Article

Synthesis of Functionalized Thietanes via Electrophilic Carbenoid-Induced Ring Expansion of Thiiranes with Sulfonium Acylmethylides as Carbene Precursors

Jun Dong, Hongguang Du, and Jiaxi Xu

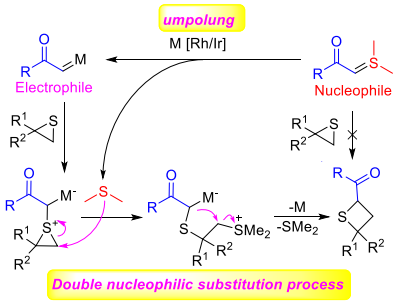
J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b01152 • Publication Date (Web): 12 Aug 2019

Synthesis of Functionalized Thietanes via Electrophilic Carbenoid-Induced Ring Expansion of Thiiranes with Sulfonium Acylmethylides as Carbene Precursors

Jun Dong, Hongguang Du, and Jiaxi Xu*

State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

Supporting Information



ABSTRACT: Various functionalized thietanes were prepared from thiiranes *via* an electrophilic ring expansion with rhodium carbenoids as electrophiles generated from safe and readily accessible dimethylsulfonium acylmethylides. The reaction appears to proceed through electrophilic metallocarbenoid-induced activation of thiiranes, nucleophilic ring-opening of the activated thiiranes with dimethyl sulfide as a transient nucleophile, and nucleophilically intramolecular cyclization. The umpolung from the nucleophilic ylides to the electrophilic carbenoids plays an important role in both the activation and ring-opening of thiiranes, and subsequent cyclization. The current method provides a new strategy for the efficient preparation of functionalized thietanes from readily available thiiranes.

INTRODUCTION

Thietanes are pharmaceutically important cores or moieties of some biological compounds, such as thietanose nucleosides,[1] and spiroannulated glycothietane nucleosides as the thiaanalogues of antiviral (anti-HIV and HSV) oxetanocin A and their conformationally restricted analogues,[2] the thia derivatives of docetaxel, D-ring modified anticancer drug taxoids,[3] and thiathromboxane A2 (Figure 1).[4]

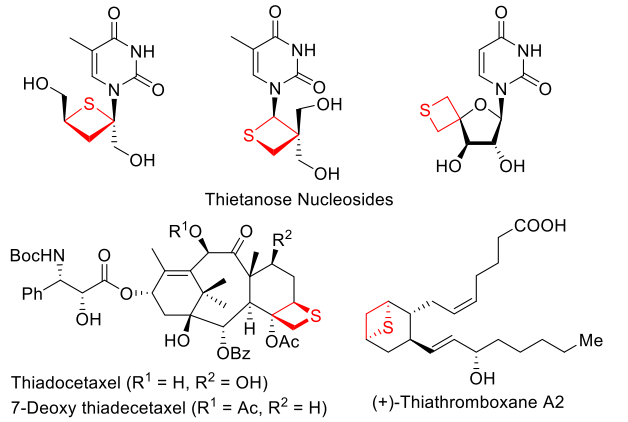


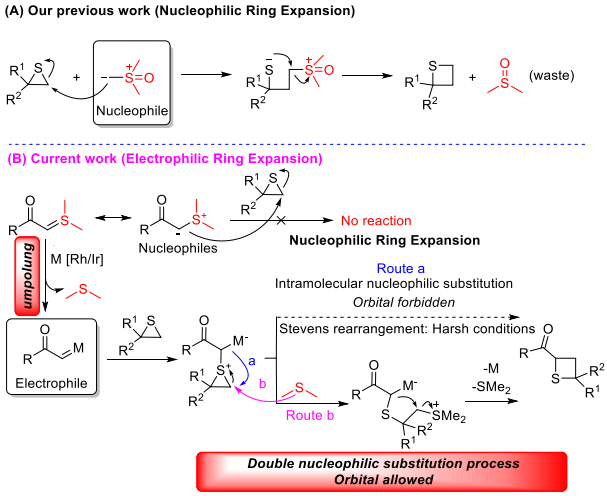
Figure 1. Pharmaceutically Important Compounds with the Thietane Ring as Crucial Cores.

Thietanes also serve as important intermediates in organic synthesis for the preparation of sulfur-containing compounds and thiaheterocycles.[5] Although thietanes have been widely applied in organic synthesis and medicinal chemistry, their synthetic methods are very limited to date.[6] One traditional route is intermolecular double substitutions of 1,3-dihaloalkanes,[1b] sulfonates of 3-haloalkan-1-ols, or disulfonates of alkane-1,3-diols with sodium sulfide.[1a] Another alternative method is [2+2] photocycloaddition, Paterno-Büchi like cycloaddition, of alkenes and thiocarbonyl compounds,[7] especially cyclic thioimides, to afford spirocyclic amidothietanes.[8] Alkylidenethietanes have been prepared via the amine-catalyzed tunable formal [2+2] cycloadditions of allenoates and dithioesters.[9] 3-Substituted thietanes have been prepared through the reactions of (1-chloroalkyl)thiiranes, especially epithiochlorohydrin, and various nucleophiles.[10]

Sulfur ylides (sulfonium and sulfoxonium methylides) have been used as universal synthetic precursors for various chemical transformations.[11] They have been widely applied as sources of methylene synthons to synthesize small cyclic compounds through a nucleophilic attack and intramolecular ring closure sequence, for example, syntheses of oxiranes, aziridines, and cyclopropanes with electrophilic aldehydes, imines, and enones;[12] and preparations of azetidines,[13] oxetanes,[14] and thietanes [15] with strained aziridines, oxiranes, and thiiranes as electrophiles, respectively. However, the nucleophilic ring expansions have been applied in only limited cases. In most cases, only dimethylsulfonium and/or sulfoxonium methylides have been used as nucleophiles in the nucleophilic ring expansions for the preparation of four-membered heterocycles.[13a,13b,14,15] When the methods were extended to functionalized sulfur ylides, especially with electron-withdrawing groups, the ring expansion generally did not occur, except for the reactions of the aziridines bearing electron-withdrawing substituents with dimethylsulfonium and sulfoxonium 2-phenyl-2-oxoethylide ylides.[13c,13d]

Simultaneously, sulfur ylides can also act as the precursors of electrophilic metallocarbenoids after an umpolung conversion with transition metal catalysts.[16] However, the most recent application of this type of metallocarbenoids is only limited to the insertion of acidic X–H (X = C, N, O, S) bonds and cyclopropanations.[11a,17] The development of reactions involving sulfur-ylide-derived metallocarbenoids for a wide range of applications is in high demand since the method with ylides as the carbenoid precursors can offer some advantages of safety, stability, and easy operation over that with diazo compounds as carbenoid precursors.[11a,18] Most sulfur ylides are safe in large-scale preparation, crystallizable, and bench-stable.[18] Thus, it is possible to replace diazo compounds with sulfur ylides in metallocarbenoid reactions.[19]

The carbenoid-induced electrophilic ring expansions of four-membered heterocycles into five-membered heterocycles have been realized in limited cases.[20] The transformation occurs because the ring strain of the four-membered ring releases. Although the reactions of three-membered heterocycles containing heteroatoms (O, N, and S) with metallocarbenoids generated from diazo compound precursors have been explored, six-membered heterocyclic products were obtained accompanied by the removal of heteroatoms during the reactions.[21,22] Because the four-membered rings are still strained rings, it is certain difficult transformation from three-membered rings directly to four–membered rings through a ring expansion, compared with other larger rings.[21b,22] Until 2017, the first example was reported on the strained aziridines with electrophilic one-carbon sources to trigger a ring-opening and ring-closing cascade to yield azetidines.[23] However, the reaction was applied only in the designed special bicyclic methyleneaziridines.



Scheme 1. Synthesis of Thietanes from Thiiranes

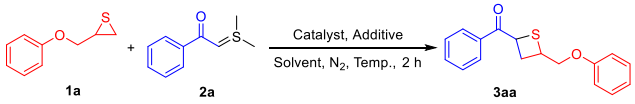
Considering that the carbon atoms of thiiranes are less electrophilic due to less polar C–S bond (similar electronegativities of sulfur and carbon), unfavorably reacting with electron-deficient ylides. However, their sulfur atom is more nucleophilic. We hope to convert nucleophilic sulfur ylides into electrophilic metallocarbenoids through an umpolung under the catalysis of transition metal catalysts to initiate the reaction with the nucleophilic thiirane sulfur atom. Herein, we present an electrophilic ring expansion for the conversion of strained thiiranes into strained thietanes directly

with sulfur ylide-generated metallocarbenoids as electrophiles and dimethyl sulfide as a transient nucleophile and leaving group, resulting in a favorable double nucleophilic substitution process (Scheme 1). The current method is a new strategy for the synthesis of functionalized strained thietanes from readily accessible thiiranes.

RESULTS AND DISCCUSION

At the outset of this study, 2-(phenoxymethyl)thiirane (**1a**) and 2-(dimethyl-λ^4-sulfanylidene)-1-phenylethan-1-one (sulfonium methylide **2a**) were employed as the model substrates to optimize reaction conditions. We first optimized the reactant ratio (Table 1, entries 1–5). When the ratio of **1a**:**2a** was increased from 1:1 to 1:1.5 to 1:2 (Table 1, entries 1, 3, and 4), the yield increased from 34% to 59% to 76% with similar ratios of *cis*:*trans* from 1:0.89 to 1:0.90. However, when the ratio of **1a**:**2a** was increased to 1:2.5, the yield was slightly decreased to 73% (Table 1, entry 5). Solvents were also screened, when polar solvent MeCN was used, product **3aa** was obtained in 27% yield with a ratio of *cis*:*trans* 1:0.62 (Table 1, entry 6). Product **3aa** was obtained in 64% and 68% yields, respectively, when the weak polar solvents toluene and dioxane were used (Table 1, entries 7 and 8). We further optimized the amount of additive pentaerythritol, which was usually used as a ligand in the carbenoid-participated reactions[17f] (Table 1, entries 9–11). When the amount of pentaerythritol was 10 mol%, the yield was only 57% with a ratio of *cis*:*trans* of 1:0.90 (Table 1, entry 9). Next, the amount of additive pentaerythritol was increased to 30 mol% and 40 mol%, the yield decreased slightly (Table 1, entries 10 and 11). Then, we carried out further optimizations with 10 mol% of pentaerythritol as an additive at different reaction temperatures and found that when the temperature was decreased to 70 °C or increased to 90 °C, the yield dropped slightly (Table 1, entries 12 and 13). Furthermore, we screened catalysts and found that $Rh_2(CH_3CO_2)_4$, $Rh_2(C_7H_{15}CO_2)_4$, $[Rh(COD)Cl]_2$, and $[Ir(COD)Cl]_2$[17d] were also able to give the corresponding product **3aa** (Table 1, entries 14–17). When $Rh_2(CH_3CO_2)_4$ and $Rh_2(C_7H_{15}CO_2)_4$ were used as the catalysts, the yields of **3aa** were only 47% and 41% with the ratios of *cis*:*trans* 1:0.97 and 1:1, respectively (Table 1, entries 14 and 15). Fortunately, using catalyst $[Rh(COD)Cl]_2$ got 79% NMR yield and 58% isolated yield of product **3aa** (Table 1, entry 16). Comparing with catalyst $[Rh(COD)Cl]_2$, the catalyst $[Ir(COD)Cl]_2$ only gave product **3aa** in 48% yield with a *cis*:*trans* ratio of 1:1 (Table 1, entry 17). Moreover, the amounts of catalysts $Rh_2(CF_3CO_2)_4$ and $Rh_2(CH_3CO_2)_4$ were reduced to half and it was found that the catalyst $Rh_2(CF_3CO_2)_4$ had no significant effect on the yield of product **3aa** (Table 1, entry 18). Diazoacetophenone was also tested instead of **2a** as the carbene precursor, no desired product **3aa** was observed (Table 1, entries 20 and 21). No product **3aa** was detected when no catalyst was used (Table 1, entry 22) and similar results were obtained without pentaerythritol as an additive under the catalysis of $[Rh(COD)Cl]_2$ (Table 1, entry 23). But the yield decreased obviously when the reaction was conducted without pentaerythritol as an additive under the catalysis of $Rh_2(CF_3CO_2)_4$ (Table 1, entry 24).

Table 1. Optimization for the Reaction of 2-(Phenoxymethyl)thiirane (**1a**) and Sulfonium Ylide **2a**[a]

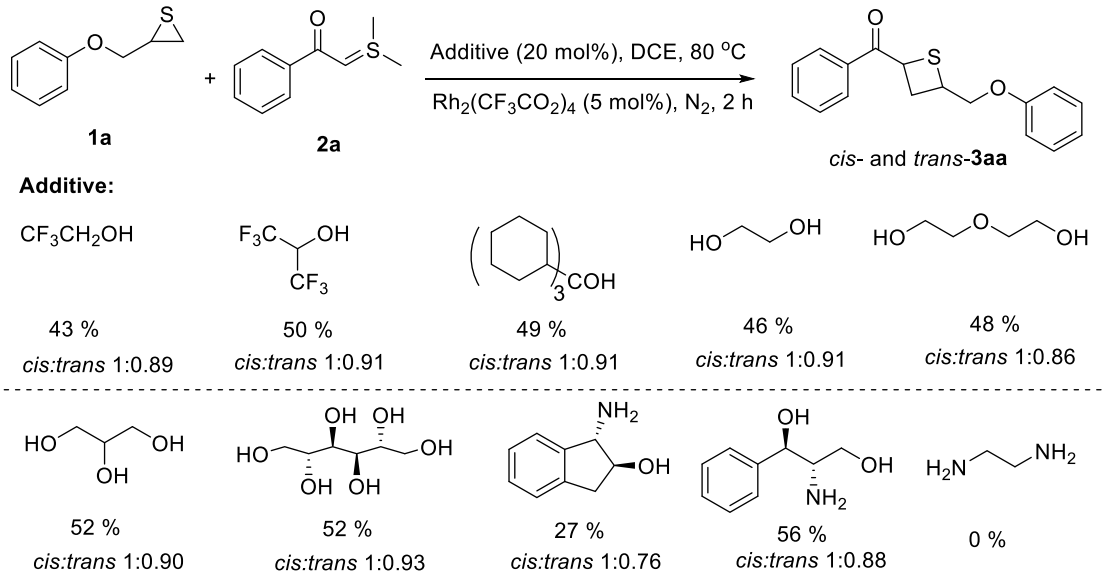


Entry	**1a** (mmol)	**2a** (mmol)	Catalyst (mol%)	Additive (mol%)	Solvent (1 mL)	Temp. (°C)	Yield (%)[b]	*Cis:trans*
1	0.125	0.125	$(CF_3CO_2)_4Rh_2$ (5)	$C(CH_2OH)_4$ (20)	DCE	80	34	1: 0.89
2	0.1875	0.125	$(CF_3CO_2)_4Rh_2$ (5)	$C(CH_2OH)_4$ (20)	DCE	80	32	1: 0.89
3	0.125	0.1875	$(CF_3CO_2)_4Rh_2$ (5)	$C(CH_2OH)_4$ (20)	DCE	80	59	1: 0.90
4	**0.125**	**0.25**	**$(CF_3CO_2)_4Rh_2$ (5)**	**$C(CH_2OH)_4$ (20)**	**DCE**	**80**	**76**	**1: 0.89**
5	0.125	0.3125	$(CF_3CO_2)_4Rh_2$ (5)	$C(CH_2OH)_4$ (20)	DCE	80	73	1: 0.92
6	0.125	0.25	$(CF_3CO_2)_4Rh_2$ (5)	$C(CH_2OH)_4$ (20)	MeCN	80	27	1: 0.62
7	0.125	0.25	$(CF_3CO_2)_4Rh_2$ (5)	$C(CH_2OH)_4$ (20)	Toluene	80	64	1: 1
8	0.125	0.25	$(CF_3CO_2)_4Rh_2$ (5)	$C(CH_2OH)_4$ (20)	dioxane	80	68	1: 1
9	0.125	0.25	$(CF_3CO_2)_4Rh_2$ (5)	$C(CH_2OH)_4$ (10)	DCE	80	57	1: 0.89
10	0.125	0.25	$(CF_3CO_2)_4Rh_2$ (5)	$C(CH_2OH)_4$ (30)	DCE	80	75	1: 0.85
11	0.125	0.25	$(CF_3CO_2)_4Rh_2$ (5)	$C(CH_2OH)_4$ (40)	DCE	80	74	1: 0.84
12	0.125	0.25	$(CF_3CO_2)_4Rh_2$ (5)	$C(CH_2OH)_4$ (20)	DCE	70	62	1: 0.86
13	0.125	0.25	$(CF_3CO_2)_4Rh_2$ (5)	$C(CH_2OH)_4$ (20)	DCE	90	51	1: 0.80
14	0.125	0.25	$(CH_3CO_2)_4Rh_2$ (5)	$C(CH_2OH)_4$ (20)	DCE	80	47	1: 0.97
15	0.125	0.25	$(C_7H_{15}CO_2)_4Rh_2$ (5)	$C(CH_2OH)_4$ (20)	DCE	80	41	1: 1
16	**0.125**	**0.25**	**$[Rh(COD)Cl]_2$ (5)**	**$C(CH_2OH)_4$ (20)**	**DCE**	**80**	**79/58[c]**	**1: 0.93**
17	0.125	0.25	$[Ir(COD)Cl]_2$ (5)	$C(CH_2OH)_4$ (20)	DCE	80	48	1: 1

18	0.125	0.25	$(CF_3CO_2)_4Rh_2$ (2.5)	$C(CH_2OH)_4$ (20)	DCE	80	74	1: 0.84
19	0.125	0.25	$[Rh(COD)Cl]_2$ (2.5)	$C(CH_2OH)_4$ (20)	DCE	80	46	1: 0.77
20	0.125	0.25	$(CF_3CO_2)_4Rh_2$ (5)	$C(CH_2OH)_4$ (20)	DCE	80	0[d]	-
21	0.125	0.25	$[Ir(COD)Cl]_2$ (5)	$C(CH_2OH)_4$ (20)	DCE	80	0[d]	-
22	0.125	0.25	None	$C(CH_2OH)_4$ (20)	DCE	80	0	-
23	0.125	0.25	$[Rh(COD)Cl]_2$ (5)	None	DCE	80	78	1: 0.93
24	0.125	0.25	$(CF_3CO_2)_4Rh_2$ (5)	None	DCE	80	52	1: 0.89

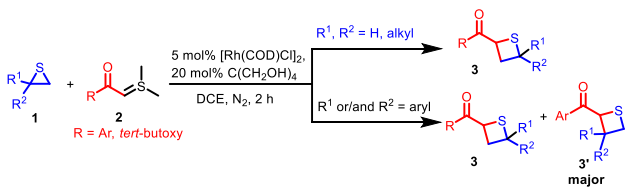
[a] Reactions were conducted on a 0.125 mmol scale of **1a** in 1 mL of solvent. [b] NMR yield of the crude product **3aa** using 1,3,5-trimethoxybenzene as an internal standard. [c] Isolated yield. [d] Diazoacetophenone as starting material instead of **2a**.

Table 2. Optimization for Additives in the Reaction of 2-(Phenoxymethyl)thiirane (**1a**) and Sulfonium Ylide **2a**[a]



[a] NMR yield of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

To further improve the yield and stereoselectivity of the product **3aa**, different alcohols, including primary, secondary, tertiary alcohols, diols, triol, and enantiopure hexaol, vicinal amino alcohols, were tested. However, both yield and stereoselectivity were not further improved. Ethane-1,2-diamine was also tried. No reaction occurred (Table 2).



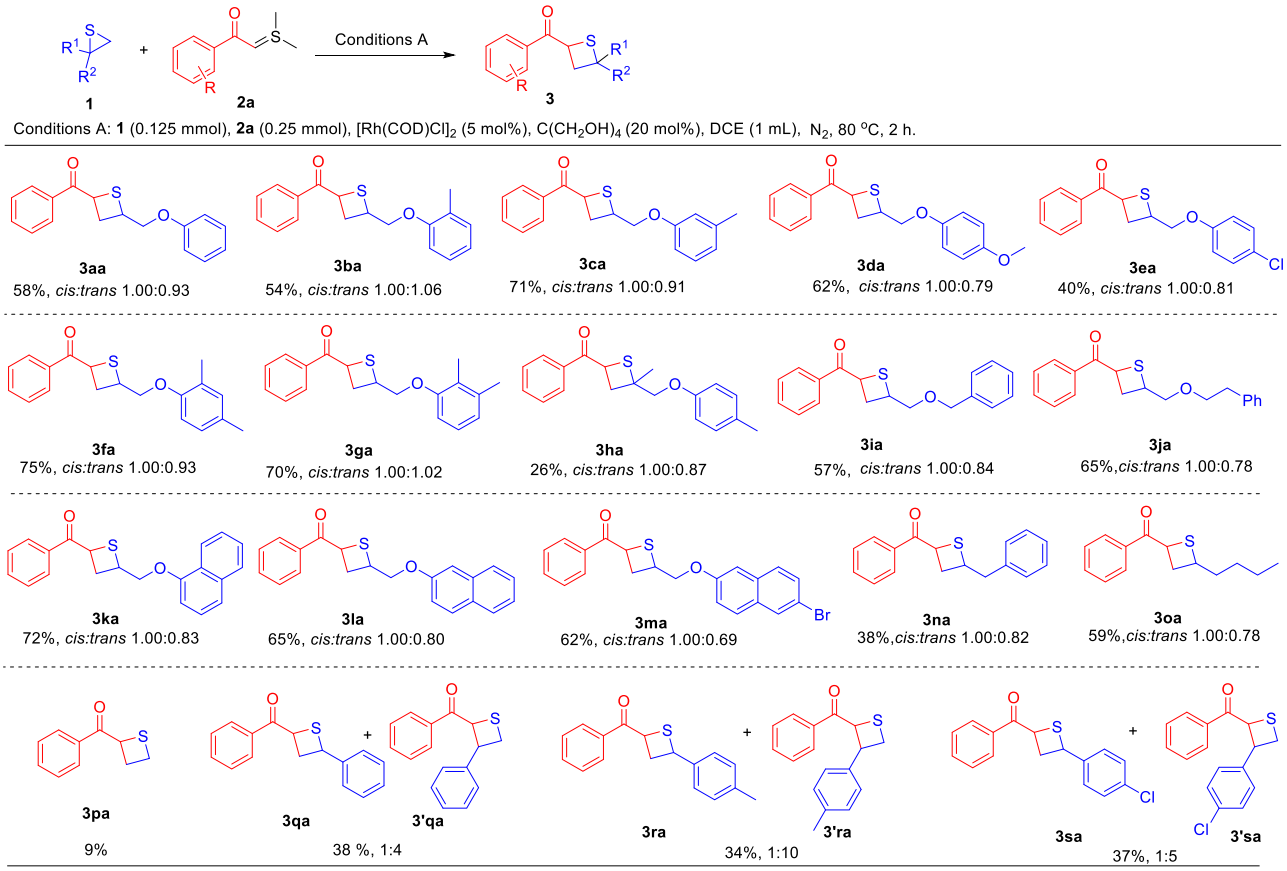
Scheme 2. Synthesis of Thietanes from Thiiranes.

With the optimized reaction conditions, the reaction scope was then evaluated (Scheme 2, Table 3). Various thiiranes **1** were subjected to the optimal conditions with sulfonium benzoylmethylide **2a**. The results are presented in Table 3. Phenoxymethylthiirane (**1a**) and electron-rich *ortho*- and *meta*-methylphenoxymethylthiiranes (**1b-c**) gave the corresponding products **3ba-ca** in moderate to good isolated yields of 54% and 71%. We further extended to more electron-rich 4-methoxyphenoxymethylthiirane (**1d**), affording product **3da** in a moderate yield of 62%. However, electron-deficient 2-(4-chlorophenoxymethyl)thiirane (**1e**) produced the desired product **3ea** in a low yield of 40%. In comparison with monosubstituted phenoxymethylthiiranes **1a-e**, more electron-rich dimethyl substituted phenoxymethylthiiranes **1f** and **1g** gave rise to the corresponding products **3fa** and **3ea** in high yields of 75% and 70%, respectively. For geminal 2,2-disubstituted thiiranes, electron-rich 2-(4-methylphenoxy)methyl-2-methylthiirane (**1h**) was converted into 2,2,4-trisubstituted thietane **3ha** in a low yield of 26%. This is very different from the previous results of the nucleophilic ring expansion with trimethylsulfoxonium iodide as the ylide source.[15] Furthermore, both benzyloxymethylthiirane (**1i**) and (2-phenylethoxymethyl)thiirane (**1j**) generated the corresponding products **3ia** and **3ja** in moderate yields of 57% and 65%, respectively. We further extended thiiranes **1** from phenoxymethylthiiranes to naphthyloxymethylthiiranes, (naphthalen-1-yloxymethyl)thiirane (**1k**), (naphthalen-2-yloxymethyl)thiirane (**1l**), and (6-bromonaphthalen-2-yloxymethyl) thiirane (**1m**), affording the corresponding products **3ka–3ma** in moderate yields of 62% to 72%. Aliphatic

2-butylthiirane (**1o**) also gave rise to the corresponding product **3oa** in a moderate yield of 59%. For unsubstituted thiirane (**1p**), product **3pa** was obtained in a very low yield of 9% possibly due to its high volatility, resulting in a deviation of its amount involved in the reaction from the added amount.

Furthermore, aromatic 2-arylthiiranes **1q–1s** were attempted. Relatively low yields were obtained because of their instability. At the same time, the formation of the corresponding olefins after desulfurization was also observed in GC-MS analysis during monitoring the reaction progress. 2-Arylthiiranes show different regioselectivity in the electrophilic ring expansion and 2,3-disubstituted thietanes **3'** were obtained as major products because dimethyl sulfide favorably attacks the more electrophilic benzylic carbon atom in 2-arylthiiranes after they nucleophilically attacked the metallocarbenoids generated from sulfonium ylides and the rhodium catalyst (Scheme 4).

Table 3. Synthesis of Thietanes **3** from Different Thiiranes **1**



After investigating different substituted thiiranes **1**, the scope of sulfur ylides **2** was studied (Table 4). Generally, (dimethyl-λ^4-sulfanylidene)-1-arylethan-1-ones **2b** and **2c** bearing electron-donating groups worked well to deliver the desired products **3ab** and **3ac** in 60% and 80% yields, while (dimethyl-λ^4-sulfanylidene)-1-arylethan-1-ones **2d–2h** with electron-withdrawing groups also worked to give rise to the desired products **3ad–3ah** in satisfactory to moderate yields (40%–70%). After replacing the phenyl group with naphthyl, the corresponding product **3ai** was obtained in 34% yield. Furthermore, a sterically hindered cyclic aliphatic sulfur ylide, (1-adamantan-1-yl)-2-(dimethyl-l4-sulfanylidene)ethan-1-one (**2j**) was prepared and reacted with thiirane **1a** to afford the desired product **3aj** in 70% yield. *Tert*-butyl 2-(dimethyl-λ^4-sulfanylidene)acetate (**2k**) was also tried to produce the corresponding product **3ak** in a yield of 40%.

There had been a few reports on the reactions of diazo carbonyl compound-generated carbenoids and thietanes for the synthesis of the five-membered heterocycle thiacyclopentanes through the ring expansion.[20a,20c] Compared with diazo carbonyl compounds, sulfur ylides had obvious advantages as carbene precursors. Therefore, besides the studies on the expansion of thiiranes, the sulfur ylide carbene precursors were also used for the ring expansion reactions of thietane.

Thietane (**4**) and sulfur ylide **2a** were selected as model substrates for the reaction optimization (Table 5). The rhodium catalysts gave the desired products in low yields (Table 5, entries 1–3). Fortunately, a moderate yield was obtained under the catalysis of $[Ir(COD)Cl]_2$ (Table 5, entry 4). $CuSO_4$ was also attempted as catalyst, but no reaction occurred (Table 5, entry 5). The catalyst $[Ir(COD)Cl]_2$ was finally selected as the optimal catalyst for the electrophilic ring expansion of thietane.

Table 4. Synthesis of Thietanes **3** from Different Sulfonium Ylides (Dimethyl-λ^4-sulfanylidene)-1-arylethan-1-ones **2**

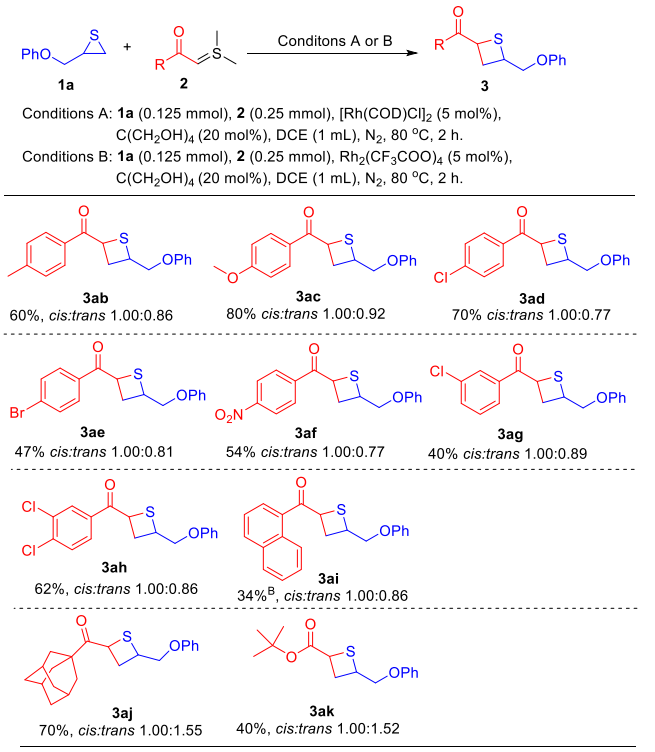
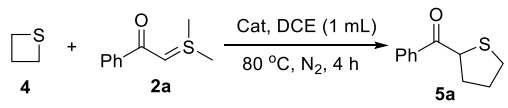


Table 5. Optimization for the reaction of thietane (**4**) and sulfonium ylide (**2a**)

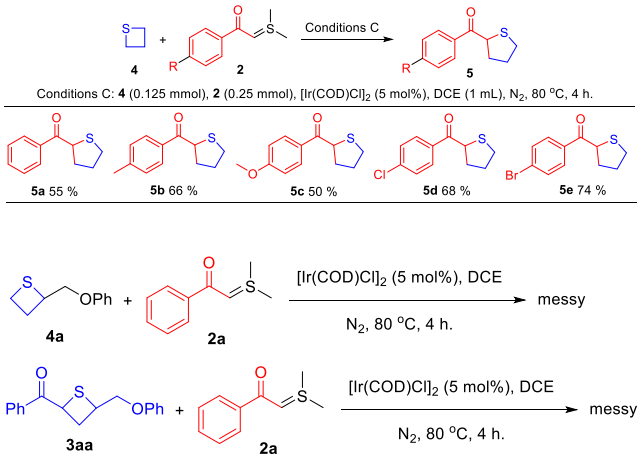


Entry	**4** (mmol)	**2a** (mmol)	Catalyst (5 mol%)	Yield (%)[a]
1	0.125	0.25	$Rh_2(CF_3CO_2)_4$	7
2	0.125	0.25	$Rh_2(OAc)_4$	10
3	0.125	0.25	$[Rh(COD)Cl]_2$	13
4	**0.125**	**0.25**	**$[Ir(COD)Cl]_2$**	**58 (55)[b]**
5	0.125	0.25	$CuSO_4$	NR

[a] NMR yield of the crude product using 1,3,5-trimethoxybenzene as an internal standard. [b] Yield of the isolated product.

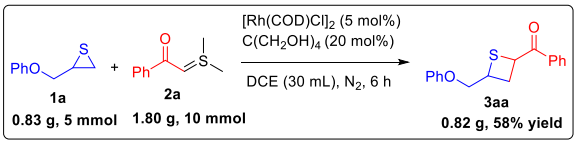
Under the optimal conditions, thietane (**4**) was used as an electrophile to react with different (dimethyl-λ^4-sulfanylidene)-1-arylethan-1-ones **2**. The results are presented in Table 6. (Dimethyl-λ^4-sulfanylidene)-1-phenylethan-1-one (**2a**) gave the desired product **5a** in 55% yield. Electron-rich (dimethyl-λ^4-sulfanylidene)-1-arylethan-1-ones **2b** and **2c** yielded the corresponding products **5b** and **5c** in 66% and 50% yields, respectively, while electron-deficient (dimethyl-λ^4-sulfanylidene)-1-arylethan-1-ones **2d** and **2e** produced the desired products **5d** and **5e** in 68% and 74% yields, respectively.

Table 6. Synthesis of Thiacyclopentanes **5** from Thietane **4**

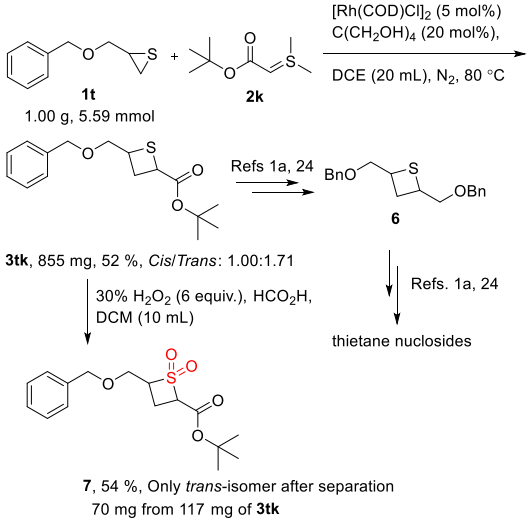


Scheme 3. Attempted Reactions of Substituted Thietanes and Sulfur Ylide **2a**.

Substituted thietanes, monosubstituted 2-phenoxymethylthietane (**4a**) and disubstituted thietane **3aa** were further explored in the ring expansion. However, only messy mixture products were obtained (Scheme 3). This is the reason why further ring expansion product thiacyclopentane derivatives were not observed in the ring expansion of thiiranes.



Scheme 4. Gram-Scale Reaction.



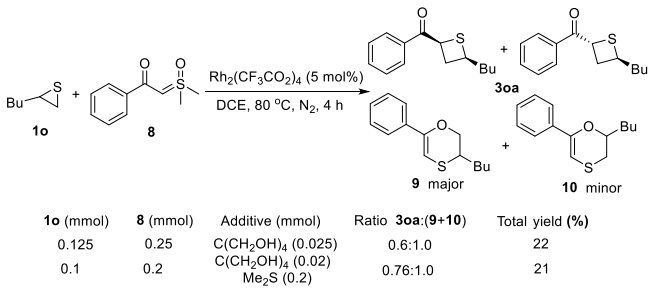
Scheme 5. Further derivations of the synthetic thietane **3tk**.

To demonstrate the practical utility of the method, a gram-scale synthesis of **3aa** was performed, and a moderate yield was realized (Scheme 4). To show further synthetic utility, this strategy was applied to the synthesis of the thietane derivative **3tk**, which could be converted easily into **6** for the synthesis of thietane nucleosides by referring literature method (Scheme 5).[1a,24] Sulfone **7** was obtained in 54% yield by the oxidation of

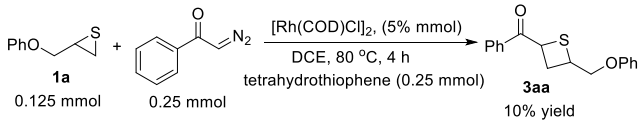
thietane **3tk** with H_2O_2/HCO_2H. Only *trans*-isomeric product was obtained after silica gel column separation (Scheme 5).[25]

To further understand the reaction mechanism and to extend the scope of sulfur ylides, 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one (**8**) was prepared and subjected to the ring expansion. The reaction of 2-butylthiirane (**1o**) and sulfur ylide **8** afforded the desired product **3oa** in 8% yield with a *cis* and *trans* ratio of 1:0.43 accompanied with 2,3-dihydro-1,4-oxathiines **9** and **10** in 14% yield as byproducts under conditions A.[26] The yield of the desired product **3oa** was slightly increased to 9% when dimethyl sulfide was added as an additive due to favorable formation of six-membered 2,3-dihydro-1,4-oxathiines (Scheme 6).

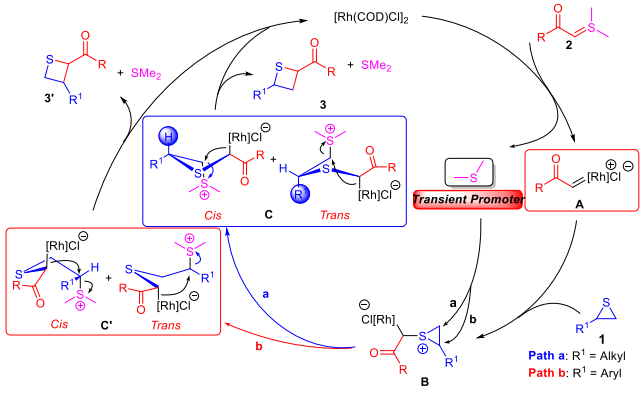
The reaction of thiirane **1a** and diazoacetophenone was further tested in the presence of sulfide additives. Although no desired product **3aa** was observed in the absence of sulfide additives, the desired product **3aa** was obtained in a trace amount in the presence of dimethyl sulfide and in 10% yield in the presence of tetrahydrothiophene. The results reveal that sulfide can promote the ring expansion (Scheme 7)



Scheme 6. Reaction of 2-Butylthiirane and Sulfoxonium Benzoylmethylide Ylide **8**.



Scheme 7. Reaction of 2-Phenoxymethylthiirane and Diazoacetophenone.



Scheme 8. Proposed the reaction mechanism.

The above results indicate that dimethyl sulfide plays a crucial role in the reaction, first as a nucleophile, and then as a leaving group, because other carbene precursors (dimethyl(oxo)-λ^4-sulfanylidene)-1-phenylethan-1-one (**8**) gave the desired product **3aa** in a low yield accompanied by 2,3-dihydro-1,4-oxathiines **9** and **10** as byproducts due to weak nucleophilicity of dimethyl sulfoxide (Scheme 6). Diazoacetophenone without dimethyl sulfide does not work under reaction conditions (Table 1, entries 20 and 21), but works in the presence of tetrahydrothiophene (Scheme 7). After obtaining the above information, we proposed the following reaction mechanism (Scheme 8), first, (dimethyl-λ^4-sulfanylidene)-1-arylethan-1-ones (sulfur ylides) **2** react with the metal Rh catalyst to form metallocarbenoid intermediates **A** by loss of dimethyl sulfide.[17a,17b] Then thiiranes **1** as nucleophiles attack the intermediates **A**, generating thiirane sulfonium intermediates **B**.[21b,22b] Intermediates **B** are activated thiiranium derivatives and can be attacked by dimethyl sulfide to generate ring-opened intermediates **C** (and **C'**) depending on the substituents of thiiranes.[27] In the ring opening reaction, all 2-alkylthiiranes are attacked on their less substituted ring carbon atom followed by intramolecularly nucleophilic attack to afford mixtures of *cis*- and *trans*-products **3** (Path **a**). However, all 2-arylthiiranes are attacked on their more substituted benzylic ring carbon atom mainly to give rise to ring-opened intermediates **C'** as major intermediates followed by intramolecularly nucleophilic attack to deliver thietanes **3'** as major products (Path **b**). The regioselectivity is similar to that in the Lewis acid $AgNO_3$-catalyzed ring opening reactions of thiiranes.[27]

To identify the function of dimethyl sulfide: acceleration or deceleration of the reaction because Me_2S may poison the active catalyst or disfavor the formation of intermediate **A**, under optimal conditions, we conducted the model reaction with additional 2 equiv. of Me_2S, giving product **3aa** in 79%, the same as that without additional Me_2S. We can conclude that Me_2S does not poison the active catalyst. We also carried out the model reaction in a round-bottom flask with a reflux condenser, affording product **3aa** in 72% yield, slightly lower than that in a pressure tube (79% yield, Table 1, entry 16), indicating the reaction maybe very fast. Before the escape of the generated Me_2S from the reaction mixture, the reaction almost finished. To verify the assumption, we determined the product yields at different reaction times for the model reaction. The profile of yield *vs* time is shown in Figure 2. The results indicate that the reaction occurred very fast, almost complete during 15 mins., showing a high turnover number.

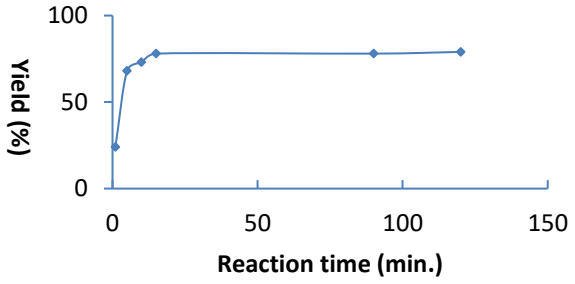
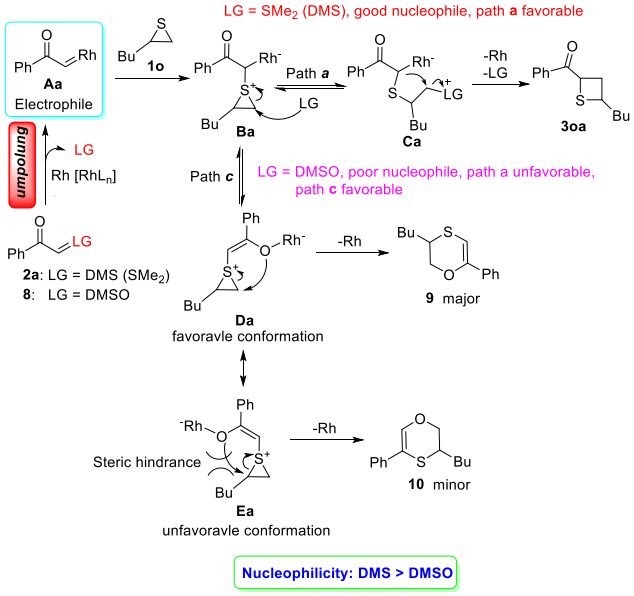


Figure 2. Profile of Yield *vs* Time for the Reaction of **1a** and **2a**.

The reactions of 2-(dimethyl-λ^6-sulfanylidene)-1-phenylethan-1-one (**2a**) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one (**8**) with 2-butylthiirane (**1o**) show different chemoselectivity. The former produced thietane **3oa** as only product (Table 3). However, the later gave rise to a mixture products of thietane **3oa**, 3-butyl-6-phenyl-2,3-dihydro-1,4-oxathiine (**9**) and 2-butyl-6-phenyl-2,3-dihydro-1,4-oxathiine (**10**) due to poor nucleophilicity of DMSO. Dimethyl sulfide (DMS) is a good nucleophile, favorably nucleophilically attacking the less ring carbon atom in the thiirane in the intermediate **Ba** to generate intermediate **Ca**, which undergoes an intramolecularly nucleophilic cyclization to afford thietane **3oa** (Path **a**). However, DMSO is a poor nucleophile, path **a** is not favorable, the competitive path **c** occurs. The intermediate **Ba** converts into its enolic forms **Da** (favorable conformation) and **Ea** (unfavorable conformation), which undergo intramolecular ring-opening reactions on their less and more substituted ring carbon atoms, respectively, to afford products **9** and **10** (Scheme 9).



Scheme 9. Rationale on the Different Chemoseletivity in the Reactions of 2-(Dimethyl-λ^6-sulfanylidene)-1-phenylethan-1-one (**2a**) and 2-(Dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one (**8**) with 2-Butylthiirane (**1o**).

All the results support that dimethyl sulfide serves as a transient nucleophile and a leaving group in the synthesis of thietanes from thiiranes through the carbene-induced electrophilic ring expansion. Dimethyl sulfide participation changes unfavorable Stevens rearrangement into favorable double nucleophilic substitution, making the electrophilic ring expansion smoothly.

CONCLUSIONS

The current reaction presents a new method for the synthesis of functionalized thietanes from readily available thiiranes through the electrophilic ring expansion strategy. The strategy effectively utilizes the tension of thiiranes and the nucleophilicity of the sulfur atom in thiiranes to react with the metallocarbenoids generated from safe and relatively easy-to-prepared carbene precursors, (dimethyl-λ^4-sulfanylidene)-1-arylethan-1-ones or *tert*-butyl 2-(dimethyl-λ^4-sulfanylidene)acetate. 2-Alkyl and 2-arylthiiranes show different regioselectivity in their electrophilic ring expansion. The umpolung from the nucleophilic ylides to the electrophilic carbenoids plays an important role in both the activation and ring-opening of less electrophilic thiiranes, even in subsequent intramolecular substitution because the released dimethyl sulfide during the umpolung acts as a nucleophile and leaving group in the subsequent double nucleophilic substitution process. This strategy provides an efficient route to prepare functionalized thietanes. Next, more work has to be done to achieve highly stereochemical control in the preparation of the expanded products.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all materials were purchased from commercial suppliers. Flash column chromatography was performed using silica gel (normal phase, 200-300 mesh) from Branch of Qingdao Haiyang Chemical Industry. Petroleum ether (PE) used for column chromatography is 60−90 °C fraction, and the removal of residue solvent was accomplished under rotovap. Reactions were monitored by thin-layer chromatography on silica gel GF254 coated 0.2 mm plates from Institute of Yantai Chemical Industry. The plates were visualized under UV light, as well as other TLC stains (10% phosphomolybdic acid in ethanol; 1% potassium permanganate in water; 10 g of iodine absorbed on 30 g of silica gel). ^{1}H and ^{13}C {1H} NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ with TMS as an internal standard, and the chemical shifts (δ) are reported in parts per million (ppm). All coupling constants (*J*) in ^{1}H NMR spectra are absolute values given in hertz (Hz) with peaks labeled as singlet (s), broad singlet (brs), doublet (d), triplet (t), quartet (q), and multiplet (m). The IR spectra (KBr pellets, *v* [cm^{-1}]) were taken on a Nicolet 5700 FTIR spectrometer. HRMS measurements were carried out on an Agilent LC/MSD TOF mass spectrometer. LRMS measurements were carried out on Thermo Trace 1300/ISQ QD system. Melting points were obtained on a Yanaco MP-500 melting point apparatus and are uncorrected.

General Procedure for the Synthesis of Sulfur Ylides 2a-2j.[28]

To a solution of 2-bromoacetophenone (1.99 g, 10 mmol) in acetone (15 mL) was added dimethyl sulfide (620 mg, 10 mmol). After the mixture had been stirred at room temperature for 12 h, the residue was filtered and washed with acetone. The solid product was used as sulfonium bromide without further purification. The corresponding sulfonium bromide was added to a solution of NaOH (400 mg, 10 mmol) in water (10 mL). The solution was stirred at room temperature for 30 min and then extracted several times with dichloromethane. The combined organic layers were washed with water and brine sequentially, dried over Na_2SO_4, filtered, and concentrated. The sulfur ylide obtained can be used directly without further purification. **2a−2i** were prepared by the general procedure.

2-(Dimethyl-λ⁴-sulfanylidene)-1-phenylethan-1-one (2a).[28b] Yellow solid 700 mg, 51% yield. M.p.: 37–38 °C, Lit.[28c] M.p.: 56–57 °C). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.81 – 7.74 (m, 2H, ArH), 7.36 – 7.31 (m, 3H, ArH), 4.33 (br s, 1H), 2.92 (s, 6H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 182.6, 140.7, 129.3, 127.6, 126.1, 51.5, 28.3.

2-(Dimethyl-λ⁴-sulfanylidene)-1-(p-tolyl)ethan-1-one (2b).[28b] Yellow solid 533 mg, 55% yield. M.p.: 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.68 (d, *J* = 8.3 Hz, 2H, ArH), 7.14 (d, *J* = 7.9 Hz, 2H, ArH), 4.30 (s, 1H), 2.99 – 2.98 (m, 6H), 2.35 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 183.2, 139.5, 138.1, 128.5, 126.3, 49.9, 28.5, 21.3.

2-(Dimethyl-λ⁴-sulfanylidene)-1-(4-methoxyphenyl)ethan-1-one (2c).[28b] Yellow solid 620 mg, 37% yield. M.p.: 106–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.74 – 7.71 (m, 2H, ArH), 6.85 – 6.83 (m, 2H, ArH), 4.25 (s, 1H), 3.803 – 3.796 (m, 3H), 2.96 – 2.94 (m, 6H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 182.6, 160.7, 133.5, 127.8, 113.0, 55.2, 50.4, 28.7.

1-(4-Chlorophenyl)-2-(dimethyl-λ⁴-sulfanylidene)ethan-1-one (2d).[28d] White solid 939 mg, 44% yield. M.p.: 119–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.69 (d, *J* = 8.5 Hz, 2H, ArH), 7.28 (d, *J* = 8.5 Hz, 2H, ArH), 4.26 (s, 1H), 2.97 (s, 6H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 181.7, 139.3, 135.3, 127.9, 127.7, 50.9, 28.3.

1-(4-Bromophenyl)-2-(dimethyl-λ⁴-sulfanylidene)ethan-1-one (2e).[28b] Yellow solid 1.27 g, 84% yield. M.p.: 112–113 °C, Lit.[28c] M.p: 121–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.60 (d, *J* = 8.4 Hz, 2H, ArH), 7.42 (d, *J* = 8.5 Hz, 2H, ArH), 4.27 (s, 1H), 2.92 (s, 6H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 181.5, 139.7, 130.8, 127.9, 123.7, 51.5, 28.3.

2-(Dimethyl-λ⁴-sulfanylidene)-1-(4-nitrophenyl)ethan-1-one (2f).[28b] Yellow solid 1.37 g, 94% yield. M.p.: 119–120 °C, Lit.[28c] M.p.: 110–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 8.18 – 8.15 (m, 2H, ArH), 7.89 – 7.87 (m, 2H, ArH), 4.42 (s, 1H), 3.02 – 3.01 (s, 6H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 180.1, 148.3, 146.7, 127.2, 123.2, 53.6, 28.0.

1-(3-Chlorophenyl)-2-(dimethyl-λ⁴-sulfanylidene)ethan-1-one (2g). Yellow liquid 1.22 g, 65%. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.74 (t, *J* = 1.9 Hz, 1H, ArH), 7.61 (dt, *J* = 7.4, 1.5 Hz, 1H, ArH) 7.30 – 7.22 (m, 2H, ArH), 4.27 (s, 3H), 2.93 (s, 6H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 180.9, 142.7, 133.7, 129.1, 129.0, 126.4, 124.3, 52.1, 28.2. IR (KBr): *ν* = 1574, 1516, 872, 843 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{10}H_{12}ClOS^+$: 215.0292, found: 215.0292.

1-(3,4-Dichlorophenyl)-2-(dimethyl-λ⁴-sulfanylidene)ethan-1-one (2h). Yellowish solid 1.08 g, 58%. M.p.: 136–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.85 – 7.84 (m, 1H, ArH), 7.60 – 7.52 (m, 1H, ArH), 7.40 – 7.34 (m, 1H, ArH), 4.26 – 4.25 (m, 1H), 2.97 – 2.96 (m, 6H). ^{13}C {1H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 180.0, 140.9, 133.1, 132.0, 129.8, 128.4, 125.5, 51.7, 28.2. IR (KBr): *ν* = 1569, 1515, 1395, 846 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{10}H_{11}Cl_2OS^+$: 248.9902, found: 248.9902.

2-(Dimethyl-λ⁴-sulfanylidene)-1-(naphthalen-1-yl)ethan-1-one (2i). White solid 550 mg, 75%. M.p.: 160–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 8.47 (d, *J* = 7.9 Hz, 2H, ArH), 7.85 – 7.69 (m, 2H, ArH), 7.48 – 7.37 (m, 3H, ArH), 4.07 (br s, 1H), 3.05 (s, 6H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 175.2, 133.7, 130.6, 128.4, 127.9, 126.3, 125.9, 125.5, 124.9, 124.4, 54.8, 28.7. IR (KBr): *ν* = 1510, 1405, 839 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{14}H_{15}OS^+$: 231.0838, found: 231.0838.

(1-Adamantan-1-yl)-2-(dimethyl-l4-sulfanylidene)ethan-1-one (2j). White solid 677 mg, 87%. M.p.: 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 3.67 (s, 1H), 3.83 – 3.82 (m, 6H), 1.96 (br s, 3H), 1.77 (br s, 3H), 1.70 – 1.64 (m, 6H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 197.7, 48.1, 42.5, 40.1, 37.0, 28.7, 28.7. IR (KBr): *ν* = 2899, 2847, 1483, 850 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{14}H_{23}OS^+$: 239.1464, found: 239.1465.

Synthesis of Sulfur Ylide 2k.[29]

A 50 mL round-bottomed flask was charged with *tert*-butyl bromoacetate (5.00 g, 25.7 mmol), acetone (15 mL), and dimethylsulfide (5.1 mL, 69 mmol). The reaction vessel was sealed and the reaction mixture was stirred at room temperature overnight, during which the product precipitated. The solid product was then filtered and washed several times with cold acetone and dried under reduced pressure to give the product as a white crystalline solid (6.62 g, 25.7 mmol, quant.). The product was used in the subsequent step without further purification or characterization. A 25 mL round-bottomed flask was charged with (2-(*tert*-butoxy)-2-oxoethyl)dimethylsulfonium bromide (1.82 g, 7.10 mmol) and $CHCl_3$ (8 mL). The reaction mixture was allowed to stir for 5 min until the reaction mixture had become homogeneous. The reaction mixture was cooled to 0 °C and saturated aq. K_2CO_3 (4.6 mL) and aq. NaOH solution (1 mL, 12 M, 7.2 mmol) were added in quick succession with vigorous stirring. The reaction mixture immediately became heterogeneous and the reaction mixture was brought to r.t. and stirred. After 15 min the reaction mixture was filtered, and the top organic layer was separated from the aqueous layer. The aqueous layer was extracted once with $CHCl_3$. The combined organics were dried over K_2CO_3 and concentrated under reduced pressure to provide the crude product as an off-white solid in quantitative yield (1.25 g, 7.09 mmol), which was used in the subsequent step without further purification.

tert-Butyl 2-(dimethyl-λ⁴-sulfanylidene)acetate (2k).[29b] White solid quantitative yield (1.25g). M.p.: 61–63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 2.69 (br s, 1H), 2.60 (s, 6H), 1.33 (s, 9H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 170.5, 76.8, 32.9, 30.7, 29.0.

General Procedure for the Synthesis of Sulfur Ylide 8.[30]

In a 125 mL flame-dried round bottom flask attached to a reflux condenser, under argon atmosphere, potassium *tert*-butoxide (3.0 g, 27.2 mmol) and 27.0 mL of anhydrous THF were added. Then, trimethylsulfoxonium iodide (4.48 g, 20.4 mmol) was added in one portion. After the suspension was refluxed for 2 hours, the mixture was cooled to 0 °C followed by slow addition of benzoyl chloride (956 mg, 6.8 mmol). The reaction temperature was allowed to warm to room temperature and the mixture was stirred for additional 3 hours. After that, 70 mL of water was added and the product was extracted with a CH_2Cl_2:*i*-PrOH (3:1, *v*/*v*) mixture (8×20 mL). The organic phase was washed with water (3×10 mL), dried over Na_2SO_4, and the solvent was removed on a rotary evaporator. The crude material was purified by recrystallization from a mixture of petroleum and ethyl acetate.

(Dimethyl(oxo)-λ⁴-sulfanylidene)-1-phenylethan-1-one (8). White solid 760 mg, 70% yield. M.p.: 127–128 °C, Lit.[30] M.p.: 119–121 °C. R_f = 0.33, 5% methol in dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.84 – 7.74 (m, 2H, ArH), 7.48 – 7.34 (m, 3H, ArH), 4.98 (s, 1H), 3.52 – 3.47 (m, 6H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 182.3, 138.8, 130.7, 128.1, 126.5, 68.2, 42.4.

General Procedure for the Synthesis of Thietanes 3

Conditions A: A pressure tube was charged with $[Rh(COD)Cl]_2$ (3 mg, 5 mol %), $C(CH_2OH)_4$ (3 mg, 20 mol%), thiirane (0.125 mmol), sulfoxonium ylide (0.25 mmol), and DCE (1 mL). The reaction mixture was stirred under N_2 conditions at 80 °C in an oil bath for 2 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA (10:1, *v*/*v*) as eluent to afford the product **3**.

Conditions B: A pressure tube was charged with $(CF_3CO_2)_4Rh_2$ (4 mg, 5 mol %), $C(CH_2OH)_4$ (3 mg, 20 mol%), thiirane (0.125 mmol), sulfoxonium ylide (0.25 mmol), and DCE (1 mL). The reaction mixture was stirred under N_2 conditions at 80 °C in an oil bath for 2 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA (10:1, *v*/*v*) as eluent to afford the product **3**.

2-(Benzoyl)-4-(phenoxymethyl)thietane (3aa). White solid 20 mg, 58% yield. M.p.: 94–97 °C. R_f = 0.24, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.80 – 7.76 (m, 2H, ArH), 7.56 – 7.52 (m, 1H, ArH), 7.45 – 7.41 (m, 2H, ArH), 6.97 – 6.89 (m, 1H, ArH), 6.93 – 6.83 (m, 2H, ArH), 4.81 – 4.77 (m, 1H), 4.30 (dd, *J* = 9.7, 6.3 Hz, 1H), 4.23 – 4.19 (m, 1H), 4.01 – 3.88 (m, 1H), 3.68 (ddd, *J* = 12.5, 8.8, 5.7 Hz, 1H), 2.80 (ddd, *J* = 12.6, 8.5, 5.5 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 196.3, 196.1, 158.5, 158.4, 133.9, 133.6, 133.53, 133.47, 129.5, 129.4, 128.8, 128.29, 128.28, 121.2, 121.0, 114.73, 114.66, 72.9, 72.6, 37.5, 36.8, 36.4, 35.7, 28.9, 28.3. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.80 – 7.76 (m, 2H, ArH), 7.56 – 7.52 (m, 1H, ArH), 7.45 – 7.41 (m, 2H, ArH), 6.97 – 6.89 (m, 1H, ArH), 6.93 – 6.83 (m, 2H, ArH), 4.81 – 4.77 (m, 1H), 4.23 – 4.19 (m, 1H), 4.07 (dd, *J* = 9.4, 7.3 Hz, 1H), 4.01 – 3.88 (m, 1H), 3.37 (ddd, *J* = 12.6, 6.2, 6.2 Hz, 1H), 3.10 (ddd, *J* = 12.8, 8.7, 8.7 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 196.3, 196.1, 158.5, 158.4, 133.9, 133.6, 133.53, 133.47, 129.5, 129.4, 128.8, 128.29, 128.28, 121.2, 121.0, 114.73, 114.66, 72.9, 72.6, 37.5, 36.8, 36.4, 35.7, 28.9, 28.3. IR (KBr): *ν* = 2942, 2860, 1682, 1598, 1586, 1496, 1387 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{17}O_2S^+$: 285.0944, found: 285.0945.

2-(Benzoyl)-4-((2-methylphenyloxy)methyl)thietane (3ba). Gold yellow liquid 20 mg, 57% yield. R_f = 0.26, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.84 – 7.80 (m, 2H, ArH), 7.60 – 7.55 (m, 1H, ArH), 7.49 – 7.44 (m, 2H, ArH), 7.20 – 7.10 (m, 2H, ArH), 7.92 – 7.79 (m, 2H, ArH), 4.86 – 4.82 (m, 1H), 4.34 (dd, *J* = 9.7, 6.1 Hz, 1H), 4.25 (dd, *J* = 9.5, 6.3 Hz, 1H), 4.12 – 3.96 (m, 1H), 3.73 (ddd, *J* = 12.6, 8.8, 5.6 Hz, 1H), 2.86 (ddd, *J* = 12.5, 8.5, 5.5 Hz, 1H), 2.25 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 196.2, 196.1, 156.6, 156.5, 133.9, 133.6, 133.52, 133.47, 130.8, 130.7, 128.8, 128.30, 128.28, 127.05, 126.99, 126.8, 126.7, 120.9, 120.8, 111.5, 111.4, 73.0, 72.7, 37.6, 36.8, 36.7, 35.9, 28.9, 28.2, 16.2, 16.1. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.84 – 7.80 (m, 2H, ArH), 7.60 – 7.55 (m, 1H, ArH), 7.49 – 7.44 (m, 2H, ArH), 7.20 – 7.10 (m, 2H, ArH), 7.92 – 7.79 (m, 2H, ArH), 4.86 – 4.82 (m, 1H), 4.25 (dd, *J* = 9.5, 6.3 Hz, 1H), 4.12 – 3.96 (m, 2H), 3.44 (ddd, *J* = 12.7, 6.3, 6.3 Hz, 1H), 3.12 (ddd, *J* = 12.9, 8.5, 8.5 Hz, 1H), 2.18 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 196.2, 196.1, 156.6, 156.5, 133.9, 133.6, 133.52, 133.47, 130.8, 130.7, 128.8, 128.30, 128.28, 127.05, 126.99, 126.8, 126.7, 120.9, 120.8, 111.5, 111.4, 73.0, 72.7, 37.6, 36.8, 36.7, 35.9, 28.9, 28.2, 16.2, 16.1. IR (KBr): *ν* = 2855, 1682, 1597, 1495, 1382 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{19}O_2S^+$: 299.1100, found: 299.1100.

2-(Benzoyl)-4-((3-methylphenyloxy)methyl)thietane (3ca). Gold yellow solid 26 mg, 71% yield. M.p.: 52–53 °C. R_f = 0.26, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.83 – 7.80 (m, 2H, ArH), 7.59 – 7.55 (m, 1H, ArH), 7.48 – 7.44 (m, 2H, ArH), 7.21 – 7.13 (m, 1H, ArH), 6.82 – 6.67 (m, 3H, ArH), 4.82 (dd, *J* = 8.5, 5.9 Hz, 1H), 4.32 (dd, *J* = 9.8, 6.4 Hz, 1H), 4.26 – 4.21 (m, 1H), 4.04 – 3.91 (m, 1H), 3.71 (ddd, *J* = 12.6, 8.8, 5.7 Hz, 1H), 2.83 (ddd, *J* = 12.6, 8.5, 5.5 Hz, 1H), 2.35 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 196.3, 196.1, 158.5, 158.4, 139.6, 139.5, 133.8, 133.6, 133.5, 133.4, 129.2, 129.1, 128.8, 128.29, 128.28, 122.0, 121.9, 115.6, 115.5, 111.5, 72.9, 72.6, 37.5, 36.8, 36.4, 35.7, 28.9, 28.3, 21.5, 21.4. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.83 – 7.80 (m, 2H, ArH), 7.59 – 7.55 (m, 1H, ArH), 7.48 – 7.44 (m, 2H, ArH), 7.21 – 7.13 (m, 1H, ArH), 6.82 – 6.67 (m, 3H, ArH), 4.82 (dd, *J* = 8.5, 5.9 Hz, 1H), 4.26 – 4.21 (m, 1H), 4.09 (dd, *J* = 9.4, 7.3 Hz, 1H), 4.04 – 3.91 (m, 1H), 3.40 (ddd, *J* = 12.6, 6.2, 6.2 Hz, 1H), 3.13 (ddd, *J* = 12.9, 8.7, 8.7 Hz, 1H), 2.32 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 196.3, 196.1, 158.5, 158.4, 139.6, 139.5, 133.8, 133.6, 133.5, 133.4, 129.2, 129.1, 128.8, 128.29, 128.28, 122.0, 121.9, 115.6, 115.5, 111.5, 72.9, 72.6, 37.5, 36.8, 36.4, 35.7, 28.9, 28.3, 21.5, 21.4. IR (KBr): *ν* = 2943, 2861, 1682, 1598, 1583, 1385 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{19}O_2S^+$: 299.1100, found: 299.1100.

2-(Benzoyl)-4-((4-methoxyphenoxy)methyl)thietane (3da). Yellow green solid 24 mg, 62% yield. M.p.: 71–75 °C. R_f = 0.28, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.82 – 7.79 (m, 2H, ArH), 7.59 – 7.55 (m, 1H, ArH), 7.48 – 7.44 (m, 2H, ArH), 6.90 – 6.79 (m, 4H, ArH), 4.84 – 4.80 (m, 1H), 4.29 (dd, *J* = 9.8, 6.3 Hz, 1H), 4.22 – 4.17 (m, 1H), 4.02 – 3.89 (m, 1H), 3.78 (s, 3H), 3.70 (ddd, *J* = 12.6, 8.8, 5.6 Hz, 1H), 2.82 (ddd, *J* = 12.6, 8.5, 5.5 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 196.2, 196.0, 157.2, 157.1, 133.8, 133.6, 133.5, 129.4, 129.3, 128.83, 128.82, 128.29, 128.28, 126.1, 125.9, 116.02, 115.95, 73.2, 73.0, 37.4, 36.7, 36.2, 35.5, 28.8, 28.2. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.82 – 7.79 (m, 2H, ArH), 7.59 – 7.55 (m, 1H, ArH), 7.48 – 7.44 (m, 2H, ArH), 6.90 – 6.79 (m, 4H, ArH), 4.84 – 4.80 (m, 1H), 4.22 – 4.17 (m, 1H), 4.05 (dd, *J* = 9.3, 7.3 Hz, 1H), 4.02 – 3.89 (m, 1H), 3.76 (s, 3H), 3.39 (ddd, *J* = 12.6, 6.2, 6.2 Hz, 1H), 3.11 (ddd, *J* = 12.8, 8.6, 8.6 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 196.2, 196.0, 157.2, 157.1, 133.8, 133.6, 133.5, 129.4, 129.3, 128.83, 128.82, 128.29, 128.28, 126.1, 125.9, 116.02, 115.95, 73.2, 73.0, 37.4, 36.7, 36.2, 35.5, 28.8, 28.2. IR (KBr): *ν* = 2933, 1680, 1596, 1581,

1508, 1384 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ $C_{18}H_{19}O_3S^+$: 315.1049, found: 315.1054.

2-(Benzoyl)-4-((4-chlorophenoxy)methyl)thietane (3ea). Yellow green liquid 16 mg, 40% yield. R_f = 0.35, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.82 – 7.79 (m, 2H, ArH), 7.59 – 7.55 (m, 1H, ArH), 7.48 – 7.44 (m, 2H, ArH), 7.25 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 4.83 – 4.79 (m, 1H), 4.29 (dd, *J* = 9.7, 6.2 Hz, 1H), 4.22 – 4.18 (m, 1H), 4.01 – 3.90 (m, 1H), 3.71 (ddd, *J* = 12.6, 8.8, 5.6 Hz, 1H), 2.81 (ddd, *J* = 12.7, 8.5, 5.5 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.2, 196.0, 157.2, 157.1, 133.8, 133.6, 133.5, 129.4, 129.3, 128.83, 128.82, 128.29, 128.28, 126.1, 125.9, 116.02, 115.95, 37.4, 36.7, 36.2, 35.5, 28.8, 28.2. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.82 – 7.79 (m, 2H, ArH), 7.59 – 7.55 (m, 1H, ArH), 7.48 – 7.44 (m, 2H, ArH), 7.21 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 4.83 – 4.79 (m, 1H), 4.22 – 4.18 (m, 1H), 4.06 (dd, *J* = 9.4, 7.3 Hz, 1H), 4.01 – 3.90 (m, 1H), 3.38 (ddd, *J* = 12.9, 6.1, 6.1 Hz, 1H), 3.13 (ddd, *J* = 12.9, 8.7, 8.7 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.2, 196.0, 157.2, 157.1, 133.8, 133.6, 133.5, 129.4, 129.3, 128.83, 128.82, 128.29, 128.28, 126.1, 125.9, 116.02, 115.95, 37.4, 36.7, 36.2, 35.5, 28.8, 28.2. IR (KBr): ν = 2942, 2858, 1681, 1596, 1581, 1491, 1385 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}ClO_2S^+$: 319.0554, found: 319.0548.

2-Benzoyl-4-((2,4-dimethylphenoxy)methyl)thietane (3fa). Orange solid 29 mg, 75% yield. M.p.: 85–89 °C. R_f = 0.43, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.86 – 7.76 (m, 2H, ArH), 7.59 – 7.55 (m, 1H, ArH), 7.49 – 7.44 (m, 2H, ArH), 7.09 – 7.01 (m, 1H, ArH), 6.83 – 6.68 (m, 2H, ArH), 4.86 – 4.81 (m, 1H), 4.32 (dd, *J* = 9.7, 6.1 Hz, 1H), 4.26 – 4.19 (m, 1H), 4.13 – 3.95 (m, 1H), 3.72 (ddd, *J* = 12.6, 8.8, 5.6 Hz, 1H), 2.86 (ddd, *J* = 12.5, 8.5, 5.6 Hz, 1H), 2.29 (s, 3H), 2.17 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.2, 196.1, 156.4, 156.2, 138.1, 137.9, 133.9, 133.6, 133.5, 133.4, 128.9, 128.8, 128.5, 128.3, 125.8, 125.7, 125.52, 125.46, 122.8, 122.7, 109.5, 109.4, 73.4, 73.1, 37.6, 36.8, 36.7, 35.9, 28.9, 28.3, 20.05, 20.02, 11.6, 11.5. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.86 – 7.76 (m, 2H, ArH), 7.59 – 7.55 (m, 1H, ArH), 7.49 – 7.44 (m, 2H, ArH), 7.09 – 7.01 (m, 1H, ArH), 6.83 – 6.68 (m, 2H, ArH), 4.86 – 4.81 (m, 1H), 4.26 – 4.19 (m, 1H), 4.13 – 3.95 (m, 2H), 3.43 (ddd, *J* = 12.3, 6.1, 6.1 Hz, 1H), 3.11 (ddd, *J* = 13.0, 8.6, 8.6 Hz, 1H), 2.25 (s, 3H), 2.10 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.2, 196.1, 156.4, 156.2, 138.1, 137.9, 133.9, 133.6, 133.5, 133.4, 128.9, 128.8, 128.5, 128.3, 125.8, 125.7, 125.52, 125.46, 122.8, 122.7, 109.5, 109.4, 73.4, 73.1, 37.6, 36.8, 36.7, 35.9, 28.9, 28.3, 20.05, 20.02, 11.6, 11.5. IR (KBr): ν = 2940, 2859, 1682, 1597, 1582, 1384 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{21}O_2S^+$: 313.1257, found: 313.1253.

2-(Benzoyl)-4-((2,3-dimethylphenoxy)methyl)thietane (3ga). White solid 27 mg, 70% yield. M.p.: 55–58 °C. R_f = 0.43, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.84 – 7.80 (m, 2H, ArH), 7.59 – 7.55 (m, 1H, ArH), 7.49 – 7.44 (m, 2H, ArH), 7.97 – 7.91 (m, 2H, ArH), 6.76 (d, *J* = 7.9 Hz, 1H), 4.85 – 4.81 (m, 1H), 4.31 (dd, *J* = 9.8, 6.1 Hz, 1H), 4.23 – 4.19 (m, 1H), 4.09 – 3.94 (m, 1H), 3.71 (ddd, *J* = 12.5, 8.8, 5.6 Hz, 1H), 2.85 (ddd, *J* = 12.5, 8.5, 5.5 Hz, 1H), 2.28 – 2.15 (m, 6H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.2, 196.1, 154.5, 154.4, 133.9, 133.6, 133.5, 133.4, 131.6, 131.5, 130.2, 130.0, 128.8, 128.29, 128.27, 126.94, 126.89, 126.83, 126.78, 111.7, 111.6, 73.4, 73.1, 37.6, 36.8, 36.7, 35.9, 28.9, 28.3, 20.44, 20.42, 16.1, 16.0. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.84 – 7.80 (m, 2H, ArH), 7.59 – 7.55 (m, 1H, ArH), 7.49 – 7.44 (m, 2H, ArH), 7.97 – 7.91 (m, 2H, ArH), 6.70 (d, *J* = 8.9 Hz, 1H), 4.85 – 4.81 (m, 1H), 4.23 – 4.19 (m, 1H), 4.09 – 3.94 (m, 2H), 3.42 (ddd, *J* = 12.6, 6.3, 6.3 Hz, 1H), 3.10 (dt, *J* = 13.0, 8.6, 8.6 Hz, 1H), 2.28 – 2.15 (m, 6H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.2, 196.1, 154.5, 154.4, 133.9, 133.6, 133.5, 133.4, 131.6, 131.5, 130.2, 130.0, 128.8, 128.29, 128.27, 126.94, 126.89, 126.83, 126.78, 111.7, 111.6, 73.4, 73.1, 37.6, 36.8, 36.7, 35.9, 28.9, 28.3, 20.44, 20.42, 16.1, 16.0. IR (KBr): ν = 2920, 1682, 1612, 1581, 1503, 1383, 1302 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{21}O_2S^+$: 313.1257, found: 313.1266.

2-(Benzoyl)-4-methyl-4-((4-methylphenoxy)methyl)thietane (3ha). Golden yellow liquid 10 mg, 26% yield. R_f = 0.15, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.85 – 7.79 (m, 2H, ArH), 7.59 – 7.53 (m, 1H, ArH), 7.48 – 7.43 (m, 2H, ArH), 7.06 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 4.80 – 4.76 (m, 1H), 4.24 (d, *J* = 9.2 Hz, 1H), 4.08 (d, *J* = 9.3 Hz, 1H), 3.57 (dd, *J* = 12.8, 5.7 Hz, 1H), 2.75 (dd, *J* = 12.8, 8.8 Hz, 1H), 2.27 (s, 3H), 1.80 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.43, 196.41, 156.9, 156.7, 133.9, 133.5, 133.4, 130.4, 130.1, 129.9, 129.8, 128.8, 128.7, 128.4, 128.3, 114.64, 114.58, 45.81, 45.79, 35.3, 35.2, 34.2, 33.5, 28.5, 28.0, 20.49, 20.46. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.85 – 7.79 (m, 2H, ArH), 7.59 – 7.53 (m, 1H, ArH), 7.48 – 7.43 (m, 2H, ArH), 7.12 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 4.80 – 4.76 (m, 1H), 4.10 (d, *J* = 9.1 Hz, 1H), 3.98 (d, *J* = 9.1 Hz, 1H), 3.44 (dd, *J* = 12.7, 6.9 Hz, 1H), 2.92 (dd, *J* = 12.6, 8.4 Hz, 1H), 2.31 (s, 3H), 1.61 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.43, 196.41, 156.9, 156.7, 133.9, 133.5, 133.4, 130.4, 130.1, 129.9, 129.8, 128.8, 128.7, 128.4, 128.3, 114.64, 114.58, 45.81, 45.79, 35.3, 35.2, 34.2, 33.5, 28.5, 28.0, 20.49, 20.46. IR (KBr): ν = 2927, 2863, 1685, 1608, 1512, 1384 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{21}O_2S^+$: 313.1257, found: 313.1257.

2-(Benzoyl)-4-((benzyloxy)methyl)thietane (3ia). Light yellow liquid 21 mg, 57% yield. R_f = 0.35, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.82 – 7.79 (m, 2H, ArH), 7.59 – 7.54 (m, 1H, ArH), 7.48 – 7.43 (m, 2H, ArH), 7.37 – 7.27 (m, 5H, ArH), 4.75 (dd, *J* = 8.5, 5.5 Hz, 1H), 4.62 (s, 2H), 3.91 – 3.73 (m, 3H), 3.64 – 3.58 (m, 1H), 2.72 (ddd, *J* = 12.6, 8.5, 5.0 Hz, 1H), ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.4, 196.3, 138.01, 137.98, 133.9, 133.7, 133.5, 133.4, 128.8, 128.44, 128.38, 128.31, 128.28, 127.74, 127.68, 75.8, 75.0, 73.3, 73.2, 37.5, 37.1, 36.8, 36.4, 28.9, 28.5. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.82 – 7.79 (m, 2H, ArH), 7.59 – 7.54 (m, 1H, ArH), 7.48 – 7.43 (m, 2H, ArH), 7.37 – 7.27 (m, 5H, ArH), 4.80 (dd, *J* = 8.5, 6.5 Hz, 1H), 4.53 (s, 2H), 3.91 – 3.73 (m, 2H), 3.64 – 3.58 (m, 1H), 3.30 (ddd, *J* = 13.0, 6.6, 6.6 Hz, 1H), 3.01 (ddd, *J* = 12.8, 8.6, 8.6 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.4, 196.3, 138.01, 137.98, 133.9, 133.7, 133.5, 133.4, 128.8, 128.44, 128.38, 128.31, 128.28, 127.74,

127.68, 75.8, 75.0, 73.3, 73.2, 37.5, 37.1, 36.8, 36.4, 28.9, 28.5. IR (KBr): ν = 2939, 2863, 1681, 1596, 1581 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{19}O_2S^+$: 299.1100, found: 299.1100.

2-(Benzoyl)-4-((phenethoxy)methyl)thietane (3ja). Colorless liquid 25 mg, 65% yield. R_f = 0.35, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.81 – 7.77 (m, 2H, ArH), 7.57 – 7.54 (m, 1H, ArH), 7.47 – 7.43 (m, 2H, ArH), 7.31 – 7.17 (m, 5H, ArH), 4.71 (dd, *J* = 8.5, 5.6 Hz, 1H), 3.85 – 3.54 (m, 6H), 2.92 (t, *J* = 7.1 Hz, 2H), 2.66 (ddd, *J* = 12.2, 8.5, 4.9 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.4, 196.2, 138.8, 138.7, 133.9, 133.6, 133.5, 133.4, 128.89, 128.86, 128.8, 128.7, 128.32, 128.28, 126.2, 126.1, 76.3, 75.8, 72.23, 72.19, 37.5, 37.1, 36.8, 36.33, 36.27, 36.1, 28.9, 28.4. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.81 – 7.77 (m, 2H, ArH), 7.57 – 7.54 (m, 1H, ArH), 7.47 – 7.43 (m, 2H, ArH), 7.31 – 7.17 (m, 5H, ArH), 4.78 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.85 – 3.54 (m, 5H), 3.26 (ddd, *J* = 12.9, 6.5, 6.5 Hz, 1H), 2.99 (ddd, *J* = 12.8, 8.6, 8.6 Hz, 1H), 2.86 (t, *J* = 7.2 Hz, 2H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.4, 196.2, 138.8, 138.7, 133.9, 133.6, 133.5, 133.4, 128.89, 128.86, 128.8, 128.7, 128.32, 128.28, 126.2, 126.1, 76.3, 75.8, 72.23, 72.19, 37.5, 37.1, 36.8, 36.33, 36.27, 36.1, 28.9, 28.4. IR (KBr): ν = 2857, 1682, 1597, 1581 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{21}O_2S^+$: 313.1257, found: 313.1258.

2-Benzoyl-4-((naphthalen-1-yloxy)methyl)thietane (3ka). Golden yellow liquid 30 mg, 72% yield. R_f = 0.39, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 8.29 – 8.25 (m, 1H, ArH), 7.85 – 7.34 (m, 10H, ArH), 6.87 (d, *J* = 7.4 Hz, 1H, ArH), 4.90 – 4.84 (m, 1H), 4.51 (dd, *J* = 9.6, 6.2 Hz, 1H), 4.46 – 4.39 (m, 1H), 4.24 – 4.09 (m, 1H), 3.79 (ddd, *J* = 12.6, 8.8, 5.5 Hz, 1H), 2.95 (ddd, *J* = 12.6, 8.5, 5.7 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.2, 196.1, 154.2, 154.1, 134.5, 134.4, 133.8, 133.6, 133.55, 133.50, 128.8, 128.3, 127.5, 127.4, 126.5, 126.4, 125.73, 125.71, 125.6, 125.5, 125.3, 125.2, 121.90, 121.86, 120.8, 120.6, 105.12, 105.10, 73.0, 72.8, 37.6, 36.8, 36.6, 35.7, 29.0, 28.3. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 8.22 – 8.18 (m, 1H, ArH), 7.85 – 7.34 (m, 10H, ArH), 6.81 (d, *J* = 7.4 Hz, 1H), 4.90 – 4.84 (m, 1H), 4.46 – 4.39 (m, 1H), 4.29 (dd, *J* = 9.5, 7.3 Hz, 1H), 3.52 (ddd, *J* = 12.7, 6.3, 6.3 Hz, 1H), 3.19 (ddd, *J* = 12.9, 8.7, 8.7 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.2, 196.1, 154.2, 154.1, 134.5, 134.4, 133.8, 133.6, 133.55, 133.50, 128.8, 128.3, 127.5, 127.4, 126.5, 126.4, 125.73, 125.71, 125.6, 125.5, 125.3, 125.2, 121.90, 121.86, 120.8, 120.6, 105.12, 105.10, 73.0, 72.8, 37.6, 36.8, 36.6, 35.7, 29.0, 28.3. IR (KBr): ν = 3062, 2868, 1689, 1581, 1509 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{19}O_2S^+$: 335.1100, found: 335.1100.

2-(Benzoyl)-4-((naphthalen-2-yloxy)methyl)thietane (3la). Light green liquid 27 mg, 65% yield. R_f = 0.38, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.83 – 7.09 (m, 12H, ArH), 4.86 – 4.81 (m, 1H), 4.44 (dd, *J* = 9.7, 6.3 Hz, 1H), 4.38 – 4.33 (m, 1H), 4.19 – 3.98 (m, 1H), 3.75 (ddd, *J* = 12.6, 8.8, 5.7 Hz, 1H), 2.87 (ddd, *J* = 12.6, 8.5, 5.5 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.3, 196.1, 156.5, 156.4, 134.4, 133.8, 133.6, 133.55, 133.49, 129.5, 129.4, 129.15, 129.07, 128.8, 128.31, 128.29, 127.7, 127.6, 126.8, 126.7, 126.4, 126.3, 123.8, 123.7, 118.8, 118.7, 107.0, 73.0, 72.7, 37.6, 36.8, 36.4, 35.6, 29.0, 28.3. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.83 – 7.09 (m, 12H, ArH), 4.86 – 4.81 (m, 1H), 4.38 – 4.33 (m, 1H), 4.23 (dd, *J* = 9.6, 7.3 Hz, 1H), 4.19 – 3.98 (m, 1H), 3.46 (ddd, *J* = 12.6, 6.1, 6.1 Hz, 1H), 3.18 (ddd, *J* = 12.9, 8.7, 8.7 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.3, 196.1, 156.5, 156.4, 134.4, 133.8, 133.6, 133.55, 133.49, 129.5, 129.4, 129.15, 129.07, 128.8, 128.31, 128.29, 127.7, 127.6, 126.8, 126.7, 126.4, 126.3, 123.8, 123.7, 118.8, 118.7, 107.0, 73.0, 72.7, 37.6, 36.8, 36.4, 35.6, 29.0, 28.3. IR (KBr): ν = 2922, 2853, 1681, 1599, 1581, 1510 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{19}O_2S^+$: 335.1100, found: 335.1098.

2-(Benzoyl)-4-((((6-bromonaphthalen-2-yl)oxy)methyl)thietane (3ma). White solid 32 mg, 62% yield. M.p.: 109–115 °C. R_f = 0.33, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.92 – 7.09 (m, 11H, ArH), 4.85 – 4.81 (m, 1H), 4.43 (dd, *J* = 9.7, 6.3 Hz, 1H), 4.36 – 4.32 (m, 1H), 4.09 – 3.98 (m, 1H), 3.75 (ddd, *J* = 12.5, 8.8, 5.6 Hz, 1H), 2.87 (ddd, *J* = 13.3, 8.5, 5.5 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.2, 196.0, 156.8, 156.6, 133.8, 133.6, 133.52, 133.50, 132.9, 130.2, 130.1, 129.7, 129.64, 129.59, 129.57, 128.82, 128.80, 128.6, 128.5, 128.39, 128.36, 128.28, 128.26, 119.81, 119.75, 117.3, 117.2, 106.98, 106.96, 72.9, 72.7, 37.5, 36.7, 36.3, 35.6, 28.9, 28.2. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.92 – 7.09 (m, 11H, ArH), 4.85 – 4.81 (m, 1H), 4.36 – 4.32 (m, 1H), 4.21 (dd, *J* = 9.5, 7.3 Hz, 1H), 4.09 – 3.98 (m, 1H), 3.45 (ddd, *J* = 12.4, 6.0, 6.0 Hz, 1H), 3.18 (ddd, *J* = 13.0, 8.8, 8.8 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.2, 196.0, 156.8, 156.6, 133.8, 133.6, 133.52, 133.50, 132.9, 130.2, 130.1, 129.7, 129.64, 129.59, 129.57, 128.82, 128.80, 128.6, 128.5, 128.39, 128.36, 128.28, 128.26, 119.81, 119.75, 117.3, 117.2, 106.98, 106.96, 72.9, 72.7, 37.5, 36.7, 36.3, 35.6, 28.9, 28.2. IR (KBr): ν = 2942, 1680, 1590, 1500, 1389 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{18}BrO_2S^+$: 413.0205, found: 413.0203.

(4-Benzylthietan-2-yl)(phenyl)methanone (3na). Colorless liquid 10 mg, 38% yield. R_f = 0.63, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.80 – 7.77 (m, 2H, ArH), 7.59 – 7.51 (m, 1H, ArH), 7.48 – 7.40 (m, 2H, ArH), 7.30 – 7.15 (m, 5H, ArH), 4.62 (dd, *J* = 8.6, 4.3 Hz, 1H), 4.03 – 3.90 (m, 1H), 3.56 (ddd, *J* = 12.4, 8.3, 4.3 Hz, 1H), 3.19 (dd, *J* = 13.8, 6.4 Hz, 1H), 3.14 – 3.04 (m, 1H), 2.80 (ddd, *J* = 12.3, 8.6, 7.0 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.6, 196.2, 138.2, 138.0, 134.1, 133.8, 133.5, 133.3, 128.8, 128.7, 128.62, 128.61, 128.5, 128.4, 128.3, 126.7, 126.6, 45.2, 45.1, 40.8, 39.6, 36.3, 32.2, 31.7. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.86 – 7.81 (m, 2H, ArH), 7.59 – 7.51 (m, 1H, ArH), 7.48 – 7.40 (m, 2H, ArH), 7.30 – 7.15 (m, 5H, ArH), 4.77 (dd, *J* = 8.1, 7.2 Hz, 1H), 4.03 – 3.90 (m, 1H), 3.36 (ddd, *J* = 12.5, 7.3, 7.3 Hz, 1H), 3.14 – 3.04 (m, 1H), 3.02 – 2.92 (m, 2H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.6, 196.2, 138.2, 138.0, 134.1, 133.8, 133.5, 133.3, 128.8, 128.7, 128.62, 128.61, 128.5, 128.4, 128.3, 126.7, 126.6, 45.2, 45.1, 40.8, 39.6, 36.3, 32.2, 31.7. IR (KBr): ν = 2922, 2849, 1716, 1681, 1635, 1449, 1169 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{17}OS^+$: 269.0995, found: 269.0995.

2-(Benzoyl)-4-(butyl)thietane (3oa). Yellow green liquid 17 mg, 59% yield. R_f = 0.40, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.76 – 7.72 (m, 2H, ArH), 7.50 – 7.46 (m, 1H, ArH), 7.39 – 7.35 (m, 2H, ArH), 4.57 (dd, *J* = 8.6, 4.3 Hz, 1H), 3.67 – 3.61 (m, 1H), 3.49 (ddd, *J* = 12.5, 8.3, 4.4 Hz, 1H), 2.63 – 2.53 (m, 1H), 1.85 – 0.78 (m, 9H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.6, 196.4, 134.1, 133.8, 133.4, 133.2, 128.71, 128.68, 128.34, 128.26, 40.4, 39.15, 39.07, 38.9, 36.7, 36.6, 32.7, 32.3, 28.7, 28.4, 22.3, 22.2, 14.0. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.76 – 7.72 (m, 2H, ArH), 7.50 – 7.46 (m, 1H, ArH), 7.39 – 7.35 (m, 2H, ArH), 4.72 (dd, *J* = 7.7, 7.7 Hz, 1H), 3.67 – 3.61 (m, 1H), 3.16 (ddd, *J* = 12.3, 7.5, 7.5 Hz, 1H), 2.90 (ddd, *J* = 12.3, 8.2, 8.2 Hz, 1H), 1.85 – 0.78 (m, 9H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.6, 196.4, 134.1, 133.8, 133.4, 133.2, 128.71, 128.68, 128.34, 128.26, 40.4, 39.15, 39.07, 38.9, 36.7, 36.6, 32.7, 32.3, 28.7, 28.4, 22.3, 22.2, 14.0. IR (KBr): ν = 2956, 2929, 2857, 1682, 1597, 1581 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{14}H_{19}OS^+$: 235.1151, found: 235.1151.

2-Benzoylthietane (3pa). Colorless liquid 2 mg, 9% yield. R_f = 0.44, 10% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.81 – 7.79 (m, 2H, ArH), 7.60 – 7.53 (m, 1H, ArH), 7.47 – 7.44 (m, 2H, ArH), 4.85 (dd, *J* = 8.3, 6.0 Hz, 1H), 3.57 (dddd, *J* = 12.4, 9.5, 6.3, 6.3 Hz, 1H), 3.29 (ddd, *J* = 9.3, 8.7, 6.5 Hz, 1H), 3.20 (ddd, *J* = 9.4, 8.7, 5.8 Hz, 1H), 3.02 (dddd, *J* = 12.2, 9.3, 8.3, 5.8 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 197.6, 133.7, 129.1, 128.6, 40.7, 26.7, 23.0. IR (KBr): ν = 2927, 2860, 1686, 1615 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{10}H_{11}OS^+$: 179.0525, found: 179.0525.

2-(Benzoyl)-3-(phenyl)thietane (3'qa) and 2-(Benzoyl)-4-(phenyl)thietane (3qa). Colorless liquid 12 mg, 38% yield. R_f = 0.62, 10% ethyl acetate in petroleum ether. ***2-(Benzoyl)-3-(phenyl)thietane (3'qa)***. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.77 – 7.74 (m, 2H, ArH), 7.50 – 7.46 (m, 1H, ArH), 7.43 – 7.17 (m, 7H, ArH), 5.02 (ddd, *J* = 8.5, 8.5, 8.5 Hz, 1H), 4.94 (d, *J* = 7.8 Hz, 1H), 3.58 (dd, *J* = 8.7, 8.7 Hz, 1H), 3.32 (dd, *J* = 9.0, 9.0 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 195.7, 142.8, 133.9, 133.6, 128.81, 128.78, 128.6, 128.4, 127.7, 127.3, 126.5, 48.2, 43.6, 29.1. ***2-(Benzoyl)-4-(phenyl)thietane (3qa).*** ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.77 – 7.74 (m, 2H, ArH), 7.50 – 7.46 (m, 1H, ArH), 7.43 – 7.17 (m, 7H, ArH), 4.90 (dd, *J* = 8.3, 8.3 Hz, 1H), 4.63 (dd, *J* = 8.6, 3.5 Hz, 1H), 3.75 (ddd, *J* = 12.2, 8.5, 3.6 Hz, 1H), 3.15 (ddd, *J* = 12.3, 8.4, 8.4 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 195.7, 142.8, 133.9, 133.6, 128.81, 128.78, 128.6, 128.4, 127.7, 127.3, 126.5, 48.2, 43.6, 29.1. IR (KBr): ν = 2925, 2855, 1681, 1598, 1582, 1493 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{16}H_{15}OS^+$: 255.0838, found: 255.0838.

2-(Benzoyl)-3-(4-methylphenyl)thietane (3'ra) and 2-(Benzoyl)-4-(4-methylphenyl)thietane (3ra). Yellow solid 11 mg, 34% yield. M.p.: 95–98 °C. R_f = 0.68, 10% ethyl acetate in petroleum ether. ***2-(Benzoyl)-3-(4-methylphenyl)thietane (3'ra)*** ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.77 – 7.74 (m, 2H, ArH), 7.50 – 7.46 (m, 1H, ArH), 7.36 (t, *J* = 7.7 Hz, 2H, ArH), 7.24 (d, *J* = 8.0 Hz, 2H, ArH), 7.10 (d, *J* = 8.0 Hz, 2H, ArH), 4.96 (ddd, *J* = 8.4, 8.4, 8.4 Hz, 1H), 4.91 (d, *J* = 7.9 Hz, 1H), 3.55 (dd, *J* = 8.6, 8.6 Hz, 1H), 3.30 (dd, *J* = 8.9, 8.9 Hz, 1H), 2.26 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 195.8, 139.9, 137.0, 133.9, 133.6, 129.4, 128.8, 128.4, 126.4, 48.4, 43.4, 29.2, 21.1. ***2-(Benzoyl)-4-(4-methylphenyl)thietane (3ra)*** ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.79 – 7.09 (m, 9H, ArH), 4.87 (dd, *J* = 8.4, 8.4 Hz, 1H), 4.62 (dd, *J* = 8.6, 3.5 Hz, 1H), 3.72 (ddd, *J* = 12.1, 8.4, 3.6 Hz, 1H), 3.14 (ddd, *J* = 12.3, 8.4, 8.4 Hz, 1H), 2.29 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 195.8, 139.9, 137.0, 133.9, 133.6, 129.4, 128.8, 128.4, 126.4, 48.4, 43.4, 29.2, 21.1. IR (KBr): ν = 2920, 2850, 1681, 1597, 1581, 1514, 1384 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{17}H_{17}OS^+$: 269.0995, found: 269.0995.

2-(Benzoyl)-3-(4-chlorophenyl)thietane (3'sa) and 2-(Benzoyl)-4-(4-chlorophenyl)thietane (3sa). Colorless liquid 12 mg, 38% yield. R_f = 0.62, 10% ethyl acetate in petroleum ether. ***2-(Benzoyl)-3-(4-chlorophenyl)thietane (3'sa).*** ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.86 – 7.77 (m, 2H, ArH), 7.60 – 7.54 (m, 1H, ArH), 7.47 – 7.43 (m, 2H, ArH), 7.37 – 7.30 (m, 4H, ArH), 5.05 (ddd, *J* = 8.6, 8.6, 8.6 Hz, 1H), 4.94 (d, *J* = 7.9 Hz, 1H), 3.60 (dd, *J* = 8.7, 8.7 Hz, 1H), 3.38 (dd, *J* = 9.0, 9.0 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.1, 195.5, 141.4, 141.2, 133.7, 133.6, 133.4, 133.0, 128.82, 128.80, 128.76, 128.71, 128.68, 128.30, 128.26, 127.9, 48.1, 43.0, 41.5, 35.5, 35.3, 28.9. ***2-(Benzoyl)-4-(4-methylphenyl)thietane (3sa).*** ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.86 – 7.30 (m, 9H, ArH), 4.91 (dd, J = 8.2, 8.2 Hz, 1H), 4.69 (dd, *J* = 8.7, 3.6 Hz, 1H), 3.81 (ddd, *J* = 12.4, 8.5, 3.7 Hz, 1H), 3.16 (ddd, *J* = 12.4, 8.3, 8.3 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.1, 195.5, 141.4, 141.2, 133.7, 133.6, 133.4, 133.0, 128.82, 128.80, 128.76, 128.71, 128.68, 128.30, 128.26, 127.9, 48.1, 43.0, 41.5, 35.5, 35.3, 28.9. IR (KBr): ν = 2930, 2889, 1686, 1600, 1495 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{16}H_{14}ClOS^+$: 289.0448, found: 289.0447.

2-(4-Methylbenzoyl)-4-(phenoxymethyl)thietane (3ab). Green solid 25 mg, 68% yield. M.p.: 112–114 °C. R_f = 0.40, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.65 – 6.78 (m, 9H, ArH), 4.74 – 4.70 (m, 1H), 4.25 (dd, *J* = 9.7, 6.4 Hz, 1H), 4.18 – 4.13 (m, 1H), 3.95 – 3.82 (m, 1H), 3.63 (ddd, *J* = 12.6, 8.8, 5.7 Hz, 1H), 2.73 (ddd, *J* = 12.6, 8.5, 5.4 Hz, 1H), 2.32 – 3.32 (m, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.0, 195.8, 158.5, 158.4, 144.43, 144.37, 131.3, 131.1, 129.5, 129.4, 128.4, 121.2, 121.0, 114.72, 114.66, 73.0, 72.6, 37.5, 36.7, 36.3, 35.6, 28.9, 28.3, 21.7. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.65 – 6.78 (m, 9H, ArH), 4.74 – 4.70 (m, 1H), 4.18 – 4.13 (m, 1H), 4.18 – 4.13 (m, 1H), 4.02 (dd, *J* = 9.4, 7.3 Hz, 1H), 3.95 – 3.82 (m, 1H), 3.31 (ddd, *J* = 12.6, 6.2, 6.2 Hz, 1H), 3.03 (ddd, *J* = 12.8, 8.6, 8.6 Hz, 1H), 2.32 – 3.32 (m, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 196.0, 195.8, 158.5, 158.4, 144.43, 144.37, 131.3, 131.1, 129.5, 129.4, 128.4, 121.2, 121.0, 114.72, 114.66, 73.0, 72.6, 37.5, 36.7, 36.3, 35.6, 28.9, 28.3, 21.7. IR (KBr): ν = 2935, 1678, 1600, 1586, 1496, 1384 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{18}H_{19}O_2S^+$: 299.1100, found: 299.1105.

2-(4-Methoxybenzoyl)-4-(phenoxymethyl)thietane (3ac). Yellow white solid 31 mg, 80% yield. M.p.: 154–157 °C. R_f = 0.23, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.78 – 7.75 (m, 2H, ArH),

7.34 – 7.15 (m, 2H, ArH), 7.05 – 6.82 (m, 5H, ArH), 4.79 – 4.74 (m, 1H), 4.31 (dd, *J* = 9.7, 6.4 Hz, 1H), 4.24 – 4.19 (m, 1H), 4.02 – 3.87 (m, 1H), 3.84 – 3.83 (m, 3H), 3.69 (ddd, *J* = 12.6, 8.9, 5.8 Hz, 1H), 2.77 (ddd, *J* = 12.6, 8.5, 5.3 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 195. 0, 194.9, 163.8, 163.7, 158.6, 158.4, 130.6, 129.5, 129.4, 126.8, 126.6, 121.2, 121.0, 114.73, 114.66, 114.0, 73.0, 72.7, 55.5, 37.4, 36.5, 36.4, 35.7, 28.9, 28.4. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.78 – 7.75 (m, 2H, ArH), 7.34 – 7.15 (m, 2H, ArH), 7.05 – 6.82 (m, 5H, ArH), 4.79 – 4.74 (m, 1H), 4.24 – 4.19 (m, 1H), 4.08 (dd, *J* = 9.4, 7.3 Hz, 1H), 4.02 – 3.87 (m, 1H), 3.84 – 3.83 (m, 3H), 3.37 (ddd, *J* = 12.7, 6.3, 6.3 Hz, 1H), 3.07 (ddd, *J* = 12.8, 8.6, 8.6 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 195. 0, 194.9, 163.8, 163.7, 158.6, 158.4, 130.6, 129.5, 129.4, 126.8, 126.6, 121.2, 121.0, 114.73, 114.66, 114.0, 73.0, 72.7, 55.5, 37.4, 36.5, 36.4, 35.7, 28.9, 28.4. IR (KBr): *ν* = 2930, 2869, 1676, 1602, 1512, 1378 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{18}H_{19}O_3S^+$: 315.1049, found: 315.1050.

2-(4-Chlorobenzoyl)-4-(phenoxymethyl)thietane (3ad). Yellow white solid 28 mg, 70% yield. M.p.: 121–125 °C. R_f = 0.37, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.79 – 7.71 (m, 2H, ArH), 7.45 – 7.42 (m, 2H, ArH), 7.34 – 7.24 (m, 2H, ArH), 7.03 – 6.84 (m, 3H, ArH), 4.80 – 4.72 (m, 1H), 4.32 (dd, *J* = 9.8, 6.2 Hz, 1H), 4.26 – 4.21 (m, 1H), 4.06 – 3.90 (m, 1H), 3.70 (ddd, *J* = 12.6, 8.8, 5.6 Hz, 1H), 2.84 (ddd, *J* = 12.6, 8.5, 5.6 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 195.1, 194.9, 158.5, 158.4, 140.0, 139.9, 132.2, 131.9, 129.7, 129.5, 129.4, 129.2, 121.3, 121.1, 114.73, 114.66, 72.8, 72.5, 37.4, 36.6, 36.5, 35.8, 28.8, 28.2. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.79 – 7.71 (m, 2H, ArH), 7.45 – 7.42 (m, 2H, ArH), 7.34 – 7.24 (m, 2H, ArH), 7.03 – 6.84 (m, 3H, ArH), 4.80 – 4.72 (m, 1H), 4.26 – 4.21 (m, 1H), 4.09 (dd, *J* = 9.4, 7.3 Hz, 1H), 4.06 – 3.90 (m, 1H), 3.40 (ddd, *J* = 12.6, 6.2, 6.2 Hz, 1H), 3.13 (ddd, *J* = 12.9, 8.6, 8.6 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 195.1, 194.9, 158.5, 158.4, 140.0, 139.9, 132.2, 131.9, 129.7, 129.5, 129.4, 129.2, 121.3, 121.1, 114.73, 114.66, 72.8, 72.5, 37.4, 36.6, 36.5, 35.8, 28.8, 28.2. IR (KBr): *ν* = 2933, 2877, 1680, 1598, 1498 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{17}H_{16}ClO_2S^+$: 319.0554, found: 319.0556.

2-(4-Bromobenzoyl)-4-(phenoxymethyl)thietane (3ae). White solid 21 mg, 47% yield. M.p.: 147–151 °C. R_f = 0.39, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.68 – 7.65 (m, 2H, ArH), 7.61 – 7.59 (m, 2H, ArH), 7.33 – 7.24 (m, 2H, ArH), 7.00 – 6.87 (m, 3H, ArH), 4.77 – 4.74 (m, 1H), 4.32 (dd, *J* = 9.8, 6.2 Hz, 1H), 4.26 – 4.21 (m, 1H), 4.04 – 3.92 (m, 1H), 3.70 (ddd, *J* = 12.6, 8.8, 5.6 Hz, 1H), 2.84 (ddd, *J* = 12.7, 8.5, 5.6 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 195.3, 195.1, 158.5, 158.4, 132.6, 132.4, 132.2, 132.1, 129.8, 129.5, 129.4, 128.8, 128.7, 121.3, 121.1, 114.75, 114.69, 72.8, 72.5, 37.4, 36.6, 36.5, 35.8, 28.9, 28.2. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.68 – 7.65 (m, 2H, ArH), 7.61 – 7.59 (m, 2H, ArH), 7.33 – 7.24 (m, 2H, ArH), 7.00 – 6.87 (m, 3H, ArH), 4.77 – 4.74 (m, 1H), 4.26 – 4.21 (m, 1H), 4.09 (dd, *J* = 9.5, 7.3 Hz, 1H), 4.04 – 3.92 (m, 1H), 3.39 (ddd, *J* = 12.6, 6.2, 6.2 Hz, 1H), 3.13 (ddd, *J* = 12.9, 8.6, 8.6 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 195.3, 195.1, 158.5, 158.4, 132.6, 132.4, 132.2, 132.1, 129.8, 129.5, 129.4, 128.8, 128.7, 121.3, 121.1, 114.75, 114.69, 72.8, 72.5, 37.4, 36.6, 36.5, 35.8, 28.9, 28.2. IR (KBr): *ν* = 2931, 2873, 1683, 1592, 1501 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{17}H_{16}BrO_2S^+$: 363.0049, found: 363.0051.

2-(4-Nitrobenzoyl)-4-(phenoxymethyl)thietane (3af). White solid 22 mg, 54% yield. M.p.: 130–136 °C. R_f = 0.16, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 8.32 – 8.29 (m, 2H, ArH), 7.97 – 7.94 (m, 2H, ArH), 7.33 – 7.25 (m, 2H, ArH), 7.01 – 6.87 (m, 3H, ArH), 4.82 – 4.77 (m, 1H), 4.32 (dd, *J* = 9.8, 6.0 Hz, 1H), 4.26 – 4.21 (m, 1H), 4.07 – 3.97 (m, 1H), 3.70 (ddd, *J* = 12.6, 8.7, 5.2 Hz, 1H), 2.91 (ddd, *J* = 12.6, 8.4, 5.9 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 195.3, 195.1, 158.5, 158.4, 132.6, 132.4, 132.2, 132.1, 129.8, 129.5, 129.4, 128.8, 128.7, 121.3, 121.1, 114.8, 114.7, 72.8, 72.6, 37.4, 36.6, 36.5, 35.8, 28.9, 28.2. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 8.32 – 8.29 (m, 2H, ArH), 7.97 – 7.94 (m, 2H, ArH), 7.33 – 7.25 (m, 2H, ArH), 7.01 – 6.87 (m, 3H, ArH), 4.82 – 4.77 (m, 1H), 4.26 – 4.21 (m, 1H), 4.10 (dd, *J* = 9.3, 7.2 Hz, 1H), 4.07 – 3.97 (m, 1H), 3.42 (ddd, *J* = 12.9, 5.9, 5.9 Hz, 1H), 3.19 (ddd, *J* = 12.9, 8.6, 8.6 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 195.3, 195.1, 158.5, 158.4, 132.6, 132.4, 132.2, 132.1, 129.8, 129.5, 129.4, 128.8, 128.7, 121.3, 121.1, 114.8, 114.7, 72.8, 72.6, 37.4, 36.6, 36.5, 35.8, 28.9, 28.2. IR (KBr): *ν* = 2953, 2867, 1692, 1602, 1529, 1517, 1347 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{17}H_{16}NO_4S^+$: 330.0795, found: 330.0805.

2-(3-Chlorobenzoyl)-4-(phenoxymethyl)thietane (3ag). Yellow white solid 16 mg, 40% yield. M.p.: 68–72 °C. R_f = 0.41, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.82 (s, 1H, ArH), 7.69 – 7.62 (m, 1H, ArH), 7.55 – 7.50 (m, 1H, ArH), 7.42 – 7.38 (m, 1H, ArH), 7.34 – 7.24 (m, 2H, ArH), 7.02 – 6.86 (m, 3H, ArH), 4.78 – 4.74 (m, 1H), 4.33 (dd, *J* = 9.8, 6.2 Hz, 1H), 4.26 – 4.21 (m, 1H), 4.04 – 3.93 (m, 1H), 3.69 (ddd, *J* = 12.6, 8.8, 5.5 Hz, 1H), 2.85 (ddd, *J* = 12.6, 8.5, 5.6 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 195.0, 194.8, 158.5, 158.4, 135.5, 135.24, 135.23, 133.5, 133.4, 130.1, 129.5, 129.4, 128.41, 128.38, 126.3, 121.3, 121.1, 114.75, 114.68, 72.8, 72.5, 37.4, 36.7, 36.5, 35.8, 28.9, 28.2. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.82 (s, 1H, ArH), 7.69 – 7.62 (m, 1H, ArH), 7.55 – 7.50 (m, 1H, ArH), 7.42 – 7.38 (m, 1H, ArH), 7.34 – 7.24 (m, 2H, ArH), 7.02 – 6.86 (m, 3H, ArH), 4.78 – 4.74 (m, 1H), 4.26 – 4.21 (m, 1H), 4.10 (dd, *J* = 9.5, 7.3 Hz, 1H), 4.04 – 3.93 (m, 1H), 3.39 (ddd, *J* = 12.5, 6.1, 6.1 Hz, 1H), 3.14 (ddd, *J* = 12.9, 8.7, 8.7 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 195.0, 194.8, 158.5, 158.4, 135.5, 135.24, 135.23, 133.5, 133.4, 130.1, 129.5, 129.4, 128.41, 128.38, 126.3, 121.3, 121.1, 114.75, 114.68, 72.8, 72.5, 37.4, 36.7, 36.5, 35.8, 28.9, 28.2. IR (KBr): *ν* = 2950, 2865, 1688, 1600, 1583, 1496 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{17}H_{16}ClO_2S^+$: 319.0554, found: 319.0554.

2-(3,4-Dichlorobenzoyl)-4-(phenoxymethyl)thietane (3ah). Golden yellow liquid 27 mg, 68% yield. R_f = 0.33, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.86 – 7.76 (m, 1H, ArH), 7.53 – 7.49 (m, 1H, ArH), 7.47 – 7.44 (m, 1H, ArH), 7.28 – 7.14 (m, 2H, ArH), 6.94 – 6.77 (m, 3H, ArH), 4.66 – 4.61 (m, 1H), 4.24 (dd, *J* = 9.8, 6.1 Hz, 1H), 4.17 – 4.12 (m, 1H), 3.97 – 3.86 (m, 1H), 3.60 (ddd, *J* = 12.7, 8.8, 5.4 Hz, 1H), 2.77 (ddd, *J* = 12.6, 8.5, 5.7 Hz, 1H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 194.1, 193.8, 158.4, 158.3, 138.1, 133.6, 133.5, 133.2, 130.9, 130.3, 130.2, 129.5, 129.4, 127.2, 121.3, 121.1, 114.7, 114.6, 72.7, 72.4, 37.2, 36.6, 36.5, 35.8, 28.8, 28.1. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.86 – 7.76 (m, 1H, ArH), 7.53 – 7.49 (m, 1H, ArH), 7.47 – 7.44 (m, 1H, ArH), 7.28 – 7.14 (m, 2H, ArH), 6.94 – 6.77 (m, 3H, ArH), 4.66 – 4.61 (m, 1H), 4.17 – 4.12 (m, 1H), 4.01 (dd, J = 9.4, 7.3 Hz, 1H), 3.97 – 3.86 (m, 1H), 3.31 (ddd, J = 12.4, 6.0, 6.0 Hz, 1H), 3.06 (dt, J = 12.9, 8.6 Hz, 8.6 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 194.1, 193.8, 158.4, 158.3, 138.1, 133.6, 133.5, 133.2, 130.9, 130.3, 130.2, 129.5, 129.4, 127.2, 121.3, 121.1, 114.7, 114.6, 72.7, 72.4, 37.2, 36.6, 36.5, 35.8, 28.8, 28.1. IR (KBr): ν = 2929, 2861, 1688, 1602, 1495 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}Cl_2O_2S^+$: 353.0164, found: 353.0157.

2-(1-Naphthoyl)-4-(phenoxymethyl)thietane (3ai). Golden yellow liquid 14 mg, 34% yield. R_f = 0.36, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 8.80 – 8.76 (m, 1H, ArH), 7.97 (d, J = 8.2 Hz, 1H, ArH), 7.86 – 7.83 (m, 1H, ArH), 7.64 – 7.58 (m, 2H, ArH), 7.55 – 7.50 (m, 1H, ArH), 7.45 – 7.41 (m, 1H, ArH), 7.30 – 7.22 (m, 2H, ArH), 6.97 – 6.86 (m, 3H, ArH), 4.97 – 4.93 (m, 1H), 4.31 (dd, J = 9.7, 6.5 Hz, 1H), 4.27 – 4.20 (m, 1H), 4.01 – 3.91 (m, 1H), 3.70 (ddd, J = 12.6, 8.9, 5.7 Hz, 1H), 2.85 (ddd, J = 12.6, 8.5, 5.4 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 199.7, 199.5, 158.55, 158.46, 134.1, 133.5, 133.4, 131.9, 130.9, 129.5, 129.4, 128.4, 128.3, 128.2, 127.9, 127.7, 126.6, 126.0, 124.2, 121.2, 121.1, 114.7, 73.0, 72.6, 40.7, 39.1, 35.9, 35.0, 29.7, 29.2. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 8.80 – 8.76 (m, 1H, ArH), 7.97 (d, J = 8.2 Hz, 1H, ArH), 7.86 – 7.83 (m, 1H, ArH), 7.64 – 7.58 (m, 2H, ArH), 7.55 – 7.50 (m, 1H, ArH), 7.45 – 7.41 (m, 1H, ArH), 7.30 – 7.22 (m, 2H, ArH), 6.97 – 6.86 (m, 3H, ArH), 4.97 – 4.93 (m, 1H), 4.27 – 4.20 (m, 1H), 4.12 (dd, J = 9.5, 7.1 Hz, 1H), 4.01 – 3.91 (m, 1H), 3.39 (ddd, J = 12.8, 6.4, 6.4 Hz, 1H), 3.14 (ddd, J = 12.9, 8.7, 8.7 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 199.7, 199.5, 158.55, 158.46, 134.1, 133.5, 133.4, 131.9, 130.9, 129.5, 129.4, 128.4, 128.3, 128.2, 127.9, 127.7, 126.6, 126.0, 124.2, 121.2, 121.1, 114.7, 73.0, 72.6, 40.7, 39.1, 35.9, 35.0, 29.7, 29.2. IR (KBr): ν = 2927, 2857, 1676, 1599, 1496 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{19}O_2S^+$: 335.1100, found: 335.1100.

(Adamantan-1-yl)(4-(phenoxymethyl)thietan-2-yl)methanone (3aj). Colorless liquid 30 mg, 70% yield. R_f = 0.63, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.33 – 7.23 (m, 2H, ArH), 7.01 – 6.84 (m, 3H, ArH), 4.40 (dd, J = 8.4, 5.4 Hz, 1H), 4.27 – 4.22 (m, 1H), 4.18 – 4.08 (m, 1H), 3.96 – 3.84 (m, 1H), 3.47 (ddd, J = 12.4, 8.7, 5.4 Hz, 1H), 2.62 (ddd, J = 12.4, 8.4, 5.8 Hz, 1H), 2.13 – 1.63 (m, 15H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 211.2, 158.5, 129.5, 129.4, 121.1, 121.0, 114.69, 114.66, 73.0, 72.7, 46.4, 38.5, 38.4, 36.4, 35.9, 35.3, 35.1, 34.5, 29.1, 28.2, 27.9, 27.8. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.33 – 7.23 (m, 2H, ArH), 7.01 – 6.84 (m, 3H, ArH), 4.44 (dd, J = 8.4, 6.2 Hz, 1H), 4.27 – 4.22 (m, 1H), 4.18 – 4.08 (m, 1H), 3.96 – 3.84 (m, 1H), 3.18 (ddd, J = 12.6, 6.2, 6.2 Hz, 1H), 2.90 (ddd, J = 12.7, 8.7, 8.7 Hz, 1H), 2.13 – 1.63 (m, 15H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 211.2, 158.5, 129.5, 129.4, 121.1, 121.0, 114.69, 114.66, 73.0, 72.7, 46.4, 38.5, 38.4, 36.4, 35.9, 35.3, 35.1, 34.5, 29.1, 28.2, 27.9, 27.8. IR (KBr): ν = 2904, 2849, 1693, 1599, 1496, 1452, 1385 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{27}O_2S^+$: 343.1726, found: 343.1726.

tert-Butyl 4-(phenoxymethyl)thietane-2-carboxylate (3ak). Colorless liquid 14 mg, 40% yield. R_f = 0.55, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.32 – 7.26 (m, 2H, ArH), 6.96 (t, J = 7.2 Hz, 1H, ArH), 6.91 (d, J = 8.4 Hz, 2H, ArH), 4.23 (dd, J = 9.7, 6.9 Hz, 1H), 4.15 (dd, J = 9.6, 6.4 Hz, 1H), 3.98 – 3.93 (m, 2H), 3.32 (ddd, J = 12.5, 8.7, 5.7 Hz, 1H), 2.77 (ddd, J = 12.5, 8.8, 5.6 Hz, 1H), 1.49 (s, 9H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 175.8, 172.4, 158.5, 132.2, 129.8, 129.5, 121.1, 114.7, 81.5, 73.1, 72.7, 36.1, 35.7, 31.1, 27.9. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.32 – 7.26 (m, 2H, ArH), 6.96 (t, J = 7.2 Hz, 1H, ArH), 6.92 – 6.88 (m, 2H, ArH), 4.27 (dd, J = 9.6, 7.0 Hz, 1H), 4.17 – 4.13 (m, 1H), 4.00 – 3.84 (m, 2H), 3.08 (ddd, J = 12.5, 8.7, 8.7 Hz, 1H), 2.77 (ddd, J = 12.9, 6.4, 6.4 Hz, 1H), 1.47 (s, 9H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 175.8, 172.4, 158.5, 132.2, 129.8, 129.5, 121.1, 114.7, 81.5, 73.1, 72.7, 36.1, 35.7, 31.1, 27.9. IR (KBr): ν = 2978, 2935, 1726, 1600, 1497, 1392, 1368 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{15}H_{20}NaO_3S^+$: 303.1025, found: 303.1026.

tert-Butyl 4-((benzyloxy)methyl)thietane-2-carboxylate (3tk). Colorless liquid 855 mg, 52% yield. R_f = 0.31, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.38 – 7.25 (m, 5H, ArH), 4.56 (s, 2H), 3.86 (dd, J = 8.8, 5.5 Hz, 1H), 3.84 – 3.61 (m, 3H), 3.20 (ddd, J = 12.7, 8.6, 5.5 Hz, 1H), 2.65 (ddd, J = 12.6, 8.8, 5.7 Hz, 1H), 1.47 (s, 9H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 172.6, 172.3, 138.0, 128.35, 128.32, 127.7, 127.6, 81.3, 75.8, 75.1, 73.2, 73.1, 36.4, 36.0, 35.2, 31.1, 30.7, 27.9. *Cis*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.38 – 7.25 (m, 5H, ArH), 4.53 (s, 2H), 3.95 (dd, J = 8.6, 6.8 Hz, 1H), 3.84 – 3.61 (m, 3H), 2.95 (ddd, J = 12.7, 8.3, 8.3 Hz, 1H), 2.87 (ddd, J = 12.7, 6.5, 6.5 Hz, 1H), 1.45 (s, 9H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (δ, ppm) = 172.6, 172.3, 138.0, 128.35, 128.32, 127.7, 127.6, 81.3, 75.8, 75.1, 73.2, 73.1, 36.4, 36.0, 35.2, 31.1, 30.7, 27.9. IR (KBr): ν = 2979, 2937, 2859, 1727, 1496, 1477, 1392, 1368, 737, 699 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{16}H_{23}O_3S^+$: 295.1362, found: 295.1356.

Synthesis of Sulfone 7[25]

To a performic acid solution, prepared by mixing and stirring 30% H_2O_2 (0.27 mL, 2.4 mmol) and 88% HCO_2H (2.4 mL) at r.t. for 0.5 h in an ice bath, was added dropwise the thietane **3tk** (118 mg, 0.4 mmol) obtained from the above step at 0 °C over a period of 10 min. The resulting mixture was stirred and allowed to warm to r.t. for 0.5–1 h. The resulting mixture was washed with H_2O. The organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography to give the sulfone **7**.

tert-Butyl 4-((benzyloxy)methyl)thietane-2-carboxylate 1,1-dioxide (7). Colorless liquid 70 mg, 40% yield. R_f = 0.24, 10% ethyl acetate in petroleum ether. *Trans*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.39 – 7.27 (m, 5H, ArH), 4.85 (ddd,

J = 10.0, 5.8, 1.2 Hz, 1H), 4.64 – 4.54 (m, 3H), 3.91 (dd, *J* = 10.8, 7.5 Hz, 1H), 3.91 (dd, *J* = 10.8, 4.6 Hz, 1H), 2.59 (ddd, *J* = 12.2, 10.4, 5.8 Hz, 1H), 1.99 (ddd, *J* = 12.2, 10.1, 6.9 Hz, 1H), 1.51 (s, 9H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 163.2, 137.2, 128.4, 127.9, 127.8, 83.9, 79.0, 77.7, 73.4, 66.3, 27.9, 14.2. IR (KBr): *v* = 2981, 2935, 2867, 1732, 1497, 1455, 1394, 1370, 1336, 1150, 739, 700 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+Na]$^+$ calcd for $C_{16}H_{22}NaO_5S^+$: 349.1080, found: 349.1080.

General Procedure for the Synthesis of Tetrahydrothiophenes 5

Conditions C: A pressure tube was charged with $[Ir(COD)Cl]_2$ (4 mg, 5 mol %), thietane (0.125 mmol), sulfoxonium ylide (0.25 mmol), and DCE (1 mL). The reaction mixture was stirred under N_2 conditions at 80 °C in an oil bath for 4 h. After removal of solvent under reduced pressure, the residue was purified by silica gel chromatography with a mixture of petroleum ether and ethyl acetate (10:1, *v*/*v*) as eluent to afford product **5**.

2-Benzoyltetrahydrothiophene (5a). Colorless liquid 13 mg, 55% yield. R_f = 0.42, 10% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.98 – 7.92 (m, 2H, ArH), 7.60 – 7.53 (m, 1H, ArH), 7.50 – 7.43 (m, 2H, ArH), 4.74 (dd, *J* = 7.0, 4.2 Hz, 1H), 3.01 – 2.87 (m, 2H), 2.68 – 2.57 (m, 1H), 2.66 – 2.58 (m, 1H), 2.29 – 2.10 (m, 2H), 1.99 (dddd, *J* = 12.8, 8.6, 7.1, 5.9 Hz, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 196.4, 135.9, 133.1, 128.6, 49.3, 33.9, 31.3, 31.1. IR (KBr): *v* = 2930, 2874, 1687, 1599, 1452 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{11}H_{13}OS^+$: 193.0682, found: 193.0682.

2-(4-Methylbenzoyl)tetrahydrothiophene (5b). White solid 17 mg, 66% yield. M.p.: 72–74 °C. R_f = 0.33, 10% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.84 (d, *J* = 7.9 Hz, 2H, ArH), 7.26 (d, *J* = 8.1 Hz, 1H, ArH), 4.71 (dd, *J* = 7.1, 4.4 Hz, 1H), 2.98 – 2.87 (m, 2H), 2.64 – 2.56 (m, 1H), 2.41 (s, 3H), 2.28 – 2.09 (m, 2H), 2.01 – 1.93 (m, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 196.1, 143.9, 133.4, 129.3, 128.7, 49.3, 33.9, 31.3, 31.2, 21.6. IR (KBr): *v* = 2961, 2934, 2865, 1683, 1608, 1443 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{12}H_{15}OS^+$: 207.0838, found: 207.0838.

2-(4-Methoxylbenzoyl)tetrahydrothiophene (5c). White solid 14 mg, 50% yield. M.p.: 79–81 °C. R_f = 0.30, 10% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.93 (d, *J* = 8.8 Hz, 2H, ArH), 6.94 (d, *J* = 8.8 Hz, 2H, ArH), 4.69 (dd, *J* = 7.3, 4.8 Hz, 1H), 3.86 (s, 3H), 2.98 – 2.87 (m, 2H), 2.63 – 2.56 (m, 1H), 2.29 – 2.09 (m, 2H), 2.01 – 1.92 (m, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 195.2, 163.5, 130.8, 128.9, 113.8, 55.5, 49.1, 33.9, 31.4, 31.2. IR (KBr): *v* = 2964, 2934, 2862, 1678, 1602, 1511, 1454 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{12}H_{15}O_2S^+$: 223.0787, found: 223.0787.

2-(4-Chlorobenzoyl)tetrahydrothiophene (5d). Yellow solid 19 mg, 68% yield. M.p.: 54–56 °C. R_f = 0.33, 10% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.88 (d, *J* = 8.3 Hz, 2H, ArH), 7.43 (d, *J* = 8.3 Hz, 2H, ArH), 4.67 (dd, *J* = 7.1, 4.3 Hz, 1H), 2.98 – 2.88 (m, 2H), 2.64 – 2.57 (m, 1H), 2.27 – 2.10 (m, 2H), 2.02 – 1.94 (m, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 195.1, 139.5, 134.3, 130.0, 128.9, 49.3, 34.0, 31.2, 31.1, 29.7. IR (KBr): *v* = 2930, 2859, 1689, 1594, 1463 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{11}H_{12}ClOS^+$: 227.0292, found: 227.0292.

2-(4-Bromobenzoyl)tetrahydrothiophene (5e). White solid 25 mg, 74% yield. M.p.: 76–79 °C. R_f = 0.33, 10% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) (*δ*, ppm) = 7.80 (d, *J* = 8.2 Hz, 2H, ArH), 7.60 (d, *J* = 8.2 Hz, 2H, ArH), 4.66 (dd, *J* = 7.1, 4.2 Hz, 1H), 2.98 – 2.88 (m, 2H), 2.64 – 2.57 (m, 1H), 2.27 – 2.10 (m, 2H), 2.02 – 1.93 (m, 1H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) (*δ*, ppm) = 195.1, 139.5, 134.3, 130.0, 128.9, 49.3, 34.0, 31.2, 31.1, 29.7. IR (KBr): *v* = 2934, 2867, 1685, 1592 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd for $C_{11}H_{12}BrOS^+$: 270.9787, found: 270.9787.

Gram Scale Synthesis of Thietane 3aa

A pressure tube was charged with $[Rh(COD)Cl]_2$ (123 mg, 2.5 mmol, 5 mol %), $C(CH_2OH)_4$ (136 mg, 10 mmol, 20 mol%), thiirane **1a** (0.83g, 5 mmol), sulfoxonium ylide **2a** (1.80g, 10 mmol), and DCE (30 mL). The reaction mixture was stirred under N_2 conditions at 80 °C in an oil bath for 6 h. After removal of solvent under reduced pressure, the residue was purified by silica gel chromatography using PE/EA (10:1, *v*/*v*) as eluent to afford the product **3aa** (0.82g, 58%).

Gram Scale Synthesis of Thietane 3tk

A pressure tube was charged with $[Rh(COD)Cl]_2$ (137 mg, 0.28 mmol, 5 mol %), $C(CH_2OH)_4$ (151 mg, 1.11 mmol, 20 mol%), thiirane **1t** (1g, 5.59 mmol), sulfoxonium ylide **2k** (1.96g, 10 mmol), and DCE (30 mL). The reaction mixture was stirred under N_2 conditions at 80 °C in an oil bath for 7 h. After removal of solvent under reduced pressure, the residue was purified by silica gel chromatography using PE/EA (10:1, *v*/*v*) as eluent to afford the product **3tk** (0.86g, 52%).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Copies of ^{1}H and ^{13}C {^{1}H} NMR spectra for all sulfur ylides and products, and copies of NMR spectra and GC-MS profiles on mechanistic investigations (PDF)

AUTHOR INFORMATION

Corresponding Author

* E-mail: jxxu@mail.buct.edu.cn.

ORCID

Jiaxi Xu: 0000-0002-9039-4933;
Jun Dong: 0000-0002-0358-5505.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (Nos. 21572017 and 21772010) and the

Fundamental Research Funds for the Central Universities (XK1802-6).

REFERENCE and NOTES

(1) (a) Nishizono, N.; Akama, Y.; Agata, M.; Sugo, M.; Yamaguchi, Y.; Oda, K. Synthesis of Thietane Nucleoside with an Anomeric Hydroxymethyl Group. *Tetrahedron* **2011**, *67*, 358-363. (b) Nishizono, N.; Koike, N.; Yamagata, Y.; Fujii, S.; Matsuda, A. Nucleosides and Nucleotides.159. Synthesis of Thietane Nucleosides via the Pummerer Reaction as a Key Step. *Tetrahedron Lett.* **1996**, *37*, 7569-7572.

(2) Ichikawa, E.; Yamamura, S.; Kato, K. Synthesis of Enantiomerically Pure 9-[(1'*R*,2'*R*,3'*S*)-Bis(hydroxymethyl) thietan-1'-yl]adenine, 3'-Thio Analog of Oxetanocin A. *Tetrahedron Lett.* **1999**, *40*, 7385-7388.

(3) Merckle, L.; Dubois, J.; Place, E.; Thoret, S.; Gueritte, F.; Guenard, D.; Poupat, C.; Ahond, A.; Potier, P. Semisynthesis of D-Ring Modified Taxoids: Novel Thia Derivatives of Docetaxel. *J. Org. Chem.* **2001**, *66*, 5058-5065.

(4) Ohuchida, S.; Hamanaka, N.; Hayashi, M. Synthesis of Thromboxane A2 Analogs–3: (+)-Thiathromboxane A2. *Tetrahedron* **1983**, *39*, 4269-4272.

(5) Xu, W.; Xu, J. X. Regioselectivity in the Ring Opening and Expansion of Unsymmetric Thietanes. *Curr. Org. Synth.* **2016**, *13*, 73-81.

(6) (a) Carreira, E. M.; Fessard, T. C. Four-Membered Ring-Containing Spirocycles: Synthetic Strategies and Opportunities. *Chem. Rev.* **2014**, *114*, 8257-8322. (b) Sander, M. Thietanes. *Chem. Rev.* **1966**, *66*, 341-353.

(7) (a) Sakamoto, M.; Takahashi, M.; Hokari, N.; Fujita, T.; Watanabe, S. Solid-State Photochemistry: Diastereoselective Synthesis of Thietane-Fused beta-Lactams from an Acyclic Monothioimide with a Chiral Group. *J. Org. Chem.* **1994**, *59*, 3131-3134. (b) Sakamoto, M.; Hokari, N.; Takahashi, M.; Fujita, T.; Watanabe, S.; Iida, I.; Nishio, T. Chiral Thietane-Fused beta-Lactam from an Achiral Monothioimide Using the Chiral Crystal Environment. *J. Am. Chem. Soc.* **1993**, *115*, 818-818.

(8) Padwa, A.; Jacquez, M. N.; Schmidt, A. Intramolecular Photocycloaddition of Cyclic Thioimides as a Method for Heterocyclic Synthesis. *Org. Lett.* **2001**, *3*, 1781-1783.

(9) Yang, H. B.; Yuan, Y. C.; Wei, Y.; Shi, M. Amine-Catalyzed Tunable Reactions of Allenoates with Dithioesters: Formal [4+2] and [2+2] Cycloadditions for the Synthesis of 2,3-Dihydro-1,4-Oxathiines and Enantioenriched Thietanes. *Chem. Commun.* **2015**, *51*, 6430-6433.

(10) Tomashevskii, A. A.; Sokolov, V. V.; Potekhin, A. A. Reaction of 4-(*N*,*N*-Dimethylaminophenyl)magnesium Bromide with Palladium Tetrakis(triphenylphosphine). *Russ. J. Org. Chem.* **2003**, *39*, 226-234.

(11) (a) Lu, L. Q.; Li, T. R.; Wang, Q.; Xiao, W. J. Beyond Sulfide-Centric Catalysis: Recent Advances in the Catalytic Cyclization Reactions of Sulfur Ylides. *Chem. Soc. Rev.* **2017**, *46*, 4135-4149. (b) Aggarwal, V. K.; Winn, C. L. Catalytic Asymmetric Sulfur Ylide-Mediated Epoxidation of Carbonyl Compounds: Scope, Selectivity, and Applications in Synthesis. *Acc. Chem. Res.* **2004**, *37*, 611-620. (c) Li, A. H.; Dai, L. X.; Aggarwal, V. K. Asymmetric Ylide Reactions: Epoxidation, Cyclopropanation, Aziridination, Olefination, and Rearrangement. *Chem. Rev.* **1997**, *97*, 2341-2372.

(12) (a) Gololobov, Y. G.; Nesmeyanov, A. N.; lysenko, V. P.; Boldeskul, I. E. Twenty-Five Years of Dimethylsulfoxonium Ethylide (Corey's Reagent). *Tetrahedron* **1987**, *43*, 2609-2651. (b) Corey, E. J.; Chaykovsky, M. Dimethyloxosulfonium Methylide ($(CH_3)_2SOCH_2$) and Dimethylsulfonium Methylide ($(CH_3)_2SCH_2$). Formation and Application to Organic Synthesis. *J. Am. Chem. Soc.* **1965**, *87*, 1353-1364.

(13) (a) Nadir, U. K.; Sharma, R. L.; Koul, V. K. Reaction of Dimethyloxosulfonium Methylide with *N*-Arylsulfonylaziridines-Stereospecific Conversion of *N*-Arylsulfonylaziridines to *N*-Arylsulfonylazetidines. *Tetrahedron* **1989**, *45*, 1851-1858. (b) Nadir, U. K.; Koul, V. K. Reaction of Dimethyloxosulphonium Methylide with *N*-Arylsulphonyl-2-phenylaziridines: A New Synthesis of *N*-Arylsulphonyl-2-phenylazetidines. *J. Chem. Soc., Chem. Commun.* **1981**, 417-418. (c) Vaultier, M.; Danion-Bougot, R.; Danion, D.; Hamelin, J.; Carrie, R. Reaction of Azomethine Ylides with Sulfur Ylides. Novel Azetidine Synthesis. *J. Org. Chem.* **1975**, *40*, 2990-2992. (d) Vaultier, M.; Danion-Bougot, R.; Danion, D.; Hamelin, J.; Carrié, R. Reaction D'une Aziridine et D'une Oxazoline-4 Ylures D'azomethine Potentiels Avec les Ylures du Soufre, Nouvelle Methode de Synthese D'azetidines. *Tetrahedron Lett.* **1973**, *14*, 1923-1926.

(14) (a) Butova, E. D.; Barabash, A. V.; Petrova, A. A.; Kleiner, C. M.; Schreiner, P. R.; Fokin, A. A. Stereospecific Consecutive Epoxide Ring Expansion with Dimethylsulfoxonium Methylide. *J. Org. Chem.* **2010**, *75*, 6229-6235. (b) J. M. Stirling, C.; Griffiths, G. Concerted versus Stepwise Processes in Eliminative Fission of Oxacycles. *Heterocycles* **1989**, *28*, 89-92. (c) Okuma, K.; Tanaka, Y.; Kaji, S.; Ohta, H. Reaction of Dimethyloxosulfonium Methylide with Epoxides. Preparation of Oxetanes. *J. Org. Chem.* **1983**, *48*, 5133-5134.

(15) Dong, J.; Xu, J. X. Facile Synthesis of Thietanes via Ring Expansion of Thiiranes. *Org. Biomol. Chem.* **2017**, *15*, 836-844.

(16) (a) Gandelman, M.; Rybtchinski, B.; Ashkenazi, N.; Gauvin, R. M.; Milstein, D. A New General Method for the Preparation of Metal Carbene Complexes. *J. Am. Chem. Soc.* **2001**, *123*, 5372-5373. (b) Trost, B. M. Decomposition of Sulfur Ylides. Evidence for Carbene Intermediates. *J. Am. Chem. Soc.* **1966**, *88*, 1587-1588.

(17) (a) Xu, Y.; Zheng, G.; Yang, X.; Li, X. Rhodium(iii)-Catalyzed Chemodivergent Annulations Between *N*-Methoxybenzamides and Sulfoxonium Ylides via C-H Activation. *Chem. Commun.* **2018**, *54*, 670-673. (b) Wu, X.; Xiong, H.; Sun, S.; Cheng, J. Rhodium-Catalyzed Relay Carbenoid Functionalization of Aromatic C-H Bonds toward Fused Heteroarenes. *Org. Lett.* **2018**, *20*, 1396-1399. (c) Xu, Y.; Zhou, X.; Zheng, G.; Li, X. Sulfoxonium Ylides as a Carbene Precursor in Rh(III)-Catalyzed C-H Acylmethylation of Arenes. *Org. Lett.* **2017**, *19*, 5256-5259. (d) Vaitla, J.; Bayer, A.; Hopmann, K. H. Synthesis of Indoles and Pyrroles Utilizing Iridium Carbenes Generated from Sulfoxonium Ylides. *Angew. Chem. Int. Ed.* **2017**, *56*, 4277-4281. (e) Barday, M.; Janot, C.; Halcovitch, N. R.; Muir, J.; Aissa, C. Cross-Coupling of alpha-Carbonyl Sulfoxonium Ylides with C-H Bonds. *Angew. Chem. Int. Ed.* **2017**, *56*, 13117-13121. (f) Phelps, A. M.; Chan, V. S.; Napolitano, J. G.; Krabbe, S. W.; Schomaker, J. M.; Shekhar, S. Ligand-Controlled Synthesis of Azoles via Ir-Catalyzed

Reactions of Sulfoxonium Ylides with 2-Amino Heterocycles. *J. Org. Chem.* **2016**, *81*, 4158-4169.
(18) Burtoloso, A. C. B.; Dias, R. M. P.; Leonarczyk, I. A. Sulfoxonium and Sulfonium Ylides as Diazocarbonyl Equivalents in Metal-Catalyzed Insertion Reactions. *Eur. J. Org. Chem.* **2013**, *23*, 5005-5016.
(19) (a) Jia, M.; Ma, S. New Approaches to the Synthesis of Metal Carbenes. *Angew. Chem. Int. Ed.* **2016**, *55*, 9134-9166. (b) Proctor, L. D.; Warr, A. J. Development of a Continuous Process for the Industrial Generation of Diazomethane. *Org. Proc. Res. Dev.* **2002**, *6*, 884-892.
(20) (a) Lu, P.; Herrmann, A. T.; Zakarian, A. Toward the Synthesis of Nuphar Sesquiterpene Thioalkaloids: Stereodivergent Rhodium-Catalyzed Synthesis of the Thiolane Subunit. *J. Org. Chem.* **2015**, *80*, 7581-7589. (b) Bott, T. M.; Vanecko, J. A.; West, F. G. One-Carbon Ring Expansion of Azetidines via Ammonium Ylide [1,2]-Shifts: A Simple Route to Substituted Pyrrolidines. *J. Org. Chem.* **2009**, *74*, 2832-2836. (c) Nair, V.; Nair, S. M.; Mathai, S.; Liebscher, J.; Ziemer, B.; Narsimulu, K. The Rh(II) Catalyzed Reaction of Diethyl Diazomalonate with Thietanes: A Facile Synthesis of Tetrahydrothiophene Derivatives via Sulfonium Ylides. *Tetrahedron Lett.* **2004**, *45*, 5759-5762. (d) Katsuki, T.; Ito, K.; Yoshitake, M. Enantiopsecific Ring Expansion of Oxetanes: Stereoselective Synthesis of Tetrahydrofurans. *Heterocycles* **1996**, *42*, 305. (e) Kirmse, W.; Van Chiem, P.; Schurig, V. Oxygen Ylides-II.: Photochemical and Rhodium-Catalyzed Reactions of Diazomethane with (*S*)-2-Methyloxetane. *Tetrahedron Lett.* **1985**, *26*, 197-200.
(21) (a) Zhu, Z.; Espenson, J. H. Organic Reactions Catalyzed by Methylrhenium Trioxide: Reactions of Ethyl Diazoacetate and Organic Azides. *J. Am. Chem. Soc.* **1996**, *118*, 9901-9907. (b) Achard, T.; Tortoreto, C.; Poblador-Bahamonde, A. I.; Guenee, L.; Burgi, T.; Lacour, J. [CpRu]-Catalyzed Carbene Insertions into Epoxides: 1,4-Dioxene Synthesis Through $S_{(N)}1$-Like Chemistry with Retention of Configuration. *Angew. Chem. Int. Ed.* **2014**, *53*, 6140-6144.
(22) (a) Li, S. Q.; Chen, X. P.; Xu, J. X. Microwave-Assisted Copper-Catalyzed Stereoselective Ring Expansion of Three-Membered Heterocycles with α-Diazo-β-Dicarbonyl Compounds. *Tetrahedron* **2018**, *74*, 1613-1620. (b) Chen, X. P.; Xu, J. X. Synthesis of 3-Acyl-5,6-dihydro-1,4-oxathiines Through Ring Expansion of Thiiranes. *Tetrahedron Lett.* **2017**, *58*, 1651-1654.
(23) (a) Schmid, S. C.; Guzei, I. A.; Fernandez, I.; Schomaker, J. M. Ring Expansion of Bicyclic Methyleneaziridines via Concerted, Near-Barrierless [2,3]-Stevens Rearrangements of Aziridinium Ylides. *ACS Catal.* **2018**, *8*, 7907-7914. (b) Schmid, S. C.; Guzei, I. A.; Schomaker, J. M. A Stereoselective [3+1] Ring Expansion for the Synthesis of Highly Substituted Methylene Azetidines. *Angew. Chem. Int. Ed.* **2017**, *56*, 12229-12233.
(24) Shibatomi, K.; Kotozaki, M.; Sasaki, N.; Fujisawa, I.; Iwasa, S. Williamson Ether Synthesis with Phenols at a Tertiary Stereogenic Carbon: Formal Enantioselective Phenoxylation of beta-Keto Esters. *Chem. Eur. J.* **2015**, *21*, 14095-14098.
(25) Dong, J.; Xu, J. X. Safe and Metal-Free Synthesis of 1-Alkenyl Aryl Sulfides and Their Sulfones from Thiiranes and Diaryliodonium Salts. *Synthesis* **2018**, *50*, 2407-2415.
(26) The reaction of 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one (**8**) and thiirane **1a** afforded 2,3-dihydro-1,4-oxathiines **9** and **10** as byproducts. 3-Butyl-6-phenyl-2,3-dihydro-1,4-oxathiine (**9**). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.96 (d, J = 7.7 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 5.75(s, 1H), 3.92 – 3.82 (m, 1H), 3.43 (dd, J = 11.3, 5.3 Hz, 1H), 3.06 – 3.01 (m, 1H), 1.84 – 1.74 (m, 2H), 1.42 – 1.30 (m, 4H), 0.92 – 0.89 (m, 3H). 2-Butyl-6-phenyl-2,3-dihydro-1,4-oxathiine (**10**). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) = 7.96 (d, J = 7.7 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 5.73 (s, 1H), 3.92 – 3.82 (m, 1H), 3.30 (dd, J = 12.0, 4.9 Hz, 1H), 3.06 – 3.01 (m, 1H), 1.84 – 1.74 (m, 2H), 1.42 – 1.30 (m, 4H), 0.92 – 0.89 (m, 3H).
(27) (a) Zhou, C.; Xu, J. X. Regioselective Nucleophilic Ring Opening Reactions of Unsymmetric Thiiranes. *Prog. Chem.* **2012**, *24*, 238–247. (b) Huang, J. X.; Du, D.-M.; Xu, J. X. Facile Synthesis of 1,1-Disubstituted Taurines. *Synthesis* **2006**, *(2)*, 315–319. (c) Yu, H.; Cao, S. L.; Zhang, L. L.; Liu, G.; Xu, J. X. Synthesis of α-Aliphatic and β-Aromatic Substituted Taurines via the Regioselective Ammonia Ring-Opening of Thiiranes. *Synthesis* **2009**, *(13)*, 2205–2209. (d) Li, X.; Xu, J. Theoretical Calculational Investigation on the Regioselectivity of the Ring Opening of Thiiranes with Ammonia and Amines. *Tetrahedron* **2011**, *67*, 1681-1688.
(28) (a) Yuan, Z.; Fang, X.; Li, X.; Wu, J.; Yao, H.; Lin, A. 1,6-Conjugated Addition-Mediated [2+1] Annulation: Approach to Spiro[2.5]octa-4,7-dien-6-one. *J. Org. Chem.* **2015**, *80*, 11123-11130. (b) Sabounchei, S. J.; Bagherjeri, F. A.; Mozafari, Z.; Boskovic, C.; Gable, R. W.; Karamian, R. and Asadbegy, M. Synthesis and Characterization of Novel Simultaneous C and O-Coordinated and Nitrate-Bridged Complexes of Silver(I) with Carbonyl-Stabilized Sulfonium Ylides and Their Antibacterial Activities. *Dalton Trans.* **2013**, *42*, 2520-2529**.** (c) Ratts, K. W.; Yao, A. N. Stable Sulfonium Ylids. *J. Org. Chem*. **1966**, *31*, 1185-1188. (d) Sabounchei, S. J.; Bagherjeri, F. A.; Boskovic, C.; Gable, R. W.; Karamian, R.; Asadbegy, M. Binuclear Mercury(II) Complexes of Sulfonium Ylides: Synthesis, Structural Characterization and Anti-bacterial Activity. *J. Mol. Struct.* **2013**, *1034*, 265-270.

(29) (a) Amador, A. G.; Sherbrook, E. M.; Yoon, T. P. Enantioselective Photocatalytic [3 + 2] Cycloadditions of Aryl Cyclopropyl Ketones. *J. Am. Chem. Soc.* **2016**, *138*, 4722-4725. (b) Nikolaev, D. N.; Davidovich, P. B.; Piotrovskii, L. B. Synthesis of Fullerene C_{60} Monoadducts. Cyclopropanation of C_{60} with Sulfonium Ylides. *Russ. J. Org. Chem.* **2016**, *52*, 1050-1053.

(30) Gallo, Rafael D. C.; Ahmad, A.; Metzker, G.; Burtoloso, A. C. B. α,α-Alkylation-Halogenation and Dihalogenation of Sulfoxonium Ylides. A Direct Preparation of Geminal Difunctionalized Ketones. *Chem. Eur. J.* **2017**, *23*, 16980–16984.