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Organocatalytic Isomerization/Allylic Alkylation of *O*-Acylated Hemithioacetals and Its Application in Tandem Sequence to Access 2,7-Dioxabicyclo[2.2.1]heptan-3-one derivatives

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ABSTRACT: A novel protocol for the efficient preparation of *α*-hydroxy allylic thioesters *via* a Lewis base catalyzed tandem isomerization/allylic alkylation process is reported. The resulting allylic thioesters can serve as valuable scaffolds to undergo a stereoselective intramolecular cyclization to deliver 2,7-dioxabicyclo[2.2.1]heptan-3-one derivatives in a catalytically atom-economic fashion.

■ INTRODUCTION

Sulfur-embedded structural motifs are ubiquitous in numerous drug molecules, natural products and biologically important compounds.[1] Organosulfur compounds are also widely involved in a plenty of organic synthetic transformations [2]and chemically biological processes, [3] mainly due to their unique C-S bond formation and cleavage. Among them, thioesters constitute one important class of organosulfur compounds, which are not only versatile synthetic building blocks in various organic transformations, [4] but also common intermediates in many biosynthetic reactions. [5] Not surprisingly, a range of synthetic approaches have been developed for the preparation of thioesters. [6]Sulfur-substituted 1,2-enediolate involved biosynthetic or synthetic transformation represents one type of practical methods to furnish α-hydroxy thioesters. For examples, in the glyoxalase-catalyzed process, sulfur-substituted 1,2-enediolates are proven to be key intermediates to deliver targeted α-hydroxythioesters.[5a-c] Correspondingly, the isomerization of *O*-acylated hemithioacetals **1** provides an alternative synthetic strategy for direct access to *O*-acylated *α*-hydroxy thioesters *via* an intramolecular acyl migration and subsequent site-selective protonation (Figure 1a). [7] Recently, Ooi and co-workers have described a catalyst-controlled selective glycolate aldol reaction of *O*-acylated hemithioacetals**1**,[8] in which in situ generated sulfur-substituted enediolate intermediate (**III**) was trapped by aldehyde rather than proton, and afforded valuable *α*, *β*-dihydroxy carboxylic thioesters (Figure 1b). In general, the resultant *α*-hydroxy thioesters are employed as precursors of various *α*-hydroxy carbonyl compounds by discarding sulfur moiety *via* a C-S bond cleavage. In the spite of these elegant advances, the exploration of the potential utility of hemithioacetal isomerization as a means for catalytic generation and functionalization of highly basic enolates to construct structurally diverse thioesters which thereby would provide novel scaffolds to access a diversity of sulfur-containing compounds is still highly demanded.

Recently, we have demonstrated an intramolecular acylsulfenylation of electron-deficient alkene to deliver several sulfur-containing cyclic scaffolds in an atom-eco nomicfashion.[9]We envision that the combination of a Lewis base catalyzed allylic alkylation (LBCAA) of Morita–Baylis–Hillman (MBH) adducts[10] with a base promoted-hemithioacetal isomerization would enable a novel transformation to produce *α*-hydroxy allylic thioesters as fol lows: LBCAA of MBH adduct would generate catalytic

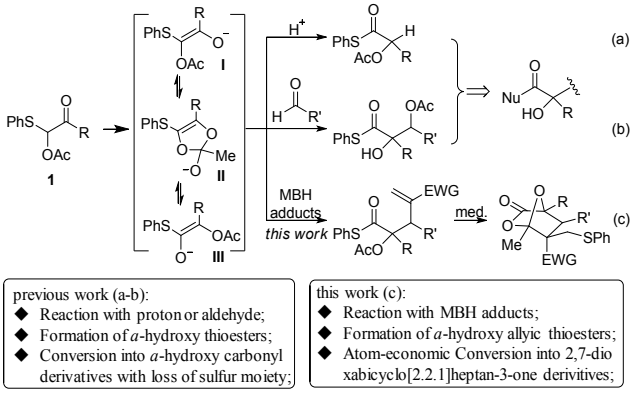


Figure 1. Synthetic strategy

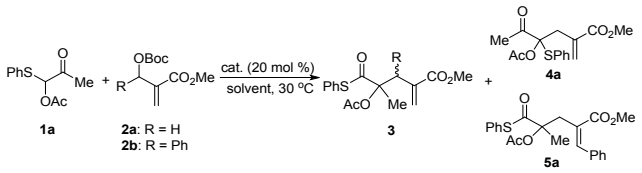
amount of *t*-butoxide and concomitant allylic electrophile, and subsequently *t*-butoxide may facilitate hemithioacetal isomerization to lead to sulfur-substituted enediolate intermediate **III**, which would undergo an allylic alkylation with electrophile to afford the desired allylic thioester. Subsequently, the resulting thioester may serve as a valuable scaffold to undergo an intramolecular cyclization

to deliver 2,7-dioxabicyclo[2.2.1]heptan-3-onesselectively in a catalytically atom-economic fashion (Figure 1c). Herein, we report our preliminary results.[11, 12]

■ RESULTS AND DISCUSSION

Our initial efforts commenced with the identification of the optimal reaction conditions fora Lewis base catalyzed hemithioacetal isomerization/allylic alkylation sequence (Table 1), in which *α*-acetoxy-*β*-ketosulfide**1a** and MBH adduct **2a** as representative substrates by using a catalytic amount of DABCO (20 mol %) in CH_3CN at 30 °C. The reaction gave the desired thioester **3aa** in 79% yield, along with **4a**, generated from enediolate **I** (entry 1). Although temperature variations had few effects on the selectivity (entries 1-3), the choice of solvent was proved to be essential to modulate the regioselectivity of this reaction. The less polar solvents delivered the mixture of regioisomers with poor selectivities, while polar solvents afforded superior results which identified DMSO to be the best regarding yield and regioselectivity (entries 4-7). Further screening of catalysts revealed that DMAP was superior to DABCO, and can provide the excellent regioselectivity in CH_3CN (entries 8-10).

Table 1. Optimization of Reaction Conditions[a]



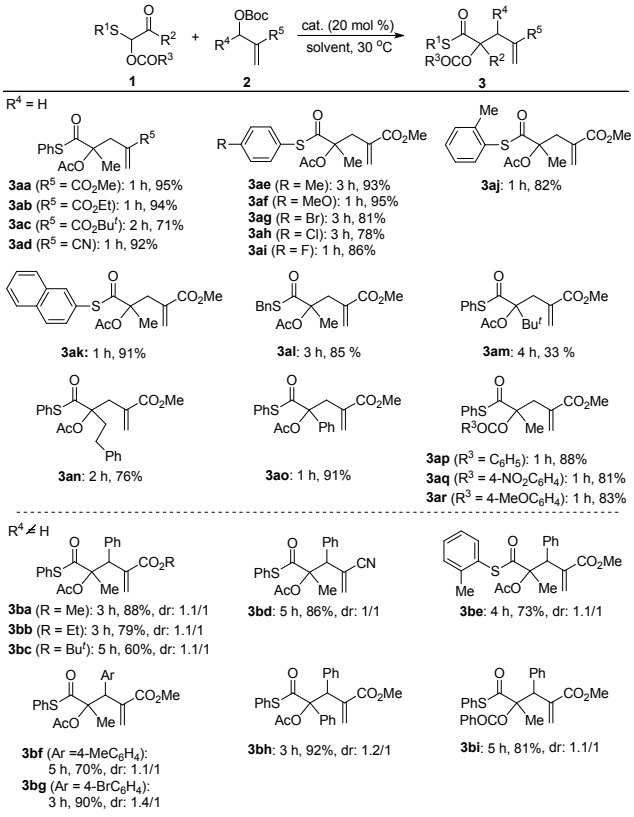
Entry	**2**	cat.	solvent	*T* (°C)	*t* (*h*)	R	Yield (%) [b]
1	**2a**	DABCO	MeCN	30	1	H	79 (**3aa**), 16 (**4a**)
2	**2a**	DABCO	MeCN	0	2	H	78 (**3aa**), 19 (**4a**)
3	**2a**	DABCO	MeCN	-40	7	H	69 (**3aa**), 17 (**4a**)
4	**2a**	DABCO	EA	30	1	H	60 (**3aa**), 37 (**4a**)
5	**2a**	DABCO	THF	30	1	H	53 (**3aa**), 45 (**4a**)
6	**2a**	DABCO	$PhCH_3$	30	1	H	48 (**3aa**), 47 (**4a**)
7	**2a**	DABCO	DMSO	30	1	H	92 (**3aa**), 5 (**4a**)
8	**2a**	DMAP	DMSO	30	1	H	96 (**3aa**), nd(**4a**)
9	**2a**	PPh_3	DMSO	30	6	H	72 (**3aa**), nd (**4a**)
10	**2a**	DMAP	MeCN	30	1	H	95 (**3aa**), nd (**4a**)
11[c]	**2b**	DABCO	Benzene	30	3	Ph	90 (**3ba**), nd (**5a**)

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.22 mmol), and catalyst (20 mol %) in solvent (1 mL). [b] Isolated yields. [c] Inseparable mixture of **3ba** (dr((*3R*,4R**)-**3ba**/(*3R*,4S**)-**3ba**) = 1.1/1, determined by ^{1}H NMR analysis of crude product).

However, the process between **1a** and substituted MBH adduct **2b** proceeded well in the presence of DABCO (20 mol %) in benzene, and gave **3ba** in high yield, albeit with low diastereoselectivity (dr ((*3R*,4R**)-**3ba**/(*3R*,4S**)-**3ba**) = 1.1/1)(entry 11). Otherwise, the reaction gave compound **5a***via* an addition-elimination pathway[10, 13](for details see the ESI†).[14]

The scope of the developed process was further tested by the variation of sulfide **1** and **2** (Scheme 1). Firstly, the reactions between unsubstituted MBH adducts **2** with **1a** were examined. MBH adducts **2** bearing different electron-withdrawing groups were well tolerated, and MBH methyl, ethyl carbonates and cyano group substituted MBH adduct afforded the desired products (**3aa**, **3ab** and **3ad**) as sole regioisomers in excellent yields, while MBH carbonate with bulky ester group showed the less reactivity and gave product **3ae** in moderate yield. Further evaluation on the variations of sulfides **1** was studied. The reactions between *α*-acyloxy-*β*-ketosulfides bearing various aryl groups (R^1) with **2a** proceeded well and provided products in good to high yields (**3ae-3aj**), irrespective of the electronic property and substitution pattern of the substituted aromatic rings. *β*-Naphthyl and benzyl substituted sulfides can also serve as suitable substrates to give the corresponding thioesters (**3ak**, **3al**) in high yields. Besides, treatment of sulfides **1** bearing various R^2 groups such as *t*-butyl, phenethyl and phenyl with **1a** can deliver the desired allylic thioesters (**3am**-**3ao**) incorporating different groups at the *α*-position. Furthermore, the reaction was tolerant of the variations on acyl groups (R^3) of sulfides **1**, and furnished allylic thioesters (**3ap**-**3ar**) in good yields. Then, this isomerization/allylic alkylation approach was extended to substituted MBH adducts ($R^4 \neq H$). The reactions were compatible with the substitution variations on both MBH adducts and *α*-acyloxy-*β*-ketosulfides, and provided

Scheme 1. Substrate Scope of Reaction of 1 and 2 [a]

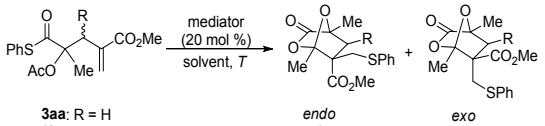


[a] Reaction conditions: R = H: **1** (0.3 mmol), **2** (0.33 mmol) and DMAP (20 mol %) in MeCN (1.5 mL). R ≠ H: **1** (0.3 mmol), **2** (0.33 mmol) and DABCO (20 mol %) in benzene (1.5 mL). Isolated yields. The dr ((*3R*,4R**)-**3**/(*3R*,4S**)-**3**) value was determined by ^{1}H NMR analysis of crude product.

thioesters incorporating contiguous quaternary and tertiary carbon centers in high yields (**3ba**-**3bi**), albeit with low diastereoslectivities.

Next, we turned our attention to study the cyclization of resultant thioesters **3** *via* a transition metal-free intramolecular cyclization (Table 2).Treatment of **3aa** with PhSLi (20 mol %) generated from thiophenol and *n*-butyllithium afforded 2,7-dioxabicyclo[2.2.1]heptan-3-one**6aa** in 70% yield (*endo*/*exo* = 3/1) in THF at 0 °C (entry 1). Interesting, not only the catalytic amount of performed PhSNa but also KOBu^t, NaOBu^t and NaOEt can facilitate this transformation to provide product **6aa** in high yield (entries 2-5), which indicated that a nucleophilic alkoxy anion may attack the carbonyl group of thioester to give thiophenolate which may serve as an authentic mediator. Bu_3P gave product **6aa** in 47% yield with low diastereoselectivity (entry 6). Notably, TBASPh gave product **6aa** with poor *endo/exo*-selectivity (1/2), in contrast to that of PhSNa (entries 2 *vs* 7), which indicated that sodium counterion was essential to obtain high diastereoselectivity. With NaOEt (20 mol %) as mediator, the survey of solvents was carried out (Table 2, entries 8-10), which indicated that less polar solvents provided the *endo*-product **6aa**, while *exo*-product **6aa** preferred to be formed in polar solvents with moderate selectivity. Finally, the loading of mediator proved to be critical to improve the selectivity, and the excellent diastereoselectivity was obtained in the presence of 10 mol% NaOEt without compromising on the productivity of this transformation (entry 11). However, when diastereo-mixture of thioester **3ba** was employed under the same reaction conditions, only (*3R*,4R**)-**3ba** can be

Table 2.Optimization of Reaction Conditions[a]



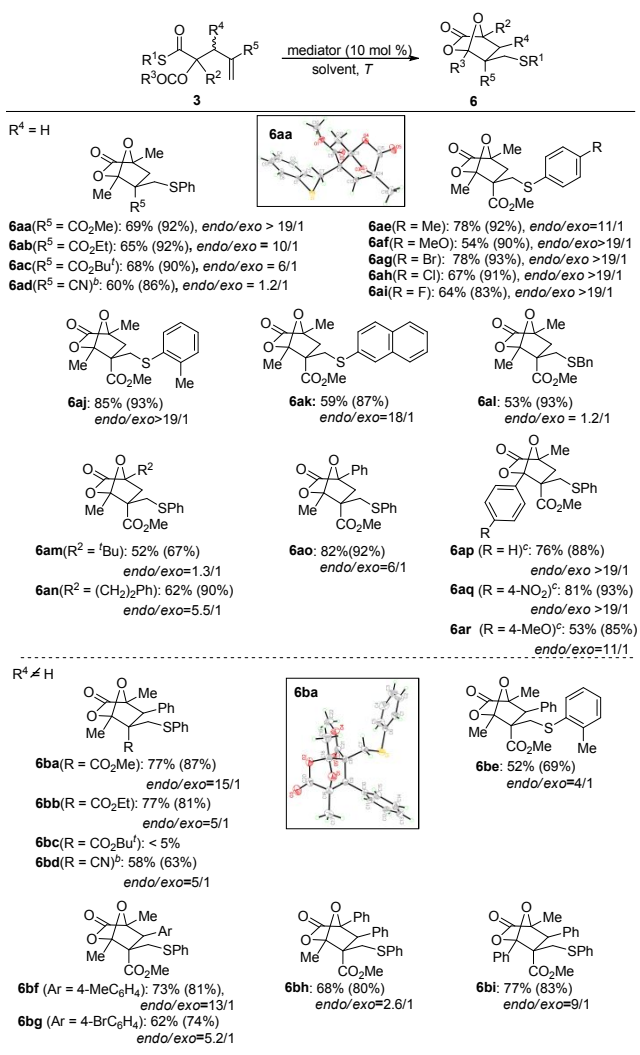
Entry	R	mediator	solvent	*T* (°C)	*t* (h)	Yield (%)[b]	*endo/exo*[b]
1[c]	H	^{n}BuLi/PhSH	THF	0	0.5	70 (**6aa**)	3/1
2	H	PhSNa	THF	0	0.5	96 (**6aa**)	6.8/1
3	H	^{t}BuOK	THF	0	1	94 (**6aa**)	5.3/1
4	H	^{t}BuONa	THF	0	1	89 (**6aa**)	10/1
5	H	EtONa	THF	0	2	92 (**6aa**)	11/1
6	H	Bu_3P	THF	rt	48	47 (**6aa**)	1.1/1
7	H	TBASPh	THF	rt	24	67 (**6aa**)	1/2
8[d]	H	EtONa	PhMe	rt	4	90 (**6aa**)	11/1
9[d]	H	EtONa	MeCN	rt	12	89 (**6aa**)	3.6/1
10[d]	H	EtONa	DMSO	rt	36	52 (**6aa**)	1/4
11[d,e]	H	EtONa	THF	rt	2	92 (**6aa**)	>19/1
12[e,f]	Ph	PhSNa	THF	rt	15	87[g] (**6ba**)	15/1

[a] Reaction conditions: **3** (0.1 mmol) and mediator (20 mol %) in solvent (0.5 mL). [b] Determined by ^{1}H NMR analysis of crude product using CH_2Br_2 as internal standard. [c] Base (20 mol %) and PhSH (20 mol %). [d] EtONa (1 *M* in DMSO). [e] Mediator (10 mol%). [f] **3ba**(dr((*3R*,4R**)-**3ba**/(*3R*,4S**)-**3ba**)= 1.1/1. [g] Based on *(3R*,4R**)-**3ba**. TBASPh: tetrabutylammonium thiophenolate.

converted into *endo*- product **6ba** in 61 % yield with *endo/exo*=15/1.[15] The additional efforts enabled this transformation to provide product **6ba** in 87% yield with high*endo/exo*-selectivity (15/1) from (*3R*,4R**)-**3ba** in the presence of PhSNa (10 nol %) (entry 12) (for details see the ESI†).[16]

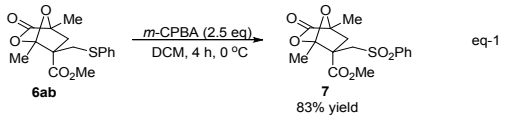
With the optimal reaction condition established, the substrate scope of this cyclization was examined. As shown in Scheme 2, this tandem sequence was applicable to a variety of allylic thioesters **3** affording bicyclic compounds **6** in high yields and good to high *endo/exo*-selectivities.[17] The reaction of allylic thioesters bearing less sterically congested carbon centers were firstly evaluated (R^4 = H). It turned out that EWG groups located at vinyl unit of **3** had considerable effects on the chemical outcome and stere

Scheme 2. Substrate Scope of Cyclization of 3[a]



[a] Reaction conditions: R = H: **3** (0.2 mmol) and EtONa (10 mol %, 1 *M* in DMSO) in THF (1 mL); R ≠ H: **3** (0.2 mmol of diastereoisomers) and PhSNa (10 mol%) in THF (1 mL). Isolated yields (R ≠ H, yields were calculated based on (*3R*,4R**)-**3**). The yields in parentheses were determined by ^{1}H NMR using CH_2Br_2 as internal standard. The endo/exo values were determined by ^{1}H NMR analysis of crude product. [b] PhSNa (20 mol%). [c] PhSNa (10 mol%).

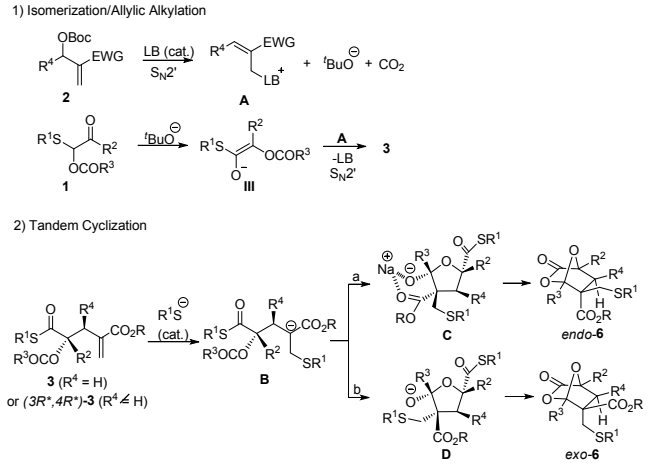
oselectivity of this transformation. High yields and selectivities of the desired products were obtained with methyl or ethyl esters as EWG groups (**6ab**-**6ac**), while steric bulk ester afforded moderate *endo/exo*-selectivity(**6ac**). Interestingly, cyano group substituted thioester gave product **6ad** in good yield with low *endo/exo*-selectivity. The electronic nature and substitution pattern of aromatic ring system (R^1) of thioester have few influences on this reaction, and the reactions provided products (**6ae**-**6ak**) in good yields with high *endo/exo*-selectivities, while benzyl analogue afforded product **6al** in good yield, but with low selectivity. Various substituents ($R^2$and R^3) at the α position or α hydroxyl group of thioesters were all tolerated (**6am**-**6ar**), which were finally positioned at the bridgehead atoms, but the selectivities seemed to be more sensitive to the variations of R^2 group of thioesters (**6am**-**6ao**). In addition, highly functionalized bicyclic products can be accessed from allylic thioesters **3**(R^4 ≠ H) incorporating contiguous quaternary and tertiary carbon centers to afford the desired products (**6ba**-**6bi**). In all cases, only (*3R*,4R**)-thioesters **3** can undergo the cyclization to provide 2,7-dioxabicyclo[2.2.1]heptan-3-ones **6**. Except forsteric bulk esteranalogue which did not afford product **6bc**, the most of tandem sequences proceeded smoothly, and provided the desired products in good to high yields (**6ba**-**6bb** and **6bd**-**6bi**). However, the selectivities of this cyclization were partially dependent on the nature of EWG (R^5) and aromatic ring system (R^1 and R^4) (**6bb, 6bd**, **6be, 6bg**). In addition, when different substituents (R^2 and R^3) at the α position or α hydroxyl group of thioesters were employed, the substituent (R^2) of thioester could exert considerable influence on the *endo/exo*-selectivities (**6bh**-**6bi**).



The practicality of this tandem sequence has been evaluated. The reaction of **1a** (3.5 mmol) with MBH adduct **2a** (1.1 equiv.) gave the desired product **3aa** in 90% yield (1.01g). The expected cyclization of **3aa** (3.6 mmol) proceeded smoothly and delivered 2,7-dioxabicyclo[2.2.1]heptan-3-one **6ba** in 67% isolated yield (778 mg, 89% yield determined by ^{1}H NMR using CH_2Br_2 as internal standard) with excellent selectivity (*endo/exo*>19/1) under the optimized reaction conditions. Furthermore, **6ba** could be readily converted into sulfone **7** in good yield in the presence of *m*-CPBA (eq-1).

The possible reaction pathways were proposed based on the above experiments. The tandem isomerization/allylic alkylation of *α*-acetoxy-*β*-ketosulfide**1** and MBH adduct **2** would deliver the desired product **3** *via* a cascade S_N2'–S_N2' pathway according to the previous procedures (Scheme 3-1).[7,8,10]The 1,4-addition of R^1SNa, initially generated from an addition of mediator to carbonyl group of thioester, to the activated C-C double bond moiety of substrate **3** would lead to intermediate **B**. Subsequently, a diastereoselective

Scheme 3. Proposed Mechanism



intramolecular 1,2-addition between anion with the carbonyl group of the substituent (R^3OC) at α hydroxyl group of thioester would prefer to afford five-membered cyclic intermediate **C** (path a), presumably due to the coordination between sodium cation and oxygen atoms of carbonyl groups. Final lactonization of intermediate **C** could give *endo*-product **6**. With regard to thioester **3**($R^4 \neq H$) incorporating contiguous quaternary and tertiary carbon centers, only (*3R*,4R**)-**3**could undergo the similar cyclization to furnish the desired *endo*-product **6** probably due to the increased interaction between *cis*-positioned thioester group and R^4 group of generated five-membered cyclic from (*3R*,4S**)-**3**.

■ CONCLUSIONS

In summary, we have demonstrated a practical tandem sequence to prepare *α*-hydroxy allylic thioesters by the combination of a LBCAA of MBH adducts with a base promoted-hemithioacetal isomerization. Subsequently, the resulting thioesters can be converted into 2,7-dioxabicyclo[2.2.1]heptan-3-one derivatives regio-selectively via a novel tandem cyclization in a catalytically atom-economic fashion. Further investigations on the mechanism and synthetic application of this transformation are being carried out in our laboratory.

■ EXPERIMENTAL SECTION

General Information. All reactions were carried out under inert atmospheric condition unless otherwise noted, and solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC) visualizing with ultraviolet light (UV), and $KMnO_4$; column chromatography purifications were carried out using silica gel. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a 400 or 500 MHz spectrometer in $CDCl_3$, and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on 100 or 125 MHz spectrometer in $CDCl_3$ unless otherwise noted. Mass spectra were recorded on the Bruker MicrOTOF Q II. Melting points were measured on a melting point apparatus and were uncorrected.

General Procedure for the Preparation of α-Acyloxy - β-Ketosulfides. For the synthesis of **1a - 1l**, [7c, 8, 18] to a solution of *β*-keto sulfoxide (1.0 mmol) and Ac_2O (0.11 mL, 1.1 mmol) in DCM (3.3 mL) was added $TsOH\cdot H_2O$ (9.5 mg, 0.05 mmol) at 0 °C. Upon completion, the reaction was quenched with saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with DCM twice. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether (60-90 °C)) to provide the desired products. For the synthesis of **1m – 1o**, [19]a solution of 1-(phenylthio)propan-2-one (1.0 mmol) and peroxyanhydride (1.1 mmol) in toluene (1 mL) was stirred in a sealed tube reactor at room temperature for 4 days. The resulting mixture was concentrated in vacuo, diluted with DCM and washed with saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with DCM twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether (60-90 °C)) to provide the desired products.

*2-Oxo-1-(phenylthio)propyl acetate (**1a**).* Yield: 58% (130 mg (petroleum ether/EtOAc = 30/1), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.42 (m, 2H), 7.41 – 7.23 (m, 3H), 6.20 (s, 1H), 2.21 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 169.6, 133.5, 129.8, 129.2, 129.1, 81.6, 26.2, 20.7. The spectral data match those previously reported.

*2-Oxo-1-(p-tolylthio)propyl acetate (**1b**).* Yield: 54% (127 mg) (petroleum ether/EtOAc = 30/1), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.15 (s, 1H), 2.33 (s, 3H), 2.23 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)δ 197.2, 169.8, 139.6, 134.1, 130.1, 126.0, 81.9, 26.32, 21.2, 20.8. The spectral data match those previously reported.

*1-((4-Methoxyphenyl)thio)-2-oxopropyl acetate (**1c**).* Yield: 53% (135 mg) (petroleum ether/EtOAc = 30/1), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 2H), 6.92 – 6.80 (m, 2H), 6.10 (s, 1H), 3.79 (s, 3H), 2.23 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 169.8, 160.9, 136.4, 119.6, 114.9, 82.0, 55.4, 26.4, 20.8. HRMS (ESI): calcd. for $C_{12}H_{14}NaO_4S$ ($[M+Na]^+$): 277.0505, found 277.0504.

*1-((4-Bromophenyl)thio)-2-oxopropyl acetate (**1d**).* Yield: 58% (176 mg) (petroleum ether/EtOAc = 30/1), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.39 (m, 2H), 7.38 – 7.31 (m, 2H), 6.18 (s, 1H), 2.24 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 169.7, 135.2, 132.5, 128.8, 123.9, 81.2, 26.3, 20.8. The spectral data match those previously reported.

*1-((4-Chlorophenyl)thio)-2-oxopropyl acetate (**1e**).* Yield: 54% (140 mg) (petroleum ether/EtOAc = 30/1), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.34 – 7.28 (m, 2H), 6.17 (s, 1H), 2.24 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.8, 169.7, 135.8, 135.1, 129.6, 128.2, 81.4, 26.3, 20.8. HRMS (ESI): calcd. for $C_{11}H_{11}ClNaO_3S$ ($[M+Na]^+$): 281.0010, found 281.0016.

*1-((4-Fluorophenyl)thio)-2-oxopropyl acetate (**1f**).* Yield: 53% (128 mg) (petroleum ether/EtOAc = 30/1), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$)δ 7.52 – 7.46 (m, 2H), 7.06 – 7.00 (m, 2H), 6.14 (s, 1H), 2.24 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.0, 169.7, 163.6 (d, *J* = 250.4 Hz), 136.5 (d, *J* = 8.4 Hz), 124.6, 116.5 (d, *J* = 21.9 Hz), 81.6, 26.3, 20.8. HRMS (ESI): calcd. for $C_{11}H_{11}FNaO_3S$ ($[M+Na]^+$): 265.0305, found 265.0307.

*2-Oxo-1-(o-tolylthio)propyl acetate (**1g**).* Yield: 55% (131 mg) (petroleum ether/EtOAc = 30/1), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.7 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.19 – 7.12 (m, 1H), 6.17 (s, 1H), 2.47 (s, 3H), 2.24 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 169.8, 141.2, 134.6, 130.8, 129.6, 129.6, 126.8, 82.1, 26.2, 21.0, 20.7. HRMS (ESI): calcd. for $C_{12}H_{14}NaO_3S$ ($[M+Na]^+$): 261.0556, found 261.0564.

*1-(Naphthalen-2-ylthio)-2-oxopropyl acetate (**1h**).* Yield: 46% (126 mg) (petroleum ether/EtOAc = 25/1), yellow solid, mp: 61–62 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 1.9 Hz, 1H), 7.85 – 7.77 (m, 3H), 7.55 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.53 – 7.49 (m, 2H), 6.28 (s, 1H), 2.26 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 169.9, 133.4, 133.1, 130.0, 129.0, 127.8, 127.2, 127.1, 126.9, 81.9, 26.3, 20.8. HRMS (ESI): calcd. for $C_{15}H_{14}NaO_3S$ ([M+Na]$^+$): 297.0556, found 297.0557.

*1-(Benzylthio)-2-oxopropyl acetate (**1i**).* Yield: 57% (136 mg) (petroleum ether/EtOAc = 30/1), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 5H), 5.92 (s, 1H), 3.89 (d, *J* = 13.1 Hz, 1H), 3.75 (d, *J* = 13.1 Hz, 1H), 2.19 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 170.1, 136.7, 129.2, 128.7, 127.6, 79.2, 34.3, 25.9, 20.6. HRMS (ESI): calcd. for $C_{12}H_{14}NaO_3S$ ([M+Na]$^+$): 261.0556, found 261.0560.

*3,3-Dimethyl-2-oxo-1-(phenylthio)butyl acetate (**1j**).* Yield: 61% (162 mg) (petroleum ether/EtOAc = 30/1), white solid, mp: 68–69 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.36 – 7.31 (m, 3H), 6.48 (s, 1H), 2.15 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.7, 170.2, 133.4, 130.9, 129.2, 129.1, 78.6, 43.4, 27.4, 20.8. HRMS (ESI): calcd. for $C_{14}H_{18}NaO_3S$ ([M+Na]$^+$): 289.0869, found 289.0870.

*2-Oxo-4-phenyl-1-(phenylthio)butyl acetate (**1k**).* Yield: 69% (217 mg) (petroleum ether/EtOAc = 30/1), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.37 – 7.23 (m, 5H), 7.23 – 7.16 (m, 1H), 7.14 – 7.11 (m, 2H), 6.18 (s, 1H), 3.11 – 2.90 (m, 1H), 2.87 – 2.71 (m, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 169.9, 140.6, 133.9, 130.0, 129.4, 129.3, 128.6, 128.5, 126.4, 81.6, 40.6, 29.5, 20.9.The spectral data match those previously reported.

*2-Oxo-2-phenyl-1-(phenylthio)ethyl acetate (**1l**).* Yield: 62% (178 mg) (petroleum ether/EtOAc = 25/1), white solid, mp: 65–66 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.91 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.37 – 7.33 (m, 1H), 7.32 – 7.27 (m, 2H), 7.05 (s, 1H), 2.23 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.0, 170.2, 134.4, 134.2, 133.8, 129.8, 129.5, 129.3, 128.9, 128.8, 79.2, 21.0. The spectral data match those previously reported.

*2-Oxo-1-(phenylthio)propyl benzoate (**1m**).* Yield: 75% (215 mg) (petroleum ether/EtOAc = 15/1), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.06 (m, 2H), 7.61 – 7.50 (m, 3H), 7.48 – 7.42 (m, 2H), 7.36 – 7.27 (m, 3H), 6.44 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 165.3, 133.9, 133.7, 130.0, 129.8, 129.3, 129.3, 128.9, 128.6, 82.3, 26.4. The spectral data match those previously reported.

*2-Oxo-1-(phenylthio)propyl 4-nitrobenzoate (**1n**).* Yield: 61% (162 mg) (petroleum ether/EtOAc = 15/1), yellow solid, mp: 85–86 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.30 (m, 2H), 8.28 – 8.24 (m, 2H), 7.54 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.41 – 7.33 (m, 3H), 6.46 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 163.7, 151.1, 134.4, 134.0, 131.2, 129.7, 129.6, 129.4, 123.9, 83.1, 26.5. The spectral data match those previously reported.

*2-Oxo-1-(phenylthio)propyl 4-methoxybenzoate (**1o**).* Yield: 52% (80 mg) (petroleum ether/EtOAc = 15/1), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 7.98 (m, 2H), 7.62 – 7.48 (m, 2H), 7.43 – 7.30 (m, 3H), 7.03 – 6.88 (m, 2H), 6.42 (s, 1H), 3.87 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 165.1, 164.1, 134.0, 132.2, 130.1, 129.4, 129.3, 121.3, 114.0, 82.1, 55.6, 26.6. The spectral data match those previously reported.

General Procedure for Preparation of Products 3. To a dried 10 mL reaction tube were added catalyst (20 mol %), α-acyloxy -β -ketosulfide**1** (0.3 mmol), MBH carbonate **2** (0.33 mmol, 1.1 equiv.),[20] and solvent (1.5 mL) under a N_2 atmosphere. The reaction was monitored by TLC. Upon completion, the reaction mixture was poured into EtOAc (10 mL), washed with saturated NH_4Cl, and the aqueous layer was extracted with EtOAc (2×10 mL). The combined organic extract was washed with saturated brine (2×10 mL), then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude mixture was purified by column chromatography (silica gel, EtOAc/Petroleum ether (60-90 °C)) to provide the desired products **3**.

*Methyl 4-acetoxy-4-methyl-2-methylene-5-oxo-5-(phenylthio)pentanoate (**3aa**).* Yield: 95% (92 mg) (petroleum ether/EtOAc = 15/1), colorless oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (brs, 5H), 6.35 (d, *J* = 1.3 Hz, 1H), 5.69 (d, *J* = 1.3 Hz, 1H), 3.75 (s, 3H), 3.17 (d, *J* = 14.2 Hz, 1H), 3.04 (d, *J* = 14.2 Hz, 1H), 2.10 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.6, 169.6, 167.5, 135.0, 134.8, 130.2, 129.6, 129.3, 127.0, 86.3, 52.2, 38.2, 22.2, 21.6. HRMS (ESI): calcd. for $C_{16}H_{19}O_5S$ ([M+H]$^+$): 323.0948, found 323.0946.

*Ethyl 4-acetoxy-4-methyl-2-methylene-5-oxo-5-(phenylthio)pentanoate (**3ab**).* Yield: 94% (95 mg) (petroleum ether/EtOAc = 15/1), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (brs, 5H), 6.35 (d, *J* = 1.4 Hz, 1H), 5.68 (d, *J* = 1.4 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.17 (d, *J* = 14.2 Hz, 1H), 3.03 (d, *J* = 14.1 Hz, 1H), 2.10 (s, 3H), 1.66 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz) δ 198.6, 169.5, 167.0, 135.1, 135.0, 129.9, 129.5, 129.2, 126.9, 86.3, 61.1, 38.1, 22.1, 21.6, 14.2. HRMS (ESI): calcd. for $C_{17}H_{21}O_5S$ ([M+H]$^+$): 337.1104, found 337.1107.

*Tert-butyl 4-acetoxy-4-methyl-2-methylene-5-oxo-5-(phenylthio)pentanoate (**3ac**).* Yield: 71% (78 mg) (petroleum ether/EtOAc = 15/1), colorless oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (brs, 5H), 6.25 (s, 1H), 5.61 (s, 1H), 3.13 (d, *J* = 14.1 Hz, 1H), 2.99 (d, *J* = 14.1 Hz, 1H), 2.10 (s, 3H), 1.65 (s, 3H), 1.49 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.6, 169.6, 166.2, 136.4, 135.1, 129.5, 129.2, 129.1, 127.1, 86.4, 81.0, 38.0, 28.1, 22.1, 21.7. HRMS (ESI): calcd. for $C_{19}H_{25}O_5S$ ([M+H]$^+$): 365.1417, found 365.1413.

*4-Cyano-2-methyl-1-oxo-1-(phenylthio)pent-4-en-2-yl acetate (**3ad**).* Yield: 92% (80 mg) (petroleum ether/EtOAc = 20/1), white solid, mp: 63–64 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (brs, 5H), 6.08 (s, 1H), 5.83(s, 1H), 3.18 (d, *J* = 14.5 Hz, 1H), 2.92 (d, *J* = 14.5 Hz, 1H), 2.21 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 169.9, 136.3, 135.0, 129.8, 129.4, 126.4, 118.5, 117.1, 85.6, 40.7, 22.9, 21.6. HRMS (ESI): calcd. for $C_{15}H_{16}NO_3S$ ([M+H]$^+$): 290.0845, found 290.0843.

*Methyl 4-acetoxy-4-methyl-2-methylene-5-oxo-5-(p-tolylthio)pentanoate (**3ae**).* Yield: 93% (94 mg) (petroleum ether/EtOAc = 15/1), colorless oil. ^{1}H NMR (500 MHz,

$CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.22 – 7.20 (m, 2H), 6.34 (d, *J* = 1.3 Hz, 1H), 5.69 (d, *J* = 1.3 Hz, 1H), 3.75 (s, 3H), 3.15 (d, *J* = 14.2 Hz, 1H), 3.03 (d, *J* = 14.2 Hz, 1H), 2.37 (s, 3H), 2.10 (s, 3H), 1.65 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0, 169.6, 167.5, 139.9, 135.0, 134.9, 130.2, 130.1, 123.4, 86.4, 52.2, 38.2, 22.3, 21.7, 21.4.HRMS (ESI): calcd. for $C_{17}H_{21}O_5S$ ($[M+H]^+$): 337.1104, found 337.1105.

*Methyl 4-acetoxy-5-((4-methoxyphenyl)thio)-4-methyl-2-methylene-5-oxopentanoate (**3af**).* Yield: 95% (100 mg) (petroleum ether/EtOAc = 15/1), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.37 – 7.27 (m, 2H), 6.99 – 6.87 (m, 2H), 6.34 (d, *J* = 1.4 Hz, 1H), 5.69 (d, *J* = 1.4 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 3.16 (d, *J* = 14.2 Hz, 1H), 3.03 (d, *J* = 14.3 Hz, 1H), 2.10 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.5, 169.6, 167.5, 160.9, 136.6, 134.9, 130.2, 117.5, 115.0, 86.3, 55.5, 52.2, 38.2, 22.3, 21.7. HRMS (ESI): calcd. for $C_{17}H_{21}O_6S$ ($[M+H]^+$): 353.1053, found 353.1046.

*Methyl 4-acetoxy-5-((4-bromophenyl)thio)-4-methyl-2-methylene-5-oxopentanoate (**3ag**).* Yield: 81% (98 mg) (petroleum ether/EtOAc = 15/1), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.46 (m, 2H), 7.31 – 7.22 (m, 2H), 6.35 (d, *J* = 1.2 Hz, 1H), 5.69 (d, *J* = 1.2 Hz, 1H), 3.75 (s, 3H), 3.16 (d, *J* = 14.2 Hz, 1H), 3.02 (d, *J* = 14.2 Hz, 1H), 2.10 (s, 3H), 1.65 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$)δ 198.1, 169.6, 167.4, 136.5, 134.7, 132.5, 130.4, 126.2, 124.4, 86.3, 52.3, 38.3, 22.2, 21.6. HRMS (ESI): calcd. for $C_{16}H_{18}BrO_5S$ ($[M+H]^+$): 401.0053, found 401.0057.

*Methyl 4-acetoxy-5-((4-chlorophenyl)thio)-4-methyl-2-methylene-5-oxopentanoate (**3ah**).* Yield: 78% (83 mg) (petroleum ether/EtOAc = 15/1), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 4H), 6.35 (d, *J* = 1.3 Hz, 1H), 5.69 (d, *J* = 1.2 Hz, 1H), 3.75 (s, 3H), 3.16 (d, *J* = 14.2 Hz, 1H), 3.02 (d, *J* = 14.2 Hz, 1H), 2.10 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 169.6, 167.4, 136.3, 136.0, 134.7, 130.3, 129.5, 125.5, 86.2, 52.2, 38.2, 22.2, 21.6. HRMS (ESI): calcd. for $C_{16}H_{18}ClO_5S$ ($[M+H]^+$): 357.0558, found 357.0551.

*Methyl 4-acetoxy-5-((4-fluorophenyl)thio)-4-methyl-2-methylene-5-oxopentanoate (**3ai**).* Yield: 86% (88 mg) (petroleum ether/EtOAc = 15/1), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.31 (m, 2H), 7.18 – 6.96 (m, 2H), 6.35 (d, *J* = 1.4 Hz, 1H), 5.69 (d, *J* = 1.4 Hz, 1H), 3.75 (s, 3H), 3.16 (d, *J* = 14.2 Hz, 1H), 3.02 (d, *J* = 14.2 Hz, 1H), 2.10 (s, 3H), 1.65 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 198.7, 169.6, 167.4, 163.7 (d, *J* = 250.0 Hz), 137.1 (d, *J* = 8.6 Hz), 134.7, 130.3, 122.3, 116.6 (d, *J* = 22.0 Hz), 86.2, 52.2, 38.2, 22.2, 21.6. HRMS (ESI): calcd. for $C_{16}H_{17}FNaO_5S$ ($[M+Na]^+$): 363.0673, found 363.0670.

*Methyl 4-acetoxy-4-methyl-2-methylene-5-oxo-5-(o-tolylthio)pentanoate (**3aj**).* Yield: 82% (83 mg) (petroleum ether/EtOAc = 15/1), white solid, mp: 54–55 °C.. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.20 (td, *J* = 7.3, 2.0 Hz, 1H), 6.34 (d, *J* = 1.4 Hz, 1H), 5.69 (d, *J* = 1.4 Hz, 1H), 3.75 (s, 3H), 3.20 (d, *J* = 14.2 Hz, 1H), 3.03 (d, *J* = 14.2 Hz, 1H), 2.33 (s, 3H), 2.10 (s, 3H), 1.66 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1, 169.6, 167.5, 143.0, 136.4, 134.9, 130.9, 130.3, 130.2, 126.7, 126.2, 86.3, 52.2, 38.0, 22.3, 21.6, 20.7. HRMS (ESI): calcd. for $C_{17}H_{21}O_5S$ ($[M+H]^+$): 337.1104, found 337.1102.

*Methyl 4-acetoxy-4-methyl-2-methylene-5-(naphthalen-2-ylthio)-5-oxopentanoate (**3ak**).* Yield: 91% (102 mg) (petroleum ether/EtOAc = 15/1), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.88 – 7.78 (m, 3H), 7.54 – 7.46 (m, 2H), 7.43 (d, *J* = 8.5 Hz, 1H), 6.36 (d, *J* = 1.4 Hz, 1H), 5.71 (d, *J* = 1.4 Hz, 1H), 3.75 (s, 3H), 3.21 (d, *J* = 14.2 Hz, 1H), 3.06 (d, *J* = 14.2 Hz, 1H), 2.12 (s, 3H), 1.69 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8, 169.6, 167.5, 135.0, 134.8, 133.7, 133.5, 131.3, 130.3, 128.9, 128.0, 127.9, 127.2, 126.6, 124.3, 86.3, 52.2, 38.2, 22.3, 21.7. HRMS (ESI): calcd. for $C_{20}H_{21}O_5S$ ($[M+H]^+$): 373.1104, found 373.1101.

*Methyl 4-acetoxy-5-(benzylthio)-4-methyl-2-methylene-5-oxopentanoate (**3al**).* Yield: 85% (86 mg) (petroleum ether/EtOAc = 20/1), colorless oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 4H), 7.26 – 7.22 (m, 1H), 6.26 (d, *J* = 1.2 Hz, 2H), 5.55 (d, *J* = 1.3 Hz, 1H), 4.11 (s, 2H), 3.72 (s, 3H), 3.10 (d, *J* = 14.1 Hz, 1H), 2.98 (d, *J* = 14.2 Hz, 1H), 2.04 (s, 3H), 1.60 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 199.9, 169.5, 167.4, 137.0, 134.7, 130.1, 129.0, 128.7, 127.4, 86.1, 52.1, 38.4, 33.3, 22.2, 21.6. HRMS (ESI): calcd. for $C_{17}H_{20}NaO_5S$ ($[M+Na]^+$): 359.0924, found 359.0923.

*Methyl 4-acetoxy-5,5-dimethyl-2-methylene-4-((phenylthio)carbonyl)hexanoate (**3am**).* Yield: 33% (36 mg) (petroleum ether/EtOAc = 20/1), colorless oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 3H), 7.41 – 7.36 (m, 2H), 6.26 (s, 1H), 5.86 (s, 1H), 3.75 (s, 3H), 3.74 (dd, *J* = 16.4, 1.2 Hz, 1H), 3.28 (dt, *J* = 16.5, 1.7 Hz, 1H), 2.20 (s, 3H), 1.14 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.4, 169.1, 167.8, 136.7, 134.9, 129.7, 129.3, 128.0, 125.9, 95.4, 52.2, 40.1, 32.0, 26.7, 22.3. HRMS (ESI): calcd. for $C_{19}H_{24}NaO_5S$ ($[M+Na]^+$): 387.1237, found 387.1234.

*Methyl 4-acetoxy-2-methylene-6-phenyl-4-((phenylthio)carbonyl)hexanoate (**3an**).* Yield: 76% (94 mg) (petroleum ether/EtOAc = 20/1), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 5H), 7.29 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 6.38 – 6.32 (d, *J* = 1.4 Hz, 1H), 5.66 (d, *J* = 1.4 Hz, 1H), 3.73 (s, 3H), 3.34 (d, *J* = 14.4 Hz, 1H), 3.16 (d, *J* = 14.4 Hz, 1H), 2.69 – 2.48 (m, 3H), 2.42 – 2.32 (m, 1H), 2.12 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.1, 169.3, 167.4, 140.8, 135.1, 135.0, 130.0, 129.7, 129.4, 128.6, 127.3, 126.3, 90.1, 52.2, 37.4, 36.3, 29.8, 21.8. HRMS (ESI): calcd. for $C_{23}H_{25}O_5S$ ($[M+H]^+$): 413.1417, found 413.1412.

*Methyl 4-acetoxy-2-methylene-5-oxo-4-phenyl-5-(phenylthio)pentanoate (**3ao**).* Yield: 91% (105 mg) (petroleum ether/EtOAc = 15/1), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.41 – 7.35 (m, 5H), 7.35 – 7.29 (m, 3H), 6.08 (d, *J* = 1.3 Hz, 1H), 5.21 (d, *J* = 1.3 Hz, 1H), 3.84 (d, *J* = 14.7 Hz, 1H), 3.51 (s, 3H), 3.39 (d, *J* = 14.7 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 169.4, 167.4, 136.7, 135.0, 134.9, 123.0, 129.6, 129.3, 128.7, 128.5, 127.0, 125.4, 89.0, 51.9, 36.7, 21.8. HRMS (ESI): calcd. for $C_{21}H_{21}O_5S$ ($[M+H]^+$): 385.1104, found 385.1095.

*4-(Methoxycarbonyl)-2-methyl-1-oxo-1-(phenylthio)pent-4-en-2-yl benzoate (**3ap**).* Yield: 88% (101 mg) (petroleum ether/EtOAc = 15/1), colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 2H), 7.62 – 7.55 (m, 1H), 7.50 – 7.37 (m, 7H), 6.35 (d, *J* = 1.3 Hz, 1H), 5.72 (d, *J* = 1.3 Hz, 1H), 3.59 (s, 3H), 3.31 (d, *J* = 14.3 Hz, 1H), 3.27 (d, *J* = 14.3 Hz, 1H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

199.0, 167.4, 165.1, 135.0, 134.9, 133.4, 130.3, 130.2, 129.9, 129.6, 129.3, 128.6, 127.0, 87.5, 52.1, 38.4, 22.7. HRMS (ESI): calcd. for $C_{21}H_{21}O_5S$ ([M+H]$^+$): 385.1104, found 385.1102.

*4-(Methoxycarbonyl)-2-methyl-1-oxo-1-(phenylthio)pent-4-en-2-yl 4-nitrobenzoate (**3aq**).* Yield: 82% (104 mg) (petroleum ether/EtOAc = 15/1), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.29 (m, 2H), 8.28 – 8.22 (m, 2H), 7.43 (brs, 5H), 6.37 (d, *J* = 1.3 Hz, 1H), 5.73 (d, *J* = 1.2 Hz, 1H), 3.63 (s, 3H), 3.38 – 3.21 (m, 2H), 1.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.3, 167.3, 163.2, 150.8, 135.7, 135.0, 134.7, 131.1, 130.6, 129.9, 129.4, 126.5, 123.7, 88.5, 52.3, 38.6, 22.7. HRMS (ESI): calcd. for $C_{21}H_{20}NO_7S$ ([M+H]$^+$): 430.0955, found 430.0950.

*4-(Methoxycarbonyl)-2-methyl-1-oxo-1-(phenylthio)pent-4-en-2-yl 4-methoxybenzoate (**3ar**).* Yield: 83% (86 mg) (petroleum ether/EtOAc = 15/1), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 7.98 (m, 2H), 7.47 – 7.33 (m, 5H), 7.01 – 6.85 (m, 2H), 6.34 (d, *J* = 1.4 Hz, 1H), 5.71 (d, *J* = 1.3 Hz, 1H), 3.86 (s, 3H), 3.60 (s, 3H), 3.36 – 3.16 (m, 2H), 1.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.2, 167.5, 164.8, 163.8, 135.0, 132.1, 130.2, 129.6, 129.3, 127.2, 122.6, 113.9, 87.2, 55.6, 52.2, 38.4, 22.8. HRMS (ESI): calcd. for $C_{22}H_{23}O_6S$ ([M+H]$^+$): 415.1210, found 415.1216.

*Methyl 4-acetoxy-4-methyl-2-methylene-5-oxo-3-phenyl-5-(phenylthio)pentanoate (**3ba**).* Yield: 88% (105 mg) (petroleum ether/EtOAc = 10/1), colorless oil(dr =1.1/1, inseparable mixture). The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.42 (s, 3H), 7.40 – 7.30 (m, 5H), 6.55 (s, 1H), 6.30 (s, 1H), 4.70 (s, 1H), 3.70 (s, 3H), 2.18 (s, 3H), 1.84 (s, 3H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$)δ 7.48 – 7.45 (m, 2H), 7.42 (s, 2H), 7.38 – 7.35 (m, 4H), 7.26 – 7.21 (m, 2H), 6.61 (s, 1H), 6.29 (s, 1H), 4.73 (s, 1H), 3.75 (s, 3H), 2.21 (s, 3H), 1.92 (s, 3H). The mixture: ^{13}C NMR (125 MHz, $CDCl_3$)δ 197.0, 196.5, 169.1, 168.9, 167.2, 167.1, 138.3, 138.0, 137.4, 136.9, 135.0, 134.8, 130.3, 130.2, 129.6, 129.5, 129.2, 129.1, 128.9, 128.4, 128.1, 127.6, 127.6, 126.7, 126.7, 89.0, 88.3, 53.1, 52.6, 52.4, 52.2, 22.5, 21.7, 21.6, 21.5. HRMS (ESI): calcd. for $C_{22}H_{23}O_5S$ ([M+H]$^+$): 399.1261, found 399.1265.

*Ethyl 4-acetoxy-4-methyl-2-methylene-5-oxo-3-phenyl-5-(phenylthio)pentanoate (**3bb**).* Yield: 79% (98 mg) (petroleum ether/EtOAc = 10/1), colorless oil (dr =1.1/1, inseparable mixture). The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.42 – 7.40 (m, 2H), 7.40 – 7.27 (m, 6H), 6.60 (s, 1H), 6.25 (s, 1H), 4.71 (s, 1H), 4.26 – 4.10 (m, 2H), 2.21 (s, 3H), 1.90 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$)δ 7.50 – 7.46 (m, 2H), 7.42 – 7.40 (m, 2H), 7.38 – 7.28 (m, 4H), 7.24 – 7.20 (m, 2H), 6.54 (s, 1H), 6.28 (s, 1H), 4.68 (s, 1H), 4.26 – 4.10 (m, 2H), 2.18 (s, 3H), 1.83 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). The mixture: ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.2, 196.6, 169.2, 169.0, 166.8, 138.6, 138.3, 137.6, 137.1, 135.1, 134.9, 130.5, 130.4, 129.6, 129.5, 129.2, 129.2, 128.7, 128.4, 128.2, 127.9, 127.6, 127.6, 126.9, 126.8, 89.1, 88.5, 61.4, 61.2, 53.2, 52.7, 22.6, 21.8, 21.7, 21.6, 14.2. HRMS (ESI): calcd. for $C_{23}H_{25}O_5S$ ([M+H]$^+$): 413.1417, found 413.1412.

*Tert-butyl 4-acetoxy-4-methyl-2-methylene-5-oxo-3-phenyl-5-(phenylthio)pentanoate (**3bc**).* Yield: 60% (79 mg) (petroleum ether/EtOAc = 20/1), colorless oil (dr =1.1/1, inseparable mixture).The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 4H), 7.35 – 7.25 (m, 4H), 7.21 – 7.17 (m, 2H), 6.47 (d, *J* = 0.8 Hz, 1H), 6.09 (s, 1H), 4.64 (s, 1H), 2.17 (s, 3H), 1.85 (s, 3H), 1.41 (s, 9H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 5H), 7.35 – 7.26 (m, 5H), 6.42 (d, *J* = 1.0 Hz, 1H), 6.17 (s, 1H), 4.62 (s, 1H), 2.14 (s, 3H), 1.79 (s, 3H), 1.38 (s, 9H). The mixture: ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.3, 196.5, 169.3, 169.1, 166.0, 166.0, 139.8, 139.5, 137.9, 137.5, 135.2, 135.0, 130.5, 130.4, 129.6, 129.5, 129.2, 128.5, 128.4, 128.1, 128.0, 127.5, 127.2, 127.0, 126.9, 89.2, 88.5, 81.5, 81.1, 53.2, 52.5, 28.0, 22.4, 21.9, 21.8, 21.4. HRMS (ESI): calcd. for $C_{25}H_{29}O_5S$ ([M+H]$^+$): 441.1730, found 441.1727.

*4-Cyano-2-methyl-1-oxo-3-phenyl-1-(phenylthio)pent-4-en-2-yl acetate (**3bd**).* Yield: 86% (94 mg) (petroleum ether/EtOAc = 20/1), colorless oil (dr =1.3/1, inseparable mixture). The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$)δ 7.57 – 7.51 (m, 2H), 7.43 – 7.28 (m, 6H), 7.09 – 7.05 (m, 2H), 6.09 (s, 1H), 6.01 (s, 1H), 3.84 (s, 1H), 2.23 (s, 3H), 1.95 (s, 3H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.44 – 7.27 (m, 8H), 5.97 (s, 1H), 5.88 (s, 1H), 3.85 (s, 1H), 2.25 (s, 3H), 1.72 (s, 3H). The mixture: ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 196.6, 169.3, 169.3, 136.2, 135.4, 135.0, 134.9, 134.8, 134.8, 130.8, 129.9, 129.7, 129.6, 129.4, 129.2, 129.1, 128.7, 128.7, 128.6, 127.7, 126.2, 122.2, 121.4, 118.4, 118.3, 88.2, 87.6, 59.4, 58.7, 21.9, 21.5, 21.5, 21.0. HRMS (ESI): calcd. for $C_{21}H_{20}NO_3S$ ([M+H]$^+$): 366.1158, found 366.1161.

*Methyl 4-acetoxy-4-methyl-2-methylene-5-oxo-3-phenyl-5-(o-tolylthio)pentanoate (**3be**).* Yield: 92% (127 mg) (petroleum ether/EtOAc = 15/1), colorless oil (dr =1.2/1, inseparable mixture). The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 6H), 7.31 – 7.23 (m, 4H), 7.23 – 7.15 (m, 5H), 6.58 (s, 1H), 6.21 (s, 1H), 5.55 (s, 1H), 3.72 (s, 3H), 2.36 (s, 3H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.46 – 7.37 (m, 7H), 7.37 – 7.32 (m, 3H), 7.29 – 7.24 (m, 3H), 6.36 (s, 1H), 5.68 (s, 1H), 5.62 (s, 1H), 3.64 (s, 3H), 2.23 (s, 3H). The mixture: ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 196.5, 168.9, 168.9, 167.2, 167.1, 138.9, 138.9, 137.9, 137.0, 135.6, 135.4, 135.0, 135.0, 131.1, 130.6, 129.6, 129.4, 129.2, 129.1, 128.8, 128.4, 128.4, 128.1, 128.0, 127.7, 127.6, 127.5, 127.4, 127.2, 127.1, 127.1, 127.0, 91.4, 91.0, 52.4, 52.2, 52.1, 50.7, 21.7, 21.6. HRMS (ESI): calcd. for $C_{23}H_{25}O_5S$ ([M+H]$^+$): 413.1417, found 413.1411.

*Methyl 4-acetoxy-4-methyl-2-methylene-5-oxo-5-(phenylthio)-3-(p-tolyl)pentanoate (**3bf**).* Yield: 68% (84 mg) (petroleum ether/EtOAc = 15/1), colorless oil (dr =1.1/1, inseparable mixture). The major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 6H), 7.23 – 7.18 (m, 1H), 7.15 – 7.07 (m, 2H), 6.54 (s, 1H), 6.23 (s, 1H), 4.65 (s, 1H), 3.70 (s, 3H), 2.32 (s, 3H), 2.15 (s, 3H), , 1.85 (s, 3H).The minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 6H), 7.23 – 7.18 (m, 1H), 7.15 – 7.07 (m, 2H), 6.47 (s, 1H), 6.21 (s, 1H), 4.60 (s, 1H), 3.65 (s, 3H), 2.30 (s, 3H), 2.12 (s, 3H), 1.78 (s, 3H). The mixture:^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 196.6, 169.2, 168.9, 167.3, 167.2, 138.4, 138.2, 137.2, 137.2, 135.0, 134.9, 134.4, 133.9, 130.2, 130.1, 129.6, 129.4, 129.2, 129.1, 128.9, 128.7, 127.9, 126.8, 89.1, 88.5, 52.7,

52.4, 52.3, 52.2, 22.5, 21.7, 21.6, 21.5, 21.1, 21.1. HRMS (ESI): calcd. for $C_{23}H_{25}O_5S$ ([M+H]$^+$): 413.1417, found 413.1410.

*Methyl 4-acetoxy-3-(4-bromophenyl)-4-methyl-2-methylene-5-oxo-5-(phenylthio)pentanoate (**3bg**).* Yield: 90% (128 mg) (petroleum ether/EtOAc = 15/1), colorless oil (dr =1.4/1, inseparable mixture). The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) 7.44 – 7.40 (m, 2H), 7.40 – 7.34 (m, 3H), 7.29 – 7.25 (m, 2H), 7.22 – 7.18 (m, 2H), 6.56 (s, 1H), 6.21 (s, 1H), 4.62 (s, 1H), 3.72 (s, 3H), 2.16 (s, 3H), 1.86 (s, 3H), 1.78 (s, 3H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 2H), 7.40 – 7.34 (m, 5H), 7.33 – 7.30 (m, 2H), 6.49 (s, 1H), 6.22 (s, 1H), 4.60 (s, 1H), 3.67 (s, 3H), 2.13 (s, 3H), 1.78 (s, 3H). The mixture: ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.9, 196.4, 169.0, 168.8, 167.0, 167.0, 138.0, 137.6, 136.5, 136.1, 135.0, 134.9, 132.1, 131.9, 131.6, 131.3, 129.7, 129.7, 129.3, 129.1, 128.4, 126.6, 126.5, 121.9, 121.9, 88.8, 88.2, 52.6, 52.4, 52.3, 22.7, 21.8, 21.7, 21.6. HRMS (ESI): calcd. for $C_{22}H_{22}BrO_5S$ ([M+H]$^+$): 477.0366, found 477.0368.

*Methyl 4-acetoxy-2-methylene-5-oxo-3,4-diphenyl-5-(phenylthio)pentanoate (**3bh**).* Yield: 92% (127 mg) (petroleum ether/EtOAc = 20/1), colorless oil (dr =1.2/1, inseparable mixture). The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 6H), 7.21 – 7.13 (m, 4H), 7.13 – 7.05 (m, 5H), 6.48 (s, 1H), 6.11 (s, 1H), 5.45 (s, 1H), 3.62 (s, 3H), 2.26 (s, 3H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.36 – 7.27 (m, 7H), 7.27 – 7.22 (m, 3H), 7.19 – 7.14 (m, 3H), 6.26 (s, 1H), 5.58 (s, 1H), 5.52 (s, 1H), 3.54 (s, 3H), 2.13 (s, 3H). The mixture: ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 196.5, 169.0, 168.9, 167.2, 167.1, 138.9, 138.9, 137.9, 137.0, 135.6, 135.4, 135.0, 135.0, 131.1, 130.6, 129.6, 129.4, 129.2, 129.1, 128.8, 128.4, 128.4, 128.1, 128.0, 127.7, 127.6, 127.5, 127.4, 127.2, 127.1, 127.1, 127.0, 91.4, 91.0, 52.4, 52.2, 52.1, 50.7, 21.7, 21.6. HRMS (ESI): calcd. for $C_{27}H_{25}O_5S$ ([M+H]$^+$): 461.1417, found 461.1407.

*4-(Methoxycarbonyl)-2-methyl-1-oxo-3-phenyl-1-(phenylthio)pent-4-en-2-yl benzoate (**3bi**).* Yield: 81% (113 mg) (petroleum ether/EtOAc = 15/1), colorless oil (dr =1.1/1, inseparable mixture). The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.04 (m, 2H), 7.61 – 7.55 (m, 1H), 7.54 – 7.44 (m, 4H), 7.40 – 7.31 (m, 5H), 7.31 – 7.20 (m, 3H), 6.57 (s, 1H), 6.31 (s, 1H), 4.84 (s, 1H), 3.66 (s, 3H), 1.96 (s, 3H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.04 (m, 2H), 7.61 – 7.55 (m, 1H), 7.54 – 7.44 (m, 4H), 7.40 – 7.31 (m, 6H), 7.31 – 7.20 (m, 2H), 6.60 (s, 1H), 6.28 (s, 1H), 4.87 (s, 1H), 3.69 (s, 3H), 2.00 (s, 3H). The mixture: ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.5, 196.7, 167.4, 167.2, 165.1, 164.8, 138.3, 137.3, 136.8, 135.1, 134.9, 133.5, 133.4, 130.6, 130.5, 130.4, 129.8, 129.8, 129.6, 129.5, 129.2, 129.2, 128.7, 128.7, 128.5, 128.3, 128.3, 127.8, 127.7, 126.9, 89.8, 89.0, 53.8, 53.2, 52.5, 52.3, 22.6, 22.0. HRMS (ESI): calcd. for $C_{27}H_{25}O_5S$ ([M+H]$^+$): 461.1417, found 461.1423.

*Methyl 4-acetoxy-2-methylene-5-oxo-4-(phenylthio)hexanoate (**4a**).* Yield: 56% (36 mg) (petroleum ether/EtOAc = 10/1), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.41 – 7.37 (m, 1H), 7.36 – 7.31 (m, 2H), 6.37 (d, *J* = 1.3 Hz, 1H), 5.75 (d, *J* = 1.2 Hz, 1H), 3.76 (s, 3H), 3.50 (d, *J* = 15.0 Hz, 1H), 3.19 (d, *J* = 15.1 Hz, 1H), 2.07 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 169.5, 167.3, 136.6, 134.2, 130.4, 129.9, 129.0, 128.9, 92.8, 52.1, 35.5, 25.4, 21.3. HRMS (ESI): calcd. for $C_{16}H_{19}O_5S$ ([M+H]$^+$): 323.0948, found 323.0939.

*Methyl (Z)-4-acetoxy-2-benzylidene-4-methyl-5-oxo-5-(phenylthio)pentanoate(**5a**).* (petroleum ether/EtOAc = 20/1), Colorless oil (*E/Z=2.4/1*, inseparable mixture). The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.47 – 7.43 (m, 1H), 7.42 – 7.36 (m, 8H), 7.34 – 7.24 (m, 2H), 3.79 (s, 3H), 3.53 (d, *J* = 14.4 Hz, 1H), 3.34 (d, *J* = 14.4 Hz, 1H), 1.87 (s, 3H), 1.54 (s, 3H).The minor isomer: 1H NMR (500 MHz, CDCl3) δ 7.47 – 7.43 (m, 3H), 7.42 – 7.36 (m, 3H), 7.34 – 7.24 (m, 2H), 7.24 – 7.20 (m, 2H), 6.75 (s, 1H), 3.33 (d, *J* = 14.1 Hz, 1H), 3.03 (d, *J* = 14.2 Hz, 1H), 2.10 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.7, 198.4, 169.6, 169.1, 143.1, 139.0, 135.7, 135.5, 135.0, 135.1, 129.6, 129.5, 129.3, 129.2, 128.8, 128.8, 128.3, 128.2, 127.6, 127.0, 126.9, 86.7, 86.4, 52.3, 51.8, 42.6, 33.3, 22.1, 21.9, 21.6, 21.4. HRMS (ESI): calcd. for $C_{22}H_{23}O_5S$ ([M+H]$^+$): 399.1261, found 399.1263.

Procedure for Preparation of Products 3aa on a larger scale. To a dried 10 mL reaction tube were added DMAP (20 mol %, 85 mg), *α*-acyloxy -*β* -ketosulfide1 (3.5 mmol, 784 mg), MBH carbonate **2a** (3.85 mmol, 831 mg), and CH_3CN (17.5 mL) under a N_2 atmosphere. The reaction was monitored by TLC. Upon completion, the reaction mixture was poured into EtOAc (80 mL), washed with saturated NH_4Cl, and the aqueous layer was extracted with EtOAc (2×40 mL). The combined organic extract was washed with saturated brine (2×50 mL), then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude mixture was purified by column chromatography (petroleum ether/EtOAc = 15/1) to provide the desired product **3aa** in 90% yield (1.01 g).

General Procedure for the Preparation of Products 6. To a dried reaction tube were added **3** (0.2 mmoL) and mediator (10 mol %) in THF (1 mL) under a N_2 atmosphere at 0 °C. The reaction was monitored by TLC. Upon completion, the reaction was quenched with saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with EtOAc (6 mL × 3), and the combined organic extract was washed with saturated brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether (60-90 °C)) to provide the desired products **6**.

*Methyl 1,4-dimethyl-3-oxo-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6aa**).* Yield: 92% (69%, 44 mg) (petroleum ether/EtOAc = 20/1), white solid, mp: 85–86 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.32 – 7.27 (m, 2H), 7.27 – 7.22 (m, 1H), 3.65 (d, *J* = 12.3 Hz, 1H), 3.49 (s, 3H), 2.92 (d, *J* = 12.2 Hz, 1H), 2.81 (d, *J* = 13.5 Hz, 1H), 1.96 (d, *J* = 13.5 Hz, 1H), 1.78 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 169.8, 134.1, 131.9, 129.2, 127.6, 112.1, 83.7, 62.1, 52.8, 41.2, 38.6, 15.1, 14.6.HRMS (ESI): calcd. for $C_{16}H_{19}O_5S$ ([M+H]$^+$): 323.0948, found 323.0944.

*Ethyl 1,4-dimethyl-3-oxo-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6ab**).* Yield: 92%

(65%, 44 mg) (petroleum ether/EtOAc = 20/1), colorless oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.32 – 7.27 (m, 2H), 7.27 – 7.22 (m, 1H), 4.02 -3.91 (m, 2H), 3.65 (d, *J* = 12.1 Hz, 1H), 2.93 (d, *J* = 12.1 Hz, 1H), 2.81 (d, *J* = 13.4 Hz, 1H), 1.94 (d, *J* = 13.4 Hz, 1H), 1.79 (s, 3H), 1.61 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 169.1, 134.4, 131.7, 129.1, 127.6, 112.1, 83.7, 62.1, 41.2, 38.5, 15.2, 14.6, 13.9.HRMS (ESI): calcd. for $C_{17}H_{21}O_5S$ ([M+H]$^+$): 337.1104, found 337.1097.

*Tert-butyl 1,4-dimethyl-3-oxo-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6ac**).* Yield: 90% (68%, 50 mg) (petroleum ether/EtOAc = 20/1), colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 3.60 (d, *J* = 11.5 Hz, 1H), 2.96 (d, *J* = 11.5 Hz, 1H), 2.72 (d, *J* = 13.3 Hz, 1H), 1.86 (d, *J* = 13.4 Hz, 1H), 1.79 (s, 3H), 1.59 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 168.3, 135.3, 130.8, 129.2, 127.2, 112.3, 83.8, 83.1, 62.5, 41.1, 38.5, 27.8, 14.7.HRMS (ESI): calcd. for $C_{19}H_{25}O_5S$ ([M+H]$^+$): 365.1417, found 365.1410.

*1,4-Dimethyl-3-oxo-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carbonitrile (**6ad**).* Yield: 86% (60%, 52 mg) (petroleum ether/EtOAc = 25/1), colorless oil (endo/exo = 1.2/1, inseparable mixture). The major isomer:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.37 – 7.26 (m, 3H), 3.26 (d, J = 13.5 Hz, 1H), 3.02 (d, J = 12.7 Hz, 1H), 2.43 (d, J = 13.7 Hz, 1H), 2.19 (d, J = 13.8 Hz, 1H), 1.81 (s, 3H), 1.61 (s, 3H).The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.37 – 7.26 (m, 3H), 3.36 (d, J = 12.8 Hz, 1H), 3.15 (d, J = 13.6 Hz, 1H), 2.43 (d, J = 13.7 Hz, 1H), 2.02 (d, J = 13.7 Hz, 1H), 1.94 (s, 3H), 1.62 (s, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 171.5, 133.9, 133.8, 131.9, 131.7, 129.5, 128.2, 128.1, 119.7, 118.3, 110.9, 110.7, 83.3, 82.7, 52.6, 51.0, 42.9, 41.7, 41.6, 38.6, 16.0, 15.1, 14.2, 14.1.HRMS (ESI): calcd. for $C_{15}H_{16}NO_3S$ ([M+H]$^+$): 290.0845, found 290.0851.

*Methyl 1,4-dimethyl-3-oxo-6-((p-tolylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6ae**).* Yield: 92% (78%, 52 mg) (petroleum ether/EtOAc = 20/1), white solid, mp: 83–84 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.63 (d, *J* = 12.3 Hz, 1H), 3.52 (s, 3H), 2.89 (d, *J* = 12.3 Hz, 1H), 2.82 (d, *J* = 13.4 Hz, 1H), 2.34 (s, 3H), 1.98 (d, *J* = 13.4 Hz, 1H), 1.79 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 169.9, 137.9, 132.5, 130.4, 129.9, 112.1, 83.7, 62.2, 52.8, 41.9, 38.5, 21.2, 15.1, 14.6. HRMS (ESI): calcd. for $C_{17}H_{21}O_5S$ ([M+H]$^+$): 337.1104, found 337.1106.

*Methyl 6-(((4-methoxyphenyl)thio)methyl)-1,4-dimethyl-3-oxo-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6af**).* Yield: 90% (54%, 44 mg) (petroleum ether/EtOAc = 20/1), colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 2H), 6.87 – 6.79 (m, 2H), 3.79 (s, 3H), 3.56 (d, *J* = 12.5 Hz, 1H), 3.49 (s, 3H), 2.81 (d, *J* = 12.5 Hz, 1H), 2.80 (d, *J* = 13.5 Hz, 1H), 1.95 (d, *J* = 13.4 Hz, 1H), 1.75 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 169.9, 159.9, 135.2, 124.1, 114.8, 112.2, 83.7, 62.3, 55.5, 52.8, 42.7, 38.5, 15.1, 14.6. HRMS (ESI): calcd. for $C_{17}H_{21}O_6S$ ([M+H]$^+$): 353.1053, found 353.1054.

*Methyl 6-(((4-bromophenyl)thio)methyl)-1,4-dimethyl-3-oxo-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6ag**).* Yield: 93% (78%, 62 mg) (petroleum ether/EtOAc = 15/1), white solid, mp: 91–92 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.30 – 7.25 (m, 2H), 3.63 (d, *J* = 12.2 Hz, 1H), 3.55 (s, 3H), 2.92 (d, *J* = 12.2 Hz, 1H), 2.82 (d, *J* = 13.5 Hz, 1H), 1.95 (d, *J* = 13.4 Hz, 1H), 1.80 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 169.8, 133.3, 132.3, 121.8, 112.0, 83.7, 62.1, 52.9, 41.3, 38.6, 15.1, 14.6.HRMS (ESI): calcd. for $C_{16}H_{18}BrO_5S$ ([M+H]$^+$): 401.0053, found 401.0052.

*Methyl 6-(((4-chlorophenyl)thio)methyl)-1,4-dimethyl-3-oxo-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6ah**).* Yield: 91% (67%, 48 mg)(petroleum ether/EtOAc = 15/1), white solid, mp: 95–96 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.30 – 7.25 (m, 2H), 3.61 (d, J = 12.2 Hz, 1H), 3.53 (s, 3H), 2.90 (d, J = 12.2 Hz, 1H), 2.80 (d, J = 13.4 Hz, 1H), 1.93 (d, J = 13.4 Hz, 1H), 1.78 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 169.8, 133.9, 133.2, 132.6, 129.3, 112.0, 83.7, 62.1, 52.9, 41.4, 38.6, 15.2, 14.6. HRMS (ESI): calcd. for $C_{16}H_{18}ClO_5S$ ([M+H]$^+$): 357.0558, found 357.0556.

*Methyl 6-(((4-fluorophenyl)thio)methyl)-1,4-dimethyl-3-oxo-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6ai**).* Yield: 83% (64%, 44 mg) (petroleum ether/EtOAc = 20/1), white solid, mp: 85–86°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.04 – 6.97 (m, 2H), 3.60 (d, *J* = 12.4 Hz, 1H), 3.51 (s, 3H), 2.86 (d, *J* = 12.4 Hz, 1H), 2.81 (d, *J* = 13.4 Hz, 1H), 1.94 (d, *J* = 13.4 Hz, 1H), 1.76 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 169.8, 162.7 (d, *J* = 248.5 Hz), 134.9 (d, *J* = 8.5 Hz), 129.0 (d, *J* = 3.6 Hz), 116.3 (d, *J* = 22.2 Hz), 112.1, 83.7, 62.2, 52.8, 42.2, 38.6, 15.1, 14.6. HRMS (ESI): calcd. for $C_{16}H_{18}FO_5S$ ([M+H]$^+$): 341.0853, found 341.0858.

*Methyl 1,4-dimethyl-3-oxo-6-((o-tolylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6aj**).* Yield: 93% (85%, 44 mg) (petroleum ether/EtOAc = 15/1), white solid, mp: 126 – 127°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 1H), 7.23 – 7.11 (m, 3H), 3.59 (d, *J* = 12.0 Hz, 1H), 3.49 (s, 3H), 2.84 (d, *J* = 12.0 Hz, 1H), 2.82 (d, *J* = 13.4 Hz, 1H), 2.41 (s, 3H), 2.00 (d, *J* = 13.4 Hz, 1H), 1.78 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 169.8, 140.1, 133.2, 132.1, 130.5, 127.8, 126.7, 112.1, 83.7, 62.0, 52.8, 40.4, 38.5, 20.7, 15.1, 14.6. HRMS (ESI): calcd. for $C_{17}H_{21}O_5S$ ([M+H]$^+$): 337.1104, found 337.1110.

*Methyl 1,4-dimethyl-6-((naphthalen-2-ylthio)methyl)-3-oxo-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6ak**).* Yield: 87% (59%, 44 mg) (petroleum ether/EtOAc = 15/1), white solid, mp: 103–104 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.72 (m, 4H), 7.53 – 7.43 (m, 3H), 3.75 (d, *J* = 12.2 Hz, 1H), 3.40 (s, 3H), 3.00 (d, *J* = 12.2 Hz, 1H), 2.84 (d, *J* = 13.5 Hz, 1H), 2.01 (d, *J* = 13.5 Hz, 1H), 1.81 (s, 3H), 1.62 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 169.9, 133.7, 132.5, 131.4, 130.4, 129.0, 128.8, 127.9, 127.4, 126.9, 126.6, 112.1, 83.7, 62.2, 52.8, 41.0, 38.6, 15.2, 14.6. HRMS (ESI): calcd. for $C_{20}H_{21}O_5S$ ([M+H]$^+$): 373.1104, found 373.1100.

*Methyl 6-((benzylthio)methyl)-1,4-dimethyl-3-oxo-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6al**).* Yield: 93% (53%, 36 mg) (petroleum ether/EtOAc = 25/1), colorless oil (endo/exo =1.3/1, inseparable mixture). The major isomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 1H), 7.35 – 7.23 (m, 4H), 3.72 (s, 3H), 3.15 (d, *J* = 11.7 Hz, 1H), 2.72 (d, *J* = 13.4 Hz, 1H), 2.48 (d, *J* = 11.8 Hz, 1H), 1.75 (d, *J* = 13.4 Hz, 1H), 1.72 (s, 3H), 1.56 (s, 3H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.20 (m, 5H), 3.65 (d, *J* = 12.2 Hz, 1H), 3.50 (s, 3H), 2.92 (d, *J* = 12.2 Hz, 1H), 2.81 (d, *J* = 13.4 Hz, 1H), 1.96 (d, *J* = 13.4 Hz, 1H), 1.79 (s, 3H), 1.61 (s, 3H). The mixture: ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 173.0, 170.4, 169.9, 137.7, 134.2, 131.9, 129.2, 129.0, 128.8, 127.7, 127.5, 112.1, 112.2, 83.7, 83.6, 62.2, 61.9, 53.1, 52.9, 41.3, 38.6, 38.6, 37.5, 37.3, 15.2, 15.1, 14.6, 14.5. HRMS (ESI): calcd. for $C_{17}H_{21}O_5S$ ([M+H]$^+$): 337.1104, found 337.1102.

*Methyl 4-(tert-butyl)-1-methyl-3-oxo-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6am**).* Yield: 67% (52%, 38 mg) (petroleum ether/EtOAc = 25/1), colorless oil (endo/exo =1.3/1, inseparable mixture). The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.33 – 7.19 (m, 3H), 3.63 (d, *J* = 12.4 Hz, 1H), 3.52 (s, 3H), 3.07 (d, *J* = 12.8 Hz, 1H), 2.63 (d, *J* = 13.5 Hz, 1H), 2.11 (d, *J* = 13.5 Hz, 1H), 1.76 (s, 3H), 1.10 (s, 9H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.33 – 7.19 (m, 3H), 3.58 (d, *J* = 12.4 Hz, 1H), 3.59 (s, 3H), 3.07 (d, *J* = 13.5 Hz, 1H), 2.87 (d, *J* = 12.4 Hz, 1H), 1.66 (s, 3H), 1.64 (d, *J* = 13.5 Hz, 1H), 1.13 (s, 9H). The mixture: ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 171.6, 170.7, 170.0, 135.1, 134.4, 131.9, 131.2, 129.2, 127.6, 127.3, 110.9, 110.8, 91.1, 90.2, 62.7, 62.1, 52.8, 52.7, 41.2, 38.8, 33.6, 32.8, 31.6, 31.6, 24.8, 24.8, 16.5, 15.1. HRMS (ESI): calcd. for $C_{19}H_{25}O_5S$ ([M+H]$^+$): 365.1417, found 365.1418.

*Methyl 1-methyl-3-oxo-4-phenethyl-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6an**).* Yield: 90% (62%, 51 mg)(petroleum ether/EtOAc = 20/1), white solid, mp: 80–81 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.32 – 7.26 (m, 4H), 7.26 – 7.18 (m, 4H), 3.65 (d, *J* = 12.4 Hz, 1H), 3.50 (s, 3H), 2.91 (d, *J* = 12.3 Hz, 1H), 2.86 – 2.71 (m, 2H), 2.76 (d, *J* = 13.7 Hz, 1H), 2.35 – 2.26 (m, 1H), 2.22 – 2.13 (m, 1H), 2.01 (d, *J* = 13.4 Hz, 1H), 1.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 169.8, 140.8, 134.2, 131.9, 129.2, 128.7, 128.4, 127.7, 126.4, 112.0, 86.0, 61.9, 52.9, 41.2, 36.9, 30.8, 30.0, 15.2. HRMS (ESI): calcd. for $C_{23}H_{25}O_5S$ ([M+H]$^+$): 413.1417, found 413.1418.

*Methyl 1-methyl-3-oxo-4-phenyl-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6ao**).* Yield: 92% (82%, 63 mg)(petroleum ether/EtOAc = 20/1), white solid, mp: 159–160 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.47 – 7.35 (m, 5H), 7.34 – 7.19 (m, 3H), 3.72 (d, *J* = 12.3 Hz, 1H), 3.52 (s, 3H), 3.24 (d, *J* = 13.4 Hz, 1H), 2.98 (d, *J* = 12.3 Hz, 1H), 2.34 (d, *J* = 13.4 Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 169.7, 134.0, 132.0, 131.8, 129.4, 129.2, 128.7, 127.7, 126.1, 112.0, 86.6, 62.2, 52.9, 41.3, 38.9, 15.2. HRMS (ESI): calcd. for $C_{21}H_{21}O_5S$ ([M+H]$^+$): 385.1104, found 385.1109.

*Methyl 4-methyl-3-oxo-1-phenyl-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6ap**).* Yield: 88% (76%, 59 mg) (petroleum ether/EtOAc = 15/1), white solid, mp: 96–97 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.37 (m, 5H), 7.35 – 7.15 (m, 5H), 3.53 (s, 3H), 3.12 (d, *J* = 12.4 Hz, 1H), 2.95 (d, *J* = 13.4 Hz, 1H), 2.87 (d, *J* = 12.5 Hz, 1H), 2.09 (d, *J* = 13.3 Hz, 1H), 1.71 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 169.7, 134.2, 131.74, 130.2, 129.1, 128.2, 127.5, 126.7, 111.6, 83.6, 63.6, 52.7, 41.6, 39.1, 14.7.HRMS (ESI): calcd. for $C_{21}H_{21}O_5S$ ([M+H]$^+$): 385.1104, found 385.1108.

*Methyl 4-methyl-1-(4-nitrophenyl)-3-oxo-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6aq**).* Yield: 93% (81%, 69 mg) (petroleum ether/EtOAc = 15/1), white solid, mp: 148–149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.27 (m, 2H), 7.71 – 7.64 (m, 2H), 7.30 – 7.21 (m, 5H), 3.52 (s, 3H), 3.05 (d, *J* = 12.4 Hz, 1H), 2.99 (d, *J* = 13.4 Hz, 1H), 2.85 (d, *J* = 12.4 Hz, 1H), 2.15 (d, *J* = 13.4 Hz, 1H), 1.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 169.3, 149.1, 136.8, 133.6, 132.1, 129.2, 128.2, 127.9, 123.3, 110.4, 84.1, 63.9, 52.9, 41.7, 38.8, 14.7. HRMS (ESI): calcd. for $C_{21}H_{20}NO_7S$ ([M+H]$^+$): 430.0955, found 430.0950.

*Methyl 1-(4-methoxyphenyl)-4-methyl-3-oxo-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6ar**).* Yield: 85% (53%, 44 mg) (petroleum ether/EtOAc = 15/1), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.30 – 7.18 (m, 5H), 6.96 – 6.91 (m, 2H), 3.84 (s, 3H), 3.52 (s, 3H), 3.14 (d, *J* = 12.4 Hz, 1H), 2.94 (d, *J* = 13.4 Hz, 1H), 2.84 (d, *J* = 12.4 Hz, 1H), 2.07 (d, *J* = 13.3 Hz, 1H), 1.70 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4, 169.7, 160.9, 134.9, 134.2, 131.6, 129.0, 128.0, 127.3, 122.2, 113.5, 111.7, 83.5, 63.5, 55.3, 52.5, 41.6, 39.0, 14.7. HRMS (ESI): calcd. for $C_{22}H_{23}O_6S$ ([M+H]$^+$): 415.1210, found 415.1208.

*Methyl 1,4-dimethyl-3-oxo-5-phenyl-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6ba**).* Yield: 87% (77%, 32 mg) (petroleum ether/EtOAc = 25/1), white solid, mp: 112–113 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 5H), 7.23 – 7.05 (m, 5H), 4.28 (s, 1H), 3.50 (s, 3H), 3.38 (d, *J* = 12.7 Hz, 1H), 3.21 (d, *J* = 12.7 Hz, 1H), 1.88 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 169.9, 136.4, 133.9, 131.3, 128.7, 128.3, 127.1, 112.0, 86.9, 67.5, 52.7, 51.0, 38.7, 15.9, 13.2. HRMS (ESI): calcd. for $C_{22}H_{23}O_5S$ ([M+H]$^+$): 399.1261, found 399.1262.

*Ethyl 1,4-dimethyl-3-oxo-5-phenyl-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6bb**).* Yield: 81% (77%, 46 mg) (petroleum ether/EtOAc = 25/1), colorless oil (endo/exo =5/1, inseparable mixture). The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 5H), 7.21 – 7.08 (m, 5H), 4.28 (s, 1H), 4.17 – 4.09 (m, 1H), 3.88 – 3.80 (m, 1H), 3.39 (d, *J* = 12.7 Hz, 1H), 3.22 (d, *J* = 12.6 Hz, 1H), 1.88 (s, 3H), 1.38 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 5H), 7.21 – 7.08 (m, 5H), 4.17 – 4.06 (m, 2H), 3.99 (s, 1H), 3.19 (d, *J* = 13.3 Hz, 1H), 3.08 (d, *J* = 13.3 Hz, 1H), 1.97 (s, 3H), 1.54 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), The mixture:^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 173.4, 170.9, 169.3, 136.7, 133.9, 132.0, 131.2, 130.0, 129.0, 128.9, 128.8, 128.5, 128.3, 127.0 126.6, 112.2, 112.0, 86.9, 84.8, 67.5, 63.1, 62.2, 62.1, 57.2, 50.9, 38.7, 36.7, 18.4, 15.9, 14.1, 14.0, 13.8, 13.2. HRMS (ESI): calcd. for $C_{23}H_{25}O_5S$ ([M+H]$^+$): 413.1417, found 413.1413.

*1,4-Dimethyl-3-oxo-5-phenyl-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carbonitrile (**6bd**).* Yield: 63%

(58%, 22 mg) (petroleum ether/EtOAc = 25/1), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 5H), 7.38 – 7.26 (m, 5H), 3.46 (d, *J* = 13.1 Hz, 1H), 3.39 (d, *J* = 13.1 Hz, 1H), 3.27 (s, 1H), 2.08 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 134.2, 133.3, 131.3, 130.4, 129.5, 129.2, 128.8, 127.9, 117.4, 111.0, 86.3, 60.6, 56.7, 40.5, 16.5, 12.8. HRMS (ESI): calcd. for $C_{21}H_{20}NO_3S$ ([M+H]$^+$): 366.1158, found 366.1161.

*Methyl 1,4-dimethyl-3-oxo-5-phenyl-6-((o-tolylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6be**).* Yield: 69% (52%, 22 mg) (petroleum ether/EtOAc = 25/1), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 5H), 7.10 – 7.01 (m, 4H), 4.28 (s, 1H), 3.51 (s, 3H), 3.30 (d, *J* = 12.4 Hz, 1H), 3.12 (d, *J* = 12.3 Hz, 1H), 2.14 (s, 3H), 1.87 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 170.0, 139.8, 135.2, 134.0, 132.0, 130.2, 128.3, 127.3, 126.5, 112.1, 86.9, 67.2, 52.8, 51.1, 38.3, 20.7, 15.9, 13.2. HRMS (ESI): calcd. for $C_{23}H_{25}O_5S$ ([M+H]$^+$): 413.1417, found 413.1415.

*Methyl 1,4-dimethyl-3-oxo-6-((phenylthio)methyl)-5-(p-tolyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6bf**).* Yield: 81% (73%, 32 mg) (petroleum ether/EtOAc = 25/1), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.20 – 7.09 (m, 7H), 4.24 (s, 1H), 3.49 (s, 3H), 3.38 (d, *J* = 12.8 Hz, 1H), 3.20 (d, *J* = 12.8 Hz, 1H), 2.35 (s, 3H), 1.87 (s, 3H), 1.36 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 170.0, 138.1, 136.6, 131.1, 130.6, 130.2, 129.7, 128.8, 127.0, 112.0, 87.0, 67.4, 52.7, 50.7, 38.6, 21.3, 15.9, 13.2. HRMS (ESI): calcd. for $C_{23}H_{25}O_5S$ ([M+H]$^+$): 413.1417, found 413.1412.

*Methyl 5-(4-bromophenyl)-1,4-dimethyl-3-oxo-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6bg**).* Yield: 74% (62%, 34 mg) (petroleum ether/EtOAc = 20/1), colorless oil(endo/exo = 5.2/1, inseparable mixture). The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 1H), 7.29 – 7.24 (m, 2H), 7.23 – 7.08 (m, 6H), 4.25 (s, 1H), 3.51 (s, 3H), 3.43 (d, *J* = 12.8 Hz, 1H), 3.10 (d, *J* = 12.8 Hz, 1H), 1.87 (s, 3H), 1.35 (s, 3H). The minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 5H), 7.41 – 7.37 (m, 2H), 7.29 – 7.24 (m, 1H), 7.23 – 7.08 (m, 1H), 4.03 (s, 1H), 3.64 (s, 3H), 3.25 (d, *J* = 13.3 Hz, 1H), 3.01 (d, *J* = 13.3 Hz, 1H), 1.92 (s, 3H), 1.52 (s, 3H). The mixture: ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 173.1, 171.2, 169.7, 136.3, 136.0, 133.0, 132.1, 131.3, 131.0, 130.3, 129.0, 127.2, 126.8, 123.0, 122.6, 112.2, 111.9, 86.7, 84.8, 67.5, 63.5, 56.1, 52.9, 52.8, 50.6, 38.4, 36.7, 18.2, 15.8, 14.0, 13.2. HRMS (ESI): calcd. for $C_{22}H_{22}BrO_5S$ ([M+H]$^+$): 477.0366, found 477.0370.

*Methyl 1-methyl-3-oxo-4,5-diphenyl-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6bh**).*Yield: 80% (68%, 34 mg) (petroleum ether/EtOAc = 20/1), white solid, mp: 151–152 °C. (endo/exo =2.6/1, inseparable mixture). The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) 7.33 – 7.22 (m, 2H), 7.22 – 7.05 (m, 13H), 4.81 (s, 1H), 3.60 (s, 1H), 3.54 (s, 3H), 3.41 (d, *J* = 12.9 Hz, 1H), 3.22 (d, *J* = 12.2 Hz, 1H), 2.01 (s, 3H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 4H), 7.33 – 7.22 (m, 11H), 4.31 (s, 1H), 3.60 (s, 3H), 3.35 (d, *J* = 13.3 Hz, 1H), 3.20 (d, *J* = 13.2 Hz, 1H), 2.06 (s, 3H). The mixture:^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 171.4, 171.2, 169.8, 136.5, 136.5, 133.6, 131.8, 131.2, 131.0, 130.8, 130.2, 129.2, 128.8, 128.9, 128.6, 128.4, 128.2, 128.1, 127.8, 127.0, 126.7, 126.5, 126.3, 112.0, 111.9, 90.6, 86.8, 67.7, 63.7, 58.5, 52.8, 52.7, 51.8, 38.9, 36.9, 18.4, 16.1. HRMS (ESI): calcd. for $C_{27}H_{25}O_5S$ ([M+H]$^+$): 461.1417, found 461.1420.

*Methyl 4-methyl-3-oxo-1,5-diphenyl-6-((phenylthio)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**6bi**).* Yield: 77% (83%, 37 mg) (petroleum ether/EtOAc = 20/1), white solid, mp: 165–166 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 3H), 7.50 – 7.32 (m, 7H), 7.08 – 7.01 (m, 3H), 6.89 – 6.82 (m, 2H), 4.46 (s, 1H), 3.51 (s, 3H), 3.14 (d, *J* = 12.8 Hz, 1H), 2.84 (d, *J* = 12.9 Hz, 1H), 1.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 169.9, 136.2, 133.9, 130.6, 130.6, 130.3, 128.7, 128.4, 128.2, 126.9, 126.6, 111.9, 86.9, 68.9, 52.5, 51.2, 38.8, 13.4. HRMS (ESI): calcd. for $C_{27}H_{25}O_5S$ ([M+H]$^+$): 461.1417, found 461.1414.

Procedure for the Preparation of Products 6aa on a larger scale. To a dried reaction tube were added **3aa** (3.6 mmol, 1.16 g) and EtONa (10 mol %, 1 *M* in DMSO) in THF (18 mL) under a N_2 atmosphere at 0 °C. The reaction was monitored by TLC. Upon completion, the reaction was quenched with saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with EtOAc (50 mL × 3), and the combined organic extract was washed with saturated brine (70 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/EtOAc = 20/1) to provide the desired product **6aa** in 67% yield (778 mg).

Procedure for the Preparation of Compound 7. To a stirred solution of **6ab** (0.2 mmol, 65 mg) in DCM (2 mL) was added *m*-CPBA (0.46 mmol, 105.8 mg) in portion-wise addition at 0 °C. The reaction mixture was stirred for 30 min, then warmed to room temperature. After completion, the reaction was diluted with DCM (8 mL) and washed with 5% aqueous K_2CO_3 (10 mL) and 5% $NaHCO_3$ (10 mL) solution. The aqueous layer was extracted with DCM (3 × 10 mL), the combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. The mixture was purified by column chromatography (silica gel, EtOAc/Petroleum ether) to provide compound **7**.

*Methyl 1,4-dimethyl-3-oxo-6-((phenylsulfonyl)methyl)-2,7-dioxabicyclo[2.2.1]heptane-6-carboxylate (**7**).* Yield: 83% (59 mg) (petroleum ether/EtOAc = 10/1), white solid, mp: 150–151 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.7 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 2H), 3.99 (d, *J* = 13.5 Hz, 1H), 3.65 (s, 3H), 3.21 (d, *J* = 13.5 Hz, 1H), 2.90 (d, *J* = 13.9 Hz, 1H), 2.52 (d, *J* = 13.8 Hz, 1H), 1.66 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 168.9, 139.8, 134.4, 129.6, 128.2, 111.5, 84.4, 60.7, 57.9, 53.4, 36.7, 15.0, 14.5. HRMS (ESI): calcd. for $C_{16}H_{19}O_7S$ ([M+H]$^+$): 355.0846, found 355.0854.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at athttp://pubs.acs.org.

^{1}H and ^{13}C NMR spectra, X-ray crystallography data.

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Notes

The authors declare no competing financial interest.

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(15) The cyclization of *syn*-**3ba** did not occur under the optimized reaction conditions.

(16) The relative configurations of major diastereomeric 2,7-dioxabicyclo[2.2.1]heptan-3-one *endo*-**6aa** and *endo*-**6ba** were determined on the basis of X-ray crystal structural analyses.

(17) The products **6** are prone to be decomposable by flash column chromatograph.

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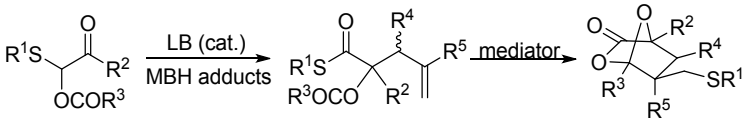
R1S
O
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MBH adducts
R1S
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1 **3** *endo*-**6**