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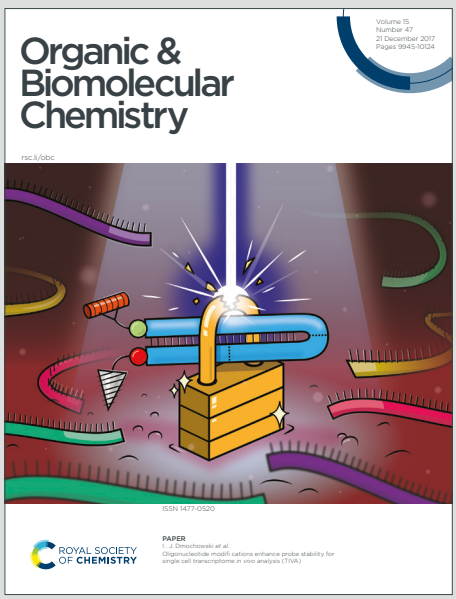




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# Access to 1,3-Oxazine-2,4-diones/1,3-thiazine-2,4-diones via Organocatalytic $CO_2$/COS Incorporation into Allenamides

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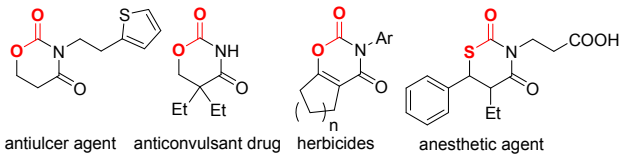
Organocatalyzed [4+2] annulation of $CO_2$/COS with allenamides is firstly reported to synthesize 1,3-oxazine-2,4-diones and 1,3-thiazine-2,4-diones in moderate to excellent yields under mild reaction conditions. The catalytic potential of a series of Lewis base $CO_2$ and COS adducts are particularly noted for this process, which features high regio- and chemo-selectivity, step-economy, facile scalability, and easy product derivatization. This study offers the potential for the application of organocatalytic systems for $CO_2$ and COS chemical transformation.

## Introduction

The development of efficient catalytic transformation of carbon dioxide ($CO_2$) to high-value-added chemicals and polymers, has received more and more attention from both academics and industry.[1] Carbonyl sulfide (COS) is another trace gas in the atmosphere, which is easily oxidized to $SO_2$ in the troposphere, thus leading to significant environment harm.[2] Along with the rapid development of the modern industry, the anthropogenic COS release is increasing obviously, so practical attempts are being undertaken towards the potential transformation of COS to reduce emissions.[3] As $CO_2$-like molecules, some activation modes and catalytic systems for COS conversion have been successfully developed with reference of $CO_2$-related research achievements.[3-4]

Six-membered heterocyclic compounds, such as 1,3-oxazine-2,4-diones and 1,3-thiazine-2,4-diones, are important scaffolds found in medicinal chemistry. For example, some of them have been practically used as antiulcer agents, anticonvulsant drug, anesthetic agent and herbicides in chemical science, as shown in scheme 1.[5] Using $CO_2$ or COS as a useful and sustainable C1 synthon, direct [4+2] annulation to construct functionalized 1,3-oxazine-2,4-diones/1,3-thiazine-2,4-diones is a very promising approach. To the best of our knowledge, up to now, the only precedent is the stoichiometric cyclization reaction of $CO_2$ with allenamides to synthesize 1,3-oxazine-2,4-diones in the presence of $K_2CO_3$ or $Cs_2CO_3$, as reported by Ma et al.[6] Thus, the development of a catalytic method for rapid construction of structurally diverse substituted 1,3-oxazine-2,4-diones/1,3-thiazine-2,4-diones in a green and sustainable manner, is highly desired.




**Scheme 1.** Representative bioactive 1,3-oxazine-2,4-diones and 1,3-thiazine-2,4-diones.

Lewis base-COX (X=O/S) adducts as an emerging type of organocatalytic systems have been rapidly developed by our group,[7] especially for catalytic [3+2] annulation of COX with propargylic compounds, such as propargylic alcohol, propargylic amines and propargylic amides as substrates to construct value-added five membered heterocyclic compounds under mild reaction conditions.[8] Taking inspiration from these studies, we are curious whether suitable Lewis base-COX adducts might display significantly catalytic activity for the synthesis of six-membered heterocyclic compounds. Herein, we firstly report the direct [4+2] annulation of $CO_2$/COS with allenamides in the presence of $CO_2$/COS adducts of *N*-heterocyclic olefins as organocatalysts, to selectively synthesize 1,3-oxazine-2,4-diones and 1,3-thiazine-2,4-diones under mild reaction conditions.

## Results and discussion

Initially, the annulation of $CO_2$ with *N*-benzyl 4-methyl-2,3-pentadienamide **2a** as the model reaction was evaluated, as shown in Table 1. A series of LB-$CO_2$ adducts (**1a-1k**), including *N*-heterocyclic carbenes-$CO_2$ adducts (NHC-$CO_2$), imidazole-derived highly polarized alkenes-$CO_2$ adducts (NHO-$CO_2$), and pyrimidine-derived highly polarized alkenes-$CO_2$ adducts

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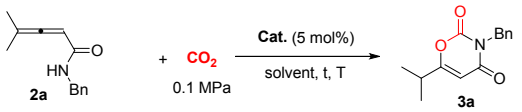
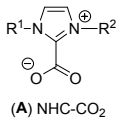
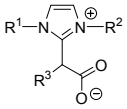
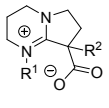
**Table 1.** Optimization of the reaction conditions for [4+2] annulation of **2a** with $CO_2$.[a]





(**A**) NHC-$CO_2$


(**B**) NHO-$CO_2$


(**C**) THPE-$CO_2$

**1a**: $R^1 = R^2$ = -**Dip**
**1b**: $R^1 = R^2$ = -**Mes**
**1c**: $R^1 = R^2$ = -$^i$Pr
**Dip** = 2,6-diisopropylphenyl
**Mes** = 2,4,6-trimethylphenyl

**1d**: $R^1$ = -**Dip**; $R^2 = R^3$ = -Me
**1e**: $R^1$ = -**Dip**; $R^2$ = -Et; $R^3$ = -Me
**1f**: $R^1$ = -**Dip**; $R^2$ = -$^i$Pr; $R^3$ = -Me
**1g**: $R^1 = R^2 = R^3$ = -Me

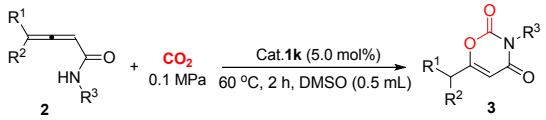
**1h**: $R^1$ = -Me; $R^2$ = -H
**1i**: $R^1 = R^2$ = -Me
**1j**: $R^1$ = -Bu; $R^2$ = -H
**1k**: $R^1$ = -Bn; $R^2$ = -H

| Entry | Cat. | Solvent | T (°C) | t (h) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | **1a** | DMSO | 25 | 2 | 5 |
| 2 | **1b** | DMSO | 25 | 2 | 5 |
| 3 | **1c** | DMSO | 25 | 2 | 19 |
| 4 | **1d** | DMSO | 25 | 2 | 16 |
| 5 | **1e** | DMSO | 25 | 2 | 11 |
| 6 | **1f** | DMSO | 25 | 2 | 6 |
| 7 | **1g** | DMSO | 25 | 2 | 5 |
| 8 | **1h** | DMSO | 25 | 2 | 13 |
| 9 | **1i** | DMSO | 25 | 2 | 14 |
| 10 | **1j** | DMSO | 25 | 2 | 6 |
| 11 | **1k** | DMSO | 25 | 2 | 36 |
| 12 | **1k** | THF | 25 | 2 | 33 |
| 13 | **1k** | $CH_3CN$ | 25 | 2 | 5 |
| 14 | **1k** | DMF | 25 | 2 | 31 |
| 15 | **1k** | DCM | 25 | 2 | 15 |
| 16 | **1k** | DMSO | 25 | 24 | 90 |
| 17 | **1k** | DMSO | 60 | 2 | 91 |
| 18 | - | DMSO | 25 | 2 | NR[c] |

[a] The reaction was carried out using 0.5 mmol of **2a** and 5.0 mol% of **Cat.** in DMSO (0.5 mL) with a $CO_2$ balloon at 25 °C for 2 h. [b] Determined by $^1$H NMR spectroscopy with 1,2,4,5-tetramethylbenzene as the internal standard. [c] No Reaction.

(THPE-$CO_2$), were employed as organocatalysts for this transformation. The catalytic runs were directly performed in DMSO solution and monitored by $^1$H NMR spectroscopy, using 5.0 mol % loading of LB-$CO_2$ adducts, working at 25 °C and atmospheric pressure of $CO_2$. For NHC-$CO_2$ catalytic systems, *N*-alkyl **1c** (entry 3) showed higher activity than *N*-aryl **1a** and **1b** (entries 1 and 2), and 6-isopropyl-1,3-oxazine-2,4-dione **3a** as the desired product, was obtained in 19% yield. Furthermore, the highly polarized alkenes-$CO_2$ adducts were evaluated (entries 4-11) and the most satisfactory result was obtained with **1k** (entry 11). When changing the solvent to THF, $CH_3CN$, DMF or DCM, the yield was decreased in different level under the same conditions (entries 12-15). Meanwhile, prolonging the reaction time to 24 h or increasing reaction temperature to 60 °C could improve the yield of **3a** obviously (entries 16 and 17). Control experiments also revealed that LB-$CO_2$ adducts were mandatory for this carboxylic cyclization (entry 18).

**Table 2. LB-$CO_2$ 1k** catalyzed annulation of different 2,3-allenamides with $CO_2$.[a]




| Entry | Substrate | $R^1$ | $R^2$ | $R^3$ | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | **2b** | -Me | -Et | -Bn | 93 |
| 2 | **2c** | -Me | -*n*Hex | -Bn | 87 |
| 3 | **2d** | -Et | -Et | -Bn | 96 |
| 4 | **2e** | -Me | -*i*Pr | -Bn | 89 |
| 5 | **2f** | | -$(CH_2)_5$- | -Bn | 99 |
| 6 | **2g** | | -$(CH_2)_4$- | -Bn | 99 |
| 7 | **2h** | -Me | -Ph | -Bn | 99 |
| 8 | **2i** | -Me | -Me | -*n*Bu | 97 |
| 9 | **2j** | -Me | -Me | -*i*Pr | 50 |
| 10 | **2k** | -Me | -Me | -*cyclo*Hex | 17[a]/46[c] |
| 11 | **2l** | -Et | -Et | -$CH_2C{\equiv}CH$ | 78 |

[a] The reaction was carried out using 0.5 mmol of **2** and 5.0 mol% of Cat.**1k** in DMSO with a $CO_2$ balloon at 60 °C for 2 h. [b] The yields were determined by $^1$H NMR analysis with 1,2,4,5-tetramethylbenzene as the internal standard. [c] The reaction was conducted at 100 °C for 6 h.

The substrate scope of the reaction was then explored using DMSO as solvent and working at 5.0 mol % **1k** loading, 60 °C, and 0.1 MPa of $CO_2$, as standard conditions (Table 2). Variation of $R^1$ and $R^2$ unit using ethyl, *iso*-propyl, *n*-hexyl, *cyclo*-pentyl, *cyclo*-hexyl or phenyl groups resulted in no obvious influence on the results, delivering the corresponding **3a-3h** in good to excellent yields. Then, the alteration of $R^3$ moiety was investigated. When the $R^3$ group was substituted with *n*-butyl group, the corresponding product **3i** was afforded in 93% yield. However, when the $R^3$ group was changed to *iso*-propyl or *cyclo*-hexyl group, **3j** and **3k** were obtained in only moderate yields, even at 100 °C for 6h, presumably due to steric hindrance. It is worth noting that 2,3-allenamide containing propargyl group on the nitrogen atom (**2l**) was also well tolerated to provide the corresponding **3l** as the sole product, and no five-membered oxazolidinone was detected.

Having established LB-$CO_2$ catalyzed [4+2] annulation of $CO_2$ with allenamides, COS was further introduced for this process in the presence of the corresponding COS adducts of LB as organocatalysts. The experiment results indicated that LB-COS catalyzed [4+2] annulation of COS with allenamides could effectively carry out at 60 °C and 1.0 MPa of COS. LB-COS adduct **S1j** showed the highest activity to selectively obtain 6-isopropyl-1,3-thiazine-2,4-dione **4a** with 96% yield (see Supporting Information for details). With optimal conditions in hand, the substrate scope was then screened and the results are demonstrated in Table 3. Variation of $R^1$ and $R^2$ unit had no obvious influence on the results, and the corresponding **4b-4h** were generated in good to excellent yields. Whereas, the steric

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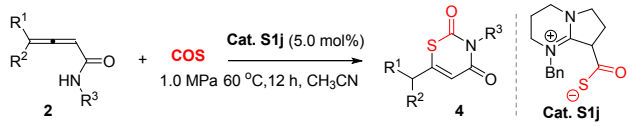
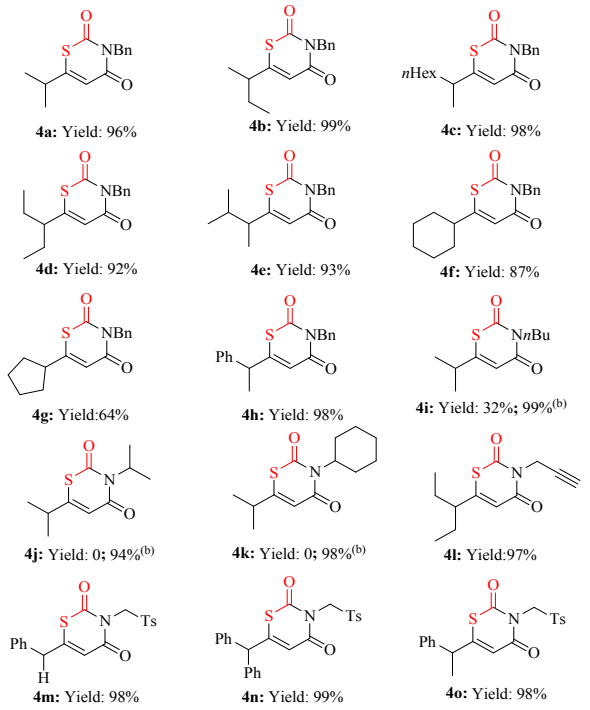
**Table 3.** LB-COS **S1j** catalyzed annulation of different 2,3-allenamides with COS.[a]




[a] General reaction conditions: substrate **2** (0.5 mmol), THPE-COS adduct Cat. **S1j** (5.0 mol%), COS (1.0 MPa), $CH_3CN$ (0.8 mL), 60 °C, 12 h. Determined by $^1H$ NMR spectroscopy with 1,2,4,5-tetramethylbenzene as the internal standard. [b] 100 °C, DMSO (0.4 mL).

demand of the *N*-substituents strongly influences the reaction rate. Only 32% yield of **4i** was achieved with the *N*-butylated substrate **2i**, whereas no desired products were detected for the *N*-isopropyl and cyclohexyl substrates. Gratifyingly, the target products **4i-4k** could be generated in high yields when increasing the reaction temperature to 100 °C. Noting that *N*-propargyl **2l** and tosylmethyl substrates (**2m-2o**) were well-tolerated in this process, affording the desired products **4l-4o** in excellent yields. Moreover, the final structure proof of **4h** was unequivocally determined by single-crystal X-ray diffraction analysis (Figure 1).

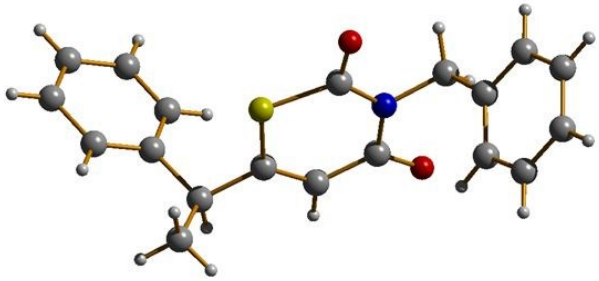
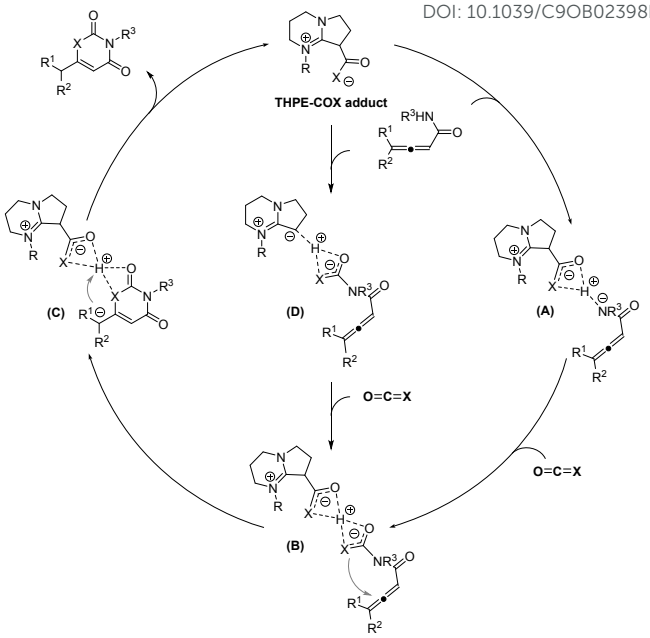
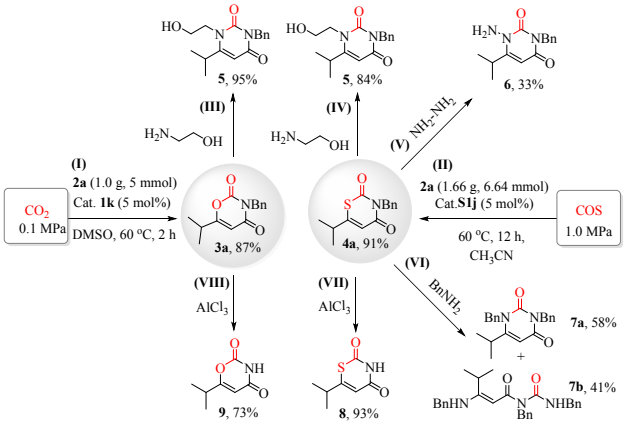


**Figure 1**. X-ray crystallographic structure of **4h**.




**Scheme 2.** Proposed mechanism

Based on the mechanistic studies (Supporting Information Scheme S1, and Figure S2-S21) and previous literatures,[6,9] the possible mechanistic pathway is shown in Scheme 2. Firstly, THPE-COX adducts should act primarily as a base to activate allenamides, thus generating intermediate **A**. Furthermore, intermediate A may attack the carbon atom of free $CO_2$/COS to form carbamate/thiocarbamate **B**. Alternatively, intermediate **B** could also be generated by intramolecular nucleophilic attack of allenamide N-position onto the THPE-COX adduct to form intermediate **D**, and followed activation of another free COX.[9] Then, the intramolecular nucleophilic addition from the carbamate/thiocarbamate anion to the allene central carbon and the subsequent pronation of the alkyl anion lead to the




**Scheme 3.** Gram-scale synthesis and chemical transformations of **3a** and **4a**. **III**: **3a**, ethanolamine, EtOH, reflux, 24 h; **IV**: **4a**, ethanolamine, EtOH, reflux, 24 h; **V**: **4a**, $NH_2NH_2$, EtOH, reflux, 4 h; **VI**: **4a**, benzylamine, EtOH, reflux, 22 h; **VII**: **4a**, $AlCl_3$, benzene, 50 °C, 2 h; **VIII**: **3a**, $AlCl_3$, benzene, 50 °C, 4 h. (see Supporting Information for detailed experimental procedures)

formation of 1,3-oxazine-2,4-diones/1,3-thiazine-2,4-diones and regeneration of free THPE-COX adducts.

To further demonstrate the utility of the annulation reaction, we conducted the gram-scale synthesis of **3a** and **4a** in 87% and 91%, respectively (Scheme 3. **I** and **II**). Moreover, the products can be easily transformed to other synthetically useful building blocks. When using various primary amines as external nucleophiles, oxazine-2,4-diones **3a** and thiazine-2,4-dione **4a** were easily converted in one step to functionalized pyrimidine-2,4-diones (**5-7**), which are a class of the most important heterocycles exhibiting remarkable pharmacological activity.[10] Furthermore, the debenzylation of **3a** and **4a** could smoothly carry out to form **9** and **8** in 73% and 93%, respectively.

## Conclusions

In summary, a series of LB-$CO_2$/COS adducts are presented as organocatalysts for [4+2] annulation of $CO_2$/COS with allenamides to directly construct functionalized 1,3-oxazine-2,4-diones and 1,3-thiazine-2,4-diones under mild reaction conditions. Notably, this reaction features high selectivity, high atom economy, smooth scalability and easy derivation of important structures.

## Experimental

### General information

Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under a dry argon atmosphere. NHC-$CO_2$ adducts,[11] NHO-$CO_2$ adducts,[8a, 8e] THPE-$CO_2$ adducts[8g,8i] and 2,3-allenamides[12] were prepared according to a reported procedure. COS and $CO_2$ (>99%), and all other reagents were used without further purification.

### General procedure for LB-$CO_2$ adducts catalyzed [4+2] annulation of $CO_2$ with allenamides.

In a glove box, a 10 mL Schlenk flask equipped with a magnetic stir bar was charged with *N*-benzyl-4-methylpenta-2,3-alkenamide **2a** (0.5 mmol), LB-$CO_2$ adduct **1k** (5.0 mol%), 1,2,4,5-tetramethylbenzene (0.5 mmol) and DMSO (0.5 mL), successively. The flask was then evacuated and filled with $CO_2$ with a balloon and the reaction was stirred at 60 °C for 2 hours. After the reaction was completed as monitored by TLC and quenched with 5 mL of $H_2O$, extracted with DCM (10 mL × 3), washed with brine, and dried over anhydrous $Na_2SO_4$. After filtration and evaporation, the residue was purified by column chromatography (eluent: petroleum ether / ethyl acetate = 5:1) to give the product **3a**. White solid. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.2 Hz, 2H), 7.41 – 7.20 (m, 3H), 5.75 (s, 1H), 5.03 (s, 2H), 2.79 – 2.48 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 172.55, 161.57, 149.16, 135.70, 129.32, 128.54, 128.07, 98.57, 44.95, 31.95, 19.27.

**3b**. Colorless liquid. (Following the procedure for the preparation of **3a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.1 Hz, 2H), 7.38 – 7.27 (m, 3H), 5.75 (s, 1H), 5.10 – 4.99 (m, 2H), 2.41 (h, *J* = 6.8 Hz, 1H), 1.74 – 1.63 (m, 1H), 1.52 (dp, *J* = 14.3, 7.2 Hz, 1H), 1.20 (d, *J* = 6.9 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 171.63, 161.49, 149.23, 135.69, 129.30, 128.55, 128.07, 99.67, 44.98, 39.06, 26.53, 16.91, 11.40.

**3c**. Colorless liquid. (Following the procedure for the preparation of **3a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.38 – 7.25 (m, 3H), 5.74 (s, 1H), 5.03 (s, 2H), 2.46 (h, *J* = 6.9 Hz, 1H), 1.71 – 1.60 (m, 1H), 1.54 – 1.37 (m, 1H), 1.28 (dd, *J* = 11.9, 5.6 Hz, 8H), 1.19 (d, *J* = 6.9 Hz, 3H), 0.87 (t, *J* = 6.9 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 171.89, 161.53, 135.71, 129.34, 128.55, 128.08, 99.52, 44.98, 37.61, 33.56, 31.62, 29.07, 26.96, 22.59, 17.41, 14.05. **HRMS(ESI)**: calcd for $C_{19}H_{26}NO_3$: 316.1913 $[M+H]^+$. Found: 316.1904 $[M+H]^+$. **IR** $\nu_{C=O}$: 1700, 1654 $cm^{-1}$ (vs).

**3d**. Colorless liquid. (Following the procedure for the preparation of **3a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.26 (m, 3H), 5.75 (s, 1H), 5.03 (s, 2H), 2.27 – 2.04 (m, 1H), 1.65 – 1.55 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 170.26, 161.32, 149.30, 135.58, 129.23, 128.56, 128.06, 101.22, 47.01, 45.02, 24.71, 11.60. **HRMS(ESI)**: calcd for $C_{17}H_{21}O_3$: 273.1491 $[M+H]^+$. Found: 273.1438 $[M+H]^+$. **IR** $\nu_{C=O}$: 1697, 1650 $cm^{-1}$ (vs).

**3e**. Colorless liquid. (Following the procedure for the preparation of **3a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.1 Hz, 2H), 7.31 (dd, *J* = 16.1, 9.0 Hz, 3H), 5.73 (s, 1H), 5.03 (s, 2H), 2.26 (p, *J* = 6.6 Hz, 1H), 1.95 (dq, *J* = 13.3, 6.5 Hz, 1H), 1.15 (d, *J* = 6.9 Hz, 3H), 0.95 – 0.89 (m, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 171.40, 161.42, 149.17, 135.72, 129.23, 128.54, 128.04, 100.33, 44.99, 44.10, 30.50, 20.84, 18.88, 13.81. **HRMS(ESI)**: calcd for $C_{16}H_{20}NO_3$: 274.1443 $[M+H]^+$. Found: 274.1435 $[M+H]^+$. **IR** $\nu_{C=O}$: 1700, 1650 $cm^{-1}$ (vs).

**3f**. White solid. (Following the procedure for the preparation of **3a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, J = 7.2 Hz, 2H), 7.37 – 7.25 (m, 3H), 5.72 (s, 1H), 5.02 (s, 2H), 2.29 (t, J = 9.0 Hz, 1H), 1.93 (d, J = 7.8 Hz, 2H), 1.83 (d, J = 5.9 Hz, 2H), 1.72 (d, J = 12.5 Hz, 1H), 1.40 – 1.24 (m, 5H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 171.75, 161.66, 149.23, 135.73, 129.33, 128.53, 128.06, 98.72, 44.93, 41.26, 29.57, 25.52. **HRMS(ESI)**: calcd for $C_{17}H_{20}NO_3$: 286.1443 $[M+H]^+$. Found: 286.1438 $[M+H]^+$. **IR** $\nu_{C=O}$: 1700, 1658 $cm^{-1}$ (vs).

**3g**. White solid. (Following the procedure for the preparation of **3a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.1 Hz, 2H), 7.27 – 7.20 (m, 3H), 5.70 (s, 1H), 4.95 (s, 2H), 2.70 (p, *J* = 7.8 Hz, 1H), 1.96 – 1.80 (m, 2H), 1.69 (s, 2H), 1.59 (d, *J* = 11.1 Hz, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 171.10, 161.52, 149.25, 135.73, 129.32, 128.53, 128.06, 99.06, 44.93, 42.73, 30.40, 25.41. **HRMS(ESI)**: calcd for $C_{16}H_{18}NO_3$: 272.1287 $[M+H]^+$. Found: 272.1283 $[M+H]^+$. **IR** $\nu_{C=O}$: 1697, 1654 $cm^{-1}$ (vs).

**3h**. White solid. (Following the procedure for the preparation of **3a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.0 Hz, 2H), 7.38 – 7.20 (m, 8H), 5.72 (s, 1H), 5.01 – 4.91 (m, 2H), 3.74 (q, *J* = 7.1 Hz, 1H), 1.53 (d, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ

170.35, 161.42, 148.93, 139.27, 135.68, 129.38, 129.04, 128.58, 128.14, 127.90, 127.73, 100.20, 45.05, 43.08, 18.02.

**3i**. Colorless liquid. (Following the procedure for the preparation of **3a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.73 (s, 1H), 3.97 – 3.78 (m, 2H), 2.76 – 2.55 (m, 1H), 1.69 – 1.57 (m, 2H), 1.43 – 1.31 (m, 2H), 1.24 (d, *J* = 6.9 Hz, 6H), 0.95 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 172.36, 161.68, 149.13, 98.50, 41.74, 31.90, 29.38, 20.00, 19.26, 13.67.

**3j**. Colorless liquid. (Following the procedure for the preparation of **3a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.69 (s, 1H), 5.06 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.63 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.45 (d, *J* = 6.9 Hz, 6H), 1.23 (d, *J* = 6.9 Hz, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 172.31, 162.15, 148.11, 98.70, 45.92, 31.77, 19.23, 18.87. **HRMS(ESI)**: calcd for $C_{10}H_{16}NO_3$: 198.1130 $[M+H]^+$. Found: 198.1121 $[M+H]^+$. **IR** $\nu_{C=O}$: 1700, 1659 $cm^{-1}$ (vs).

**3k**. White solid. (Following the procedure for the preparation of **3a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.69 (s, 1H), 4.65 (tt, *J* = 12.2, 3.8 Hz, 1H), 2.67 – 2.58 (m, 1H), 2.29 (qd, *J* = 12.4, 3.4 Hz, 2H), 1.84 (dd, *J* = 13.4, 2.4 Hz, 2H), 1.68 – 1.61 (m, 3H), 1.42 – 1.26 (m, 3H), 1.23 (d, *J* = 6.9 Hz, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 172.26, 162.27, 148.33, 98.72, 54.02, 31.76, 28.26, 26.09, 25.05, 19.24. **HRMS(ESI)**: calcd for $C_{13}H_{20}NO_3$: 238.1443 $[M+H]^+$. Found: 328.1435 $[M+H]^+$. **IR** $\nu_{C=O}$: 1698, 1658 $cm^{-1}$ (vs).

**3l**. Colorless liquid. (Following the procedure for the preparation of **3a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.79 (s, 1H), 4.65 (s, 2H), 2.26 (s, 1H), 2.21 (dd, *J* = 13.6, 6.5 Hz, 1H), 1.71 – 1.56 (, 4H), 0.92 (t, *J* = 7.5 Hz, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 170.66, 160.21, 148.41, 101.01, 76.84, 71.78, 47.08, 31.01, 24.72, 11.56. **HRMS(ESI)**: calcd for $C_{12}H_{16}NO_3$: 222.1130 $[M+H]^+$. Found: 222.1122 $[M+H]^+$. **IR** $\nu_{C=O}$: 1694, 1654 $cm^{-1}$ (vs).

**General procedure for LB-COS adducts catalyzed [4+2] annulation of COS with allenamides.**

In a glove box, a 20 mL autoclave containing a stirring bar was charged with *N*-benzyl-4-methylpenta-2,3-alkenamide **2a** (0.5 mmol), LB-COS adduct **S1j** (5.0 mol%), 1,2,4,5-tetramethylbenzene (0.5 mmol), and acetonitrile (0.5 mL), successively. Then the autoclave was charged with COS (1.0 MPa). After stirring at 60 °C for 12 hours, the reaction were stopped by cooling the autoclave in an ice bath, and unreacted carbonyl sulfide was slowly vented. The crude reaction mixture was purified by column chromatography (eluent: petroleum ether / ethyl acetate = 5:1) to obtain **4a**. Colorless liquid. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.0 Hz, 2H), 7.28 (dt, *J* = 16.6, 4.7 Hz, 3H), 6.37 (s, 1H), 5.18 (s, 2H), 2.79 – 2.56 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 165.2, 164.0, 160.0, 136.3, 129.3, 128.6, 127.9, 113.4, 44.7, 35.4, 21.8. **HRMS(ESI)**: calcd for $C_{14}H_{15}NO_2S$: 262.0896 $[M+H]^+$. Found: 262.0897 $[M+H]^+$. **IR** $\nu_{C=O}$: 1689, 1651 $cm^{-1}$ (vs).

**4b**. Colorless liquid. (Following the procedure for the preparation of **4a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.39 (m, 2H), 7.28 (dq, *J* = 14.2, 7.0 Hz, 3H), 6.35 (s, 1H), 5.17 (s, 2H), 2.54 – 2.37 (m, 1H), 1.67 – 1.46 (m, 2H), 1.21 (d, *J* = 6.9 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.2, 163.8, 159.0, 136.2, 129.3, 128.5, 127.9, 114.2, 44.7, 42.8, 28.9, 19.7, 11.7. **HRMS(ESI)**: calcd for $C_{15}H_{17}NO_2S$: 276.1053 $[M+H]^+$. Found: 276.1051 $[M+H]^+$. **IR** $\nu_{C=O}$: 1684, 1652 $cm^{-1}$ (vs).

**4c**. Yellow liquid. (Following the procedure for the preparation of **4a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.9 Hz, 2H), 7.28 (dt, *J* = 8.4, 6.8 Hz, 3H), 6.35 (s, 1H), 5.17 (s, 2H), 2.61 – 2.40 (m, 1H), 1.61 – 1.40 (m, 2H), 1.37 – 1.13 (m, 12H), 0.87 (t, *J* = 6.6 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.2, 163.8, 159.3, 136.2, 129.3, 128.5, 127.8, 114.1, 44.6, 41.3, 35.9, 31.6, 29.1, 27.1, 22.6, 20.2, 14.1. **HRMS(ESI)**: calcd for $C_{19}H_{17}NO_2S$:324.1053 $[M+H]^+$. Found: 324.1053 $[M+H]^+$. **IR** $\nu_{C=O}$: 1688, 1651 $cm^{-1}$ (vs).

**4d**. Yellow liquid. (Following the procedure for the preparation of **4a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.9 Hz, 2H), 7.38 – 7.18 (m, 3H), 6.35 (s, 1H), 5.18 (s, 2H), 2.32 – 2.12 (m, 1H), 1.73 – 1.40 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.2, 163.5, 157.5, 136.2, 129.3, 128.5, 127.8, 115.3, 50.9, 44.7, 27.2, 11.8. **HRMS(ESI)**: calcd for $C_{15}H_{17}NO_2S$:290.1209 $[M+H]^+$. Found: 290.1213 $[M+H]^+$. **IR** $\nu_{C=O}$: 1689, 1651 $cm^{-1}$ (vs).

**4e**. Colorless liquid. (Following the procedure for the preparation of **4a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.0 Hz, 2H), 7.29 – 7.09 (m, 3H), 6.25 (s, 1H), 5.08 (s, 2H), 2.30 – 2.04 (m, 1H), 1.73 – 1.57 (m, 1H), 1.09 (d, *J* = 7.0 Hz, 3H), 0.84 (t, *J* = 6.6 Hz, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.1, 163.7, 158.8, 136.2, 129.2, 128.4, 127. 8, 114.5, 48.1, 44.6, 32.6, 21.1, 19.5, 17.0. **HRMS(ESI)**: calcd for $C_{12}H_{15}NO_2S$:290.1209 $[M+H]^+$. Found: 290.1207 $[M+H]^+$. **IR** $\nu_{C=O}$: 1686, 1647 $cm^{-1}$ (vs).

**4f**. Yellow liquid. (Following the procedure for the preparation of **4a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 6.8 Hz, 2H), 7.41 – 7.26 (m, 3H), 6.41 (s, 1H), 5.23 (s, 2H), 2.37 (m, *J* = 11.0 Hz, 1H), 1.91 (m, *J* = 17.7, 9.9 Hz, 4H), 1.77 (d, *J* = 12.6 Hz, 1H), 1.49 – 1.17 (m, 5H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.2, 163.9, 158.9, 136.2, 129.2, 128.4, 127.8, 113.4, 44.9, 44.5, 32.1, 25.9, 25.4. **HRMS(ESI)**: calcd for $C_{17}H_{19}NO_2S$: 302.1209 $[M+H]^+$. Found: 302.1211 $[M+H]^+$. **IR** $\nu_{C=O}$: 1683, 1651 $cm^{-1}$ (vs).

**4g**. White solid. (Following the procedure for the preparation of **4a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.25 – 7.11 (m, 3H), 6.29 (s, 1H), 5.08 (s, 2H), 2.78 – 2.65 (m, 1H), 1.97 – 1.85 (m, 2H), 1.74 – 1.62 (m, 2H), 1.62 – 1.46 (m, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.2, 162.8, 156.9, 135.3, 128.2, 127.4, 126.8, 112.6, 45.1, 43. 6, 31.3, 24.2. **HRMS(ESI)**: calcd for $C_{16}H_{17}NO_2S$:288.1053 $[M+H]^+$. Found: 288.1052 $[M+H]^+$. **IR** $\nu_{C=O}$: 1686, 1651 $cm^{-1}$ (vs).

**4h**. White solid. (Following the procedure for the preparation of **4a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.1 Hz, 2H), 7.35 – 7.13 (m, 8H), 6.43 (s, 1H), 5.12 (s, 2H), 3.79 (q, *J* = 7.0 Hz, 1H), 1.55 (d, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.8, 163.7, 157.6, 140.2, 136.1, 129.2, 129.0, 128.4, 127.9, 127.8,

127.5, 114.4, 45.5, 44.6, 19.6. **HRMS(ESI)**: calcd for $C_{19}H_{25}NO_2S$:332.1679 $[M+H]^+$. Found: 332.1680 $[M+H]^+$. **IR** $\nu_{C=O}$: 1682, 1651 $cm^{-1}$ (vs).

**4i**. Yellow liquid. (Following the procedure for the preparation of **4a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 6.35 (s, 1H), 4.07 – 3.85 (m, 2H), 2.78 – 2.62 (m, 1H), 1.59 (dt, *J* = 15.3, 7.6 Hz, 2H), 1.36 (dq, *J* = 14.8, 7.4 Hz, 2H), 1.26 (d, *J* = 6.9 Hz, 6H), 0.94 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 165.0, 164.1, 159.7, 113.3, 41.8, 35.4, 29.8, 29.8, 21.8, 20.3, 13.8. **HRMS(ESI)**: calcd for $C_{11}H_{17}NO_2S$: 228.1053 $[M+H]^+$. Found: 228.1051 $[M+H]^+$. **IR** $\nu_{C=O}$: 1689, 1655 $cm^{-1}$ (vs).

**4j**. Colorless liquid. (Following the procedure for the preparation of **4a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.22 (d, *J* = 0.7 Hz, 1H), 5.19 (hept, *J* = 6.9 Hz, 1H), 2.69 – 2.48 (m, 1H), 1.38 (d, *J* = 6.9 Hz, 6H), 1.17 (d, *J* = 6.9 Hz, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.9, 164.6, 159.7, 113.6, 77.5, 77.2, 76.8, 47.3, 35.1, 21.6, 19.4. **HRMS(ESI)**: calcd for $C_{10}H_{15}NO_2S$: 214.0896 $[M+H]^+$. Found: 214.0898 $[M+H]^+$. **IR** $\nu_{C=O}$: 1688, 1657 $cm^{-1}$ (vs).

**4k**. White solid. (Following the procedure for the preparation of **4a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.30 (s, 1H), 4.85 (tt, *J* = 12.2, 3.7 Hz, 1H), 2.67 (hept, *J* = 6.8 Hz, 1H), 2.33 (qd, *J* = 12.3, 3.3 Hz, 2H), 1.87 – 1.78 (m, 2H), 1.63 (dd, *J* = 7.7, 3.6 Hz, 3H), 1.45 – 1.27 (m, 3H), 1.25 (d, *J* = 6.9 Hz, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.1, 164.8, 159.6, 113.6, 55.7, 35.1, 28.7, 26.4, 25.3, 21.6. **HRMS(ESI)**: calcd for $C_{13}H_{19}NO_2S$: 254.1209 $[M+H]^+$. Found: 254.1213 $[M+H]^+$. **IR** $\nu_{C=O}$: 1687, 1651 $cm^{-1}$ (vs).

**4l**. Yellow liquid. (Following the procedure for the preparation of **4a**, eluent: petroleum ether / ethyl acetate = 5:1) **$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.39 (s, 1H), 4.76 (d, *J* = 2.3 Hz, 2H), 2.40 – 2.14 (m, 2H), 1.73 – 1.61 (m, 2H), 1.55 (tt, *J* = 14.5, 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.3, 162.4, 157.9, 115.0, 77.5, 71.1, 51.0, 30.5, 27.2, 27.0, 11.7. **HRMS(ESI)**: calcd for $C_{12}H_{15}NO_2S$: 238.0896 $[M+H]^+$. Found: 235.0895 $[M+H]^+$. **IR** $\nu_{C=O}$: 1695, 1651 $cm^{-1}$ (vs).

**4m**. Yellow liquid. (Following the procedure for the preparation of **4a**, eluent: petroleum ether / ethyl acetate = 5:3) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.28 (m, 5H), 7.24 – 7.14 (m, 2H), 6.34 (s, 1H), 5.43 (s, 2H), 3.78 (s, 2H), 2.44 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.0, 161.9, 153.7, 145.5, 136.3, 134.0, 130.0, 129.3, 129.3, 128.7, 128.3, 115.4, 60.4, 42.2, 21.9. **HRMS(ESI)**: calcd for $C_{19}H_{17}NO_4S_2$: 388.0672 $[M+H]^+$. Found: 388.0667 $[M+H]^+$. **IR** $\nu_{C=O}$: 1698, 1656 $cm^{-1}$ (vs).

**4n**. Yellow liquid. (Following the procedure for the preparation of **4a**, eluent: petroleum ether / ethyl acetate = 5:3) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.28 (m, 8H), 7.25 – 7.13 (m, 4H), 6.20 (d, *J* = 1.2 Hz, 1H), 5.44 (s, 2H), 5.15 (s, 1H), 2.44 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.0, 161.9, 156.7, 145.4, 137.7, 136.1, 129.9, 129.1, 128.6, 128.2, 117.1, 60.4, 57.0, 21.8. **HRMS(ESI)**: calcd for $C_{25}H_{21}NO_4S_2$: 464.0985 $[M+H]^+$. Found: 464.0983 $[M+H]^+$. **IR** $\nu_{C=O}$: 1698, 1662 $cm^{-1}$ (vs).

**4o**. Yellow liquid. (Following the procedure for the preparation of **4a**, eluent: petroleum ether / ethyl acetate = 5:3) **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.32 (dd, *J* = 7.5, 3.8 Hz, 3H), 7.24 – 7.20 (m, 2H), 6.45 (s, 2H), 5.42 (s, 1H), 3.87 (q, *J* = 7.0 Hz, 3H), 2.44 (s, 2H), 1.63 (d, *J* = 7.1 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.1, 162.2, 158.8, 145.5, 139.9, 136.2, 130.0, 129.3, 128.7, 128.3, 127.6, 113.9, 60.4, 45.8, 21.8, 19.8. **HRMS(ESI)**: calcd for $C_{20}H_{19}NO_4S_2$: 402.0828 $[M+H]^+$. Found: 402.0847 $[M+H]^+$. **IR** $\nu_{C=O}$: 1698, 1658 $cm^{-1}$ (vs).

## Crystallography

Supplementary crystallographic data was deposited at the Cambridge Crystallographic Data Centre (CCDC) under the numbers CCDC 1859584 (**4h**) and can be obtained free of charge from via www.ccdc.cam.ac.uk/data_request.cif.

## Conflicts of interest

There are no conflicts to declare.

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# Access to 1,3-Oxazine-2,4-diones/1,3-thiazine-2,4-diones via Organocatalytic $CO_2$/COS Incorporation into Allenamides

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Lewis base-$CO_2$/COS adducts were firstly studied as organocatalysts for [4+2] annulation of $CO_2$/COS with allenamides to selectively synthesize 1,3-Oxazine-2,4-diones/1,3-thiazine-2,4-diones.