd, J = 8.6 and 7.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 135.7, 129.5, 129.0, 125.7, 77.8, 71.0. HRMS-ESI: calcd for $C_9H_8NaO_3$ $(M + Na)^+$ 187.0371, found 187.0367. Enantiomer separation was accomplished with a Chiracel OD-H column using hexanes/*i*-PrOH = 70:30) and a flow rate of 1 mL min^{-1} to give retention times of 8.8 (*R*) and 10.0 (*S*) min.[24] When (*R*)-**2a** was used, (*R*)-**3a** was observed as the major enantiomer.

4-(4-Chlorophenyl)-1,3-dioxolan-2-one (**3b**). This material (378 mg) was formed in a 95% yield and the analytical data are in accord with those reported in the literature.[34] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.34 (d, 2H, 8.5 Hz), 7.33 – 7.26 (d, 2H, 8.5 Hz), 5.65 (t, *J* = 8 Hz, 1H), 4.79 (t, *J* = 8.5 Hz, 1H), 4.28 (dd, *J* = 8.6 Hz and 7.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 135.4, 134.2, 129.2, 127.2, 77.1, 71.8. HRMS-ESI: calcd for $C_9H_7ClNaO_3$ $(M + Na)^+$ 220.9981, found 220.9978.

4-(4-Fluorophenyl)-1,3-dioxolan-2-one (**3c**). This material (341 mg) was formed in a 93% yield and the analytical data are in accord with those reported in the literature.[34] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 2H), 7.17 – 7.06 (m, 2H), 5.66 (t, *J* = 8 Hz, 1H), 4.79 (t, *J* = 8.5 Hz, 1H), 4.31 (dd, *J* = 8.6 and 7.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2 (d, *J* = 249 Hz), 154.6, 131.5 (d, *J* = 3.3 Hz), 127.9 (d, *J* = 8.5 Hz), 116.2 (d, *J* = 22.1 Hz), 77.4, 71.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.1. HRMS-ESI: calcd for $C_9H_7FNaO_3$ $(M + Na)^+$ 205.0277, found: 205.0271.

4-(4-Methoxyphenyl)-1,3-dioxolan-2-one (**3d**). This material (380 mg) was formed in a 98% yield and the analytical data are in accord with those reported in the literature.[35] The product decomposed upon column chromatography. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 5.62 (t, *J* = 8.0 Hz, 1H), 4.75, (t, *J* = 8.4 Hz), 4.34 (t, *J* = 8.4 Hz, 1H), 3.83 (s, 3H).

4-(4-Nitrophenyl)-1,3-dioxolan-2-one (**3e**). This material (409 mg) was formed in a 98% yield and the analytical data are in accord with those reported in the literature.[36] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 5.83 (t, *J* = 7.9 Hz, 1H), 4.91, (t, *J* = 8.5 Hz), 4.32 (t, *J* = 8.2 Hz, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 154.1, 148.4, 142.7, 126.5, 124.3, 76.3, 70.6.

4-(Phenoxymethyl)-1,3-dioxolan-2-one (**3f**). This material (384 mg) was formed in a 99% yield and the analytical data are in accord with those reported in the literature.[34] ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.31 (t, *J* = 7.8 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.1 Hz), 5.09 – 4.96 (m, 1H), 4.60 (t, *J* = 8.5 Hz, 1H), 4.51 (dd, *J* = 6.0 and 8.4 Hz, 1H), 4.24 (dd, *J* = 10.5 and 3.8 Hz, 1H), 4.12 (dd, *J* = 10.5 and 3.8 Hz, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 157.7, 154.7, 129.5, 121.8, 114.5, 74.1, 66.7, 66.1. HRMS-ESI: calcd for $C_{10}H_{10}NaO_4$ (M+Na)$^+$ 217.0477, found 217.0475.

4-(Chloromethyl)-1,3-dioxolan-2-one (**3g**). This material (267 mg) was formed in a 98% yield and the analytical data are in accord with those reported in the literature.[34] ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.04 – 4.91 (m, 1H), 4.59 (t, *J* = 8.2 Hz, 1H), 4.41 (dd, *J* = 5.5 and 8.0 Hz, 1H), 3.83 – 3.68 (m, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 154.3, 74.3, 66.7, 44.1. HRMS-ESI: calcd for $C_4H_5ClNaO_3$ (M+Na)$^+$ 158.9825, found: 158.9821.

4-(But-3-en-1-yl)-1,3-dioxolan-2-one (**3h**). This material (256 mg) was formed in a 90% yield and the analytical data are in accord with those reported in the literature.[34] ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.84 – 5.66 (m, 1H), 5.10 – 4.96 (m, 2H), 4.77 – 4.63 (m, 1H), 4.50 (t, *J* = 8.1 Hz, 1H), 4.05 (t, *J* = 7.8 Hz, 1H), 2.32 – 2.05 (m, 2H), 1.98 – 1.81 (m, 1H), 1.81 – 1.65 (m, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 154.9, 136.0, 116.1, 76.2, 69.2, 32.8, 28.4. HRMS-ESI: calcd for $C_7H_{10}NaO_3$ (M+Na)$^+$ 165.0528, found 165.0526.

4-Vinyl-1,3-dioxolan-2-one (**3i**). This material (222 mg) was formed in a 97% yield and the analytical data are in accord with those reported in the literature.[34] ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.92 – 4.78 (m, 1H), 5.50 – 5.33 (m, 2H), 5.09 (q, *J* = 7.4 Hz, 1H), 4.56 (t, *J* = 8.3 Hz, 1H), 4.10

(t, J = 8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 132.0, 120.9, 77.2, 68.9. HRMS-ESI: calcd for $C_5H_6NaO_3$ $(M + Na)^+$ 137.0215, found: 137.0211.

4-Benzyl-1,3-dioxolan-2-one (**3j**). This material (345 mg) was formed in a 97% yield and the analytical data are in accord with those reported in the literature.[37] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 3H), 7.26 – 7.21 (m, 2H), 5.01 – 4.91 (m, 1H), 4.46 (t, J = 8.2 Hz, 1H), 4.18 (dd, J = 8.6 and 6.9 Hz, 1H), 3.16 (dd, J = 14.2 and 6.3 Hz, 1H), 3.01 (dd, J = 14.1 and 6.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 133.8, 129.2, 128.8, 127.4, 76.7, 68.4, 39.4. MS-ESI: calcd for $C_{10}H_{14}NO_3$ $(M + NH_4)^+$ 196.1, found 196.1.

4-((Benzyloxy)methyl)-1,3-dioxolan-2-one (**3k**). This material (396 mg) was formed in a 95% yield and the analytical data are in accord with those reported in the literature.[38] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H), 4.85 – 4.75 (m, 1H), 4.58 (dd, J = 17.5 and 12.0 Hz, 2H), 4.45 (t, J = 8.4 Hz, 1H), 4.35 (dd, J = 8.4 and 6.0 Hz, 1H), 3.70 (dd, J = 11.0 and 3.7 Hz, 1H) 3.59 (dd, J = 11.1 and 3.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 137.0, 128.3, 127.8, 127.5, 74.9, 73.4, 68.7, 66.1. MS-ESI: calcd for $C_{11}H_{12}NaO_4$ $(M + Na)^+$ 231.1, found: 231.1. Enantiomer separation was achieved on a Chiracel OD-H column using hexanes/*i*-PrOH = 80 : 20 and a flow rate of 1.0 mL/min to give retention times of 22.0 and 32.4 min. When the (*R*)-enantiomer of **2k** was used only the stereoisomer of **3k** eluting at 22.0 min was observed.

4-Phenyl-1,3-dioxolan-2-one-4-d (**3a-*d***). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.25 (m, 5H), 4.79 (d, J = 8.6 Hz, 1H), 4.33 (d, J = 8.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 135.7, 129.6, 129.4, 125.9, 77.5 (t, J = 24 Hz), 71.1. MS-ESI: calc for $C_9H_7DNaO_3$ $(M + Na)^+$ 188.0, found 188.0.

4-Phenyl-1,3-dioxolan-2-one-5,5-d_2 (**3a-$\boldsymbol{d_2}$**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 3H), 7.38 – 7.30 (m, 2H), 5.70 (s, 1H), 4.80 (m, 0.14H), 4.35 (m, 0.14H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 135.8, 129.8, 129.3, 125.9, 77.8, 70.8 (quintet, $J = 24$ Hz). MS-ESI: calc for $C_9H_6D_2NaO_3$ $(M + Na)^+$ 189.1, found 189.1.

Computations. Different orientations of hydrogen bonded complexes between **T7** and **2a** were fully optimized with Spartan 14[39] using B3LYP[40] and the 6-31G(d,p) basis set except for iodine, which was treated with the LANL2DZ pseudopotential.[41] Subsequent structures for **4**, **6**, and transition states leading to their formation were also located. Single point energies, reoptimizations and vibrational frequencies for select species were computed with Gaussian 09[42] using the aug-cc-pVDZ[43] and 6-311G(d) all electron basis set for iodine.[44] Thereafter, B3LYP/aug-cc-pVDZ/6-311+G(d) single point energies were computed.

Supporting Information Available: Additive, racemization and application scope data, NMR spectra, HPLC chromatograms, computed structures and energies, and the complete citation to ref. 42. This material is available free of charge via the internet at http://pubs.acs.org.

Competing financial interests: The authors declare no competing financial interests.

ACKNOWLEDGMENT

We wish to thank Mr. Curtis Payne for his assistance in determining the absolute chirality of **3a** when (*R*)-**2a** was used as the starting material. Generous support from the National Science Foundation (CHE-1665392), the Petroleum Research Fund (55631-ND4) as administered by the American Chemical Society, and the Minnesota Supercomputer Institute for Advanced Computational Research are gratefully acknowledged. The work carried out in Linz was supported by the Austrian Science Funds (FWF): Project No. P26387-N28. Computational resources were provided by the super-computing facilities of the Université catholique de

Louvain (CISM/UCL) and the Consortium des Équipements de Calcul Intensif en Fédération Wallonie Bruxelles (CÉCI) funded by the Fond de la Recherche Scientifique–FNRS de Belgique (F.R.S.-FNRS) under convention 2.5020.11. The NMR spectrometers used were acquired in collaboration with the University of South Bohemia (CZ) with financial support from the European Union through the EFRE INTERREG IV ETC-AT-CZ program (project M00146, „RERI-uasb"). Raphaël Robiette is a Maître de recherche of the F.R.S.-FNRS.

References

1. Tans, P., NOAA/ESRL (www.esrl.noaa.gov/gmd/ccgg/trends/) and Keeling, R., Scripps Institution of Oceanography (scrippsco2.ucsd.edu/).

2. (a) Trogler, W. C. The Environmental Chemistry of Trace Atmospheric Gases. *J. Chem. Educ.* **1995**, *72*, 973-976. (b) Quadrelli, E. A.; Centi, G.; Duplan, J.-L.; Perathoner, S. Carbon Dioxide Recycling: Emerging Large-Scale Technologies with Industrial Potential. *ChemSusChem* **2011**, *4*, 1194-1215. (c) Martín, R.; Kleij, A. W. Myth or Reality? Fixation of Carbon Dioxide into Complex Organic Matter under Mild Conditions. *ChemSusChem* **2011**, *4*, 1259-1263. (d) Centi, G.; Iaquaniello, G.; Perathoner, S. Can We Afford to Waste Carbon Dioxide? Carbon Dioxide as a Valuable Source of Carbon for the Production of Light Olefins. *ChemSusChem* **2011**, *4*, 1265-1273. (e) Aresta, M.; Dibenedetto, A.; Angelini, A. Catalysis for the Valorization of Exhaust Carbon: from CO_2 to Chemicals, Materials, and Fuels. Technological Use of CO_2. *Chem. Rev.* **2014**, *114*, 1709-1742.

3. (a) Leitner, W. Supercritical Carbon Dioxide as a Green Reaction Medium for Catalysis. *Acc. Chem. Res.* **2002**, *35*, 746-756. (b) Omae, I. Aspects Of Carbon Dioxide Utilization. *Catal. Today* **2006**, *115*, 33-52. (c) Aresta, M.; Dibenedetto, A. Utilisation Of CO_2 As A Chemical Feedstock: Opportunities And Challenges. *Dalton Trans*. **2007**, 2975-2992. (d) D'Alessandro, D. M.; Smit, B.; Long, J. R. Carbon Dioxide Capture: Prospects for New Materials. *Angew. Chem., Int. Ed.* **2010**, *49*, 6058-6082. (e) Riduan, S.N.; Zhang, Y. Recent Developments In Carbon Dioxide Utilization Under Mild Conditions. *Dalton Trans.* **2010**, *39*, 3347-3357. (f) Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kühn, F. E. Transformation of Carbon Dioxide with Homogeneous Transition-Metal Catalysts: A Molecular Solution to a Global Challenge? *Angew. Chem. Int. Ed.* **2011**, *50*, 8510-8537.

4. (a) Jessop, P. G.; Ikariya, T.; Noyori, R. Homogeneous Hydrogenation of Carbon Dioxide. *Chem. Rev.* **1995**, *95*, 259-272. (b) Gibson, D. H. The Organometallic Chemistry of Carbon Dioxide. *Chem. Rev.* **1996**, *96*, 2063-2096. (c) Tundo, P.; Selva, M. The Chemistry of Dimethyl Carbonate. *Acc. Chem. Res.* **2002**, *35*, 706-716. (d) Sakakura, T.; Choi, J. C.; Yasuda, H. Transformation of Carbon Dioxide. *Chem. Rev.* **2007**, *107*, 2365-2387. (e) North, M.; Pasquale, R.; Young, C. Synthesis Of Cyclic Carbonates From Epoxides And CO_2. *Green Chem.* **2010**, *12*, 1514-1539.

5. (a) Shaikh, A.-A. G.; Sivaram, S. Organic Carbonates. *Chem. Rev.* **1996**, *96*, 951-976. (b) Fukuoka, S.; Kawamura, M.; Komiya, K.; Tojo, M.; Hachiya, H.; Hasegawa, K.; Aminaka, M.; Okamoto, H.; Fukawa, I.; Konno, S. A Novel Non-Phosgene Polycarbonate Production Process Using By-Product CO_2 As Starting Material. *Green Chem*. **2003**, *5*, 497-507. (c) Ochiai, B.; Endo, T. Carbon Dioxide And Carbon Disulfide As Resources For Functional Polymers. *Prog. Polym. Sci.* **2005**, *30*, 183-215. (d) Schäffner, B.; Schäffner, F.; Verevkin, S. P.; Börner, A. Organic Carbonates as Solvents in Synthesis and Catalysis. *Chem. Rev.* **2010**, *110*, 4554-4581. (e) Balaraman, E.; Gunanathan, C.; Zhang, J.; Shimon, L. J. W.; Milstein, D. Efficient Hydrogenation Of Organic Carbonates, Carbamates And Formates Indicates Alternative Routes To Methanol Based On CO_2 And CO. *Nat. Chem.* **2011**, *3*, 609-614.

6. (a) Nicolaou, K. C.; Yang, Z.; Liu, J. J.; Ueno, H.; Nantermet, P. G.; Guy, R. K.; Claiborne, C. F.; Renaud, J.; Couladouros, E. A.; Paulvannan, K.; Sorensen, E. J. Total Synthesis Of Taxol .*Nature* **1994**, *367*, 630-634. (b) Chang, H. T.; Sharpless, K. B. A Practical Route To Enantiopure 1,2-Aminoalcohols. *Tetrahedron Lett.* **1996**, *37*, 3219-3222. (c) Takata, T.; Furusho, Y.; Murakawa, K.; Endo, T.; Matsuoka, H.; Hirasa, T.; Matsuo, J.; Sisido, M. Optically Active Poly(aryl carbonates) Consisting of Axially Chiral Units. Chiral Binaphthyl Group Induced

Helical Polymer. *J. Am. Chem. Soc.* **1998**, *120*, 4530-4531. (d) Bayardon, J.; Holz, J.; Schäffner, B.; Andrushko, V.; Verevkin, S.; Preetz, A.; Börner, A. Propylene Carbonate As A Solvent For Asymmetric Hydrogenations. *Angew. Chem. Int. Ed.* **2007**, *46*, 5971-5974. (e) Yu, K. M. K.; Curcic, I.; Gabriel, J.; Tsang, S. C. E. Recent Advances in CO_2 Capture and Utilization. *ChemSusChem* **2008**, *1*, 893-899. (f) Sakakura, T.; Kohno, K. The Synthesis Of Organic Carbonates From Carbon Dioxide. *Chem. Commun.* **2009**, 1312-1330.

7. (a) Lu, X.; Liang, B.; Zhang, Y.; Tian, Y.; Wang, Y.; Bai, C.; Wang, H.; Zhang, R. Asymmetric Catalysis with CO_2: Direct Synthesis of Optically Active Propylene Carbonate from Racemic Epoxides. *J. Am. Chem. Soc.* **2004**, *126*, 3732-3733. (b) Jing, H.; Nguyen, S. T. $SnCl_4$-Organic Base: Highly Efficient Catalyst System For Coupling Reaction Of CO_2 And Epoxides. *J. Mol. Catal. A* **2007**, *261*, 12-15. (c) Zhang, X.; Jia, Y.; Lu, X.; Li, B.; Wang, H.; Sun, L. Intramolecularly Two-Centered Cooperation Catalysis For The Synthesis Of Cyclic Carbonates From CO_2 And Epoxides. *Tetrahedron Lett.* **2008**, *49*, 6589-6592. (d) Ren, Y.; Shi, Y.; Chen, J.; Yang, S.; Qi, C.; Jiang, H. Ni(Salphen)-Based Metal–Organic Framework For The Synthesis Of Cyclic Carbonates By Cycloaddition Of CO_2 To Epoxides. *RSC Adv.* **2013**, *3*, 2167-2170. (e) Whiteoak, C. J.; Kielland, N.; Laserna, V.; Adán, E. C. E.; Martin, E.; Kleij, A. W. A Powerful Aluminum Catalyst for the Synthesis of Highly Functional Organic Carbonates. *J. Am. Chem. Soc.* **2013**, *135*, 1228-1231. (f) Maeda, C.; Taniguchi, T.; Ogawa, K.; Ema, T. Bifunctional Catalysts Based on m-Phenylene-Bridged Porphyrin Dimer and Trimer Platforms: Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides. *Angew. Chem. Int. Ed.* **2015**, *54*, 134-138. (g) Xu, F.; Cheng, W.; Yao, X.; Sun, J.; Sun, W.; Zhang, S. Thiourea-Based Bifunctional Ionic Liquids As Highly Efficient Catalysts For The CycloAddition Of CO_2 To Epoxides. *Catal. Lett.* **2017**, *147*, 1654-1664.

8. (a) Peng, J.; Deng, Y. Cycloaddition Of Carbon Dioxide To Propylene Oxide Catalyzed By Ionic Liquids. *New. J. Chem.* **2001**, *25*, 639-641. (b) Kawanami, H.; Sasaki, A.; Matsui, K. Ikushima, Y. A Rapid And Effective Synthesis Of Propylene Carbonate Using A Supercritical CO_2–Ionic Liquid System. *Chem. Commun.* **2003**, *39*, 896-897. (c) He, L.; Yasuda, H.; Sakakura, T. New Procedure For Recycling Homogeneous Catalyst: Propylene Carbonate Synthesis Under Supercritical CO_2 Conditions. *Green Chem.* **2003**, *5*, 92-94. (d) Xie, H.; Li, S.; Zhang, S. Highly Active, Hexabutylguanidinium Salt/Zinc Bromide Binary Catalyst For The Coupling Reaction Of Carbon Dioxide And Epoxides. *J. Mol. Catal. A: Chem.* **2006**, *250*, 30-34. (e) Sun, J.; Wang, L.; Zhang, S.; Li, Z.; Zhang, X.; Dai, W.; Mori, R. $ZnCl_2$/Phosphonium Halide: An Efficient Lewis Acid/Base Catalyst For The Synthesis Of Cyclic Carbonate. *J. Mol. Catal. A: Chem.* **2006**, *256*, 295-300. (f) Lee, J. K.; Kim, Y. J.; Choi, Y. S.; Lee, H.; Lee, J. S.; Hong, J.; Jeong, E.-K.; Kim, H. S.; Cheong, M. Zn-Containing Ionic Liquids Bearing Dialkylphosphate Ligands For The Coupling Reactions Of Epoxides And CO_2. *Appl. Catal., B* **2012**, *111-112*, 621-627. (g) Song, Y.; Cheng, C.; Jing, H. Aza-Crown Ether Complex Cation Ionic Liquids: Preparation And Applications In Organic Reactions. *Chem. Eur. J.* **2014**, *20*, 12894-12900. (h) Jiang, X.; Gou, F.; Fu, X.; Jing, H. Ionic Liquids-Functionalized Porphyrins As Bifunctional Catalysts For Cycloaddition Of Carbon Dioxide To Epoxides. *J. CO2 Util.* **2016**, *16*, 264-271.

9. Sun, J.; Han, L.; Cheng, W.; Wang, J.; Zhang, X.; Zhang, S. Efficient Acid-Base Bifunctional Catalysts for the Fixation of CO_2 with Epoxides under Metal- and Solvent-Free Conditions. *ChemSusChem* **2011**, *4*, 502-507.

10. (a) Shen, Y.; Duan, W.; Shi, M. Chemical Fixation of Carbon Dioxide Co-Catalyzed by a Combination of Schiff Bases or Phenols and Organic Bases. *Eur. J. Org. Chem.* **2004**, 3080-3089. (b) Whiteoak, C. J.; Nova, A.; Maseras, F.; Kleij, A. W. Merging Sustainability with

Organocatalysis in the Formation of Organic Carbonates by Using CO_2 as a Feedstock. *ChemSusChem*, **2012**, *5*, 2032-2038. (c) Whiteoak, C. J.; Henseler, A. H.; Ayats, C.; Kleij, A. W.; Pericàs, M. A. Conversion Of Oxiranes And CO_2 To Organic Cyclic Carbonates Using A Recyclable, Bifunctional Polystyrene-Supported Organocatalyst. *Green Chem.* **2014**, *16*, 1552-1559. (d) Sopeña, S.; Fiorani, G.; Martín, C.; Kleij, A. W. Highly Efficient Organocatalyzed Conversion of Oxiranes and CO_2 into Organic Carbonates. *ChemSusChem* **2015**, *8*, 3248-3254. (e) Okada, M.; Nishiyori, R.; Kaneko, S.; Igawa, K.; Shirakawa, S. KI–Tetraethylene Glycol Complex as an Effective Catalyst for the Synthesis of Cyclic Thiocarbonates from Epoxides and CS_2. *Eur. J. Org. Chem.* **2018**, 2022-2027.

11. (a) Xiao, B.; Sun, J.; Wang, J.; Liu, C.; Cheng, W. Triethanolamine/KI: A Multifunctional Catalyst for CO_2 Activation and Conversion with Epoxides into Cyclic Carbonates. *Synth. Commun.* **2013**, *43*, 2985-2997. (b) Werner, T.; Büttner, H. Phosphorus-Based Bifunctional Organocatalysts for the Addition of Carbon Dioxide and Epoxides. *ChemSusChem* **2014**, *7*, 3268-3271. (c) Wilhelm, M. E.; Anthofer, M. H.; Cokoja, M.; Markovits, I. I. E.; Herrmann, W. A.; Kühn, F. E. Cycloaddition of Carbon Dioxide and Epoxides using Pentaerythritol and Halides as Dual Catalyst System. *ChemSusChem*, **2014**, *7*, 1357-1360. (d) Büttner, H.; Steinbauer, J.; Werner, T. Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide by Using Bifunctional One-Component Phosphorus-Based Organocatalysts. *ChemSusChem* **2015**, *8*, 2655-2669. (e) Alves, M.; Grignard, B.; Gennen, S.; Méreau, R.; Detrembleur, C.; Jerome, C.; Tassaing, T. Organocatalytic Promoted Coupling Of Carbon Dioxide With Epoxides: A Rational Investigation Of The Cocatalytic Activity Of Various Hydrogen Bond Donors. *Catal. Sci. Technol.* **2015**, *5*, 4636-4643.

12. (a) Han, L.; Choi, H.-J.; Choi, S.-J.; Liu, B.; Park, D.-W. Ionic Liquids Containing Carboxyl Acid Moieties Grafted Onto Silica: Synthesis And Application As Heterogeneous Catalysts For Cycloaddition Reactions Of Epoxide And Carbon Dioxide. *Green Chem*. **2011**, *13*, 1023-1028. (b) Tharun, J.; Mathai, G.; Kathalikkattil, A. C.; Roshan, R.; Kwak, J.-Y.; Park, D.-W. Microwave-Assisted Synthesis Of Cyclic Carbonates By A Formic Acid/KI Catalytic System. *Green Chem*. **2013**, *15*, 1673-1677. (c) Dai, W.; Jin, B.; Luo, S.; Luo, X.; Tu, X.; Au, C. -T. Functionalized Phosphonium-Based Ionic Liquids As Efficient Catalysts For The Synthesis Of Cyclic Carbonate From Expoxides And Carbon Dioxide. *Applied Catalysis A: General* **2014**, *470*, 183-188.

13. (a) Hardman-Baldwin, A. M.; Mattson, A. E. Silanediol‐Catalyzed Carbon Dioxide Fixation. *ChemSusChem* **2014**, *7*, 3275-3278. (b) de J. Velásquez-Hernández, M.; Torres-Huerta, A.; Hernández-Balderas, U.; Martínez-Otero, D.; Núñez-Pineda, A.; Jancik, V. Novel Route To Silanetriols And Silanediols Based On Acetoxysilylalkoxides. *Polyhedron* **2017**, *122*, 161-171.

14. Sopeña, S.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. Pushing the Limits with Squaramide-Based Organocatalysts in Cyclic Carbonate Synthesis. *ACS Catal.* **2017**, *7*, 3532-3539.

15. Gennen, S.; Alves, M.; Méreau, R.; Tassaing, T.; Gilbert, B.; Detrembleur, C.; Jerome, C.; Grignard, B. Fluorinated Alcohols as Activators for the Solvent‐Free Chemical Fixation of Carbon Dioxide into Epoxides. *ChemSusChem* **2015**, *8*, 1845-1849.

16. Rulev, Y. A.; Gugkaeva, Z. T.; Lokutova, A. V.; Maleev, V. I.; Peregudov, A. S.; Wu, X.; North, M.; Belokon, Y. N. Carbocation/Polyol Systems as Efficient Organic Catalysts for the Preparation of Cyclic Carbonates. *ChemSusChem* **2017**, *10*, 1152-1159.

17. Fan, Y.; Kass, S. R. Electrostatically Enhanced Thioureas. *Org. Lett.* **2016**, *18*, 188-191.

18. Alunni, S.; Pero, A.; Reichenbach, G. Reactivity Of Ions And Ion Pairs In The Nucleophilic Substitution Reaction On Methyl P-Nitrobenzenesulfonate. *J. Chem. Soc. Perkin Trans. 2* **1998**, 1747-1750.

19. Solid carbon dioxide was added to a stainless steel vessel to achieve the higher pressure. This undoubtedly led to some variation in the reaction temperature but only a 16% conversion was observed after 1.5 h and this is virtually the same (18%) as when an atmospheric pressure of CO_2 was used.

20. Fan, Y.; Kass, S. R. Quantification of Catalytic Activity for Electrostatically Enhanced Thioureas via Reaction Kinetics and a UV−Vis Spectroscopic Measurement. J. *Org. Chem.*, submitted for publication.

21. (a) Aoyagi, N.; Furusho, Y.; Endo, T. Remarkably Efficient Catalysts of Amidine Hydroiodides for the Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides under Mild Conditions. *Chem. Lett.* **2012**, *41*, 240-241. (b) Liu, X.; Zhang, S.; Song, Q.; Liu, X.; Ma, R.; He, L. Cooperative Calcium-Based Catalysis With 1,8-Diazabicyclo[5.4.0]-Undec-7-Ene For The Cycloaddition Of Epoxides With CO_2 At Atmospheric Pressure. *Green Chem.* **2016**, *18*, 2871-2876.

22. Marques-Lopez, E.; Alcaine, A.; Tejero, T.; Herrera, R. P. Enhanced Efficiency of Thiourea Catalysts by External Brønsted Acids in the Friedel–Crafts Alkylation of Indoles. *Eur. J. Org. Chem.* 2011, 3700-3705.

23. We also examined the catalytic performance of added organic salts, acids and bases under the same reaction conditions for comparison. More details are provided in the supporting information.

24. (a) Zhao, D.; Liu, X.-H.; Shi, Z.-Z.; Zhu, C.-D.; Zhao, Y.; Wang, P.; Sun, W.-Y. Three Powerful Dinculear Metal-Organic Catalysts For Converting CO_2 Into Organic Carbonates.

Dalton Trans. **2016**, *45*, 14184-14190. (b) Wang, L.; Zhang, G.; Kodama, K.; Hirose, T. An Efficient Metal- And Solvent-Free Organocatalytic System For Chemical Fixation of CO_2 Into Cyclic Carbonates Under Mild Conditions. *Green Chem.* **2016**, *18*, 1229-1233. (c) Zhou, F.; Xie, S.-L.; Gao, X.-T.; Zhang, R.; Wang, C.-H.; Yin, G.-Q.; Zhou, J. Activation Of (Salen)CoI Complex By Phosphorane For Carbon Dioxide Transformation At Ambient Temperature And Pressure. *Green Chem.* **2017**, *19*, 3908-3915.

25. Single point B3LYP/aug-cc-pVDZ/6-311+G(d)//B3LYP/aug-cc-pVDZ/6-311G(d) energies were used but the B3LYP/aug-cc-pVDZ/6-311G(d) optimized values are all within 0.13 kcal mol^{-1} of the given values.

26. A transition structure involved in the conversion of **6** to **4** was located, and the displacement of iodide by the sulfur atom of the deprotonated thiourea was found to have a B3LYP/aug-cc-pVDZ/6-311+G(d) barrier that is 37.5 kcal mol^{-1} (i.e., 9.3 kcal mol^{-1} smaller than for TS_S).

27. Riches, S. L.; Saha, C.; Filgueira, N. F.; Grange, E.; McGarrigle, E. M.; Aggarwal, V. K. On the Mechanism of Ylide-Mediated Cyclopropanations: Evidence for a Proton-Transfer Step and Its Effect on Stereoselectivity. *J. Am. Chem. Soc*. **2010**, *132,* 7626-7630.

28. Edwards, D. R.; Du, J.; Crudden, C. M. Synthesis of the Core Structure of Cruentaren A. *Org. Lett.* **2007**, *9*, 2397-2999.

29. Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Zani, P. Reactions Of Stilbene Episulphoxides And Episulphides With Organolithium Compounds. Evidence For Attack At Sulphur And At Proton. *Tetrahedron Lett.* **1979**, *20*, 3987-3990.

30. Torde, R. G.; Therrien, A. J.; Shortreed, M. R.; Smith, L. M.; Lamos, S. M. Multiplexed Analysis of Cage and Cage Free Chicken Egg Fatty Acids Using Stable Isotope Labeling and Mass Spectrometry. *Molecules*, **2013**, *18*, 14977-14988.

31. Bertucci, M. A.; Lee, S. J.; Gagne, M. R. Thiourea-Catalyzed Aminolysis Of N-Acyl Homoserine Lactones. *Chem. Commun.* **2013**, *49*, 2055-2057.

32. Varga, S.; Jakab, G.; Drahos, L.; Holczbauer, T.; Czugler, M.; Soos, T. Double Diastereocontrol in Bifunctional Thiourea Organocatalysis: Iterative Michael–Michael–Henry Sequence Regulated by the Configuration of Chiral Catalysts. *Org. Lett.* **2011**, *13*, 5416-5419.

33. Additional signals in the spectra appear to be due to the presence of a tautomer.

34. (a) Rokicki, G.; Kuran, W.; Pogorzelska-Marciniak, B. Cyclic Carbonates From Carbon Dioxide And Oxiranes. *Monatsh. Chem*. **1984**, *115*, 205-214. (b) Corsano, S.; Strappaghetti, G.; Ferrini, R.; Sala, R. Synthesis of Compounds with a Possible Ca-Antagonist and P-Blocking Activity. *Arch. Pharm.* **1988**, *321*, 731-734. (c) Clegg, W.; Harrington, R. W.; North, M.; Pasquale, R. Cyclic Carbonate Synthesis Catalysed by Bimetallic Aluminium–Salen Complexes. *Chem. Eur. J.* **2010**, *16*, 6828-6843. (d) Wu, L.; Yang, H.; Wang, H.; Lu, J. Electrosynthesis Of Cyclic Carbonates From CO_2 And Epoxides On A Reusable Copper Nanoparticle Cathode. *RSC Adv* **2015**, *5*, 23189-23192. (e) Büttner, H.; Steinbauer, J.; Werner, T. Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide by Using Bifunctional One - Component Phosphorus - Based Organocatalysts. *ChemSusChem* **2015**, *8*, 2655-2659. (f) Kumatabara, Y.; Okada, M.; Shirakawa, S. Triethylamine Hydroiodide as a Simple Yet Effective Bifunctional Catalyst for CO_2 Fixation Reactions with Epoxides under Mild Conditions. *ACS Sustainable Chem. Eng.* **2017**, *5*, 7295-7301. (g) Tiffner, M.; Gonglach, S.; Haas, M.; Schöfberger, W.; Waser, M. CO_2 Fixation with Epoxides under Mild Conditions with a Cooperative Metal Corrole/Quaternary Ammonium Salt Catalyst System. *Chem. Asian J.* **2017**, *12*, 1048-1051.

35. Iwasaki, T.; Kihara, N.; Endo, T. Reaction of Various Oxiranes and Carbon Dioxide. Synthesis and Aminolysis of Five-Membered Cyclic Carbonates. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 713-719.

36. Buckley, B. R.; Patel, A. P.; Wijayantha, K. G. U. 'Ring-Expansion Addition' Of Epoxides Using Applied Potential: An Investigation Of Catalysts For Atmospheric Pressure Carbon Dioxide Utilization. *RSC Adv.* **2014**, *4*, 58581-58590.

37. Kozak, J. A.; Wu, J.; Su, X.; Simeon, F.; Hatton, T. A.; Jamison, T. F. Bromine-Catalyzed Conversion of CO_2 and Epoxides to Cyclic Carbonates under Continuous Flow Conditions. *J. Am. Chem. Soc.* **2013**, *135*, 18497-18501.

38. Kaneko, S.; Shirakawa, S. Potassium Iodide–Tetraethylene Glycol Complex as a Practical Catalyst for CO_2 Fixation Reactions with Epoxides under Mild Conditions. *ACS Sustainable Chem. Eng.* **2017**, *5*, 2836-2840.

39. Spartan 14v1.2 (2014) Wavefunction, Inc., Irvine.

40. (a) Becke, A. D. Density‐Functional Thermochemistry. III. The Role Of Exact Exchange. *J. Chem. Phys*. **1993**, *98*, 5648-5652. (b) Lee, C.; Yang, W.; Parr, R. G. Development Of The Colle-Salvetti Correlation-Energy Formula Into A Functional Of The Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789.

41. (a) Hay, P. J.; Wadt, W. R. Ab Initio Effective Core Potentials For Molecular Calculations. Potentials For The Transition Metal Atoms Sc To Hg. *J. Chem. Phys.*, **1985**, *82*, 270-283. (b) Wadt, W. R.; Hay, P. J. Ab Initio Effective Core Potentials For Molecular Calculations. Potentials For Main Group Elements Na To Bi. *J. Chem. Phys.*, **1985**, *82*, 284-298. (c) Hay, P. J.; Wadt, W. R. Ab Initio Effective Core Potentials For Molecular Calculations. Potentials For K To Au Including The Outermost Core Orbitals. *J. Chem. Phys.*, **1985**, *82*, 299-310.

42. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A., *et al*. Gaussian 09. Gaussian, Inc., Wallingford CT, 2009.

43. Dunning, Jr., T. H. Gaussian Basis Sets For Use In Correlated Molecular Calculations. I. The Atoms Boron Through Neon And Hydrogen. *J. Chem. Phys*. **1989**, *90*, 1007-1023.

44. Glukhovstev, M. N.; Pross, A.; McGrath, M. P.; Radom, L. Extension Of Gaussian ‐ 2 (G2) Theory To Bromine- and Iodine-Containing Molecules: Use Of Effective Core Potentials. *J. Chem. Phys*. **1995**, *103*, 1878-1885.