

Synthesis of Cyclic Organic Carbonates Using Atmospheric Pressure CO₂ and Charge-Containing Thiourea Catalysts

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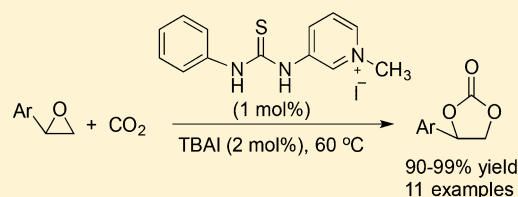
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S Supporting Information

ABSTRACT: Cycloadditions of epoxides with CO₂ 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 CO₂ 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 (CO₂) is a problematic greenhouse gas of great concern in the Earth's atmosphere. Its atmospheric concentration has been rapidly rising over the past 50 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 CO₂ 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 nontoxic 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 squaramides¹⁴ 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-(CF₃)₂C₆H₃NH)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 nonpolar media. Inspired by these results, we decided to examine their ability to catalyze the cycloadditions of epoxides

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with CO₂. The catalytic performance of eight such derivatives (**T1**–**T8**, Figure 1) is reported herein.

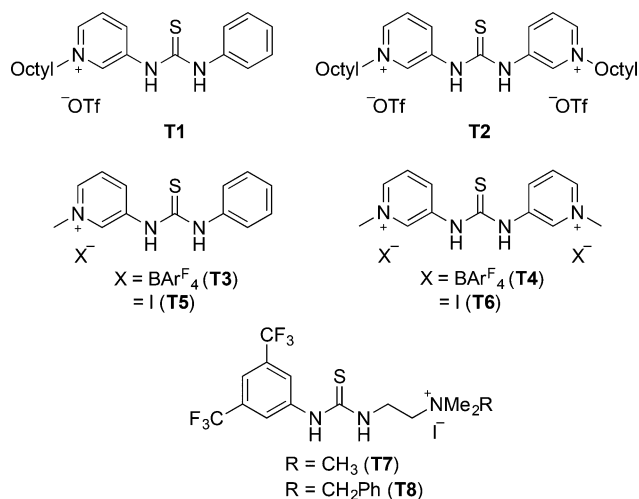
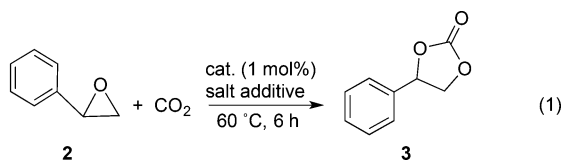


Figure 1. Charge-containing thiourea salts examined in this work.

RESULTS AND DISCUSSION

To initiate our study upon the chemical fixation of CO₂ into epoxides using charged thiourea salts as catalysts, we first examined the reaction of 2-phenyloxirane (**2**) with CO₂ to afford the phenyl-substituted carbonate **3** (eq 1). Under mild



solvent-free conditions at 60 °C with an atmospheric pressure of CO₂, 1 mol % of **T1** and a halide salt, the cyclic carbonate was formed with moderate conversions after 6 h (Table 1).

Table 1. Catalytic Performance of **T1** with Various Halide Salt Co-Catalysts in the Fixation of CO₂ into 2-Phenyloxirane^a

entry	additive	(mol %)	conversion (%) ^b
1	(Bu) ₄ NI	1	57
2	(Bu) ₄ NBr	1	41
3	(Bu) ₄ NCl	1	20
4	(Ph ₃ P) ₂ NCl	1	19
5	none		0
6 ^c	(Bu) ₄ NI	1	29
7 ^c	(Bu) ₄ NI	2	56
8	(Bu) ₄ NI	2	74
9	(Bu) ₄ NI	3	65
10	(Bu) ₄ NI	5	66
11	(Bu) ₄ NI	10	53
12 ^d	(Bu) ₄ NI	2	16

^aUnless 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 CO₂. ^bReaction conversions were obtained after 6 h by ¹H NMR. ^cNo thiourea catalyst was used. ^dThe reaction was carried out under 4.0 MPa of CO₂ and analyzed after 1.5 h.

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 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 nucleophilicity of I[−]. A reaction was also carried out at an elevated pressure of CO₂ (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 CO₂ 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.

Upon the basis of 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 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^F₄[−]) were explored.¹⁷ In the absence of a nucleophile, no carbonate was produced (entries 3 and 6) and the monocharged 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 CO₂ by activating the latter reagent.²¹ When we added 2 mol % of 4-dimethylaminopyridine (DMAP) along with **T5** and TBAI, no improvement was observed (entry 13). This is consistent with our observation that an increase in the CO₂ 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,

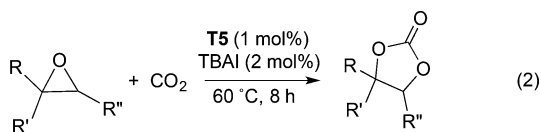
Table 2. Catalyst and Additive Screening for the Reaction of 2-Phenyloxirane with CO₂^a

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) ₂ CS	2	48
21	1	2	40

^aThese transformations were carried out for 6 h with 1 mol % of the catalyst and atmospheric pressure (0.1 MPa) CO₂ at 60 °C. ^bProduct conversions were obtained by ¹H NMR. ^cTetra-*n*-heptylammonium iodide was used instead of TBAI. ^d4-Dimethylaminopyridine (DMAP, 2 mol %) was added. ^eAcetic acid (1 mol %) was added. ^fTrifluoroacetic acid (1 mol %) was added.

reactions were carried out with diphenylthiourea and (3,5-(CF₃)₂C₆H₃NH)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 atm pressure of CO₂, 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.

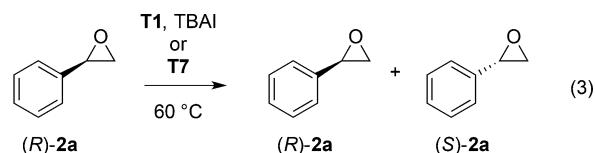
To address the mechanism of this transformation further, (*R*)-2-phenyloxirane (2a, ≥ 99% ee) and (*R*)-2-(benzyloxymethyl)oxirane (2k, ≥ 99% ee) were reacted with T5 as illustrated in eq 2, and the isolated products were both obtained in 95% yields with 86% ee for 3a and ≥99% ee for 3k. The absolute configuration of the major enantiomer in both cases corresponded to retention of configuration (*R*) by

Table 3. Reaction Scope with the Use of the T5/TBAI Binary Catalyst System

entry	epoxide (and carbonate 3)	yield (%)
1	R = Ph, R' = H (2a)	95
2	R = <i>p</i> -ClC ₆ H ₄ , R' = H (2b)	95
3	R = <i>p</i> -FC ₆ H ₄ , R' = H (2c)	93
4	R = <i>p</i> -MeOC ₆ H ₄ , R' = H (2d)	98 ^a
5	R = <i>p</i> -O ₂ NC ₆ H ₄ , R' = H (2e)	98 ^b
6	R = PhOCH ₂ , R' = H (2f)	99
7	R = ClCH ₂ , R' = H (2g)	98
8	R = CH ₂ =CHCH ₂ CH ₂ , R' = H (2h)	90
9	R = CH ₂ =CH, R' = H (2i)	97
10	R = PhCH ₂ , R' = H (2j)	97
11	R = BnOCH ₂ , 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.

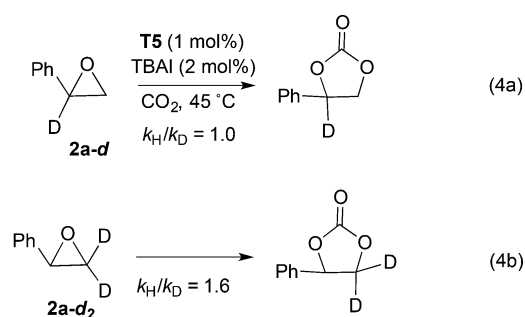
comparison to previously reported chiral HPLC data.²⁴ In accord with these findings, when enantiopure samples of 2a were heated to 60 °C in the absence of CO₂ but in the presence of T1 and TBAI (1 and 2 mol %, respectively) or T7 (1 and 3 mol %), racemization was observed to slowly occur (eq 3). In the former case, the epoxide had an 86% ee after 1 h



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)

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.

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 buildup 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% D₂) at 45 °C with 1 mol % T5 and 2 mol % TBAI (eqs 4a and b). Surprisingly, *k*_H/*k*_D = 1.0 for the monodeuterio compound and 1.6 for the dideuterio species were observed (see Table S4 for additional details). The latter secondary kinetic isotope effect is large, and taken together, these results indicate that nucleophilic attack occurs at the terminal

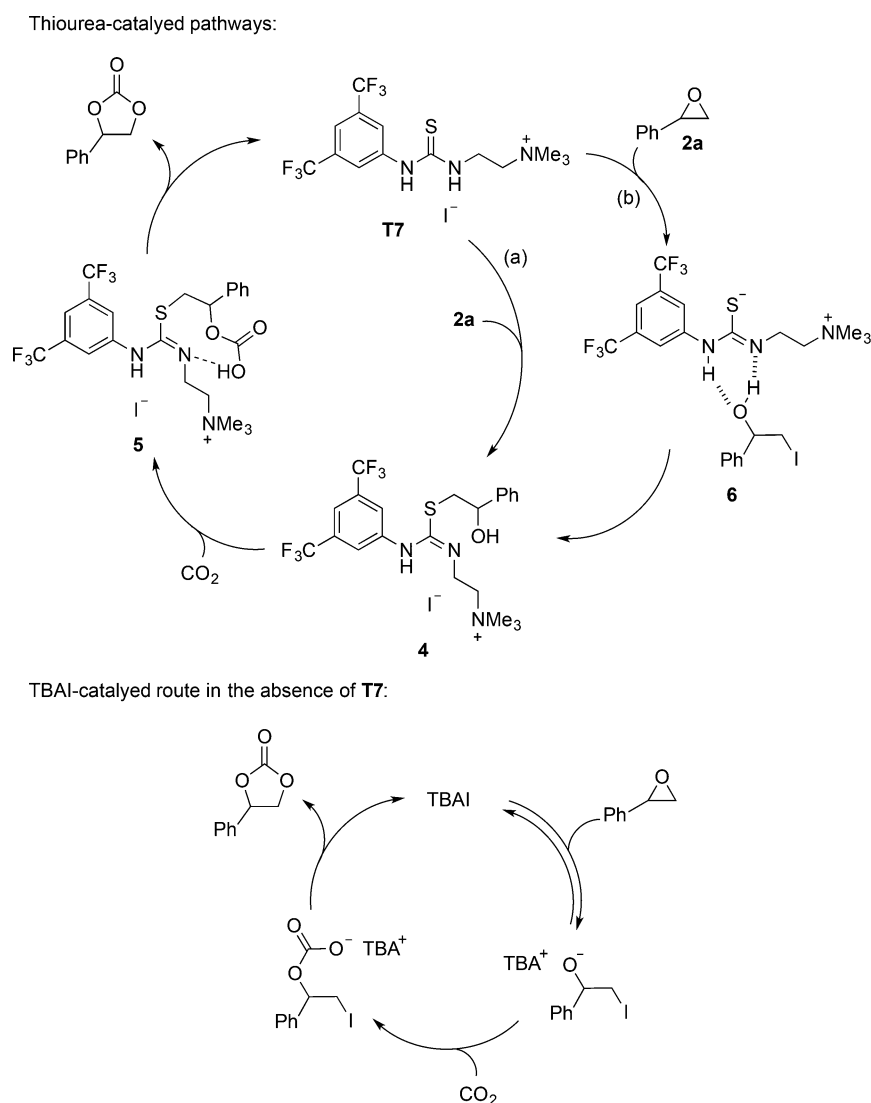


methylene carbon of 2-phenyloxirane. Additionally, when the reaction of **2a** with **T7** was monitored by ^1H NMR, a small amount of an intermediate was observed. This species (**4**) was subsequently isolated and characterized and is the product resulting from nucleophilic attack of the epoxide by 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.

In our proposed mechanism, the charge-containing thiourea catalyst acts as a nucleophile in an $\text{S}_{\text{N}}2$ 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.

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)



To address these mechanistic alternatives further, B3LYP calculations were carried out on different structural arrangements of hydrogen-bonded complexes between T7 and 2a (see the 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).

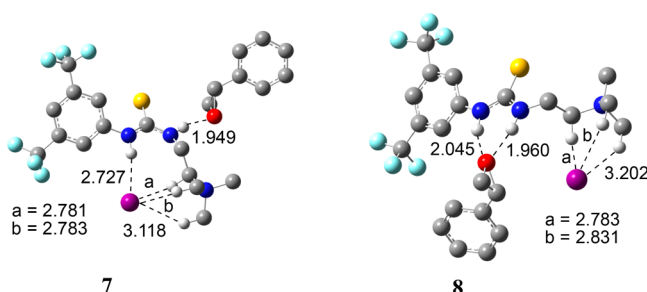


Figure 2. Fully optimized B3LYP/aug-cc-pVDZ/6-311G(d) structures, where the second all electron basis set was used for iodine. Distances are given in Å, and most of the hydrogen atoms attached to carbon are omitted for clarity sake.

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

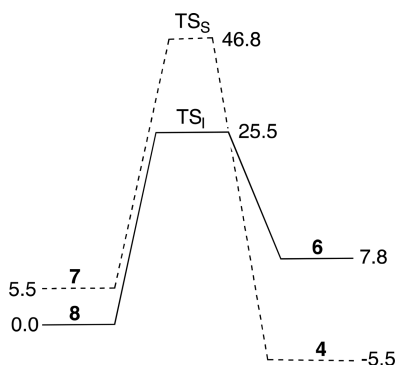


Figure 3. Computed B3LYP/aug-cc-pVDZ/6-311+G(d) single point free energy reaction diagrams for the T7 catalyzed ring opening of 2-phenyloxirane. Relative free energies are given in kcal mol⁻¹ at 298 K.

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.

CONCLUSION

A series of metal-free electrostatically enhanced thiourea catalysts T1–T8 were explored and found to induce CO₂ 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 imidazolium 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 CO₂ in a kinetically competent manner to afford the cyclic carbonate product and regenerate the thiourea catalyst.

EXPERIMENTAL SECTION

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 CO₂ atmosphere. NMR spectra were recorded on 300, 500, and 700 MHz instruments. The ¹H and ¹³C chemical shifts are given in ppm and were referenced respectively as follows: 7.26 and 77.2 (CDCl₃) and 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 × 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 CO₂. A 3-dram vial was purged with gaseous CO₂ 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 CO₂ and heated at 60 °C for 6 h. Reaction conversions were obtained by ¹H NMR in CDCl₃ 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 CDCl₃ 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 D₂O was slowly added. A ¹H NMR sample of the CDCl₃ 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 CDCl₃ (2 × 2 mL). The combined organic material was dried with Na₂SO₄, 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 ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): 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, K₂CO₃ (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 H₂O was added, and the aqueous phase was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic material was washed with brine (50 mL), dried over Na₂SO₄,

and the solvent was removed under reduced pressure to afford 720 mg (84%) of **2a-d₂** as a colorless liquid. Its analytical data are in accord with those reported in the literature.²⁸ ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): 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 Na₂SO₄ 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 colorless liquid. Its analytical data are in accord with those reported in the literature.²⁹ ¹H NMR (300 MHz, CDCl₃): δ 7.41–7.26 (m, 5H), 3.17 (d, *J* = 5.5 Hz, 1H), 2.84 (d, *J* = 5.5 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): 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 CH₂Cl₂ 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 Na₂SO₄. Removal of the solvent by rotatory evaporation afforded the crude product, which was purified by column chromatography on silica gel with CH₂Cl₂/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 ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): 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. ¹⁹F NMR (282 MHz, D₂O): δ –64.5. HRMS-ESI: calcd for C₁₄H₁₈F₆N₃S⁺ (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 CH₂Cl₂/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 CH₃CN for 15 h at room temperature. The reaction mixture was directly subjected to column chromatography on silica gel with CH₂Cl₂/MeOH (10:1) to yield 148 mg (92%) of **T8** as a white solid. ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): 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 C₂₀H₂₂F₆N₃S⁺ (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 equiv) 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 CH₂Cl₂/MeOH (20:1) as the eluent. This afforded 9 mg (36%) of **4** as a colorless oil. ¹H 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). ¹³C 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 C₂₂H₂₆F₆N₃OS⁺ (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 equiv) 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 CH₂Cl₂/MeOH (20:1) as the eluent. This afforded 7 mg (31%) of **4'** as a colorless oil. ¹H 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). ¹³C 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. HRMS-ESI: calcd for C₁₇H₂₄F₆N₃OS⁺ (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 ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): δ 154.7, 135.7, 129.5, 129.0, 125.7, 77.8, 71.0. HRMS-ESI: calcd for C₉H₈NaO₃ (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 ¹H NMR (300 MHz, CDCl₃): 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 and 7.8 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 154.5, 135.4, 134.2, 129.2, 127.2, 77.1, 71.8. HRMS-ESI: calcd for C₉H₇ClNaO₃ (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 ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): 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. ¹⁹F NMR (282 MHz, CDCl₃): δ –111.1. HRMS-ESI: calcd for C₉H₇FN₃O₃ (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. ¹H NMR (300 MHz, CDCl₃): 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 ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): 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 ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): δ 157.7, 154.7, 129.5, 121.8, 114.5, 74.1, 66.7, 66.1. HRMS-ESI: calcd for C₁₀H₁₀NaO₄ (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 ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): 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 ¹H 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). ¹³C 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 ¹H 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). ¹³C 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 ¹H 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). ¹³C 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 ¹H 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). ¹³C 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). ¹H 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). ¹³C 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: calcd for $C_9H_7DNaO_3$ ($M + Na$)⁺, 188.0; found, 188.0.

4-Phenyl-1,3-dioxolan-2-one-5,5-d₂ (3a-d₂). ¹H 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). ¹³C 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: calcd 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 14³⁹ using B3LYP⁴⁰ 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 09⁴² using the aug-cc-pVDZ⁴³ 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.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b01374.

Additive screening, racemization, application scope data, kinetic isotope data, NMR spectra, HPLC chromatograms, computed structures and energies, and the complete citation to ref 42 (PDF)

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Notes

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