JOC The Journal of Organic Chemistry

Article

Cycloaddition of Aziridine with CO2/CS2 Catalyzed by Amidato Divalent Lanthanide Complexes

Yueqin Xie, Chengrong Lu, Bei Zhao, Qianyu Wang, and Yingming Yao

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b02924 • Publication Date (Web): 16 Jan 2019

Just Accepted

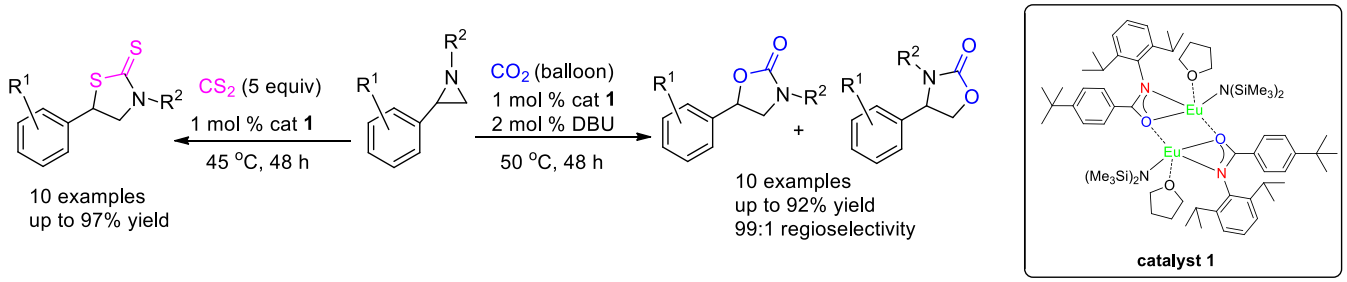
ACS Publications

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Cycloaddition of Aziridine with CO_2/CS_2 Catalyzed by Amidato Divalent Lanthanide Complexes

Yueqin Xie[a], Chengrong Lu[a,b], Bei Zhao*[a,b], Qianyu Wang and Yingming Yao[a,b]

Key Laboratory of Organic Synthesis of Jiangsu Province,[a] College of Chemistry, Chemical Engineering and Materials Science,[b] Soochow University, Suzhou 215123, People's Republic of China.



ABSTRACT: This is the first time that the amidato lanthanide amides ({L^{n}Ln[N(SiMe$_3$)$_2$]THF}$_2$ (n = 1, Ln = Eu (**1**); n = 2, Ln = Eu (**3**), Yb (**4**); HL^1 = ^{t}BuC$_6$H$_4$CONHC$_6$H$_3$(^{i}Pr)$_2$; HL^2 = C$_6$H$_5$CONHC$_6$H$_3$(^{i}Pr)$_2$) and {L^{3}Eu[N(SiMe$_3$)$_2$]THF}{L$^3{}_2$Eu(THF)$_2$} (**2**); (HL^3 = ClC$_6$H$_4$CONHC$_6$H$_3$(^{i}Pr)$_2$)) were applied in the cycloaddition reactions of aziridines with carbon dioxide (CO_2) or carbon disulfide (CS_2) under mild conditions. The corresponding oxazolidinones and thiazolidine-2-thiones were obtained in good to excellent yields with good functional group tolerance.

Introduction Oxazolidinones are the main component of a class of antimicrobial agents. [1] Also, oxazolidinones are raw material in many transformations, including aldol condensation,[2a,2b] alkylation reactions,[2c] Diels-Alder cycloaddition reactions,[2d] alcoholysis reaction,[2e] stereoselective oxidation.[2f] Consequently, the synthesis of oxazolidinones has attracted great attention. As the primary greenhouse gas, CO_2 is a growing problem in climatic change and chemical transformation of CO_2 is worthy studying.[3] Several methods using CO_2, which is often considered as an attractive C1 building block, for the formation of oxazolidinones were developed, for example, carbonylation of amino alcohols with phosgene/CO_2, [4a] reactions of propargyl/acetylenic amines/epoxy amines with CO_2,[4b-e] coupling reactions between epoxides and phenyl carbamate,[4f] and multicomponent reaction using propargylamines, arylhalides and CO_2.[4g] The study of the aziridine/CO_2 coupling reaction to obtain oxazolidinones was also discovered. Alkali metal halides were applied to the transformation.[5a] The reaction can also be catalyzed by iodine in supercritical CO_2 with good outcome. However, the scope of substrates is limited to aliphatic aziridines. (Salen)chromium(III)/4-(*N*,*N*-dimethylamino)pyridine was reported to be an effective catalyst for the coupling of CO_2 and aziridines, which successfully extended the substrates to monosubstituted *N*-aryl aziridines.[5b] Some other catalysts have also been exploited for the transformation, such as Al-based, Cr-based metal complexes and (salen)Co(I) complexes,[5b-c] small molecules,[5d] ILs,[5e] loaded macromolecule,[5f-h] and mesoporous materials.[5i-j] Although significant advantages have been made, most of them still have some problems, for instance, high pressure (60 atm), elevated temperature (120 °C), relative high catalyst loading (10 mol %) or toxic co-solvent (CH_2Cl_2) was required.

The rare-earth metal complexes, especially amidato divalent lanthanide amides,[6] have high reactivities in many transformations, including forming 2,4-quinazolidinones from CO_2 and 2-aminobenzonitriles,[6b] and carboxylation of terminal alkynes with CO_2.[7a] And also, rare-earth metal complexes showed reactivities in the reaction of epoxides with CO_2 under mild condition.[7b-7d] It indicates that rare-earth metal complexes do fairly well in the chemical fixation of CO_2. Thus, starting from CO_2 and aziridines to realize the formation of oxazolidinones catalyzed by rare-earth metal complexes is promising and quite meaningful.

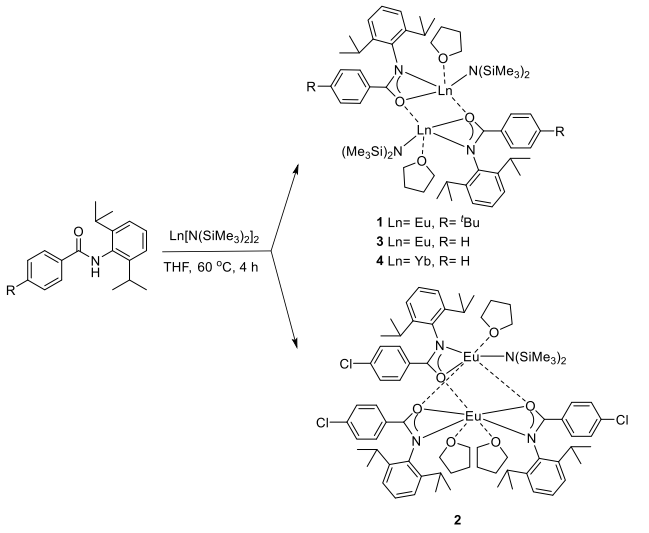
Thiazolidine-2-thiones, sulfur-substituted analogues to oxazolidinones, are also useful intermediates in pharmaceutical chemistry[8] and some enantioselective reactions (e.g aldol reactions,[9a,9b] alkylation reactions,[9c] cross-coupling reaction.[9d]). The synthetic strategies for the construction of thiazolidine-2-thione skeleton include the reaction of CS_2 with amino alcohols,[10a-10b] the tandem umpolung addition and intramolecular cyclization of bifunctional sulfur pronucleophiles on ar-

ylpropiolates with a phosphine catalyst,[10c] reaction of dibenzoylacetylene/racemic α-chloro-β,γ-alkenoate esters with CS_2 and amines,[10d] and the cyclization reaction with propargylamine and CS_2.[10e] Cycloaddition of CS_2 with aziridines is a most step- and atom-economic approach to construct thiazolidine-2-thiones. Catalysts for this transformation involve organoantimony halide,[10f] tetrabutylammonium halide,[5a] tributylphosphine,[10g] functionalized ion-exchange resin,[5g] and amine.[10h] The main drawbacks are relative limited substrates and harsh reaction conditions, such as high temperature (180 ℃) and large dose of catalysts (25 mol%). Seeking for high efficient catalyst to fulfill the cycloaddition of CS_2 with aziridines in mild condition is still necessary.

Though the properties of CS_2 and CO_2 are similar,[11] CS_2 is considered to be more reactive owing to the weaker C=S double bond.[12] It is thus divinable that the reaction of more active CS_2 with aziridines catalyzed by the amidato divalent lanthanide amides is feasible.

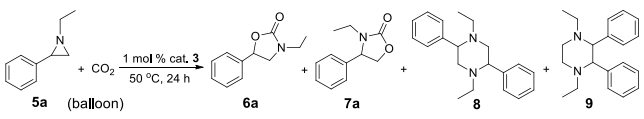
Results and Discussion Four amidato divalent lanthanide complexes were synthesized by simple metathesis of the proligand HL with appropriate lanthanide precursors $Ln[N(SiMe_3)_2]_2$ (Ln = Eu or Yb) in THF at 60 ºC (Scheme 1).

Scheme 1. Synthesis of amidato divalent lanthanide amides 1-4



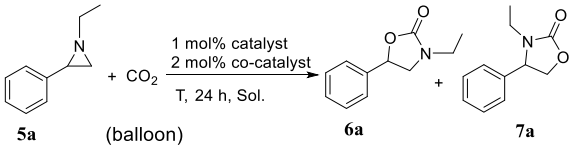
The reaction of CO_2 with *N*-ethyl-2-phenylaziridine **5a** was catalyzed by 1 mol% amidato divalent lanthanide complex **3** under ambient pressure. The preliminary result showed the formation of four kinds of products in the model reaction. Compounds **6a** and **7a** are the main products with the overall yield of 62%, while compounds **8** and **9** are dimeric products of *N*-ethyl-2-phenyl aziridine (Scheme 2). It is consistent with the results of several cases.[5g-h]

Scheme 2. Cycloaddition reaction of CO_2 with *N*-ethyl-2-phenylaziridine



To improve the yield of cycloaddition product, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added to the reaction system, which is widely regarded as a kind of reagent to gather and activate CO_2 molecule.[6b,13] The increasing yield of 74% of cycloaddition products **6a** and **7a**, with excellent regioselectivity of 99:1 was obtained after 24 hours at 50 ºC in the presence of 2 mol% DBU (Table 1, entries 2). The same increasing tendency was observed using complex **1** as the catalyst, the overall yield of **6a** and **7a** up to 90% in the presence of DBU (Table 1, entries 12 and 14). The yield of **6a** was very poor when another frequently used basic additive DABCO was added instead of DBU (Table 1, entry 13). Obviously, solvent free is optimal choice, because some representative coordinating solvent (DME, DMSO), non-coordinating polar solvent ($CHCl_3$) were tested and did not lead to higher yields (Table 1, entries 2 and 6-8). Complexes **1-4** and the precursor $Eu[N(SiMe_3)_2]_2$ were tested in the reaction. The amidato divalent europium complex **1** was proved as the optimal catalyst for cycloaddition of *N*-ethyl-2-phenylaziridine with CO_2 (Table 1, entries 2 and 9-12).

Table 1 Screening of conditions for the reaction of CO_2 and *N*-ethyl-2-phenylaziridine[a]



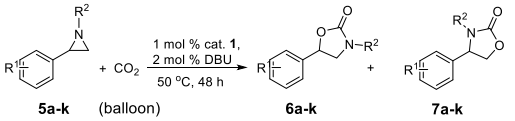
Entry	Cat.	T [ºC]	Sovent[b]	Co-catalyst	Yield [%][c]	Regiosel.[d]
1	**3**	30	-	DBU	30	99:1
2	**3**	50	-	DBU	74	99:1
3	**3**	60	-	DBU	69	98:2
4	**3**	80	-	DBU	56	98:2
5	**3**	100	-	DBU	36	96:4
6	**3**	50	DME	DBU	5	99:1
7	**3**	50	$CHCl_3$	DBU	7	98:2
8	**3**	50	DMSO	DBU	10	99:1
9	**4**	50	-	DBU	75	99:1
10	**2**	50	-	DBU	83	99:1
11	$Eu[N(SiMe_3)_2]_2$	50	-	DBU	34	99:1
12	**1**	50	-	DBU	90	98:2
13	**1**	50	-	DABCO	11	99:1
14	**1**	50	-	-	78	99:1

[a] Reaction conditions: **5a** (2.0 mmol), CO_2 (1 atm); [b] Solvent (2 mL); [c] Determined by GC with biphenyl as an internal standard; [d] Molar ratio of **6a** to **7a**.

As shown in table 2, various aziridines react with CO_2 efficiently, and the target products with high yields and excellent selectivities were obtained. The high yields of oxazolidinones were gained when the groups attached to the nitrogen atom have relative less steric hindrance (Table 2, entries 1-4). There was no significant impact of the electronic effects of the substituents on the phenyl ring, and the yields of the corresponding oxazolidinones are high as well (Table 2, entries 5-9). However, the 54% yield of oxazolidinone **6k** and **7k**, without substituent on N atom, decreased significantly. It may due to the extreme instability of the starting material **5k**. A reported case of **6k** can get a moderate yield of 80%, but 50 atmospheric pressures was required.[5f] In addition, an excellent yield of

6b (>90%) was obtained in previous reports, but the regioselectivities of **6b**:**7b** was relatively poor (90:10 [5b] or 97:3 [5i]).

Table 2 Cycloaddition reaction of various aziridines with CO_2[a]



5a-k 6a-k 7a-k

Entry	Aziridine	R^1	R^2	Yield [%][b]	Regio-sel.[c]
1	**5a**	H	Et	92	99:1
2	**5b**	H	*n*-propyl	89	99:1
3	**5c**	H	*n*-butyl	88	99:1
4	**5d**	H	*i*-butyl	79	99:1
5	**5f**	Cl	Et	83	99:1
6	**5g**	Br	Et	73	99:1
7	**5h**	Methyl	Et	87	99:1
8	**5i**	*t*-butyl	Et	82	99:1
9	**5j**	Methoxy	Et	43	99:1
10	**5k**	H	H	54	93:7

[a]Reaction condition: **5a-k** (2 mol), CO_2 (1 atm), cat **1** (1 mol%), DBU (2 mol%), solvent free; [b]Isolated yield of product; [c] Molar ratio of **6** to **7**.

Based on the previous works,[5b,14] the possible catalytic cycle of the cycloaddition of aziridines and CO_2 is proposed in scheme 3. Firstly, the starting material aziridine is activated by the europium amide through the coordination of the nitrogen atom to the Lewis acidic europium center, resulting in the formation of a Lewis acid-Lewis base complex **A**. The nucleophilic attack of the DBU activated CO_2 species **B** was favored on the partial positive charged benzylic carbon, which lead to the ring-opening of aziridine to produce intermediate **C**. Next, an intramolecular nucleophilic attack occurs to realize cyclization product **D**, meanwhile DBU is released. Obviously, the increased steric hindered R group attached to nitrogen atom has negative effect on the nucleophilic addition. Finally, product **6a** was produced via the intermolecular replacing by a new aziridine molecule, and intermediate **A** was regenerated.

Encouraged by the successful reaction of *N*-ethyl-2-phenylaziridine and CO_2, the model reaction of CS_2 with *N*-ethyl-2-phenylaziridine **5a** was catalyzed by 1 mol% amidato divalent lanthanide complex **1** smoothly, which produced the desired thiazolidine-2-thione **10a** in 77% yield at 30 °C for 24 hours. To our delight, after screening of the reaction temperature, the yield of **10a** reached up to 96% at 45 °C (Table 3, entries 1-4). Results of evaluation of reaction time and solvents proved that solvent free and 24 hours are the optimal reaction conditions (Table 3, entries 5-12). Complexes **1**-**4** and the precursor $Eu[N(SiMe_3)_2]_2$ showed similar reactivities tendency as that for the reaction of *N*-ethyl-2-phenylaziridine with CO_2.The central metal have striking difference in the catalytic reactivities, for the 15% yield of **10a** catalyzed by ytterbium complex **4** is significantly lower than 76% of the europium complex **3** (Table 3, entries 14-15). The divalent precursors $Eu[N(SiMe_3)_2]_2$ was also tested in the reaction, which gave out **10a** only 58% (Table 3, entry 16), while the yield was only 11% in the absence of catalysts (Table 3, entry 17). The results suggest that the divalent lanthanide amides modified by appropriate amidato ligands promote the model reaction of CS_2 with *N*-ethyl-2-phenylaziridine **5a**, and the divalent europium amides perform better in the transformation. Overall, the reaction catalyzed by complex **1** gave the best result of 96% at 45 ℃ after 24 h reaction, while the product **10a** can be only obtained in medium yield under higher temperature (100 or 180 °C) in other cases. [10h]

Scheme 3 A proposed mechanism for the cycloaddition of CO_2 and aziridines by amidato divalent lanthanide amides.

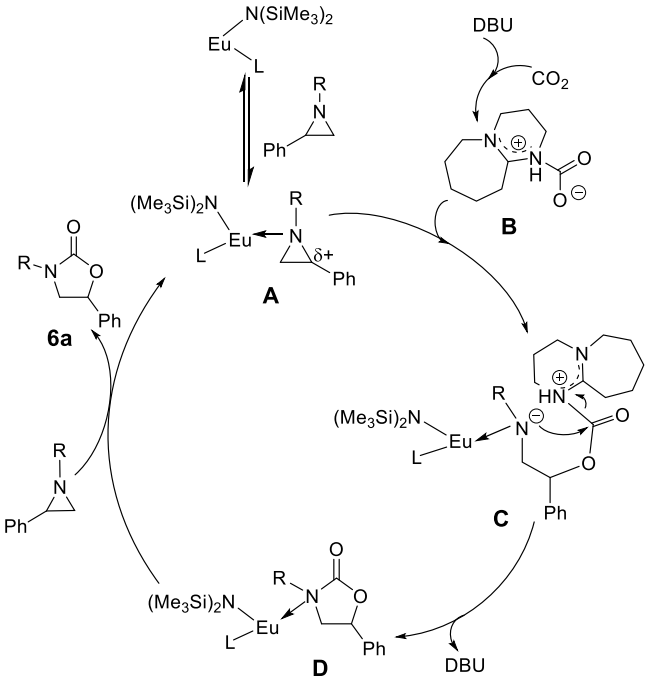
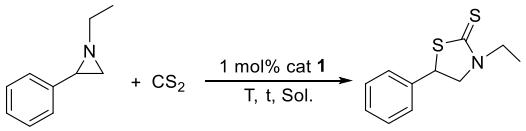


Table 3 Screening of reaction conditions[a]



5a 10a

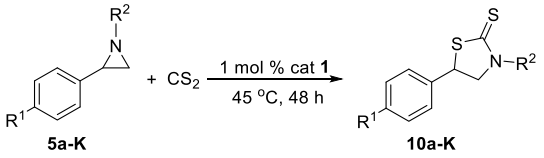
Entry	Cat	T [°C]	t [h]	Solvent[b]	Yield [%][c]
1	**1**	30	24	-	77
2	**1**	40	24	-	85
3	**1**	45	24	-	96
4	**1**	50	24	-	73
5	**1**	45	48		98
6	**1**	45	6	-	47
7	**1**	45	12	-	61
8	**1**	45	24	THF	1
9	**1**	45	24	Tol	7
10	**1**	45	24	DME	6
11	**1**	45	24	DMF	66

12	**1**	45	24	CH_3CN	77
13	**2**	45	24	-	41
14	**3**	45	24	-	76
15	**4**	45	24	-	15
16	$Eu[N(SiMe_3)_2]_2$	45	24	-	58
17	-	45	24	-	11

[a]Reaction conditions: **5a** (1 mmol), CS_2 (5 mmol), cat (1 mol %); [b]Solvent: 2 mL; [c]Determined by GC with biphenyl as an internal standard.

The results of the cycloaddition reaction of various *N*-substituted aziridines with CS_2 catalyzed by complex **1** are presented in Table 4. It shows that most of *N*-substituted aziridines reacted with CS_2 smoothly and the target products were obtained in high to excellent yields. *N*-isobutyl-2-phenylaziridine was found to be least reactive, which is probably due to the relatively high steric hindrance. An improved yield of 83% of *N*-isobutyl-5-phenylthiazolidine-2-thione **10d** was obtained by increasing catalyst loading to 3 mol % (Table 4, entry 4). Aziridines bearing strong electron-donating groups on the aromatic ring, such as *t*-butyl and methoxyl, exhibited relatively low reactivities, and gave moderate yields of 70% and 50%, respectively (Table 4, entries 9-10).

Table 4 Cycloaddition reaction of various aziridines with CS_2[a]



5a-K 10a-K

Entry	Aziridine	R^1	R^2	Yield [%][b]
1	**5a**	H	Et	95[c]
2	**5b**	H	*n*-propyl	97
3	**5c**	H	*n*-butyl	87
4	**5d**	H	*i*-butyl	35 (83[d])
5	**5e**	H	Bn	71
6	**5f**	Cl	Et	89
7	**5g**	Br	Et	85
8	**5h**	Methyl	Et	85
9	**5i**	*t*-butyl	Et	70
10	**5j**	Methoxyl	Et	50
11	**5k**	H	H	86

[a]Reaction conditions : **5a-k** (1 mmol), CS_2 (5 mmol), 48 h, solvent free; [b]Isolated yield of product; [c]Reaction time: 24 h; [d]cat **1** (3 mol %).

To gain more insight into the cyclization reaction, the reaction rate was measured. When *N*-ethyl-2-phenylaziridine **5a** was treated with 5-fold excess of CS_2, the linear plot of $Ln([\mathbf{5a}]_0/[\mathbf{5a}]_t)$ versus time indicates a first-order reaction of *N*-ethyl-2-phenylaziridine (SI.28). Furthermore, the rate order of catalyst was determined to be 1.6, which implies that both mono- and dinuclear species may exist in catalytic cycle (Fig. 1)

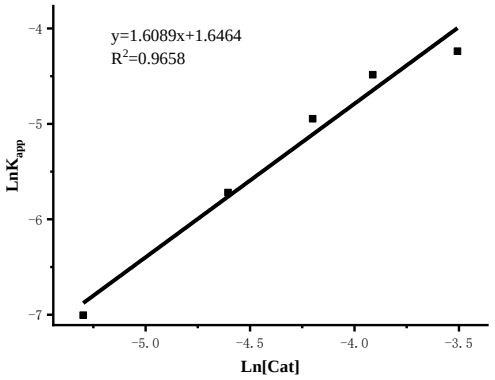
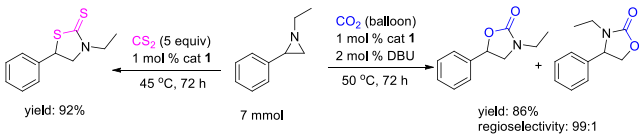


Fig. 1 Plot of LnK_{app} versus Ln[Cat.]. Conditions: complex **1**, $[\mathbf{5a}]_0 : [CS_2]_0 = 1:5$, 45 ℃, solvent free, determined by GC with biphenyl as an internal standard.

Finally, the method applied in the gram scale synthesis of compounds **6a** and **10a** were carried out in the presence of catalyst **1**, respectively. The outcomes are satisfying (Scheme **4**).

Scheme 4 Gram scale synthesis of compounds **6a** and **10a**



CONCLUSION

In summary, four amidato divalent lanthanide amides were applied to catalyze the cycloaddition reaction of aziridines with CO_2 and CS_2, respectively. The europium complex **1** $\{^tBuC_6H_4CONC_6H_3(^iPr)_2Eu[N(SiMe_3)_2]THF\}_2$ was proved to be the most efficient catalyst for the cycloaddition reactions of aziridines. Both oxazolidinones and thiazolidine-2-thiones were prepared in high to excellent yield using 1 mol% of complex **1** under mild reaction conditions. A plausible mechanism of the cycloaddition of CO_2 and aziridines by amidato divalent lanthanide amides was raised. A kinetic study reveals that it has a reverse-first-order reaction of aziridine in the reaction of aziridines with CS_2.

EXPERIMENTAL SECTION

General procedures. CO_2 was supplied from Wu Jiang Mayer industrial gas co., Ltd with a purity of >99.999%, CS_2 was supplied from Shanghai Kefei Industry Co., Ltd. Aziridines were prepared according to the reported method.[5h] Four known amidato divalent lanthanide amides, $(L^nL_n[N(SiMe_3)_2]THF\}_2$ (n = 1, Ln = Eu (1); n = 2, Ln = Eu (3), Yb (4); HL^1 = $^tBuC_6H_4CONHC_6H_3(^iPr)_2$; HL^2 = $C_6H_5CONHC_6H_3(^iPr)_2$) and $\{L^3Eu[N(SiMe_3)_2]THF\}\{L^3{}_2Eu(THF)_2\}$ (2); (HL^3 = $ClC_6H_4CONHC_6H_3(^iPr)_2$)) were prepared according to the literature methods.[6a, 6b] Solvents were distilled from sodium benzophenone ketyl under argon prior to use unless otherwise noted. ^1H, ^{13}C NMR spectra were obtained with a Bruker-400 spectrometer in $CDCl_3$. High resolution mass (HRMS) spectra were obtained using Bruker ESI-TOF. GC analyses were performed on a thermo trace 1300 gas chromatograph.

General procedure for the synthesis of aziridines.[5h] Dimethyl sulfide (12.4 g, 0.2 mol) and bromine (32.0 g, 0.2 mol) were sepa-

rately dissolved in dry dichloromethane (40 mL and 40 mL respectively). The bromine solution was then added dropwise over 30 min to an ice-cooled solution of dimethyl sulfide. During the addition, light orange crystals of bromodimethyl sulfonium bromide began to separate. Then, the crystals were collected by filtration and washed with dry ether and dried under vacuum. Olefin (160 mmol) was added dropwise to the 160 mL acetonitrile solution of the orange crystals (35.56 g, 160 mmol) in ice-water bath. During the addition, the white solid began to separate. The solution was stirred for 10 min after the addition of olefin was completed. The alkenyl sulphonium bromide were collected by filtration, dried under vacuum. To a stirred solution of alkenyl sulphonium bromide (10 mmol) in 20 mL of water at r.t., amine (20-50 mmol) was added dropwise and the resulting mixture was stirred overnight. The mixture was poured into 20 mL of saturated brine, extracted with diethyl ether (3 ×20 mL), dried with $MgSO_4$ and the solvent evaporated under reduced pressure. Pure product was obtained by distillation under reduced pressure.

Characterization data of aziridines. *1-ethyl-2-phenylaziridine (**5a**).*[5h] Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.14 (m, 5H), 2.49 – 2.38 (m, 2H), 2.28 (dt, J = 12.1, 6.1 Hz, 1H), 1.88 (d, J = 3.3 Hz, 1H), 1.63 (d, J = 6.6 Hz, 1H), 1.19 (t, J = 7.1 Hz, 3H) ppm.

*2-phenyl-1-propylaziridine (**5b**).*[5h] Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.17 (m, 5H), 2.47 – 2.39 (m, 2H), 2.28 (dt, J = 11.0, 5.5 Hz, 1H), 1.88 (d, J = 3.3 Hz, 1H), 1.63 (d, J = 6.6 Hz, 1H), 1.19 (t, J = 7.1 Hz, 3H) ppm.

*1-butyl-2-phenylaziridine (**5c**).*[5h] Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.24 (m, 5H), 2.56 (dt, J = 11.5, 7.3 Hz, 1H), 2.44 – 2.30 (m, 2H), 1.95 (d, J = 3.3 Hz, 1H), 1.67 (ddd, J = 21.2, 12.9, 6.6 Hz, 3H), 1.54 – 1.39 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H) ppm.

*1-isobutyl-2-phenylaziridine (**5d**).*[5h] Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.23 (m, 5H), 2.49 (dd, J = 11.6, 7.1 Hz, 1H), 2.36 – 2.28 (m, 1H), 2.11 (dd, J = 11.6, 6.5 Hz, 1H), 2.02 – 1.88 (m, 2H), 1.69 (d, J = 6.5 Hz, 1H), 1.01 (dt, J = 17.6, 8.8 Hz, 6H) ppm.

*1-benzyl-2-phenylaziridine (**5e**).*[5h] Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.14 (m, 10H), 3.61 (dd, J = 31.1, 13.8 Hz, 2H), 2.46 (dd, J = 6.5, 3.3 Hz, 1H), 1.95 (d, J = 3.3 Hz, 1H), 1.80 (d, J = 6.5 Hz, 1H) ppm.

*2-(4-chlorophenyl)-1-ethylaziridine (**5f**).*[5h] Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (dt, J = 30.7, 6.2 Hz, 4H), 2.42 (q, J = 7.1 Hz, 2H), 2.25 (dd, J = 6.5, 3.2 Hz, 1H), 1.82 (d, J = 3.2 Hz, 1H), 1.64 (d, J = 6.5 Hz, 1H), 1.18 (t, J = 7.1 Hz, 3H) ppm.

*2-(4-bromophenyl)-1-ethylaziridine (**5g**).*[5h] Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (t, J = 16.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 2.42 (q, J = 7.1 Hz, 2H), 2.25 (dd, J = 6.5, 3.2 Hz, 1H), 1.81 (t, J = 10.6 Hz, 1H), 1.63 (dd, J = 17.0, 4.7 Hz, 1H), 1.26 – 1.10 (m, 3H) ppm.

*1-ethyl-2-(p-tolyl)aziridine (**5h**).*[5i] Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (q, J = 8.1 Hz, 4H), 2.52 – 2.36 (m, 2H), 2.33 (s, 3H), 2.28 (dd, J = 6.5, 3.4 Hz, 1H), 1.89 (t, J = 5.3 Hz, 1H), 1.63 (d, J = 6.6 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H) ppm.

*2-(4-(tert-butyl)phenyl)-1-ethylaziridine (**5i**).* Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.37 – 7.29 (m, 2H), 7.24 – 7.14 (m, 2H), 2.52 – 2.36 (m, 2H), 2.32 – 2.24 (m, 1H), 1.90 (d, J = 3.3 Hz, 1H), 1.64 (t, J = 4.9 Hz, 1H), 1.32 (d, J = 7.4 Hz, 9H), 1.23 – 1.15 (m, 3H) ppm.

*1-ethyl-2-(4-methoxyphenyl)aziridine (**5j**).* Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 – 7.10 (m, 2H), 6.90 – 6.68 (m, 2H), 2.50 – 2.35 (m, 2H), 2.26 (dd, J = 6.5, 3.4 Hz, 1H), 1.85 (t, J = 6.1 Hz, 1H), 1.60 (d, J = 6.5 Hz, 1H), 1.21 (dt, J = 14.3, 7.1 Hz, 3H) ppm.

*2-phenylaziridine (**5k**).*[5h] Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (m, 2H), 7.21 (m, 3H), 2.95 (m, 1H), 2.15 (m, 1H), 1.74 (m, 1H), 0.91 (br, 1H) ppm.

General procedure for the catalytic ring-opening reaction of aziridines with CO_2. All manipulations and reactions were conducted under a purified argon atmosphere by using standard Schlenk techniques. A 5 mL Schlenk tube under dried argon was charged with complex **1** (0.02 mmol), aziridine (2 mmol) and a stirring bar. After the catalyst was dissolved, 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU, 0.04 mmol) was added into the tube. Thereafter, purging the Schlenk flask with CO_2 three times, then carbon dioxide was introduced with a balloon at ambient pressure. The reaction mixture was stirred at oil bath of 50 ℃ for 48 h, then cooled down to room temperature, quenched with ethyl acetate, then biphenyl (1 mmol) was added as an internal standard for the analysis of product yields by GC, The crude mixture was purified by column chromatography on silica gel (200−300 mesh, eluting with 20:1 petroleum ether/ethyl acetate to give desired products).

Characterization data of oxazolidinones.

3-*ethyl-5-phenyloxazolidin-2-one (**6a**).*[5h] Colorless liquid. Yield: 92%, 351.6 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.31 (m, 5H), 5.53 – 5.38 (m, 1H), 3.91 (t, J = 8.7 Hz, 1H), 3.46 – 3.24 (m, 3H), 1.16 (t, J = 7.3 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 138.3, 128.3, 125.0, 73.8, 51.1, 38.4, 12.0 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{14}NO_2$: 192.1019, found: 192.1016.

*5-phenyl-3-propyloxazolidin-2-one (**6b**).*[5h] Colorless liquid. Yield: 89%, 365.1 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.30 (m, 5H), 5.53–5.43 (m, 1H), 3.91 (t, J = 8.8 Hz, 1H), 3.42 (dd, J = 8.7, 7.4 Hz, 1H), 3.33–3.17 (m, 2H), 1.58 (h, J = 7.4 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 138.4, 128.3, 125.0, 73.8, 51.6, 45.3, 20.1, 10.5 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{15}NNaO_2$: 228.0995, found: 228.1003.

*3-butyl-5-phenyloxazolidin-2-one (**6c**).*[5h] Colorless liquid. Yield: 88%, 385.4 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.26 (m, 5H), 5.50–5.35 (m, 1H), 3.95–3.82 (m, 1H), 3.45–3.15 (m, 3H), 1.53 (dt, J = 14.3, 7.2 Hz, 2H), 1.34 (dd, J = 14.6, 7.5 Hz, 2H), 0.97–0.86 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 138.9, 128.8, 125.5, 74.3, 52.1, 43.9, 29.4, 19.8, 13.7 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{17}NNaO_2$: 242.1151, found: 242.1151.

*3-isobutyl-5-phenyloxazolidin-2-one (**6d**).*[5h] Colorless liquid. Yield: 79%, 346.2 mg; 1H NMR (400 MHz, $CDCl_3$): δ 7.45–7.29 (m, 5H), 5.47 (d, J = 7.4 Hz, 1H), 3.90 (s, 1H), 3.40 (s, 1H), 3.08 (dd, J = 9.8, 7.5 Hz, 2H), 1.95–1.77 (m, 1H), 0.91 (dd, J = 9.0, 4.4 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 138.5, 128.4, 125.0, 73.8, 52.4, 51.3, 26.4, 19.4 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{17}NNaO_2$: 242.1151, found: 242.1161.

*5-(4-chlorophenyl)-3-ethyloxazolidin-2-one (**6f**).*[5h] White solid. Yield: 83%, 373.6 mg; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.50 (dd, J = 26.0, 8.4 Hz, 4H), 5.60 (t, J = 7.9 Hz, 1H), 4.06–3.86 (m, 1H), 3.51–3.38 (m, 1H), 3.26 (tq, J = 14.0, 7.0 Hz, 2H), 1.12 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.2, 138.8, 133.6, 129.2, 128.4, 73.4, 50.9, 38.7, 12.8 ppm. HRMS

(ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{11}H_{12}ClNNaO_2$: 248.0449, found: 248.0447. MP: 59.0-66.4 °C.

5-(4-bromophenyl)-3-ethyloxazolidin-2-one ***(6g)***.[15] White solid. Yield: 73%, 392.7 mg; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.63 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 5.62–5.48 (m, 1H), 3.96 (s, 1H), 3.41–3.37 (m, 1H), 3.29–3.17 (m, 2H), 1.08 (t, J = 7.2 Hz, 3H)ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.9, 143.9, 136.88, 133.4, 126.9, 78.2, 55.6, 43.5, 17.5 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{11}H_{12}BrNNaO_2$: 291.9944, found: 291.9938. MP: 57.8-65.5 °C.

3-ethyl-5-(p-tolyl)oxazolidin-2-one ***(6h)***.[5i] White solid. Yield: 87%, 356.9 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (dd, J = 19.7, 8.1 Hz, 4H), 5.43 (t, J = 8.1 Hz, 1H), 3.89 (t, J = 8.7 Hz, 1H), 3.44–3.27 (m, 3H), 2.35 (s, 3H), 1.17 (td, J = 7.2, 0.5 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7, 138.6, 135.8, 129.5, 125.6, 74.4, 51.6, 38.9, 21.2, 12.6 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{15}NNaO_2$: 228.0995, found: 228.0998. MP: 53.6-55.9 °C.

5-(4-(tert-butyl)phenyl)-3-ethyloxazolidin-2-one ***(6i)***. White liquid. Yield: 82%, 405.3 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 5.46 (t, J = 8.1 Hz, 1H), 3.91 (t, J = 8.7 Hz, 1H), 3.49–3.28 (m, 3H), 1.33 (s, 9H), 1.19 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 151.3, 135.3, 125.3, 124.9, 73.8, 51.0, 38.4, 30.8, 12.1 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{21}NNaO_2$: 270.1465, found: 270.1464.

3-ethyl-5-(4-methoxyphenyl)oxazolidin-2-one ***(6j)***. White solid. Yield: 43%, 190.1 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8.3 Hz, 2H), 6.93 (d, J = 8.2 Hz, 2H), 5.43 (t, J = 8.0 Hz, 1H), 3.89 (t, J = 8.6 Hz, 1H), 3.82 (s, 3H), 3.40 (ddd, J = 20.4, 14.9, 7.5 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 157.7, 130.7, 127.2, 114.2, 74.3, 55.4, 51.6, 38.9, 12.6 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{15}NNaO_3$: 244.0944, found: 244.0940. MP: 68.3-72.1 °C.

5-phenyloxazolidin-2-one ***(6k)***.[5h] Colorless liquid. Yield: 54%, 176.1 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.31 (m, 5H), 5.75 (s, 1H), 5.63 (t, J = 8.2 Hz, 1H), 3.99 (t, J = 8.7 Hz, 1H), 3.60–3.50 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.41, 138.5, 128.9, 127.4, 125.8, 78.0, 48.4 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_9H_9NNaO_2$: 186.0525, found: 186.0523.

General procedure for the catalytic ring-opening reaction of aziridines with CS_2. All manipulations and reactions were conducted under a purified argon atmosphere by using standard Schlenk techniques. A 5 mL Schlenk tube under dried argon was charged with complex **1** (0.01 mmol), aziridine (1 mmol) and a stirring bar. After the catalyst was dissolved, CS_2 (5 mmol) was added into the tube. The reaction mixture was stirred at oil bath of 45 °C for 24 h, then cooled down to room temperature, quenched with ethyl acetate, then biphenyl (0.5 mmol) was added as an internal standard for the analysis of product by GC. The crude mixture was purified by column chromatography on silica gel (200−300 mesh, eluting with 20:1 petroleum ether/ethyl acetate to give desired products).

Characterization data of thiazolidine-2-thiones. *3-ethyl-5-phenylthiazolidine-2-thione* ***(10a)***.[5g] Yellow solid. Yield: 95%, 211.9 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46– 7.29 (m, 5H), 4.84 (dd, J = 8.2, 7.1 Hz, 1H), 4.38 (dd, J = 11.5, 8.4 Hz, 1H), 4.07 (dd, J = 11.6, 7.0 Hz, 1H), 3.87 (ddd, J = 14.2, 9.1, 6.9 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.7, 138.3, 128.7, 128.1, 126.8, 63.0, 46.5, 43.7, 11.2 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{14}NS_2$: 224.0562, found: 224.0557. MP: 63.3-66.9 °C.

5-phenyl-3-propylthiazolidine-2-thione ***(10b)***. Yellow solid. Yield: 97%, 229.9 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 –7.30 (m, 5H), 4.91–4.77 (m, 1H), 4.40 (dd, J = 11.6, 8.4 Hz, 1H), 4.08 (dd, J = 11.6, 6.9 Hz, 1H), 3.89–3.67 (m, 2H), 1.82–1.62 (m, 2H), 0.97 (q, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.3, 138.2, 128.7, 128.1, 126.8, 63.7, 50.3, 46.6, 19.7, 10.8 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{16}NS_2$: 238.0719, found: 238.0705. MP: 53.2-54.7 °C.

3-butyl-5-phenylthiazolidine-2-thione ***(10c)***. Yellow solid. Yield: 87%, 218.4 mg; ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.41– 7.29 (m, 5H), 4.84 (dd, J = 8.2, 7.0 Hz, 1H), 4.38 (dd, J = 11.6, 8.3 Hz, 1H), 4.05 (dt, J = 12.9, 6.4 Hz, 1H), 3.85 – 3.71 (m, 2H), 1.71–1.58 (m, 2H), 1.43–1.31 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5, 138.7, 129.1, 128.5, 127.3, 64.1, 49.1, 47.1, 28.8, 20.1, 13.8 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{18}NS_2$: 252.0875, found: 252.0866. MP: 53.4-55.1 °C.

3-isobutyl-5-phenylthiazolidine-2-thione ***(10d)***. Yellow solid. Yield: 83%, 208.4 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 –7.22 (m, 5H), 4.83–4.73 (m, 1H), 4.29 (dd, J = 11.6, 8.3 Hz, 1H), 3.98 (dd, J = 11.6, 7.1 Hz, 1H), 3.56 (qd, J = 13.4, 7.6 Hz, 2H), 2.04 (dp, J = 13.7, 6.9 Hz, 1H), 0.93–0.83 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 138.0, 128.6, 128.1, 126.9, 64.3, 55.9, 46.8, 26.9, 19.7 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{18}NS_2$: 252.0875, found: 252.0865. MP: 54.7-55.3 °C.

3-benzyl-5-phenylthiazolidine-2-thione ***(10e)***.[10b] Yellow solid. Yield: 71%, 202.4 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 –7.24 (m, 10H), 5.02 (dd, J = 33.4, 14.6 Hz, 2H), 4.86–4.74 (m, 1H), 4.23 (dd, J = 11.6, 8.4 Hz, 1H), 3.93 (dd, J = 11.7, 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 138.4, 134.9, 129.1, 129.0, 128.5, 128.4, 128.4, 127.3, 63.2, 52.7, 46.9 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{15}NNaS_2$: 308.0538, found: 308.0544. MP: 115.2-118.7 °C.

5-(4-chlorophenyl)-3-ethylthiazolidine-2-thione ***(10f)***. Yellow solid. Yield: 89%, 228.7 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.21 (m, 4H), 4.73 (dd, J = 8.2, 6.5 Hz, 1H), 4.32 (dd, J = 11.6, 8.3 Hz, 1H), 3.94 (dd, J = 11.6, 6.5 Hz, 1H), 3.79 (ddt, J = 20.8, 13.6, 6.9 Hz, 2H), 1.19 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.5, 137.0, 133.9, 128.8, 128.2, 62.9, 45.7, 43.7, 11.1 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{13}ClNS_2$: 258.0172, found: 258.0163. MP: 91.4-92.9 °C.

5-(4-bromophenyl)-3-ethylthiazolidine-2-thione ***(10g)***. Yellow solid. Yield: 85%, 255.8 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.5 Hz, 2H), 7.22–7.16 (m, 2H), 4.77–4.63 (m, 1H), 4.32 (dd, J = 11.6, 8.3 Hz, 1H), 3.94 (dd, J = 11.6, 6.5 Hz, 1H), 3.87–3.66 (m, 2H), 1.18 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.4, 137.5, 131.8, 128.5, 122.0, 62.9, 45.8, 43.7, 11.2 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{11}H_{12}BrNNaS_2$: 323.9487, found: 323.9474. MP: 103.6-105.1 °C.

3-ethyl-5-(p-tolyl)thiazolidine-2-thione ***(10h)***. Yellow solid. Yield: 85%, 201.5 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 –7.17 (m, 2H), 7.09 (d, J = 8.0 Hz, 2H), 4.79–4.71 (m, 1H), 4.28 (dd, J = 11.5, 8.3 Hz, 1H), 3.97 (dd, J = 11.6, 7.1 Hz, 1H), 3.87–3.70 (m, 2H), 2.27 (s, 3H), 1.18 (d, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 138.5, 135.6, 129.8, 127.2, 63.6, 46.8, 44.2, 21.1, 11.7 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{16}NS_2$: 238.0719, found: 238.0711. MP: 63.5-64.9 °C.

5-(4-(tert-butyl)phenyl)-3-ethylthiazolidine-2-thione ***(10i)***. Yellow solid. Yield: 70%, 195.4 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34

(d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 4.80 (dd, J = 16.1, 8.3 Hz, 1H), 4.37–4.24 (m, 1H), 4.11–3.98 (m, 1H), 3.82 (tq, J = 13.7, 6.9 Hz, 2H), 1.28–1.19 (m, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.0, 151.3, 135.0, 126.5, 125.6, 63.0, 46.3, 43.7, 34.2, 30.8, 11.2 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{22}NS_2$: 280.1188, found: 280.1187. MP: 96.6-99.8 °C.

3-ethyl-5-(4-methoxyphenyl)thiazolidine-2-thione ***(10j)***. Yellow solid. Yield: 50%, 126.5 mg; ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.21 (dd, J = 8.5, 2.6 Hz, 2H), 6.78 (dd, J = 8.4, 3.1 Hz, 2H), 4.75 (t, J = 7.3 Hz, 1H), 4.37–4.19 (m, 1H), 4.00 –3.89 (m, 1H), 3.84–3.71 (m, 2H), 3.70 (d, J = 3.9 Hz, 3H), 1.16 (dd, J = 10.5, 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2, 159.6, 130.5, 128.5, 114.4, 63.6, 55.4, 46.6, 44.2, 11.7 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{16}NOS_2$: 254.0668, found: 254.0669. MP: 54.8-55.3 °C.

5-phenylthiazolidine-2-thione ***(10k)***. Yellow solid. Yield: 86%, 167.7 mg; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.35 (s, 1H)，7.51–7.37 (m, 5H)，5.44–5.26 (m, 1H)，4.32 (dd, J = 12.1, 8.1 Hz, 1H)，4.01 (dd, J = 12.1, 6.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.2，140.0，129.3，128.6，127.7，58.4，52.8 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_{10}NS_2$: 196.0249, found: 196.0256. MP: 54.8-55.3 °C.

ASSOCIATED CONTENT

Supporting Information

Supporting Information Available: Additional experimental procedures and full spectroscopy data for all the products. This materials is available free of charge via the Internet at http://pubs.asc.org.

AUTHOR INFORMATION

Corresponding Author

*Fax: +86-512-65880305; Tel: +86-512-65880305; E-mail: zhaobei@suda.edu.cn

Notes The authors declare no competing financial interest.

ACKNOWLEDGMENT

We gratefully acknowledge financial support from the National Natural Science Foundation of China (Grant No. 21572151), the project of scientific and technologic infrastructure of Suzhou (SZS201708), and PAPD.

REFERENCES

[1] (a) Basarab, G. S.; Doig, P.; Galullo, V.; Kern, G.; Kimzey, A.; Kutschke, A.; Newman, J. P.; Morningstar, M.; Mueller, J.; Otterson, L.; Vishwanathan, K.; Zhou, F.; Gowravaram, M. Discovery of novel DNA gyrase inhibiting spiropyrimidinetriones: benzisoxazole fusion with N-linked oxazolidinone substituents leading to a clinical candidate (ETX0914). *J. Med. Chem.* **2015**, *58*, 6264−6282. (b) Deshmukh, M. S.; Jain, N. Design, synthesis, and antibacterial evaluation of oxazolidinones with fused heterocyclic C-ring substructure. *Med. Chem. Lett.* **2017**, *8*, 1153−1158. (c) Ramesh, R.; Reddy, D. S. Quest for novel chemical entities through incorporation of silicon in drug scaffolds. *J. Med. Chem*. **2018**, *61*, 3779−3798.

[2] (a) Crimmins, M. T.; King, B. W.; Tabet, E. A.; Chaudhary, K. Asymmetric aldol additions: use of titanium tetrachloride and (-)-sparteine for the soft enolization of *N*-acyl oxazolidinones, oxazolidinethiones, and thiazolidinethiones. *J. Org. Chem.* **2001**, *66*, 894-902. (b) Evans, D. A.; Downey, C. W.; Shaw, J. T.; Tedrow, J. S. Magnesium halide-catalyzed anti-aldol reactions of chiral *N*-acylthiazolidinethiones. *Org. Lett*. **2002**, *4*, 1127–1130. (c) Ando, Y.; Kamatsuka, T.; Shinokubo, H.; Miyake, Y. Selective α-arylation of α,β-unsaturated imides mediated by a visible light photoredox catalyst. *Chem. Commun.* **2017**, 53, 9136-9138. (d) Evans, D. A.; Chapman, K. T.; Bisaha, J. Asymmetric diels-alder cycloaddition reactions with chiral α, β-unsaturated *N*-acyloxazolidinones. *J. Am. Chem. Soc*. **1988**, 110, 1238–1256. (e) Huang, P. Q.; Geng, H. Ni-catalyzed chemoselective alcoholysis of *N*-acyloxazolidinones. *Green Chem.* **2018**, 1-7. (f) Palomino, A. G.; Romea, P.; Urp ĺ F. Stereo selective oxidation of titanium(IV) enolates with oxygen. *Synthesis* **2018**, *50*, 2721–2726.

[3] Sakakura, T.; Choi, J. C.; Yasuda, H. Transformation of carbon dioxide. *Chem. Rev*. **2007**, *107*, 2365-2387.

[4] (a) Khusnutdinova, J. R.; Garg, J. A.; Milstein, D. Combining low-pressure CO_2capture and hydrogenation to form methanol. *ACS Catal*. **2015**, *5*, 2416−2422. (b) Liu, A. H.; Ma, R.; Song, C.; Yang, Z. Z.; Yu, A.; Cai, Y.; He, L. N.; Zhao, Y. N.; Yu, B.; Song, Q. W. Equimolar CO_2 capture by *N*-substituted amino acid salts and subsequent conversion. *Angew. Chem. Int. Ed*. **2012**, *51*, 11306-11310. (c) Hase, S.; Kayaki, Y.; Ikariya, T. NHC-gold(I) complexes as effective catalysts for the carboxylative cyclization of propargylamines with carbon dioxide. *Organometallics*. **2013**, *32*, 5285−5288; (d) Gao, X. T.; Gan, C. C.; Liu, S. Y.; Zhou, F.; Wu, H. H.; Zhou, J. Utilization of CO_2 as a C1 building block in a tandem asymmetric A^3 coupling-carboxylative cyclization sequence to 2-oxazolidinones. *ACS Catal*. **2017**, *7*, 8588−8593. (e) Lee, Y.; Choi, J.; Kim, H. Stereocontrolled, divergent, Al(lll)-catalyzed coupling of chiral *N*-aryl epoxy amines and CO_2. *Org. Lett.* **2018**, *20*, 5036−5039; (f) Birrell, J. A.; Jacobsen , E. N. A practical method for the synthesis of highly enantioenriched trans-1,2-amino alcohols. *Org. Lett*, **2013**, *15*, 2895-2897. (g) Patricia, G. D.; Fehr, L.; Rusconi, G.; Nevado, C. Palladium-catalyzed incorporation of atmospheric CO_2 : efficient synthesis of functionalized oxazolidinones. *Chem. Sci*. **2016**, *7*, 3914-3918.

[5] (a) Sudo, A.; Morioka, Y.; Koizumi, E.; Sanda, F.; Endo, T. Highly efficient chemical fixations of carbon dioxide and carbon disulfide by cycloaddition to aziridine under atmospheric pressure. *Tetrahedron Lett*. **2003**, *44*, 7889–7891. (b) Miller, A. W.; Nguyen, S. T. (Salen)chromium(III)/DMAP: an efficient catalyst system for the selective synthesis of 5-substituted oxazolidinones from carbon dioxide and aziridines. *Org. Lett*. **2004**, *6*, 2301-2304. (c) Zhou, F.; Xie, S. L.; Gao, X. T.; Zhang, R.; Wang, C. H.; Yina, G. Q.; Zhou, J. Activation of (salen)Col complex by phosphorene for carbon dioxide transformation at ambient temperature and pressure. *Green Chem.* **2017**, *19*, 3908-3915. (d) Saptal, V. B.; Bhanage, B. M. *N*-heterocyclic olefins as robust organocatalyst for the chemical conversion of carbon dioxide to value-added chemicals. *ChemSusChem*. **2016**, *9*, 1-7. (e) Yang, Z. Z.; Li, Y. N.; Wei, Y. Y.; He, L. N. Protic onium salts-catalyzed synthesis of 5-aryl-2-oxazolidinones from aziridines and CO_2 under mild conditions. *Green Chem*. **2011**, *13*, 2351-2353. (f) Watile, R. A.; Bagal, D. B.; Deshmukh, K. M.; Dhake, K. P.; Bhanage, B. M. Polymer supported diol functionalized ionic liquids: An efficient, heterogeneous and recyclable catalyst for 5-aryl-2-oxazolidinones synthesis from CO_2 and aziridines under mild and solvent free condition. *J. Mol. Catal. A: Chem.* **2011**, *351*, 196-203.(g) Liu, A. H.; He, L. N.; Peng, S. Y.; Pan, Z. D.; Wang, J. L.; Gao, J. Environmentally benign chemical fixation of CO_2 catalyzed by the functionalized ion-exchange resins. *Sci. China Chem*. **2010**, *53*, 1578-1584. (h) Du, Y.; Wu, Y.; Liu, A. H.; He, L. N. Quaternary ammonium bromide functionalized polyethylene glycol: a highly efficient and recyclable catalyst for selective synthesis of 5-aryl-2-oxazolidinones from carbon dioxide and aziridines under solvent-free conditions. *J. Org. Chem.* **2008**, *73*, 4709-4712. (i) Lin, X. Z.; Yang, Z. Z.; He, L. N.; Yuan, Z. Y. Mesoporous zirconium phosphonates as efficient catalysts for chemical CO_2 fixation. *Green Chem*. **2015**, *17*, 795-798. (j) Tian, Y. M.; Shi, Z. Q. Acid-base bifunctional periodic mesoporous metal phosphonates for synergistically and heterogeneously catalyzing CO_2 conversion. *ACS Catal*. **2014**, *4*, 3847-3855.

[6] (a) Ding, H.; Lu,C. R.; Hu, X. L.; Zhao, B.; Wu, B.; Yao, Y. M. Addition of terminal alkynes to aromatic nitriles catalyzed by divalent lanthanide amides supported by amidates: synthesis of ynones. *Synlett* **2013**, *24*, 1269–1274. (b) Wang, Q. Y.; Lu, C. R.; Zhao, B.; Yao, Y. M. Synthesis and characterization of amidato divalent lanthanide

complexes and their use in forming 2,4-quinazolidinones from CO_2 and 2-aminobenzonitriles. *Eur. J. Org. Chem.* **2016**, 2555–2559.

[7] (a) Cheng, H.; Zhao, B.; Yao, Y. M.; Lu, C. R. Carboxylation of terminal alkynes with CO_2 catalyzed by bis(amidate) rare-earth metal amides. *Green Chem*. **2015**, *17*, 1675-1682. (b) Qin, J.; Xu, B.; Zhang, Y.; Yuan, D.; Yao, Y. M. Cooperative rare earth metal–zinc based heterometallic catalysts for copolymerization of CO_2 and cyclohexene oxide. *Green Chem*. **2016**, *18*, 4270–4275. (c) Zhao, Z. W.; Qin, J.; Zhang, C.; Wang, Y. R.; Yuan, D.; Yao, Y. M. Recyclable single-component rare-earth metal catalysts for cycloaddition of CO_2 and epoxides at atmospheric pressure. *Inorg. Chem*. **2017**, *56*, 4568-4575.

[8] (a) Ahn, J. H.; Kim, S. J.; Ryu, S. E.; Choi, J. K. Synthesis and biological evaluation of rhodanine derivatives as PRL-3 inhibitors. *Bioorg. Med. Chem. Lett*. **2006**, *16*, 2996−2999. (b) Opletalova, V.; Dolezel, J.; Kralova, K.; Pesko, M.; Kunes, J.; Jampilek, J. Synthesis and characterization of (z)-5-arylmethylidenerhodanines with photosynthesis-inhibiting properties. *Molecules* **2011**, *16*, 5207–5227. (c) Almeida, A. M.; Oliveira, B. A.; Castro, P. P.; Mendonc ¸C. C.; Furtado, R. A.; Nicolella, H. D.; Silva, V. L.; Diniz, C. G.; Tavares, D. C.; Silva, H.; Almeida, M. V. Lipophilic gold(I) complexes with 1,3,4-oxadiazol-2-thione or 1,3-thiazolidine-2-thione moieties: synthesis and their cytotoxic and antimicrobial activities. *Biometals.* **2017**, *30*, 841-857. (d) Anitha, M.; Swamy, K. C. K. Synthesis of thiazolidinethiones, iminothiazolidines and oxazolidines via the base promoted cyclisation of epoxy-sulfonamides and heterocumulenes. *Org. Biomol. Chem*. **2018**, *16*, 402-413.

[9] (a) Evans, D. A.; Downey, C. W.; Shaw, J. T.; Tedrow, J. S. Magnesium halide-catalyzed anti-aldol reactions of chiral N-acylthiazolidinethiones. *Org. Lett*. **2002**, *4*, 1127-1130. (b) Evans, D. A.; Downey, C. W.; Hubbs, J. L. Ni(II) bis(oxazoline)-catalyzed enantioselective syn aldol reactions of *N*-propionylthiazolidinethiones in the presence of silyl triflate. *J. Am. Chem. Soc*. **2003**, *125*, 8706-8707. (c) Nagao, Y.; Kumagai, T.; Tamai, S.; Abe, T.; Kuramoto, Y.; Taga, T.; Aoyagi, S.; Nagase, Y.; Ochiai, M.; Inoue, Y.; Fujita, E. Highly diastereoselective alkylation onto 4-acetaxy-2-azetidinones employing tin(I1) enolates of C4-chiral 3-acyl- 1,3-thiazolidine-2-thiones. *J. Am. Chem. Soc*. **1986**, *108*, 4673-4675. (d) Baiget, J.; Cosp, A.; Galvez, E.; Pinal, L. G.; Romea, P.; Urpı, F. On the influence of chiral auxiliaries in the stereoselective cross-coupling reactions of titanium enolates and acetals. *Tetrahedron* **2008**, *64*, 5637-5644.

[10] (a) Chen, N.; Jia, W.; Xu, J. A versatile synthesis of various substituted taurines from vicinal amino alcohols and aziridines. *Eur. J. Org. Chem.* **2009**, 5841–5846. (b) Medini, H.; Mekni, N. H.; Boujlel, K. Electrochemically generated base synthesis of thiazolidine-2-thiones. *J. Sul. Chem.* **2015**, 1-7. (c) Gabillet, S.; Lecercle ´, D.; Loreau, O.; Carboni, M.; De ´zard, S. J. M. Gomis, F. Taran, Phosphine-catalyzed construction of sulfur heterocycles. *Org. Lett*. **2007**, *9*, 3925-3927. (d) Jacobine, A. M.; Posner, G. H. Three-component, one-flask synthesis of rhodanines (thiazolidinones). *J. Org. Chem*. **2011**, *76*, 8121-8125. (e) Nechaev, A. A.; Peshkov, A. A.; Hecke, K. V.; Peshkov, V. A.; Eycken, E. V. V. Synthesis of thiazolidine-2-thiones through a one-pot A3-coupling–carbon disulfide incorporation process. *Eur. J. Org. Chem.* **2017**, 1063-1069. (f) Nomura, R.; Nakano, T.; Nishio, Y.; Ogawa, S.; Ninagawa, A.; Matsuda, H. Regioselective cycloaddition of 1,2-disubstituted aziridines to heterocumulenes catalyzed by organoantimony halides. *Chem. Ber*. **1989**, *122*, 2407-2409. (g) Wu, J. Y.; Luo, Z. B.; Dai, L. X.; Hou, X. L. Tributylphosphine-catalyzed cycloaddition of aziridines with carbon disulfide and isothiocyanate. *J. Org. Chem*. **2008**, *73*, 9137-9139. (h) Sengoden, M.; Vijay, M.; Balakumar, E.; Punniyamurthy, T. Efficient pyrrolidine catalyzed cycloaddition of aziridines with isothiocyanates, isoselenocyanates and carbon disulfide "on water". *RSC Adv.* **2014**, *4*, 54149-54157.

[11] (a) Ample, F.; Curulla, D.; Fuster, F.; Clotet, A.; Ricart, J. M. Adsorption of CO and CN^- on transition metal surfaces: a comparative study of the bonding mechanis. *Surf. Sci*. **2002**, 139-154. (b) Stewart, C. A.; Dickie, D. A.; Parkes, M. V.; Saria, J. A.; Kemp, R. A. Reactivity of bis(2,2,5,5-tetramethyl-2,5-disila-1-azacyclopent-1-yl)tin with CO_2, OCS, and CS_2 and comparison to that of bis[bis(trimethylsilyl)amido]tin. *Inorg. Chem*. **2010**, *49*, 11133-11141. (c) Seif, A.; Ebrahimi, S.; Vessally, E.; Goodarzi, M. Comparative study on the stabilities and properties of heterodimers containing the intermolecular interactions of CF_2Cl_2 with the isoelectronic and isostructure species of N_2O and CO_2. *Struct. Chem.* **2013**, *24*, 1737-1745.

[12] (a) Miller, P. W.; Bender, D. [^{11}C] Carbon disulfide: a versatile reagent for PET radiolabelling. *Chem. Eur. J.* **2012**, *18*, 433-436. (b) Wang, Y. B.; Sun, D. S.; Zhou, H.; Zhang, W. Z.; Lu, X. B. CO_2, COS and CS_2 adducts of *N*-heterocyclic olefins and their application as organocatalysts for carbon dioxide fixation. *Green Chem.* **2015**, *17*, 4009-4015. (c) Zhang, C. J.; Yang, J. L.; Hu, L. F.; Zhang, X. H. Anionic copolymerization of carbonyl sulfide with epoxides via alkali metal alkoxides. *Chin. J. Chem*. **2018**, *36*, 625-629.

[13] (a) Wang, C. M.; Luo, H. M.; Luo, X. Y.; Li, H. R.; Dai, S. Equimolar CO_2 capture by imidazolium-based ionic liquids and superbase systems. *Green Chem.* **2010**, *12*, 2019-2023. (b) Yang, Z. Z.; He, L. N.; Zhao, Y. N.; Li , B.; Yu, B. CO_2 capture and activation by superbase/polyethylene glycol and its subsequent conversion. *Energy Environ. Sci*. **2011**, *4*, 3971-3975.

[14] (a) Liu, X.; Zhang, S.; Song, Q. W.; Liu, X. F.; Ma, R.; He, L. N. 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.

[15] Liu, A. H.; Dang, Y. L.; Zhou, H.; Zhang, J. J.; Lu, X. B. CO_2 adducts of carbodicarbenes: robust and versatile organocatalysts for chemical transformation of carbon dioxide into heterocyclic compounds. *ChemCatChem*. **2018**, *10*, 2686-2692.