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A novel tandem [4⁺+2] cycloaddition–elimination reaction: 2-alkenyl-4,4-dimethyl-1,3-oxathianes as synthetic equivalents for α,β-unsaturated thioaldehydes

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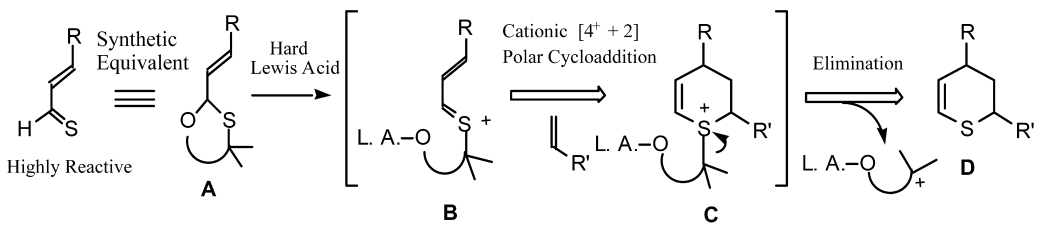
Abstract—The first tandem cationic [4⁺+2] polar cycloaddition–elimination reaction of 1-thia-1,3-butadienyl cations **B** with olefins to afford directly 3,4-dihydro-2*H*-thiopyrans **D** is described. The cations **B** were easily accessible by treatment of monothioacetals **A**, particularly the 2-alkenyl-4,4-dimethyl-1,3-oxathianes **1**, with a hard Lewis acid. In this novel reaction, 2-alkenyl-4,4-dimethyl-1,3-oxathianes were utilized as synthetic equivalents for highly reactive α,β-unsaturated thioaldehydes. The effect of geminal dimethyl substituents on the oxathianes **1** and the mechanistic aspect of the reaction are considered. The reaction's asymmetric version was also investigated using a chiral oxathiane **4** derived from (−)-(1*R*,2*R*,5*R*)-2-(1-mercapto-1-methylethyl)-5-methylcyclohexanol. Although the enantioselectivities were moderate, the whole process can be done under odorless conditions.

1. Introduction

It is usually difficult to control the abnormally high reactivity of α,β-unsaturated thioaldehydes and aliphatic thioketones because they easily polymerize or dimerize even at low temperature. For example, thioacrolein, generated by pyrolysis of diallyl sulfide, polymerizes at low temperature[1] and methyl vinyl thioketone readily dimerizes through a hetero Diels–Alder reaction.[2] However, the α,β-unsaturated thioketones used in this cycloaddition[3] and its asymmetric versions[4]are limited in most cases to relatively stable phenyl thioketone derivatives (such as thiochalcone). For all of this, little attention has been directed toward the Diels–Alder trapping of α,β-unsaturated thioaldehydes.[5] Synthetic equivalents of these highly reactive thioaldehydes or ketones are therefore needed for use in new types of organic reactions. Although thienium cations can be subjected to cationic [2⁺+4] polar cycloadditions as hetero dienophiles[6] or to cationic [4⁺+2] polar cycloadditions as 2-thia-1,3-butadienes,[7] there is no precedent for cationic [4⁺+2] polar cycloadditions as 1-thia-1,3-butadienes (i.e. α,β-unsaturated thioaldehydes). Consequently, we have developed a novel tandem [4⁺+2] cycloaddition–elimination reaction[8] of 2-alkenyl-4,4-dimethyl-1,3-oxathianes **A** with olefins to give 3,4-dihydro-2*H*-thiopyrans **D**, as shown in Scheme 1. Recently, a similar reaction was developed using α,β-unsaturated oxathiolanes and styrene derivatives.[9] These reactions can be formally categorized as hetero Diels–Alder reactions of α,β-unsaturated thioaldehydes with olefins to afford heterocyclic adducts containing a sulfur atom.[10] We report herein a full account of the novel tandem [4⁺+2] cycloaddition–elimination reaction as well as its asymmetric version.



Scheme 1. A strategy for a novel tandem cationic [4⁺+2] polar cycloaddition–elimination reaction.

Keywords: α,β-unsaturated thioaldehydes; stereochemistry; cycloaddition.

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During the course of our studies on the development of new organic reactions utilizing 1,3-mercapto alcohols,[11] we envisioned the elimination of the exocyclic substituent on the sulfur atom of the cationic cycloadduct **C** prepared through [4+2] cycloaddition of the α,β-unsaturated thienium cation **B** with an olefin that would constitute a novel cycloaddition reaction to give 3,4-dihydro-2*H*-thiopyrans **D**. It is usually difficult to synthesize this type of 3,4-dihydro-2*H*-thiopyran via cycloaddition of an α,β-unsaturated thioaldehyde because of its high reactivity. The 1,3-oxathiane **A** must have *gem*-dimethyl groups at the position adjacent to the sulfur atom to facilitate the elimination of the exocyclic substituent on the sulfur atom. Therefore, we selected 2-alkenyl-4,4-dimethyl-1,3-oxathianes (**A**) as the starting monothioacetals for the generation of the α,β-unsaturated thienium cation **B** promoted by a selective coordination of a hard Lewis acid to the oxygen of the monothioacetal **A**. The *gem*-dimethyl groups would also retard the coordination of the Lewis acid to the sulfur atom because of steric hindrance and would direct the reaction toward formation of the thienium cation intermediate **B**.

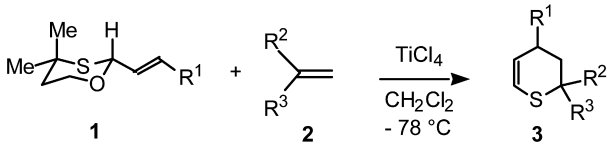
2. Results and discussion

2.1. Tandem [4+2] cycloaddition–elimination reactions of 2-alkenyl-4,4-dimethyl-1,3-oxathianes (1) with olefins

The results of tandem [4+2] cycloaddition–elimination reactions of 2-alkenyl-4,4-dimethyl-1,3-oxathianes **1** with olefins **2** are summarized in Table 1. Treatment of **1a** and 1,1-diphenylethylene (**2a**) with titanium tetrachloride in dichloromethane at −78°C gave the desired 3,4-dihydro-2*H*-thiopyran **3aa** in 88% yield (entry 1). The reaction of **1a** with α-methylstyrene **2b** afforded **3ab** in lower yield than the reaction with **2a** (entry 2). Titanium tetraisopropoxide resulted in no reaction. The other Lewis acids (dimethylaluminum chloride, stannic tetrachloride, and boron trifluoride etherate) gave poor yields (<10%). The reaction of **1a** with other α-alkylstyrenes **2c–e** also afforded **3ac–3ae** in moderate yields (entries 3–5).

Although the reaction of 4′-bromo-α-methylstyrene **2f** gave the 3,4-dihydro-2*H*-thiopyran **3af** (entry 6), the *o*-bromo- and *o*-methoxy substituents on the phenyl group of α-methylstyrene resulted in unreacted recovered starting material. The reactions of **1b** having the 4-methoxyphenyl substituent as R^1 proceeded slowly to give the corresponding dihydrothiopyrans **3ba**, **3bb** and **3bd**, but the yields were higher than those of **3ab** and **3ad** (entries 7–9). The electron donating effect of the *p*-methoxy group on the phenyl substituent obviously affected the stability of the thienium cation intermediate (**B**). On the other hand, the electron withdrawing (4-bromo and 3-trifluoromethyl) groups on the phenyl ring resulted in low yields of 3,4-dihydro-2*H*-thiopyran **3ca** and **3da** (entries 10 and 11). In these cases, γ-vinylated alcohols (see Scheme 3) were formed in 37 and 17% yield, respectively. 1,3-Oxathianes having an alkyl substituent at R^1 also afforded 3,4-dihydro-2*H*-thiopyrans **3ea** and **3fa** in moderate yields (entries 12 and 13). All these reactions showed *cis* diastereoselectivity varying from 10:1 to 1.2:1. The stereochemistry was determined by NOE experiments between the methyl proton and the methine proton adjacent to the phenyl ring of the diastereomer *cis*-**3ab** (Table 1, entry 2) isolated by silica gel chromatography. The *cis* and *trans* stereochemistry of the

Table 1. A tandem [4+2] cycloaddition–elimination reaction of oxathiane **1** with olefin **2**



1 **2** **3**

Entry	Oxathiane **1**		Olefin **2**				$TiCl_4$ (equiv.)	Time	Product **3**		
		R^1		R^2	R^3	Equiv.				Yield[a] (%)	Ratio[b] (*cis*/*trans*)
1	**1a**	Ph	**2a**	Ph	Ph	4	1.2	15 h	**3aa**	88	–
2	**1a**	Ph	**2b**	Ph	Me	4	1.0	1 h	**3ab**	38	2:1
3	**1a**	Ph	**2c**	Ph	Et	4	1.0	1 h	**3ac**	37	2:1
4	**1a**	Ph	**2d**	Ph	Pr	4	1.0	1 h	**3ad**	42	2:1
5	**1a**	Ph	**2e**	Ph	Bn	5	1.0	26 h	**3ae**	48	3.3:1
6	**1a**	Ph	**2f**	4-BrPh	Me	5	1.2	3 h	**3af**	31	2.5:1
7[c]	**1b**	4-MeOPh	**2a**	Ph	Ph	4	1.2	3 d	**3ba**	76	–
8	**1b**	4-MeOPh	**2b**	Ph	Me	4	1.2	3 d	**3bb**	77	10:1
9[d]	**1b**	4-MeOPh	**2d**	Ph	Pr	5	1.2	4 d	**3bd**	65	1.2:1
10	**1c**	4-BrPh	**2a**	Ph	Ph	4	1.0	1 d	**3ca**	24[e]	–
11	**1d**	3-CF_3Ph	**2a**	Ph	Ph	4	1.0	1.5 h	**3da**	34[f]	–
12	**1e**	$PhCH_2$	**2a**	Ph	Ph	4	1.0	1 h	**3ea**	54	–
13	**1f**	Me	**2a**	Ph	Ph	4	1.0	0.5 h	**3fa**	37	–

[a] Isolated yield.
[b] Determined by ^{1}H NMR.
[c] The reaction was conducted at −30°C.
[d] The reaction was conducted at −50°C.
[e] γ-Vinylated alcohol (37%) was obtained.
[f] γ-Vinylated alcohol (17%) was obtained.

other compounds was determined by comparison of the chemical shifts of the olefinic protons of 3,4-dihydro-2*H*-thiopyran **3**.

2.2. Asymmetric version of tandem [4$^+$+2] cycloaddition–elimination reactions

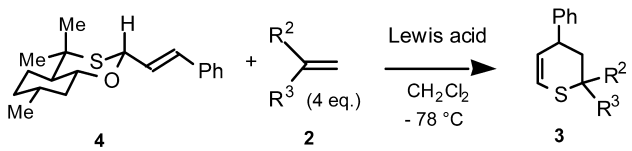
Although 3-mercapto-3-methylbutanol, used in the preparation of the oxathiane **1**, is a malodorous mercapto alcohol, (−)-(1*R*,2*R*,5*R*)-2-(1-mercapto-1-methylethyl)-5-methylcyclohexanol[12] does not have the common thiol-like foul smell. It was therefore suitable as a chiral and odorless 1,3-mercapto alcohol having geminal dimethyl groups to prepare the oxathiane in order to test the asymmetric version of the reaction. The chiral oxathiane **4** derived from (−)-(1*R*,2*R*,5*R*)-2-(1-mercapto-1-methylethyl)-5-methylcyclohexanol was subjected to the tandem [4$^+$+2] cycloaddition–elimination reaction with olefin **2**, and the results are summarized in Table 2.

Treatment of **4** and 1,1-diphenylethylene (**2a**) with titanium tetrachloride in dichloromethane at −78°C then at −40°C gave the desired 3,4-dihydro-2*H*-thiopyran **3aa** in 82% yield (entry 1). The optical purity (51% ee) of (+)-**3aa** was determined by HPLC analysis using a chiral stationary column (Daicel CHIRALCEL OJ). The absolute configuration of (+)-**3aa** was determined to be *S* by X-ray crystallographic analysis (see Experimental). 5-Methyl-2-(1-methylethenyl)cyclohexanol [isopulegol] was isolated in 29% as the fragment from the chiral auxiliary. In the above reaction, the use of dichloropyrocatecholatotitanium[13] resulted in recovery of the starting material **4** in 86% yield. The reaction of the chiral oxathiane **4** and 2-phenylpropene (**2b**) with titanium tetrachloride was tested at −78°C. The enantiomeric excess of the *cis*-thiopyrans was also low and *trans*-thiopyrans were almost racemic (entry 2). Changing the Lewis acid to methylaluminum dichloride in the reaction with **2a** resulted in lower ee (entry 3). Modification of methylaluminum dichloride with bulky phenols improved the ee to 43% from 14% of the desired 3,4-dihydro-2*H*-thiopyran **3aa** (entries 4 and 5). The reaction using aluminum Lewis acids afforded the γ-vinylated alcohols in considerable yields along with 3,4-dihydro-2*H*-thiopyrans (entries 3–5). Consequently, titanium tetrachloride was the best among the Lewis acids tested. The entire reaction was odorless, even though the enantioselectivity was moderate.

2.3. The effect of geminal dimethyl substituents

In order to prove the significance of geminal dimethyl substituents on the 1,3-oxathianes **1**, we carried out the reactions of 2-styryl-1,3-oxathiane (**5**) with α-substituted styrenes **2a**,**b** or allyltrimethylsilane (**2g**), as shown in Scheme 2. The tandem reaction of **5** with **2a** or **2b** (4 equiv.) promoted by titanium tetrachloride (1 equiv.) in dichloromethane at −78°C did not proceed, and the reaction of **5** with **2g** (4 equiv.) afforded only the α-allylated alcohol **6** in 25% yield (see Section 4 for identification of **6**). On the other hand, the reaction of oxathiane **1a** having geminal

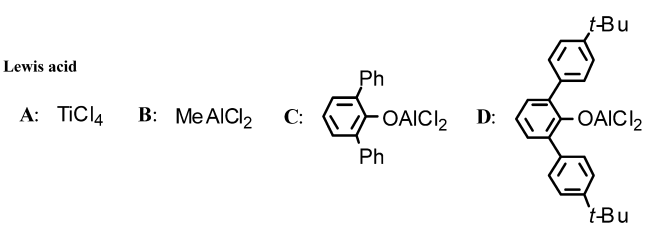
Table 2. A tandem [4$^+$+2] cycloaddition–elimination reaction of a chiral oxathiane **4** with olefin **2**



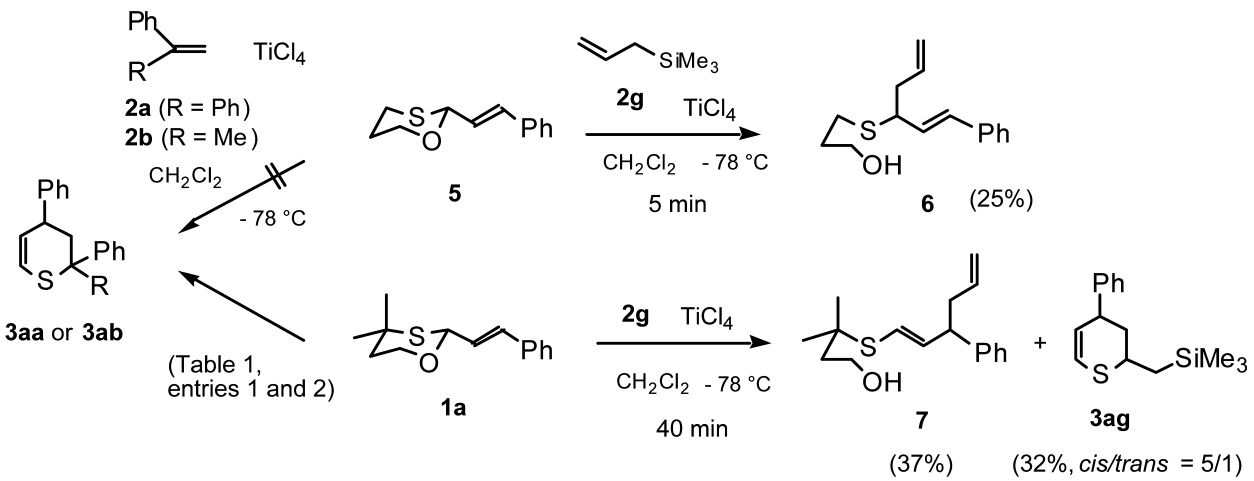
4 2 3

Entry	Olefin **2**			Lewis acid (equiv.)	Time (h)	Product **3**			
		R^2	R^3				Yield[a] (%)	Ratio[b] (*cis*/*trans*)	E.e. (%)[c] (*cis*/*trans*)
1[d]	**2a**	Ph	Ph	**A** (1.0)	17	**3aa**	82	–	51
2	**2b**	Ph	Me	**A** (1.0)	17	**3ab**	21	4:1	26:0
3	**2a**	Ph	Ph	**B** (4.0)	17	**3aa**	45[e]	–	14
4	**2a**	Ph	Ph	**C** (2.0)	17	**3aa**	33[f]	–	41
5	**2a**	Ph	Ph	**D** (2.0)	18	**3aa**	37[g]	–	43

Lewis acid



[a] Isolated yield.
[b] Determined by ^{1}H NMR.
[c] Enantiomeric excesses were determined by chiral HPLC analyses using Daicel CHIRALCEL OJ (hexane/isopropanol=99/1).
[d] The reaction was conducted at −78°C, then temperature was raised to −40°C.
[e] γ-Vinylated alcohol (49%) was obtained.
[f] γ-Vinylated alcohol (58%) was obtained.
[g] γ-Vinylated alcohol (43%) was obtained.



Scheme 2.

dimethyl substituents with **2g** gave the γ-allylated alcohol **7** (37%) regioselectively, along with 3,4-dihydro-2*H*-thiopyran **3ag** (32%). Undoubtedly, geminal dimethyl substituents at the 4-position of 1,3-oxathianes **1** play important roles in the novel tandem [4$^+$+2] cycloaddition–elimination reaction, i.e. promotion of the reaction and regioselectivity of the products.

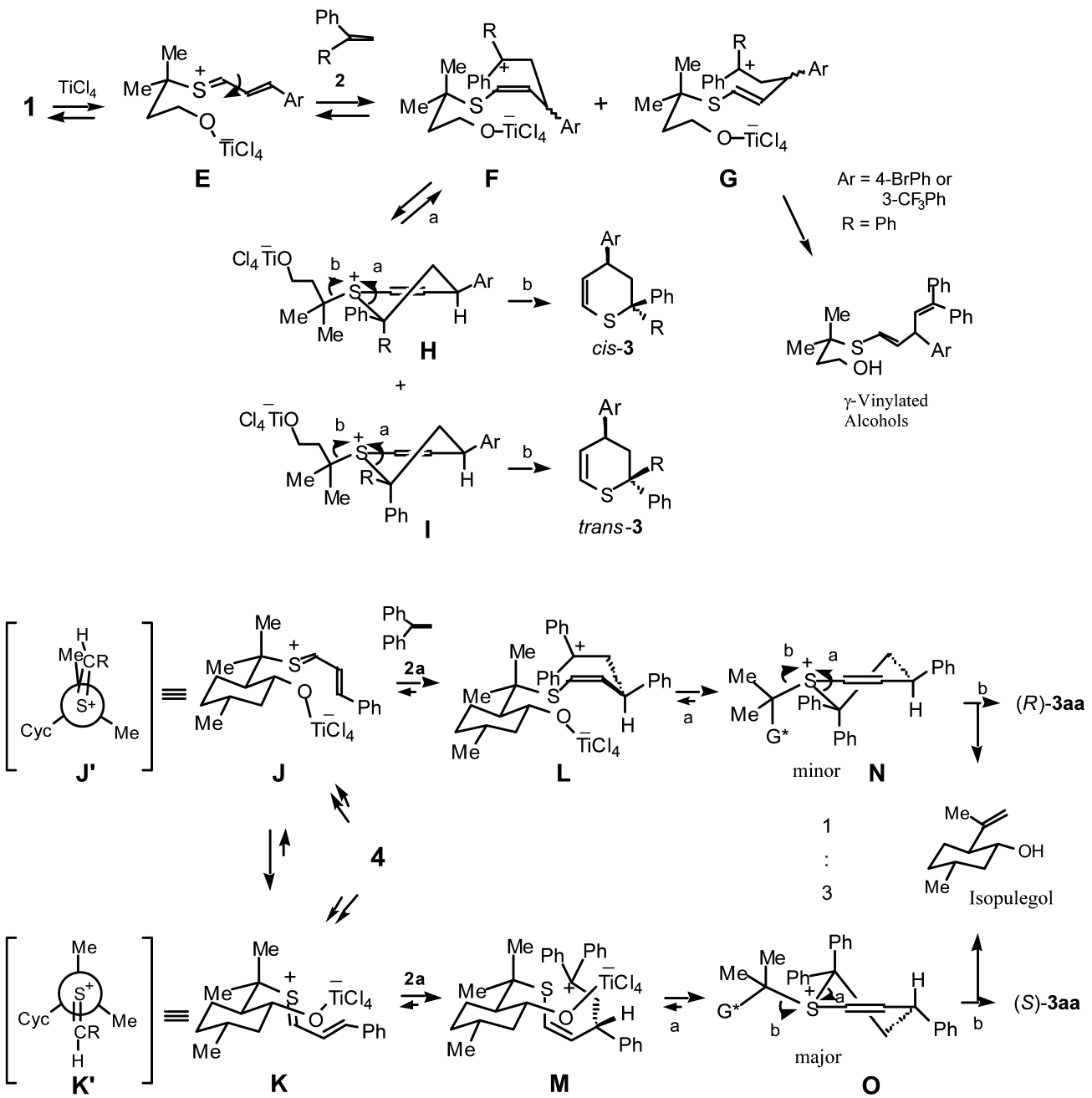
2.4. Mechanistic aspects

The generation of 3,4-dihydro-2*H*-thiopyrans **3** can be formally interpreted as being the result of a hetero Diels–Alder reaction of an α,β-unsaturated thioaldehyde with an olefin. However, we could rule out the mechanism of the concerted process (hetero Diels–Alder reaction) and concluded that this novel cationic [4$^+$+2] polar cycloaddition proceeded via a stepwise process for the following reasons: (1) using normal olefins such as 1-hexene, 3-phenyl-1-propene, 2-hexyl-1-octene, and methyl acrylate did not give 3,4-dihydro-2*H*-thiopyrans in this reaction, (2) the reactive olefins were limited to α-substituted styrenes and allylsilane, which generate stable cations through attack of an electrophile, (3) the ee's of *cis*- and *trans*-**3ab** were not equal (Table 2, entry 2), and (4) in some cases γ-vinylated alcohols were formed via a stepwise mechanism. In addition, the generation of free thiocinnamaldehyde from the thienium cation **E** can probably be excluded, because the starting 1,3-oxathiane **1a** was recovered in 87% yield when **1a** was treated with titanium tetrachloride (1.0 equiv.) in dichloromethane at −78°C for 1 h. A plausible reaction mechanism for oxathianes **1** and **4** with the olefin **2** is illustrated in Scheme 3.

The selective coordination of titanium tetrachloride with the oxygen of 1,3-oxathiane **1** would initially generate the α,β-unsaturated thienium cation **E**. After rotation to the *s-cis* conformation of **E**, electrophilic attack on a styrene derivative would give the carbocation intermediate **F**, whereas the intermediate **G** would be formed from **E** without the rotation to its *s-cis* conformation. The subsequent cyclization by sulfur in the (*Z*)-vinyl sulfide **F** would form the sulfonium intermediates **H** and **I**, but the (*E*)-vinyl sulfide **G** could not cyclize because of the strong strain in the 6-membered ring and would be transformed into **F** via reversion to **E** or would give γ-vinylated alcohols by the elimination of a proton in some cases (Ar=electron deficient phenyl substituent or using aluminum Lewis acid). The cleavage of the carbon–sulfur bond of the sulfonium intermediates **H** and **I** via path b would result in the cationic [4$^+$+2] polar cycloaddition reaction to give 3,4-dihydro-2*H*-thiopyrans **3**, while the cleavage of the other carbon–sulfur bond, via path a, would lead back to the intermediate **F**. The *cis* selectivity might be attributed to the stability of the sulfonium intermediates **H** and **I**. The sulfonium intermediate **H** should be more stable than **I** because the two phenyl substituents assume the equatorial position in the half chair conformation. The enantioselectivity of the asymmetric version of this novel tandem reaction using chiral oxathiane **4** was moderate (up to 51%). The resulting thienium cation **J** would reach equilibrium with the cation **K** through C–S bond rotation. The cation **K** would be more stable than the cation **J** due to the eclipsed conformation of **J**′, as shown in the Newman projection. Presence of this equilibrium must be a reason of the low enantioselectivity. Nucleophilic attacks of the olefin to the cations **J** and **K** give the cations **L** and **M**, respectively. The major enantiomer (*S*)-**3aa** should be formed through the sulfonium cation intermediate **O** with the elimination of isopulegol.

3. Conclusion

We have exploited a novel tandem [4$^+$+2] cycloaddition–elimination reaction using 1,3-oxathianes **1** as synthetic equivalents of α,β-unsaturated thioaldehydes to give 3,4-dihydro-2*H*-thiopyrans **3**. This is the first reaction of cationic [4$^+$+2] polar cycloaddition utilizing a 1-thia-1,3-butadienyl cation derived from 2-alkenyl-4,4-dimethyl-1,3-oxathianes. An asymmetric version of this reaction with a chiral 1,3-oxathiane **4** resulted in moderate enantiomeric excesses. It can be concluded that this novel tandem cycloaddition–elimination reaction probably proceeds via a stepwise mechanism due to our experimental evidence. In these reactions, γ-vinylated alcohols or γ-allylated alcohols accompanied the 3,4-dihydro-2*H*-thiopyrans **3** in some cases. This chemistry will be reported elsewhere. It is worth noting that, because of their high reactivity, it is difficult to synthesize α,β-unsaturated thioaldehydes;



Scheme 3. A plausible reaction mechanism.

however, α,β-unsaturated 1,3-oxathianes, as substrates in this reaction, can be easily prepared from the corresponding aldehydes by monothioacetalization using 1,3-mercapto alcohols. This tandem reaction therefore offers a new method of controlling the high reactivity toward polymerization of α,β-unsaturated thioaldehydes.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were obtained with a VARIAN GEMINI 2000/200, XL-300, INOVA-400NB or JEOL JNM-AL300 spectrometer with tetramethylsilane as internal standard. Infrared spectra were measured with a Shimazu FTIR-8300 spectrometer. Low and high-resolution mass spectra were determined on either a JEOL JMS GC-mate (EI) or a JEOL JMX SX 102A QQ (FAB) mass spectrometers. Preparative high performance liquid chromatography was performed on a Japan Analytical Industry Co.LTD., LC 908 series, silica gel column (JAIGEL SIL-043-15) or a GPC column (JAIGEL 1H and 2H). Silica gel 60 (230–400 mesh Merck) was used for column chromatography. Silica gel F_{254} plates (Merck) were used for thin layer chromatography and preparative thin layer chromatography (ptlc). Visualization was performed using UV light, iodine, and 12-molybdo(VI) phosphoric acid *n*-hydrate in EtOH. Melting points were taken on a micro hot-stage apparatus (Yanagimoto) and are uncorrected.

4.2. Materials

Dichloromethane was distilled from CaH_2, after washing with water. Most of the reagents were obtained from Wako Pure Chemical Industries, Ltd, Nacalai Tesque, Inc., Tokyo Chemical Industries, Ltd, or Aldrich Chemical Inc. *trans*-4-Phenyl-2-butenal was prepared by the reported procedure.[14]

4.3. General methods for the synthesis of 3-mercapto-3-methyl-1-butanol

To an ethanol solution (80 mL) of ethyl 3,3-dimethylacrylate (14.7 g, 115.1 mmol) was added benzyl mercaptan (21.4 g, 172.6 mmol) followed by addition of an ethanol (2 mL) solution of sodium ethoxide (4.3 mmol) at room temperature. The resultant mixture was stirred for 1 d. Additional benzyl mercaptan (10.7 g, 86.3 mmol) was added, and the reaction solution was heated and stirred at 50°C for 12 h. The reaction solution was poured into 1N HCl, and concentrated in vacuo. The aqueous layer was extracted with AcOEt, dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude mixture was purified by silica gel column chromatography to give ethyl 3-methyl-3-benzylthiobutanoate (29.1 g, 100%). To a tetrahydrofuran suspension (150 mL) of lithium aluminum hydride (9.62 g, 253.6 mmol) was added dropwise a tetrahydrofuran (50 mL) solution of ethyl 3-methyl-3-benzylthiobutanoate (29.1 g, 115.3 mmol) at 0°C, and the mixture was refluxed for 1.5 h. The reaction mixture was quenched with a saturated Na_2SO_4 solution, dried (Mg_2SO_4), filtered, and concentrated in vacuo. An ether (100 mL) solution of the crude residue was added to a solution of liq. NH_3 (300 mL) and ether (150 mL) solution of sodium (11.9 g, 518.7 mmol) at −78°C. The reaction mixture was stirred for 1.5 h. The reaction mixture was quenched with solid NH_4Cl until its purple color disappeared, then liq. NH_3 was evaporated. After neutralization with conc. HCl, the aqueous layer was extracted with AcOEt, dried (Mg_2SO_4), filtered, and concentrated in vacuo. The crude residue was purified by silica gel column chromatography to give 3-mercapto-3-methyl-1-butanol (12.1 g, 2 steps 87%).

4.3.1. Ethyl 3-methyl-3-benzylthiobutanoate. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.19 (m, 5H), 4.15 (q, J=7.1 Hz, 2H), 3.80 (s, 2H), 2.61 (s, 2H), 1.47 (s, 6H), 1.28 (t, J=7.1 Hz, 3H); IR ($CHCl_3$): 3034, 3011, 2981, 2931, 1724, 1494, 1454, 1369, 1317, 1194, 1107, 1032 cm^{-1}; FAB-MS *m/z*: 253 (M^++H, 17), 252 (M^+, 8), 154 (100); HRMS calcd for $C_{14}H_{21}O_2S$ (M^++H): 253.1262, found 253.1267.

4.3.2. 3-Benzylthio-3-methyl-1-butanol. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.23 (m, 5H), 3.83 (t, J=6.4 Hz, 2H), 3.78 (s, 2H), 2.30 (br, 1H, OH), 1.86 (t, J=6.4 Hz, 2H), 1.37 (s, 6H); IR ($CHCl_3$): 3730–2940 (br), 3620, 3086, 3065, 3034, 3007, 2964, 2932, 2897, 1603, 1494, 1454, 1387, 1367, 1261, 1126, 1069, 1028, 1016, 982, 968 cm^{-1}; FAB-MS *m/z*: 211 (M^++H, 75), 210 (M^+, 38), 154 (100); HRMS calcd for $C_{12}H_{19}O_2S$ (M^++H): 211.1157, found 211.1151.

4.3.3. 3-Mercapto-3-methyl-1-butanol. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.87 (t, J=6.6 Hz, 2H), 1.89 (t, J=6.6 Hz, 2H), 1.81 (s, 1H, SH), 1.43 (s, 6H) (OH proton was not observed); IR ($CHCl_3$): 3730–3160 (br), 3620, 3011, 2968, 2928, 2895, 1458, 1369, 1126, 1070, 1022 cm^{-1}; EI-MS (20 eV) *m/z*: 120 (M^+, 12), 87 (28), 86 (70), 75 (21), 71 (44), 69 (100), 41 (28); HRMS calcd for $C_5H_{12}OS$ (M^+): 120.0609, found 120.0599.

4.4. General procedure for the preparation of 4,4-dimethyl-1,3-oxathianes (1a–d)

To a dichloromethane solution of 3-mercapto-3-methyl-1-butanol was added the α,β-unsaturated aldehydes followed by addition of boron trifluoride etherate at 0°C, and the reaction mixture was stirred at room temperature. The reaction mixture was neutralized with a saturated $NaHCO_3$ solution, and the aqueous layer was extracted with $CHCl_3$, washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography gave the 4,4-dimethyl-1,3-oxathianes (**1a–d**).

4.4.1. *trans*-4,4-Dimethyl-2-styryl-1,3-oxathiane (1a). According to the general procedure, the reaction was carried out using 3-mercapto-3-methyl-1-butanol (1.5 g, 12.5 mmol), *trans*-cinnamaldehyde (2.5 g, 18.7 mmol), boron trifluoride etherate (0.46 mL, 3.7 mmol), and CH_2Cl_2 (15 mL). Reaction time; 40 min. **1a** (2.9 g, 99%). Colorless powder; mp 32.8–33.0°C (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.23 (m, 5H), 6.77 (dd, J=16.0, 1.2 Hz, 1H), 6.23 (dd, J=16.0, 5.7 Hz, 1H), 5.52 (dd, J=5.7, 1.2 Hz, 1H), 4.16 (ddd, A part of AB, J=12.4, 4.4, 2.2 Hz, 1H), 3.88 (dt, B part of AB, J=12.4, 2.2 Hz, 1H), 1.97 (dt, A part of AB, J=12.4, 4.4 Hz, 1H), 1.55 (s, 3H), 1.49 (dt, B part of AB, J=12.4, 2.2 Hz, 1H), 1.32 (s, 3H); IR ($CHCl_3$): 3009, 2968, 2939, 2928, 2901, 2870, 1497, 1460, 1448, 1387, 1367, 1279, 1140, 1103, 1074, 1038, 1007, 986, 964, 691 cm^{-1}; EI-MS (70 eV) *m/z*: 234 (M^+, 100), 201 (4), 165 (12), 147 (27), 133 (38), 131 (59), 115 (36), 104 (54), 102 (37), 91 (13), 87 (36), 70 (79), 69 (71); HRMS calcd for $C_{14}H_{18}OS$ (M^+): 234.1078, found 234.1075; Anal. calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74. Found: C, 71.96; H, 7.71.

4.4.2. *trans*-2-(*p*-Methoxystyryl)-4,4-dimethyl-1,3-oxathiane (1b). According to the general procedure, the reaction was performed using 3-mercapto-3-methyl-1-butanol (1.0 g, 8.3 mmol) *trans*-*p*-methoxycinnamaldehyde (1.3 g, 7.9 mmol), boron trifluoride etherate (0.2 mL, 1.7 mmol), and CH_2Cl_2 (10 mL). Reaction time; 50 min. **1b** (1.7 g, 78%). Colorless powder; mp 41.1–41.8°C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J=8.8 Hz, 2H), 6.83 (d, J=8.8 Hz, 2H), 6.70 (dd, J=15.9, 0.7 Hz, 1H), 6.09 (dd, J=15.9, 5.8 Hz, 1H), 4.15 (ddd, A part of AB, J=12.0, 4.3, 2.4 Hz, 1H), 3.87 (dt, B part of AB, J=12.0, 2.0 Hz, 1H), 3.80 (s, 3H), 1.96 (dt, A part of AB, J=13.4, 4.4 Hz, 1H), 1.54 (s, 3H), 1.48 (dt, B part of AB, J=16.1, 2.4 Hz, 1H), 1.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.5, 131.5, 128.9, 127.9, 123.6, 113.9, 79.3, 65.8, 55.2, 40.9, 39.3, 32.3, 26.8; IR ($CHCl_3$): 3032, 3024, 3011, 2964, 2937, 2901, 2868, 2839, 1607, 1512, 1460, 1248, 1175, 1138, 1036, 966 cm^{-1}; EI-MS (20 eV) *m/z*: 264 (M^+, 60), 231 (5), 162 (25), 161 (24), 147 (22), 134 (100), 131 (19), 121 (12), 70 (14), 69 (14); HRMS calcd for

$C_{15}H_{20}O_2S$ (M^+): 264.1184, found 264.1191. Anal. calcd for $C_{15}H_{20}O_2S$: C, 68.14; H, 7.62. Found: C, 68.27; H, 7.75.

4.4.3. *trans*-2-(*p*-Bromostyryl)-4,4-dimethyl-1,3-oxathiane (1c). According to the general procedure, the reaction was carried out using 3-mercapto-3-methyl-1-butanol (42 mg, 0.35 mmol), *trans*-*p*-bromocinnamaldehyde (73 mg, 0.35 mmol), boron trifluoride etherate (4 μL, 0.04 mmol), and CH_2Cl_2 (4 mL). Reaction time; 20 min. **1c** (61 mg, 56%). Colorless powder; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J=8.3 Hz, 2H), 7.23 (d, J=8.3 Hz, 2H), 6.70 (br d, J=16.0 Hz, 1H), 6.23 (dd, J=16.0, 5.3 Hz, 1H), 5.50 (dd, J=5.3, 1.4 Hz, 1H), 4.16 (ddd, A part of AB, J=12.2, 4.2, 2.0 Hz, 1H), 3.87 (dt, B part of AB, J=12.2, 2.0 Hz, 1H), 1.98 (dt, A part of AB, J=12.2, 4.2 Hz, 1H), 1.55 (s, 3H), 1.49 (dt, B part of AB, J=12.2, 2.0 Hz, 1H), 1.31 (s, 3H); IR ($CHCl_3$): 3013, 2963, 2939, 3870, 1601, 1489, 1462, 1138, 1072, 1011 cm^{-1}; EI-MS (70 eV) *m*/*z*: 314 (M^++2, 16), 312 (M^+, 15), 211 (12), 184 (16), 182 (16), 147 (11), 131 (67), 116 (23), 103 (46), 102 (77), 87 (3), 77 (26), 74 (34), 70 (100), 69 (91), 56 (51), 55 (45); HRMS calcd for $C_{14}H_{17}BrOS$ (M^+): 312.0183, found 312.0181.

4.4.4. *trans*-4,4-Dimethyl-2-(*m*-trifluoromethylstyryl)-1,3-oxathiane (1d). According to the general procedure, the reaction was done using 3-mercapto-3-methyl-1-butanol (60 mg, 0.50 mmol), *trans*-*m*-trifluoromethylcinnamaldehyde (100 mg, 0.50 mmol), boron trifluoride etherate (6 μL, 0.05 mmol), and CH_2Cl_2 (6 mL). Reaction time; 70 min. **1d** (128 mg, 85%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (br s, 1H), 7.54 (d, J=7.7 Hz, 1H), 7.48 (d, J=7.7 Hz, 1H), 7.42 (t, J=7.7 Hz, 1H), 6.80 (dd, J=16.1, 1.3 Hz, 1H), 6.30 (dd, J=16.1, 5.5 Hz, 1H), 5.53 (dd, J=5.5, 1.3 Hz, 1H), 4.17 (ddd, A part of AB, J=12.5, 4.4, 2.4 Hz, 1H), 3.89 (dt, B part of AB, J=12.5, 2.4 Hz, 1H), 1.95 (br dt, A part of AB, J=14.2, 4.4 Hz, 1H), 1.56 (s, 3H), 1.50 (dt, B part of AB, J=14.2, 2.4 Hz, 1H), 1.32 (s, 3H); IR ($CHCl_3$): 2970, 2939, 2901, 2870, 1458, 1443, 1335, 1272, 1254, 1169, 1134, 1072, 964 cm^{-1}; EI-MS (70 eV) *m*/*z*: 302 (M^+, 60), 283 (8), 215 (11), 199 (12), 183 (10), 172 (16), 151 (17), 131 (20), 102 (43), 87 (38), 74 (30), 70 (97), 69(100), 56 (44); HRMS calcd for $C_{15}H_{17}OF_3S$ (M^+): 302.0952, found 302.0949.

4.4.5. *trans*-4,4-Dimethyl-2-(3-phenyl-1-propenyl)-1,3-oxathiane (1e). To an ethereal (10 mL) solution of 3-mercapto-3-methyl-1-butanol (53 mg, 0.44 mmol) was added *trans*-4-phenyl-2-butenal (64 mg, 0.44 mmol) followed by addition of anhydrous lithium perchlorate (47 mg, 0.44 mmol) at room temperature. The reaction mixture was stirred for 3 d. The reaction mixture was then neutralized with a saturated $NaHCO_3$ solution, and the aqueous layer was extracted with AcOEt, washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography gave **1e** (62 mg, 57%). Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.33–7.11 (m, 5H), 6.03 (ddt, J=16.0, 6.6, 1.0 Hz, 1H), 5.56 (ddt, J=16.0, 6.8, 1.5 Hz, 1H), 5.31 (dd, J=6.8, 1.0 Hz, 1H), 4.08 (ddd, A part of AB, J=12.5, 4.2, 2.2 Hz, 1H), 3.79 (dt, B part of AB, J=12.5, 2.2 Hz, 1H), 3.38 (br d, J=6.6 Hz, 2H), 1.90 (br dt, J=12.7, 4.2 Hz, 1H), 1.49 (s, 3H), 1.44 (dt, J=12.7, 2.2 Hz, 1H), 1.39 (s, 3H); IR ($CHCl_3$): 3005, 2966, 2928, 2901, 2870, 1458, 1250, 1138, 1069, 972 cm^{-1}; EI-MS (70 eV) *m*/*z*: 248 (M^+, 21), 157 (13), 146 (100), 129 (25), 117 (23), 115 (23), 102 (28), 91 (22), 87 (25), 74 (20), 69 (65), 56 (26); HRMS calcd for $C_{15}H_{20}OS$ (M^+): 248.1235, found 248.1232.

4.4.6. 4,4-Dimethyl-2-(1-propenyl)-1,3-oxathiane (1f). To an ethereal (20 mL) solution of 3-mercapto-3-methyl-1-butanol (875 mg, 7.28 mmol) was added crotonaldehyde (510 mg, 7.28 mmol) followed by addition of anhydrous lithium perchlorate (774 mg, 7.28 mmol) at 0°C. The reaction mixture was stirred at room temperature for 3 d. The reaction mixture was then neutralized with a saturated $NaHCO_3$ solution, the aqueous layer was extracted with AcOEt, washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography gave **1f** (982 mg, 78%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (dqm, J=15.4, 6.6 Hz, 1H), 5.54 (ddm, J=15.4, 6.3 Hz, 1H), 5.26 (br d, J=6.3 Hz, 1H), 4.07 (ddd, A part of AB, J=12.4, 4.2, 2.4 Hz, 1H), 3.80 (dt, B part of AB, J=12.4, 2.4 Hz, 1H), 1.89 (dtm, A part of AB, J=13.5, 4.2 Hz, 1H), 1.71 (dm, J=6.6 Hz, 1H), 1.49 (s, 3H), 1.42 (br dt, B part of AB, J=13.5, 2.4 Hz, 1H), 1.27 (s, 3H); IR ($CHCl_3$): 3005, 2966, 2939, 2901, 2870, 1674, 1458, 1368, 1254, 1142, 1092, 1069, 1003, 964, 941 cm^{-1}; EI-MS (70 eV) *m*/*z*: 172 (M^+, 28), 157 (6), 130 (15), 102 (100), 87 (54), 74 (41), 70 (82), 69 (86), 58 (80); HRMS calcd for $C_9H_{16}OS$ (M^+): 172.0922, found 172.0919.

4.5. General procedure for the preparation of α-substituted styrene derivatives (2c–2f)

To a THF solution of methyltriphenylphosphonium bromide was added *n*-butyllithium (hexane solution) at 0°C. After the mixture stirred for 5 min, a THF solution of a carbonyl compound (propiophenone, butyrophenone, benzyl phenyl ketone or *p*-bromoacetophenone) was added at 0°C. Hydrochloric acid (1N) was added to the reaction mixture, and the aqueous layer (pH 5) was extracted with AcOEt, washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude residue was purified by silica gel column chromatography (hexane) to give the α-substituted styrene derivatives **2c–2f**.

4.5.1. 2-Phenyl-1-butene (2c). According to the general procedure, the reaction was performed using methyltriphenylphosphonium bromide (13.5 g, 38 mmol), propiophenone (5.0 g, 38 mmol), and *n*-butyllithium (14.9 mL, 2.53 M in hexane, 38 mmol), and THF (50 mL). Reaction time; 14 h. **2c** (3.2 g, 64%). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.23 (m, 5H), 5.27 (s, 1H), 5.06 (dd, J=2.9, 1.5 Hz, 1H), 2.51 (dm, J=7.4 Hz, 2H), 1.10 (t, J=7.4 Hz, 3H); IR ($CHCl_3$): 3082, 3059, 3032, 2970, 2934, 2875, 1628, 1599, 1574, 1495, 1463, 1443, 1375, 1234, 1082, 1028 cm^{-1}; EI-MS (20 eV) *m*/*z*: 132 (M^+, 100), 117 (94), 97 (34), 85 (55), 71 (74), 57 (73); HRMS calcd for $C_{10}H_{12}$ (M^+):132.0939, found 132.0941.

4.5.2. 2-Phenyl-1-pentene (2d). According to the general procedure, the reaction was carried out using methyltriphenylphosphonium bromide (4.8 g, 13.5 mmol), butyrophenone (1.0 g, 6.7 mmol), *n*-butyllithium (8.4 mL, 1.6 M in hexane, 13.5 mmol), and THF (40 mL). Reaction time;

29 h. **2d** (789 mg, 80%). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.38 (m, 2H), 7.37–7.23 (m, 3H), 5.26 (d, J=1.7 Hz, 1H), 5.05 (dd, J=2.9, 1.4 Hz, 1H), 2.46 (br t, J=7.4 Hz, 2H), 1.48 (sextet, J=7.4 Hz, 2H), 0.92 (t, J=7.4 Hz, 3H); IR ($CHCl_3$): 3082, 3059, 3030, 2961, 2934, 2872, 1626, 1495, 1456, 1379, 1028, 901 cm^{-1}; EI-MS (20 eV) *m/z*: 146 (M^+, 28), 131 (47), 118 (100), 71 (12), 57 (11); HRMS calcd for $C_{11}H_{14}$ (M^+):146.1096, found 146.1081.

4.5.3. 2,3-Diphenyl-1-propene (2e). According to the general procedure, the reaction was carried out using methyltriphenylphosphonium bromide (18.2 g, 50.6 mmol), benzyl phenyl ketone (10 g, 50.6 mmol), *n*-butyllithium (20.1 mL, 2.53 M in hexane, 50.6 mmol), and THF (300 mL). Reaction time; 24 h. **2e** (1.4 g, 8%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.43 (m, 2H), 7.32–7.17 (m, 8H), 5.51 (t, J=0.8 Hz, 1H), 5.04–5.02 (m, 1H), 3.85 (br s, 2H); IR ($CHCl_3$): 3086, 3063, 2924, 2855, 1628, 1601, 1493, 1450, 1072, 1030, 903 cm^{-1}; EI-MS (20 eV) *m/z*: 194 (M^+, 39), 179 (49), 145 (31), 129 (33), 116 (100), 103 (42), 91 (21), 58 (18); HRMS calcd for $C_{15}H_{14}$ (M^+):194.1096, found 194.1097.

4.5.4. *p*-Bromo-α-methylstyrene (2f). According to the general procedure, the reaction was effected using methyltriphenylphosphonium bromide (4.3 g, 12.0 mmol), *p*-bromoacetophenone (2 g, 10.0 mmol), *n*-butyllithium (7.5 mL, 1.6 M in hexane, 12.1 mmol), and THF (40 mL). Reaction time; 48 h. **2f** (1.9 g, 94%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J=8.6 Hz, 2H), 7.32 (d, J=8.6 Hz, 2H), 5.37 (br s, 1H), 5.10 (m, 1H), 2.12 (br s, 3H); IR ($CHCl_3$): 3090, 3032, 3009, 2976, 2949, 2922, 1628, 1589, 1558, 1490, 1456, 1392, 1375, 1307, 1296, 1250, 1115, 1072, 1045, 1009, 899, 833, 806 cm^{-1}; EI-MS (70 eV) *m/z*: 198 (M^++2, 99), 196 (M^+, 100), 183 (31), 181 (26), 117 (82), 115 (66), 102 (64), 85 (13), 71 (50), 57 (62); HRMS calcd for C_9H_9Br (M^+):195.9887, found 195.9881.

4.6. General procedure for the tandem [4$^+$+2] cycloaddition–elimination reaction of 4,4-dimethyl-1,3-oxathianes 1 with styrene derivatives. (Table 1)

To a dichloromethane solution of a 4,4-dimethyl-1,3-oxathiane **1** was added the styrene derivative **2** followed by addition of titanium tetrachloride (1.0 M dichloromethane solution) at −78°C. The reaction mixture was quenched with a saturated $NaHCO_3$ solution, the aqueous layer was extracted with $CHCl_3$, washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography gave the 3,4-dihydro-2*H*-thiopyrans **3**.

4.6.1. 2,2,4-Triphenyl-3,4-dihydro-2*H*-thiopyran (3aa). According to the general procedure, the reaction was carried out using *trans*-4,4-dimethyl-2-styryl-1,3-oxathiane (**1a**) (30 mg, 0.13 mmol), 1,1-diphenylethylene (**2a**) (92 mg, 0.51 mmol), titanium tetrachloride (0.14 mL, 1.0 M in a dichloromethane solution, 0.14 mmol), and dichloromethane (4 mL). Reaction time; 15 h. **3aa** (37 mg, 88%). Prisms; mp 132.5–134.0°C (AcOEt); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J=8.1 Hz, 2H), 7.41–7.16 (m, 13H), 6.36 (dd, J=10.0, 2.2 Hz, 1H), 5.75 (dd, J=10.0, 2.0 Hz, 1H), 2.92–2.81 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.1, 144.9, 144.4, 128.6, 128.5, 128.3, 128.1, 127.7, 127.1, 126.9, 126.7, 126.6, 124.8, 121.7, 56.0, 44.1, 39.6; IR ($CHCl_3$): 3060, 2900, 1601, 1491, 1445, 1300, 1013, 934 cm^{-1}; EI-MS (70 eV) *m/z*: 328 (M^+, 33), 295 (40), 217 (21), 198 (41), 180 (100), 165 (68), 147 (85), 115 (25), 103 (13), 91 (53), 77 (17); HRMS calcd for $C_{23}H_{20}S$ (M^+): 328.1286, found 328.1291. Anal. calcd for $C_{23}H_{20}S$: C, 84.10; H, 6.14. Found: C, 83.77; H, 6.00.

4.6.2. 2-Methyl-2,4-diphenyl-3,4-dihydro-2*H*-thiopyran (3ab). According to the general procedure, the reaction was conducted using *trans*-4,4-dimethyl-2-styryl-1,3-oxathiane (**1a**) (30 mg, 0.13 mmol), α-methylstyrene (**2b**) (61 mg, 0.51 mmol), titanium tetrachloride (0.13 mL, 1.0 M in a dichloromethane solution, 0.13 mmol), and dichloromethane (4 mL). Reaction time; 1 h. **3ab** (13 mg, 38%). The resulting diastereomeric mixture was separated by preparative high performance liquid chromatography (Japan Analytical Industry Co.LTD., LC 908 series, silica gel column; JAIGEL SIL-043-15, hexane). *cis*-**3ab**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J=7.2 Hz, 2H), 7.38–7.20 (m, 8H), 6.37 (dd, J=10.2, 2.2 Hz, 1H), 5.86 (dd, J=10.2, 2.2 Hz, 1H), 3.71–3.64 (m, 1H), 2.25 (t, A part of AB, J=13.4 Hz, 1H), 2.15 (dd, B part of AB, J=13.4, 6.3 Hz, 1H), 1.92 (s, 3H); IR ($CHCl_3$): 3065, 2970, 2926, 2862, 1599, 1493, 1452, 1443, 1063, 1028 cm^{-1}; EI-MS (70 eV) *m/z*: 266 (M^+, 29), 233 (31), 147 (100), 136 (22), 115 (33), 91 (38), 77 (21); HRMS calcd for $C_{18}H_{18}S$ (M^+): 226.1129, found 226.1126. Relative configuration was determined by nOe between the methyl signal (1.92 ppm) and the benzylic methine signal (3.71–3.64 ppm). *trans*-**3ab**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J=8.0 Hz, 2H), 7.42–7.12 (m, 8H), 6.29 (dd, J=10.1, 2.2 Hz, 1H), 5.68 (dd, J=10.1, 2.2 Hz, 1H), 2.94 (ddt, J=12.3, 5.0, 2.2 Hz, 1H), 2.51 (dd, A part of AB, J=13.4, 5.0 Hz, 1H), 2.21 (dd, B part of AB, J=13.4, 12.3 Hz, 1H), 1.66 (s, 3H); IR ($CHCl_3$): 3065, 2926, 2868, 1601, 1491, 1452, 1377, 1302, 1065, 1030 cm^{-1}; EI-MS (70 eV) *m/z*: 266 (M^+, 24), 233 (29), 148 (31), 147 (100), 136 (31), 115 (33), 103 (20), 91 (50), 77 (23); HRMS calcd for $C_{18}H_{18}S$ (M^+): 266.1129, found 266.1124. The nOe was not observed between the methyl signal (1.66 ppm) and the benzylic methine signal (2.94 ppm).

4.6.3. 2-Ethyl-2,4-diphenyl-3,4-dihydro-2*H*-thiopyran (3ac). According to the general procedure, the reaction was performed using *trans*-4,4-dimethyl-2-styryl-1,3-oxathiane (**1a**) (30 mg, 0.13 mmol), 2-phenyl-1-butene (**2c**) (67 mg, 0.51 mmol), titanium tetrachloride (0.13 mL, 1.0 M in a dichloromethane solution, 0.13 mmol), and dichloromethane (4 mL). Reaction time; 1 h. **3ac** (13.5 mg, 37%). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J=8.4 Hz, 0.33H, minor diastereomer), 7.45 (d, J=8.4 Hz, 0.67H, major diastereomer), 7.41–7.12 (m, 9H), 6.31 (dd, J=10.1, 2.3 Hz, 1H), 5.83 (dd, J=10.1, 2.2 Hz, 0.67H, major diastereomer), 5.65 (dd, J=10.1, 1.0 Hz, 0.33H, minor diastereomer), 3.73–3.62 (m, 0.67H, major diastereomer), 2.98–2.92 (m, 0.33H, minor diastereomer), 2.63–2.45 (m, 1H), 2.45–1.98 (m, 3H), 0.80 (t, J=7.2 Hz, 2.11H, major diastereomer), 0.79 (t, J=7.5 Hz, 0.99H, minor diastereomer); IR ($CHCl_3$): 3084, 3063, 2970, 2937, 2878,

1601, 1493, 1452, 1379, 1306, 1078, 1032, 1001, 914 cm^{-1}; EI-MS (70 eV) *m/z*: 280 (M^+, 62), 251 (64), 147 (100), 115 (44), 91 (76); HRMS calcd for $C_{19}H_{20}S$ (M^+): 280.1286, found 280.1282.

4.6.4. 2,4-Diphenyl-2-propyl-3,4-dihydro-2*H*-thiopyran (3ad). According to the general procedure, the reaction was carried out using *trans*-4,4-dimethyl-2-styryl-1,3-oxathiane (**1a**) (30 mg, 0.13 mmol), 2-phenyl-1-pentene (**2d**) (74 mg, 0.51 mmol), titanium tetrachloride (0.13 mL, 1.0 M in a dichloromethane solution, 0.13 mmol), and dichloromethane (4 mL). Reaction time; 1 h. **3ad** (16 mg, 42%). The resulting diastereomeric mixture was separated by preparative high performance liquid chromatography (Japan Analytical Industry Co.LTD, LC 908 series, silica gel column; JAIGEL SIL-043-15, hexane). *cis*-**3ad**: colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.46–7.42 (m, 2H), 7.38–7.20 (m, 8H), 6.31 (dd, *J*=10.0, 2.4 Hz, 1H), 5.83 (dd, *J*=10.0, 2.4 Hz, 1H), 3.66 (ddt, *J*=12.0, 5.3, 2.4 Hz, 1H), 2.56 (dd, *J*=13.7, 5.3 Hz, 1H), 2.42–2.18 (m, 3H), 1.40–1.20 (m, 1H), 1.16–0.98 (m, 1H), 0.88 (t, *J*=7.2 Hz, 3H); IR ($CHCl_3$): 3063, 3032, 2961, 2936, 2874, 1601, 1493, 1452, 1309, 1103, 1078, 1032, 862 cm^{-1}; EI-MS (20 eV) *m/z*: 294 (M^+, 81), 261 (56), 251 (100), 217 (20), 164 (48), 148 (54), 147 (76), 134 (32), 131 (31), 118 (37), 91 (88); HRMS calcd for $C_{20}H_{22}S$ (M^+): 294.1442, found 294.1447. *trans*-**3ad**: colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.64–7.58 (m, 2H), 7.43–7.35 (m, 2H), 7.32–7.16 (m, 4H), 7.15–7.09 (m, 2H), 6.28 (dd, *J*=10.1, 1.5 Hz, 1H), 5.65 (dd, *J*=10.1, 1.2 Hz, 1H), 2.95–2.89 (m, 1H), 2.48 (dd, A part of AB, *J*=13.1, 4.8 Hz, 1H), 2.23 (dd, B part of AB, *J*=13.1, 12.4 Hz, 1H), 2.00–1.84 (m, 2H), 1.42–1.22 (m, 1H), 1.09–0.90 (m, 1H), 0.79 (t, *J*=7.3 Hz, 3H); IR ($CHCl_3$): 3063, 3032, 3020, 2961, 2934, 2874, 1601, 1493, 1452, 1445, 1030, 1000, 858 cm^{-1}; EI-MS (70 eV) *m/z*: 294 (M^+, 37), 261 (32), 251 (70), 217 (20), 164 (16), 148 (36), 147 (100), 118 (35), 115 (48), 103 (22), 91 (77), 77 (18); HRMS calcd for $C_{20}H_{22}S$ (M^+): 294.1442, found 294.1445.

4.6.5. 2-Benzyl-2,4-diphenyl-3,4-dihydro-2*H*-thiopyran (3ae). According to the general procedure, the reaction was carried out using *trans*-4,4-dimethyl-2-styryl-1,3-oxathiane (**1a**) (50 mg, 0.21 mmol), 2,3-diphenyl-1-propene (**2e**) (207 mg, 1.67 mmol), titanium tetrachloride (0.21 mL, 1.0 M in a dichloromethane solution, 0.21 mmol), and dichloromethane (4 mL). Reaction time; 26 h. **3ae** (35 mg, 48%). A diastereomer mixture; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57–7.53 (m, 0.48H, minor diastereomer), 7.39–7.06 (m, 12.52H), 6.78–6.73 (m, 2H, major diastereomer), 6.37 (dd, *J*=10.0, 2.3 Hz, 0.76H, major diastereomer), 6.20 (dd, *J*=10.0, 2.3 Hz, 0.24H, minor diastereomer), 5.93 (dd, *J*=10.0, 2.3 Hz, 0.76H, major diastereomer), 5.61 (dd, *J*=10.0, 2.3 Hz, 0.24H, minor diastereomer), 3.95 (ddt, *J*=12.0, 5.5, 2.3 Hz, 0.76H, major diastereomer), 3.65 (d, A part of AB, *J*=14.1 Hz, 0.76H, major diastereomer), 3.56 (d, B part of AB, *J*=14.1 Hz, 0.76H, major diastereomer), 3.31 (d, A part of AB, *J*=13.4 Hz, 0.24H, minor diastereomer), 3.13 (d, B part of AB, *J*=13.4 Hz, 0.24H, minor diastereomer), 3.04 (ddt, *J*=12.2, 4.9, 2.3 Hz, 0.24H, minor diastereomer), 2.77 (dd, A part of AB, *J*=14.0, 4.9 Hz, 0.24H, minor diastereomer), 2.48 (dd, A part of AB, *J*=13.0, 5.5 Hz, 0.76H, major diastereomer), 2.33 (dd, B part of AB, *J*=14.0, 12.2 Hz, 0.24H, minor diastereomer), 2.22 (dd, B part of AB, *J*=13.0, 12.0 Hz, 0.76H, major diastereomer); IR ($CHCl_3$): 3086, 3063, 3036, 2920, 2855, 1601, 1495, 1452, 1306, 1078, 1032, 864 cm^{-1}; EI-MS (20 eV) *m/z*: 342 (M^+, 3), 251 (100), 217 (16), 121 (10), 115 (12), 91 (24); HRMS calcd for $C_{24}H_{22}S$ (M^+): 342.1442, found 342.1432. Relative configuration was determined by nOe between the benzylic methylene proton and the benzylic methine proton of the major *cis* diastereomer [major diastereomer=*cis*, minor diastereomer=*trans*].

4.6.6. 2-(*p*-Bromophenyl)-2-methyl-4-phenyl-3,4-dihydro-2*H*-thiopyran (3af). According to the general procedure, the reaction was conducted using *trans*-4,4-dimethyl-2-styryl-1,3-oxathiane (**1a**) (30 mg, 0.13 mmol), *p*-bromo-α-methylstyrene (**2f**) (126 mg, 0.64 mmol), titanium tetrachloride (0.15 mL, 1.0 M in a dichloromethane solution, 0.15 mmol), and dichloromethane (4 mL). Reaction time; 3 h. **3af** (13 mg, 31%). The resulting diastereomeric mixture was separated by preparative high performance liquid chromatography (Japan Analytical Industry Co.LTD., LC 908 series, silica gel column; JAIGEL SIL-043-15). *cis*-**3af**: colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J*=6.1 Hz, 2H), 7.42 (d, *J*=6.1 Hz, 2H), 7.37–7.21 (m, 5H), 6.35 (dd, *J*=10.2, 2.3 Hz, 1H), 5.86 (dd, *J*=10.2, 2.3 Hz, 1H), 3.65 (ddt, *J*=11.7, 6.0, 2.3 Hz, 1H), 2.22 (br t, A part of AB, *J*=13.4 Hz, 1H), 2.13 (dd, B part of AB, *J*=13.4, 6.0 Hz, 1H), 1.88 (s, 3H); IR ($CHCl_3$): 3100, 3070, 2928, 2862, 1601, 1562, 1474, 1454, 1416, 1296, 1080, 995, 910, 868 cm^{-1}; EI-MS (20 eV) *m/z*: 346 (M^++2, 23), 344 (M^+, 22), 313 (21), 311 (21), 232 (12), 216 (17), 214 (16), 199 (40), 197 (39), 188 (45), 147 (100), 130 (40), 91 (14); HRMS calcd for $C_{18}H_{17}BrS$ (M^+): 344.0234, found 344.0230. *trans*-**3af**: colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (br s, 4H), 7.32–7.17 (m, 3H), 7.13 (d, *J*=8.5 Hz, 2H), 6.28 (dd, *J*=10.0, 2.4 Hz, 1H), 5.68 (dd, *J*=10.0, 2.4 Hz, 1H), 2.90 (ddt, *J*=10.0, 5.1, 2.4 Hz, 1H), 2.46 (dd, A part of AB, *J*=13.6, 5.1 Hz, 1H), 2.20 (dd, B part of AB, *J*=13.6, 10.0 Hz, 1H), 1.63 (s, 3H); IR ($CHCl_3$): 3090, 3070, 3040, 2920, 2840, 1601, 1562, 1493, 1470, 1300, 1103, 995, 860 cm^{-1}; EI-MS (70 eV) *m/z*: 346 (M^++2, 14), 344 (M^+, 14), 313 (12), 311 (13), 232 (10), 217 (11), 148 (35), 147 (100), 130 (38), 115 (37), 91 (21), 77 (10); HRMS calcd for $C_{18}H_{17}BrS$ (M^+): 344.0234, found 344.0230.

4.6.7. 4-(*p*-Methoxyphenyl)-2,2-diphenyl-3,4-dihydro-2*H*-thiopyran (3ba). According to the general procedure, the reaction was performed using *trans*-2-(*p*-methoxystyryl)-4,4-dimethyl-1,3-oxathiane (**1b**) (30 mg, 0.11 mmol), 1,1-diphenylethylene (**2a**) (81 mg, 0.45 mmol), titanium tetrachloride (0.14 mL, 1.0 M in a dichloromethane solution, 0.14 mmol), and dichloromethane (4 mL). The reaction was conducted at −30°C for 3 d and afforded **3ba** (31 mg, 76%). Colorless powder; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J*=7.4 Hz, 2H), 7.36 (t, *J*=7.9 Hz, 2H), 7.30–7.16 (m, 6H), 7.07 (d, *J*=8.6 Hz, 2H), 6.84 (d, *J*=8.6 Hz, 2H), 6.33 (dd, *J*=10.0, 2.0 Hz, 1H), 5.72 (dd, *J*=10.0, 1.3 Hz, 1H), 3.79 (s, 3H), 2.89–2.75 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.3, 146.2, 144.4, 137.0, 128.6, 128.4, 128.2, 128.0, 127.1, 126.8, 126.7, 125.2, 121.4, 113.9, 56.0, 55.2, 44.2, 38.8; IR ($CHCl_3$): 3063, 3020, 2970,

2950, 2914, 2837, 1609, 1510, 1491, 1443, 1302, 1250, 1177, 1036, 833 cm^{-1}; EI-MS (20 eV) *m/z*: 358 (M^+, 33), 325 (44), 280 (11), 254 (18), 180 (50), 178 (72), 168 (54), 160 (84), 147 (100), 121 (17), 91 (18); HRMS calcd for $C_{24}H_{22}OS$ (M^+): 358.1391, found 358.1403. Anal. calcd for $C_{24}H_{22}OS$: C, 80.41; H, 6.19. Found: C, 79.98; H, 6.16.

4.6.8. 4-(*p*-Methoxyphenyl)-2-methyl-2-phenyl-3,4-dihydro-2*H*-thiopyran (3bb). According to the general procedure, the reaction was carried out using *trans*-2-(*p*-methoxystyryl)-4,4-dimethyl-1,3-oxathiane (**1b**) (30 mg, 0.11 mmol), α-methylstyrene (**2b**) (53 mg, 0.45 mmol), titanium tetrachloride (0.14 mL, 1.0 M in a dichloromethane solution, 0.14 mmol), dichloromethane (4 mL). Reaction time; 3 d. **3bb** (26 mg, 77%). A diastereomeric mixture; colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J=7.1 Hz, 0.18H, minor diastereomer), 7.54 (d, J=7.7 Hz, 1.82H, major diastereomer), 7.42–7.17 (m, 3H), 7.21 (d, J=8.6 Hz, 1.82H), 6.86 (d, J=8.6 Hz, 1.82H, major diastereomer), 6.82 (d, J=8.6 Hz, 0.18H, minor diastereomer), 6.34 (dd, J=10.2, 2.4 Hz, 0.91H, major diastereomer), 6.27 (dd, J=10.2, 2.5 Hz, 0.09H, minor diastereomer), 5.83 (dd, J=10.2, 1.5 Hz, 0.91H, major diastereomer), 5.65 (dd, J=10.0, 1.5 Hz, 0.09H, minor diastereomer), 3.79 (s, 2.73H, major diastereomer), 3.77 (s, 0.27H, minor diastereomer), 3.67–3.58 (m, 0.91H, major diastereomer), 2.92–2.86 (m, 0.09H, minor diastereomer), 2.49 (dd, J=13.5, 4.9 Hz, 0.09H, minor diastereomer), 2.30–2.13 (m, 1.91H), 1.90 (s, 2.73H, major diastereomer), 1.64 (s, 0.27H, minor diastereomer); IR ($CHCl_3$): 3061, 2961, 2936, 2912, 2866, 2837, 1610, 1601, 1512, 1464, 1445, 1302, 1259, 1240, 1177, 1036, 908, 831 cm^{-1}; EI-MS (20 eV) *m/z*: 296 (M^+, 52), 263 (90), 191 (44), 190 (100), 178 (23), 177 (40), 160 (51), 147 (71), 121 (17), 106 (59), 91 (18); HRMS calcd for $C_{19}H_{20}OS$ (M^+): 296.1235, found 296.1231.

4.6.9. 4-(*p*-Methoxyphenyl)-2-phenyl-2-propyl-3,4-dihydro-2*H*-thiopyran (3bd). According to the general procedure, the reaction was done using *trans*-2-(*p*-methoxystyryl)-4,4-dimethyl-1,3-oxathiane (**1b**) (30 mg, 0.11 mmol), 2-phenyl-1-pentene (**2d**) (83 mg, 0.45 mmol), titanium tetrachloride (0.14 mL, 1.0 M in a dichloromethane solution, 0.14 mmol), and dichloromethane (4 mL). Reaction time; 4 d. **3bd** (22 mg, 65%). A diastereomeric mixture: colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J=7.1 Hz, 0.9H, minor diastereomer), 7.44 (d, J=7.7 Hz, 1.1H, major diastereomer), 7.41–7.17 (m, 3H), 7.19 (d, J=8.6 Hz, 1.1H, major diastereomer), 7.04 (d, 8.6 Hz, 0.9H, minor diastereomer), 6.87 (d, J=8.6 Hz, 1.1H, major diastereomer), 6.81 (d, J=8.6 Hz, 0.9H, minor diastereomer), 6.39–6.23 (m, 1H), 5.79 (dd, J=10.0, 2.0 Hz, 0.55H, major diastereomer), 5.62 (dd, J=10.0, 1.3 Hz, 0.45H), 3.80 (s, 1.65H, major diastereomer), 3.78 (s, 1.35H, minor diastereomer), 3.67–3.58 (m, 0.55H, major diastereomer), 2.92–2.84 (m, 0.45H, minor diastereomer), 2.54 (dd, A part of AB, J=13.5, 5.3 Hz, 0.55H, major diastereomer), 2.47 (dd, A part of AB, J=13.0, 4.2 Hz, 0.45H, minor diastereomer), 2.40–2.16 (m, 2H), 2.02–1.84 (m, 1H), 1.40–1.21 (m, 1H), 1.13–0.92 (m, 1H), 0.89 (t, J=7.2 Hz, 1.65H, major diastereomer), 0.79 (t, J=7.4 Hz, 1.35H, minor diastereomer); IR ($CHCl_3$): 3063, 3028, 2959, 2936, 2874, 2839, 1611, 1512, 1466, 1443, 1300, 1250, 1034, 910, 833 cm^{-1}; EI-MS (70 eV) *m/z*: 324 (M^+, 35), 291 (45), 281 (42), 248 (24), 190 (31), 177 (69), 160 (43), 147 (100), 134 (74), 121 (71), 91 (80), 77 (19); HRMS calcd for $C_{21}H_{24}OS$ (M^+): 324.1548, found 324.1550.

4.6.10. 4-(*p*-Bromophenyl)-2,2-diphenyl-3,4-dihydro-2*H*-thiopyran (3ca). According to the general procedure, the reaction was performed using *trans*-2-(*p*-bromostyryl)-4,4-dimethyl-1,3-oxathiane (**1c**) (53 mg, 0.17 mmol), 1,1-diphenylethylene (**2a**) (122 mg, 0.68 mmol), titanium tetrachloride (0.17 mL, 1.0 M in a dichloromethane solution, 0.17 mmol), and dichloromethane (4 mL). Reaction time; 1 d. **3ca** (16 mg, 24%). **3ca**: Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J=8.6 Hz, 2H), 7.41 (d, J=8.6 Hz, 1H), 7.36 (t, J=7.8 Hz, 2H), 7.31–7.16 (m, 6H), 7.03 (d, J=8.6 Hz, 2H), 6.37 (dd, J=10.1, 2.2 Hz, 1H), 5.68 (dd, J=10.1, 2.2 Hz, 1H), 2.92–2.84 (m, 1H), 2.81–2.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 145.9, 144.2, 143.9, 131.6, 129.5, 128.5, 128.4, 128.0, 127.2, 126.8, 124.0, 122.3, 120.3, 55.9, 44.0, 39.2; IR ($CHCl_3$): 3063, 2930, 2910, 1605, 1489, 1443, 1404, 1296, 1072, 1011, 934, 826 cm^{-1}; EI-MS (70 eV) *m/z*: 408 (M^++2, 8), 406 (M^+, 7), 375 (12), 373 (12), 294 (6), 227 (7), 225 (7), 198 (25), 180 (100), 165 (53), 147 (34), 115 (8), 91 (12), 77 (10); HRMS calcd for $C_{23}H_{19}BrS$ (M^+): 406.0390, found 406.0393.

4.6.11. 2,2-Diphenyl-4-(*m*-trifluoromethylphenyl)-3,4-dihydro-2*H*-thiopyran (3da). According to the general procedure, the reaction was conducted using *trans*-4,4-dimethyl-2-(*m*-trifluoromethylstyryl)-1,3-oxathiane (**1d**) (50 mg, 0.17 mmol), 1,1-diphenylethylene (**2a**) (119 mg, 0.66 mmol), titanium tetrachloride (0.17 mL, 1.0 M in a dichloromethane solution, 0.17 mmol), and dichloromethane (4 mL). Reaction time; 1.5 h. **3da** (22 mg, 34%). **3da**: Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55–7.46 (m, 3H), 7.44–7.18 (m, 11H), 6.43 (dd, J=10.1, 2.4 Hz, 1H), 5.73 (dd, J=10.1, 2.4 Hz, 1H), 3.03–2.94 (m, 1H), 2.88–2.79 (m, 2H); IR ($CHCl_3$): 3060, 2950, 2920, 1601, 1493, 1447, 1331, 1169, 1130, 1072, 907 cm^{-1}; EI-MS (70 eV) *m/z*: 396 (M^+, 13), 363 (22), 215 (10), 198 (23), 180 (100), 179 (37), 165 (58), 91 (25); HRMS calcd for $C_{24}H_{19}F_3S$ (M^+): 396.1159, found 396.1163.

4.6.12. 4-Benzyl-2,2-diphenyl-3,4-dihydro-2*H*-thiopyran (3ea). According to the general procedure, the reaction was done using *trans*-4,4-dimethyl-2-(3-phenylpropenyl)-1,3-oxathiane (**1e**) (43 mg, 0.17 mmol), 1,1-diphenylethylene (**2a**) (124 mg, 0.69 mmol), titanium tetrachloride (0.17 mL, 1.0 M in a dichloromethane solution, 0.17 mmol), and dichloromethane (4 mL). Reaction time; 1 h. **3ea** (32 mg, 54%). Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.35 (m, 2H), 7.30–7.14 (m, 11H), 7.08–7.04 (m, 2H), 6.18 (dd, J=10.2, 2.3 Hz, 1H), 5.58 (dd, J=10.2, 1.5 Hz, 1H), 2.69 (d, J=8.7 Hz, 2H), 2.61 (dd, A part of AB, J=12.5, 4.3 Hz, 1H), 2.49 (t, B part of AB, J=12.5 Hz, 1H), 2.08–1.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 144.4, 139.5, 129.0, 128.4, 128.3, 128.1, 128.0, 127.0, 126.9, 126.6, 126.1, 125.1, 120.8, 55.8, 41.7, 40.8, 34.0; IR ($CHCl_3$): 3086, 3063, 3028, 2013, 2924, 2855, 1601, 1493, 1443, 1312, 1088, 1018, 910 cm^{-1}; EI-MS (70 eV) *m/z*: 342 (M^+, 9), 251 (100), 217 (61), 202 (14), 191 (13), 180 (18), 179 (19), 178 (17), 165 (33), 129 (12), 123 (13), 115 (15), 91

(40), 77 (9); HRMS calcd for $C_{24}H_{22}S$ (M^+): 342.1442, found 342.1446.

4.6.13. 4-Methyl-2,2-diphenyl-3,4-dihydro-2*H*-thiopyran (3fa). According to the general procedure, the reaction was performed using *trans*-4,4-dimethyl-2-(1-propenyl)-1,3-oxathiane (**1f**) (36 mg, 0.21 mmol), 1,1-diphenylethylene (**2a**) (150 mg, 0.83 mmol), titanium tetrachloride (0.21 mL, 1.0 M in a dichloromethane solution, 0.21 mmol), and dichloromethane (4 mL). Reaction time; 0.5 h. **3fa** (20 mg, 37%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.41 (m, 2H), 7.32–7.18 (m, 8H), 6.15 (dd, J=10.1, 2.4 Hz, 1H), 5.54 (dd, J=10.1, 2.2 Hz, 1H), 2.60 (dd, A part of AB, J=12.8, 4.9 Hz, 1H), 2.47 (dd, B part of AB, J=12.8, 11.6 Hz, 1H), 1.80–1.70 (m, 1H), 1.06 (d, J=7.2 Hz, 3H); IR ($CHCl_3$): 3063, 2963, 2932, 2870, 1601, 1493, 1443, 1308, 1034 cm^{-1}; EI-MS (70 eV) *m/z*: 266 (M^+, 67), 233 (74), 219 (17), 198 (16), 180 (100), 179 (53), 178 (37), 165 (76), 91 (53), 77 (13); HRMS calcd for $C_{18}H_{18}S$ (M^+): 266.1129, found 266.1116.

4.6.14. (1*R*,3*R*,6*R*,9*R*)-*trans*-5,5,9-Trimethyl-3-styryl-2-oxa-4-thiabicyclo[4.4.0]decane (4). To a dichloromethane (8 mL) solution of (−)-(1*R*,2*R*,5*R*)-2-(1-mercapto-1-methylethyl)-5-methylcyclohexanol[12] (250 mg, 1.33 mmol) was added cinnamaldehyde (147 mg, 1.11 mmol), followed by addition of boron trifluoride etherate (27 μL, 0.22 mmol) at 0°C. The reaction mixture was stirred at room temperature for 40 min. The reaction mixture was neutralized with saturated $NaHCO_3$ solution, and the aqueous layer was extracted with $CHCl_3$, washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography gave **4** (380 mg, 94%). Colorless solid; mp 84–85°C (hexane); $[\alpha]_D^{19}$=+59.8 (1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.20 (m, 5H), 6.75 (br d, J=16.2 Hz, 1H), 6.23 (dd, J=16.2, 5.8 Hz, 1H), 5.60 (dd, J=5.8, 1.2 Hz, 1H), 3.51 (dt, J=10.4, 4.2 Hz, 1H), 2.03 (br d, J=12.4 Hz, 1H), 1.91–1.84 (m, 1H), 1.76–1.69 (m, 1H), 1.60–1.45 (m, 2H), 1.48 (s, 3H), 1.35–1.15 (m, 2H), 1.28 (s, 3H), 1.02–0.85 (m, 1H), 0.94 (d, J=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.3, 131.7, 128.5, 127.8, 126.7, 126.0, 78.4, 77.1, 50.4, 43.7, 41.8, 34.7, 31.5, 29.4, 24.4, 22.9, 22.1; IR ($CHCl_3$): 3084, 3063, 3030, 2964, 2928, 2872, 1497, 1458, 1387, 1373, 1151, 1123, 1051, 964, 692 cm^{-1}; EI-MS (20 eV) *m/z*: 302 (M^+, 89), 155 (19), 138 (100), 137 (36), 123 (20), 95 (48), 81 (66); HRMS calcd for $C_{19}H_{26}OS$ (M^+): 302.1704, found 302.1707. Anal. calcd for $C_{19}H_{26}OS$: C, 75.40; H, 8.66. Found: C, 75.22; H, 8.65.

4.7. General procedure for the tandem [4$^+$+2] cycloaddition–elimination reaction of chiral oxathiane 4 with olefins 2 (Table 2)

To a dichloromethane solution of (1*R*,3*R*,6*R*,9*R*)-*trans*-5,5,9-trimethyl-3-styryl-2-oxa-4-thiabicyclo[4.4.0]decane (**4**) was added the olefin **2** followed by addition of a Lewis acid (1.0 M solution) at −78°C. The reaction mixture was quenched with a saturated $NaHCO_3$ solution, and the aqueous layer was extracted with $CHCl_3$, washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography gave the optically active 3,4-dihydro-2*H*-thiopyran **3** and γ-vinylated alcohol.

Dichloropyrocatecholatetitanium as a Lewis acid was prepared by the following method: To an ethereal solution (2 mL) of catechol (18 mg, 0.17 mmol) was added *n*-butyllithium (0.11 mL, 3.0 M in hexane, 0.33 mmol) at −78°C, followed by addition of titanium tetrachloride (18 μL, 0.17 mmol), and the mixture was warmed to room temperature. After concentration of the reaction solution in vacuo, dichloromethane (1 mL) was added to the resulting reddish-brown solid. The supernatant solution was added by syringe to the above reaction flask at −78°C.

4.7.1. (*S*)-2,2,4-Triphenyl-3,4-dihydro-2*H*-thiopyran (3aa). According to the general procedure, the reaction was done using (1*R*,3*R*,6*R*,9*R*)-*trans*-5,5,9-trimethyl-3-styryl-2-oxa-4-thiabicyclo[4.4.0]decane (**4**) (50 mg, 0.16 mmol), 1,1-diphenylethylene (**2a**) (119 mg, 0.66 mmol), titanium tetrachloride (0.16 mL, 1.0 M in a dichloromethane solution, 0.16 mmol), and dichloromethane (4 mL). The reaction mixture was warmed to −40°C, and stirred for 17 h to afford (*S*)-2,2,4-triphenyl-3,4-dihydro-2*H*-thiopyran (**3aa**) (45 mg, 82%). 51% ee; CHIRALCEL OJ, hexane/^{i}PrOH=99/1, flow rate=1.0 mL/min, UV=254 nm, 25°C, [major (*S*)-enantiomer; 12 min, minor (*R*)-enantiomer; 35 min].

4.8. Determination of the absolute configuration of (−)-3aa by X-ray crystallographic analysis

An enantiomeric mixture (**3aa**, 51% ee) was separated using liquid chromatography (CHIRALCEL OJ, hexane/^{i}PrOH=99/1); major enantiomer (+)-**3aa**: $[\alpha]_D^{25}$=+70.1 (0.13, $CHCl_3$), minor enantiomer (−)-**3aa**: $[\alpha]_D^{23}$=−71.6 (0.17, $CHCl_3$). Optically pure (−)-**3aa** (minor enantiomer) was obtained as prisms by recrystallization from ethyl acetate at ambient temperature. The absolute configuration of the minor enantiomer (−)-**3aa** was determined as *R* by X-ray crystallographic analysis (Fig. 1). The Flack parameter converged to 0.04381, a reliable figure for the determining the absolute configuration. Therefore, the absolute configuration of the major enantiomer of (+)-**3aa** was revealed to be *S*.

Crystal data for (*R*)-2,2,4-triphenyl-3,4-dihydro-2*H*-thiopyran [(−)-**3aa**]: $C_{23}H_{20}S$, M=328.47, orthorhombic, space group $P2_12_12_1$ (#19), a=10.657(2), b=16.064(2), c=10.471(1) Å, V=1792.5(3) Å^3, Z=4, D_c=1.217 g/cm^3, μ=15.73 cm^{-1}, T=296 K, 1905 measured reflections, 1876 unique reflections, 1876 reflections with $I>2.0\sigma(I)$ used in refinement, direct methods and Fourier techniques, R=0.116, R_w=0.202. The data were collected using a Rigaku AFC7R diffractometer with graphite-monochromated Cu Kα radiation (λ=1.54178 Å) by the ω–2θ scan technique in the range $50.57<2\theta<58.50°$. Flack parameter=0.04381. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the reference number CCDC 201692. Copies of the data can be obtained free of charge, on application to

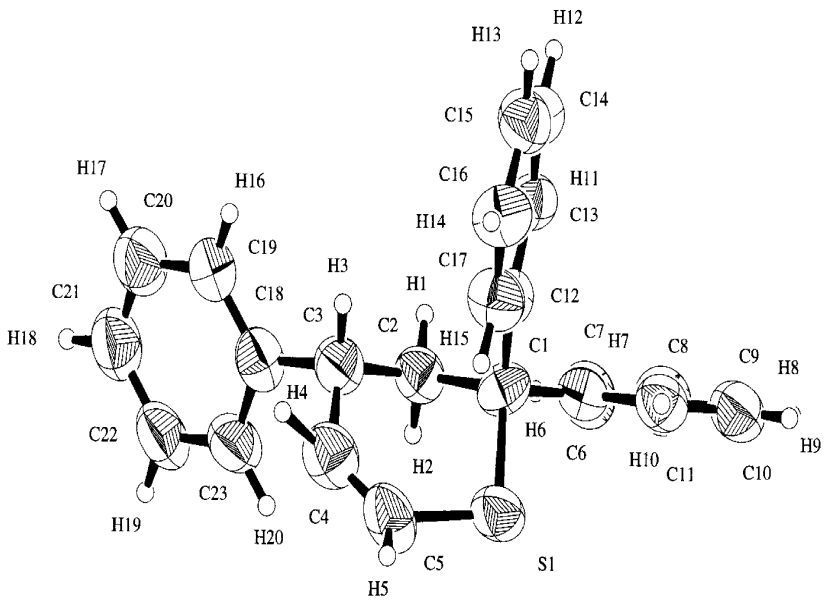


Figure 1. Minor enantiomer of (−)-**3aa**.

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4.8.1. 2-Methyl-2,4-diphenyl-3,4-dihydro-2*H*-thiopyran (3ab). According to the general procedure, the reaction was carried out using (1*R*,3*R*,6*R*,9*R*)-*trans*-5,5,9-trimethyl-3-styryl-2-oxa-4-thiabicyclo[4.4.0]decane (**4**) (150 mg, 0.49 mmol), α-methylstyrene (**2b**) (234 mg, 1.98 mmol), titanium tetrachloride (0.49 mL, 1.0 M in a dichloromethane solution, 0.49 mmol), and dichloromethane (6 mL). The reaction was conducted at −78°C for 1 h and afforded **3ab** (28 mg, 21%). The resulting diastereomeric mixture was separated by preparative high performance liquid chromatography (Japan Analytical Industry Co.LTD, LC 908 series, silica gel column; JAIGEL SIL-043-15, hexane). *cis*-**3ab**: colorless oil; CHIRALCEL OD, hexane/^{i}PrOH=99/1, flow rate=1.0 mL/min., UV=254 nm, 25°C, (minor enentiomer; 24 min, major enantiomer; 29 min), 28% ee. *trans*-**3ab**: colorless oil; CHIRALCEL OJ, hexane/^{i}PrOH=9/1, flow rate=1.0 mL/min., UV=254 nm, 25°C, (25 min, 27 min), 0% ee.

4.8.2. *trans*-5-Styryl-4-thia-7-octen-1-ol (6). The reaction was effected according to the general procedure of Table 1 using 1,3-oxathiane **5** (100 mg, 0.48 mmol), allyltrimethylsilane (**2g**) (221 mg, 1.94 mmol), titanium tetrachloride (0.48 mL, 1.0 M in a dichloromethane solution, 0.48 mmol), and dichloromethane (8 mL). The reaction was conducted at −78°C for 5 min afforded *trans*-5-styryl-4-thia-7-octen-1-ol (**6**) (30 mg, 25%) Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.20 (m, 5H), 6.38 (d, *J*=15.7 Hz, 1H), 6.02 (dd, *J*=15.7, 9.5 Hz, 1H), 5.84 (ddt, *J*=17.1, 10.1, 17.0 Hz. 1H), 5.12 (dm, *J*=17.1 Hz, 1H), 5.07 (dm, *J*=10.1 Hz, 1H), 3.73 (t, *J*=6.1 Hz, 2H), 3.44 (dt, *J*=9.5, 7.8 Hz, 1H), 2.67–2.50 (m, 2H), 2.45 (br t, *J*=7.0 Hz, 2H), 1.87–1.78 (m, 2H), 1.60 (br s, 1H, OH); IR ($CHCl_3$): 3690–3130 (br), 3626, 3082, 3065, 2930, 2883, 1639, 1599, 1493, 1448, 1437, 1250, 1069, 1043, 1003, 964, 922 cm^{-1}; EI-MS (20 eV) *m/z*: 248 (M^+, 5), 207 (33), 189 (10), 156 (73), 141 (36), 129 (43), 115 (100), 91 (35), 78 (11); HRMS calcd for $C_{15}H_{20}OS$ (M^+): 248.1235, found 248.1224. We should correct the structure of the allylated alcohol described in the preliminary communication.[8] The estimated chemical shifts of each methine proton of the γ-allylated and the α-allylated alcohol were very close. In addition, the spin system of the methine protons is the same. The NOESY experiment revealed that the product **6** was not the γ-allylated but rather the α-allylated alcohol **6**. The correlations were observed between two olefinic protons and the *o*- and *m*-protons on the phenyl ring, and no correlation was observed between the methine proton adjacent to the sulfur atom and the *o*- and *m*-protons on the phenyl ring.

4.8.3. (5*E*)-3,3-Dimethyl-7-phenyl-4-thia-5,9-decadien-1-ol (7) and 4-Phenyl-2-trimethylsilylmethyl-3,4-dihydro-2*H*-thiopyran (3ag). The reaction was carried out according to the general procedure of Table 1 using 4,4-dimethyl-1,3-oxathiane **1a** (150 mg, 0.64 mmol), allyltrimethylsilane (**2g**) (293 mg, 2.56 mmol) and titanium tetrachloride (0.64 mL, 1.0 M in a dichloromethane solution, 0.64 mmol in dichloromethane (20 mL). The reaction was conducted at −78°C for 40 min and afforded (5*E*)-3,3-dimethyl-7-phenyl-4-thia-5,9-decadien-1-ol (**7**) (66 mg, 37%) and 4-phenyl-2-trimethylsilylmethyl-3,4-dihydro-2*H*-thiopyran (**3ag**) (54 mg, 32%).

(5*E*)-3,3-Dimethyl-7-phenyl-4-thia-5,9-decadien-1-ol (**7**): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.17 (m, 5H), 6.12–6.03 (m, 2H), 5.71 (ddt, *J*=17.1, 10.2, 7.3 Hz, 1H), 5.03 (dm, *J*=17.1 Hz, 1H), 5.00 (dm, *J*=10.2 Hz, 1H), 3.80 (t, *J*=6.6 Hz, 2H), 3.45 (q, *J*=7.3 Hz, 1H), 2.50 (tt, *J*=7.3, 1.3 Hz, 2H), 1.96–1.87 (br s, 1H, OH), 1.81 (t, *J*=6.6 Hz, 2H), 1.30 (s, 6H); IR ($CHCl_3$): 3690–3120 (br), 3630, 3078, 2970, 2928, 2870, 1639, 1601, 1493, 1454, 1385, 1369, 1254, 1138, 1069, 1003, 968, 918, 833 cm^{-1}; EI-MS (20 eV) *m/z*: 276 (M^+, 1), 235 (51), 217 (3), 149(100), 115 (61), 69 (29); HRMS calcd for $C_{17}H_{24}OS$ (M^+): 276.1548, found 276.1547.

The resulting diastereomeric mixture of **3ag** was separated

by preparative high performance liquid chromatography (Japan Analytical Industry Co.LTD., LC 908 series, silica gel column; JAIGEL SIL-043-15, hexane). *cis*-**3ag**: colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.19 (m, 5H), 6.19 (dd, J=10.0, 2.0 Hz, 1H), 5.70 (dd, J=10.0, 2.0 Hz, 1H), 3.59 (ddt, J=11.8, 5.1, 2.0 Hz, 1H), 3.46 (ddt, J=11.8, 7.4, 2.2 Hz, 1H), 2.22 (ddd, A part of AB, J=13.4, 5.1, 2.2 Hz, 1H), 1.83 (dt, B part of AB, J=13.4, 11.8 Hz, 1H), 0.91 (d, J=7.5 Hz, 2H), 0.08 (s, 9H); IR ($CHCl_3$): 3063, 2955, 2905, 2866, 1601, 1493, 1450, 1250, 891, 845 cm^{-1}; FAB-MS *m/z*: 262 (M^+, 47), 154 (100); HRMS calcd for $C_{15}H_{22}SiS$ (M^+): 262.1212, found 262.1219. *trans*-**3ag**: colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.26 (m, 5H), 6.42 (dd, J=10.0, 0.6 Hz, 1H), 5.92 (dd, J=10.0, 5.0 Hz, 1H), 3.77–3.67 (m, 1H), 3.22–3.13 (m, 1H), 2.22–2.04 (m, 2H), 1.02 (dd, A part of AB, J=14.5, 6.6 Hz, 1H), 0.99 (dd, B part of AB, J=14.5, 8.3 Hz, 1H), 0.01 (s, 9H); IR ($CHCl_3$): 3063, 2955, 2909, 2862, 1601, 1493, 1454, 976, 891 cm^{-1}; FAB-MS *m/z*: 262 (M^+, 26), 261 (M^+-H, 21), 73 (100); HRMS calcd for $C_{15}H_{22}SiS$ (M^+): 262.1212, found 262.1206.

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