1,3-OXATHIANE RING FORMATION THROUGH INTRAMOLECULAR PUMMERER REACTION OF ALKYL *ortho*-HYDROXYMETHYLPHENYL SULFOXIDES

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Abstract- The intramolecular Pummerer rearrangement of 2-(2-alkylsulfinylphenyl)-2-propanols (**1a**, **1c**-**1g**) yielded 1,3-oxathianes (**2a**, **2c**-**2g**) in the presence of *p*-toluenesulfonic acid and molecular sieves 3A. Alkyl halides were converted into 1,3-oxathiane derivatives in three steps *via* this rearrangement.

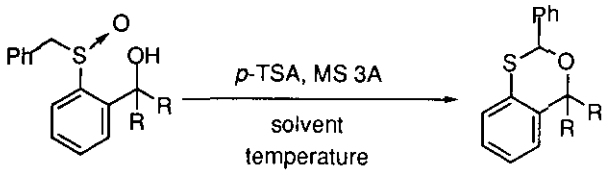
1,3-Oxathiane is a very important functional group as a masked carbonyl.[1] Recently, many useful methods for the cleavage of 1,3-oxathianes or 1,3-oxathiolanes to generate the parent carbonyl compounds have been developed.[2] Therefore, *O,S*-acetal as well as *O,O*- and *S,S*-acetals, can be expected to be widely utilized as a protecting group for carbonyl function[3] since the deprotective methods have been established. However, quite limited methods are known for the preparation of *O,S*-acetal compounds, except for the *O,S*-acetalization of carbonyl compounds.[4]

Recently, we found that γ,δ-unsaturated sulfoxides could be transformed into 1,3-oxathianes through the intramolecular Pummerer rearrangement.[5, 6] As an extension of this work, we planned to examine the Pummerer reaction of γ-hydroxy sulfoxides to form 1,3-oxathianes.

In 1997, Furukawa *et al*. reported the one-step conversion of benzyl *ortho*-hydroxymethylphenyl sulfoxide into benzaldehyde *via* the intramolecular Pummerer rearrangement.[7] Although their results are very intriguing, the utility of this reaction, in which the benzyl or naphtylmethyl group is essential in the original sulfoxides, has some limitations. In this paper, we describe the effective intramolecular Pummerer reaction of several types of alkyl *ortho*-hydroxymethylphenyl sulfoxides to obtain 1,3-oxathiane derivatives, and a short step transformation of alkyl halides into 1,3-oxathianes.[8]

In order to avoid hydrolysis of 1,3-oxathiane under the given reaction conditions, molecular sieves (MS) 3A was employed as the water trapping agent. Initially, we examined two sulfoxides (**1a**) and (**1b**) using *p*-toluenesulfonic acid (*p*-TSA) and MS 3A. As can be seen in Table 1, the reaction of **1a** with this reagent system in refluxing benzene gave 1,3-oxathiane (**2a**) in high yield (Entry 1). Even when this reaction was carried out at room temperature, **2a** was obtained in high yield (Entries 2 and 3), whereas the reaction of **1b** at room temperature afforded **2b** in low to moderate yields (Entries 4 and 5).

Table 1.



1a: R = Me
1b: R = H

2a: R = Me
2b: R = H

Entry	Sulfoxide	Solvent	Temp.	Time	Yield (%)[a]
1	**1a**	benzene	reflux	3 min	81
2	**1a**	CH_2Cl_2	rt	5 h	84 (10)[b]
3	**1a**	toluene	rt	1 h	91
4	**1b**	CH_2Cl_2	rt	5 h	18 (74)[b]
5	**1b**	toluene	rt	5 h	49 (45)[b]

a) Isolated yield. *b*) Values in parenthesis are yields of starting sulfoxide recovered.

The successful results shown in Table 1 encouraged us to attempt the transformation of alkyl halides to 1,3-oxathianes. The sequential steps are shown in the Scheme.

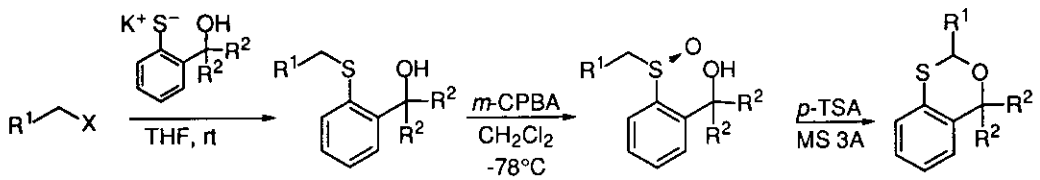
Sulfides (**5a** - **5g**) were obtained by the *S*-alkylation of thiolate (**3**) or (**4**) which is prepared from the corresponding thiol and *t*-BuOK. The nitromethylthio derivative (**5h**), however, was not obtained from bromonitromethane, but dithiosulfide (**6**) was generated.[9] Each sulfide was oxidized with *m*-chloroperbenzoic acid (*m*-CPBA) to give the corresponding sulfoxides (**1a** - **1g**). The low yield of **5f** was caused by the generation of some by-products which were detected by TLC but not isolated.

Next, the intramolecular Pummerer reactions were examined using the *p*-TSA - MS 3A system. The reaction of **1a**, **1b**, **1d** and **1g** proceeded at below room temperature to produce the 1,3-oxathiane (**2a**, **2b**, **2d** and **2g**), respectively. On the other hand, heating was necessary for sulfoxides (**1c**) and (**1f**) to complete the reaction. In the case of methyl sulfoxide (**1e**), the reaction in refluxing benzene or xylene gave **2e** in low yield although the starting **1e** was immediately consumed.

It seemed that the reactivity of this Pummerer rearrangement depended on the acidity of the hydrogen α to the sulfoxide in the substrate. Note that the 1,3-oxathiane (**2f**) could be obtained from 2-bromoethanol in three steps. This result indicates the possibility that an alkyl halide having a hydroxy group can be converted into the corresponding 1,3-oxathiane without a protecting process for the hydroxy group.

In conclusion, we have found that the intramolecular Pummerer reaction of alkyl *ortho*-hydroxymethylphenyl sulfoxide derivatives with *p*-TSA and MS 3A was effective for the formation of the 1,3-oxathianes. By use of this reaction, the three-step transformation of alkyl halides to 1,3-oxathianes, masked carbonyl equivalents, was successful. This transformation would be able to contribute to future 1,3-oxathiane chemistry.

Scheme



3: R^2 = Me
4: R^2 = H

5a: R^1 = Ph, R^2 = Me
5b: R^1 = Ph, R^2 = H
5c: R^1 = Me, R^2 = Me
5d: R^1 =  , R^2 = Me
5e: R^1 = H, R^2 = Me
5f: R^1 = CH_2OH, R^2 = Me
5g: R^1 =  , R^2 = Me
5h: R^1 = NO_2, R^2 = Me

1a: R^1 = Ph, R^2 = Me
1b: R^1 = Ph, R^2 = H
1c: R^1 = Me, R^2 = Me
1d: R^1 =  , R^2 = Me
1e: R^1 = H, R^2 = Me
1f: R^1 = CH_2OH, R^2 = Me
1g: R^1 =  , R^2 = Me

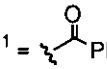
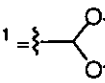
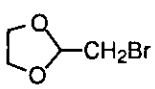
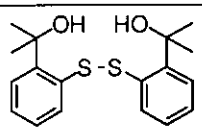
2a: R^1 = Ph, R^2 = Me
2b: R^1 = Ph, R^2 = H
2c: R^1 = Me, R^2 = Me
2d: R^1 =  , R^2 = Me
2e: R^1 = H, R^2 = Me
2f: R^1 = CH_2OH, R^2 = Me
2g: R^1 =  , R^2 = Me

Table 2

Preparation of 5		5 → 1	1 → 2	
Alkyl halide	Yield of 5 [a] (%)	Yield of 1 [a] (%)	Reaction conditions	Yield of 2 [a] (%)
$PhCH_2Br$	**5a**: 93	**1a**: 87	See Table 1	
$PhCH_2Cl$	95			
$PhCH_2Br$	**5b**: 90	**1b**: 85	See Table 1	
EtBr	**5c**: 83	**1c**: 85	benzene, reflux, 3 min	**2c**: 82
$PhCOCH_2Br$	**5d**: 96	**1d**: 85	benzene, rt, 20 min	**2d**: 64
			CH_2Cl_2, 0°C, 40 min	50
			toluene, 0°C, 40 min	90
MeI	**5e**: 95	**1e**: 85	benzene, rt, 8 h	**2e**: 13
			benzene, reflux, 3 min	36
			xylene, reflux, 3 min	49
$HOCH_2CH_2Br$	**5f**: 89	**1f**: 46	CH_2Cl_2, rt	**2f**: 0
			CH_2Cl_2, reflux, 10 h	50
			toluene, reflux, 1 h	95
	**5g**: 85 [b]	**1g**: 86	toluene, 0°C, 2 h	**2g**: 47
O_2NCH_2Br	**5h**: – [c]			

a) Isolated yield. b) Reaction was carried out under reflux.
c) 75% of disulfide (**6**) was obtained.



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ACKNOWLEDGMENT

We are grateful to the SC-NMR Laboratory of Okayama University for the use of the facilities.

EXPERIMENTAL

General: Melting points were measured with a Yanagimoto micro melting point hot-plate apparatus and are uncorrected. IR spectra were recorded on a JASCO A-102 spectrophotometer. NMR spectra were taken with a Varian VXR-500, VXR-200, or Hitachi R-1500 instrument with the chemical shifts being reported as δ ppm and couplings are expressed in Hertz. Silica gel column chromatography was carried out with Wako-gel C-200. Merck Silica-gel 60 F254 plates (No. 5744) were used for the preparative TLC.

2-(2-Mercaptophenyl)-2-propanol [10]

To a suspension of MeMgI in Et_2O (320 mL), which was prepared from Mg (10 g, 412 mmol) and MeI (22 mL, 353 mmol), was added dropwise a solution of methyl thiosalicylate (19 g, 114 mmol) in Et_2O (100 mL). After refluxing for 2 h, the reaction mixture was poured into 1N HCl aqueous solution (200 mL) at 0 °C, and extracted with Et_2O. An organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to give a yellow oil. Recrystallization with CH_2Cl_2 - pentane afforded colorless prisms (14 g, 74%), mp 43-44 °C (lit.,[10] 45-46 °C). IR (KBr) cm^{-1}: 3280, 2550. ^{1}H-NMR (60 MHz, $CDCl_3$) δ: 1.70 (s, 6H), 2.30 (br s, 1H, exchangeable with D_2O), 4.08 (s, 1H, exchangeable with D_2O), 7.07-7.31(m, 4H). *Anal.* Calcd for $C_9H_{12}OS$: C, 64.25; H, 7.19. Found: C, 64.25; H, 6.91.

2-Mercaptobenzyl alcohol

This compound was prepared by a previously reported method.[11]

Typical procedure for preparation of sulfide (5)

To a solution of 2-(2-mercaptophenyl)-2-propanol (1.01 g, 6.0 mmol) in THF (90 mL) was added *t*-BuOK (708 mg, 6.31 mmol) at 0 °C under an argon atmosphere. After stirring for 10 min, a solution of benzyl bromide (1.21 g, 6.9 mmol) was added to the mixture. The reaction mixture was stirred for 90 min at rt, poured into water, and extracted with ether. The extract was washed with brine and dried over $MgSO_4$. Evaporation of the solvent gave a residue which was purified by silica gel chromatography with hexane - CH_2Cl_2 (1:1) to leave pure **5a** (1.43 g, 93%).

2-(2-Benzylthiophenyl)-2-propanol (5a)[12]**:** Colorless prisms, mp 43-44 °C (hexane). IR ($CHCl_3$) cm^{-1}: 3500. ^{1}H-NMR (60 MHz, $CDCl_3$) δ: 1.65 (s, 6H), 3.86 (br s, 1H, exchangeable with D_2O), 4.15 (s, 2H), 7.02-7.54(m, 9H). *Anal.* Calcd for $C_{16}H_{18}OS$: C, 74.38; H, 7.02. Found: C, 74.71; H, 7.23.

2-Benzylthiophenylmethanol (5b)[13]**:** Colorless needles, mp 46.5-47.5 °C (hexane-$CHCl_3$) (lit.,[13] 48.5-49.5 °C). IR ($CHCl_3$) cm^{-1}: 3500. ^{1}H-NMR (60 MHz, $CDCl_3$) δ: 1.97 (br s, 1H, exchangeable with D_2O), 4.05 (s, 2H), 4.62 (s, 2H), 6.96-7.48 (m, 9H). *Anal.* Calcd for $C_{14}H_{14}OS$: C, 73.01; H, 6.13. Found: C, 73.33; H, 6.31.

2-(2-Ethylthiophenyl)-2-propanol (5c): Colorless oil. The spectral data of this compound were

identical with those of an authentic sample.[5b]

2-(2-Phenacylthiophenyl)-2-propanol (5d): Brown oil. IR ($CHCl_3$) cm^{-1}: 3500, 3030, 1690. ^{1}H-NMR (60 MHz, $CDCl_3$) δ: 1.67 (s, 6H), 4.40 (s, 2H), 7.11-8.03 (m, 9H). *Anal.* Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.33. Found: C, 71.06; H, 6.13.

2-(2-Methylthiophenyl)-2-propanol (5e)[14]: Colorless oil. IR ($CHCl_3$) cm^{-1}: 3500, 3030. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.70 (s, 6H), 2.52 (s, 3H), 4.20 (s, 1H, exchangeable with D_2O), 7.17-7.26 (m, 2H), 7.39-7.46 (m, 2H). HRMS (FAB) calcd for $C_{10}H_{14}OS$: 182.0765. Found: 182.0776. *Anal.* Calcd for $C_{10}H_{14}OS$: C, 65.89; H, 7.74. Found: C, 65.56; H, 7.36.

2-[2-(2-Hydroxyethyl)thiophenyl]-2-propanol (5f): Colorless prisms, mp 111-113 °C (hexane). IR (KBr) cm^{-1}: 3300, 1430, 1140, 1040, 760. ^{1}H-NMR (200 MHz, DMSO-d_6) δ: 1.59 (s, 6H), 3.02 (t, 2H, J = 7.0), 3.56 (t, 2H, J = 7.0), 7.09-7.23 (m, 2H), 7.40 (dd, 1H, J = 7.0, 1.8), 7.58 (dd, 1H, J = 7.0, 1.8). *Anal.* Calcd for $C_{11}H_{16}O_2S$: C, 62.23; H, 7.60. Found: C, 62.27; H, 7.45.

2-[2-(1,3-Dioxolan-2-yl)methylthiophenyl]-2-propanol (5g): Colorless oil. IR ($CHCl_3$) cm^{-1}: 3500, 3030, 1040. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.70 (s, 6H), 3.21 (d, 2H, J = 4.4), 3.86-4.07 (m, 4H), 4.75 (s, 1H, exchangeable with D_2O), 5.09 (t, 1H, J = 4.4), 7.20-7.24 (m, 2H), 7.43 (m, 1H), 7.55 (m, 1H). *Anal.* Calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13. Found: C, 61.12; H, 7.13.

2,2'-(2,2'-Dithiodiphenyl)-2,2'-dipropanol (6)

To a solution of 2-(2-mercaptophenyl)-2-propanol (1.02 g, 6.0 mmol) in THF (90 mL) was added *t*-BuOK (712 mg, 6.35 mmol) at 0 °C under an argon atmosphere. After stirring for 10 min, bromonitromethane (885 mg, 6.33 mmol) was added to the mixture. The reaction mixture was stirred for 10 min at rt, poured into water, and extracted with ether. The extract was washed with brine and dried over $MgSO_4$. Evaporation of the solvent gave a yellow solid which was recrystallized from hexane to give **6** (753 mg, 75%). The spectral data of this compound were identical with those of an authentic sample.[5b]

Typical procedure for oxidation of sulfide (5)

To a solution of **5a** (203 mg, 0.79 mmol) in CH_2Cl_2 (15 mL) was added *m*-CPBA (70%, 256 mg, 1.04 mmol) at -78 °C under an argon atmosphere. After stirring for 45 min at -78 °C, the reaction mixture was poured into a saturated sodium bicarbonate aqueous solution and extracted with CH_2Cl_2. The extract was washed with brine and dried over $MgSO_4$. Evaporation of the solvent gave a pale yellow solid, which was recrystallized from hexane to leave pure **1a** (187 mg, 87%).

2-(2-Benzylsulfinylphenyl)-2-propanol (1a): Colorless needles, mp 167.5-169.5 °C (hexane). IR (KBr) cm^{-1}: 3200, 1220, 1190, 990, 760, 710. ^{1}H-NMR (60 MHz, $CDCl_3$) δ: 1.58 (s, 3H), 1.68 (s, 3H), 3.23 (br s, 1H, exchangeable with D_2O), 3.81, 4.46 (ABq, 2H, J = 12.3), 7.20-7.96 (m, 9H). *Anal.* Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61. Found: C, 69.78; H, 6.51.

2-Benzylsulfinylphenylmethanol (1b)[7]: Colorless plates, mp 101.5-102.5 °C (hexane-$CHCl_3$) (lit.,[7] 99-101 °C). IR (KBr) cm^{-1}: 3300, 1005, 750, 700. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 3.16 (t, 1H, J = 5.8, exchangeable with D_2O), 4.14, 4.20 (ABq, 2H, J = 12.6), 4.54 (m, 2H), 7.00-7.07 (m, 2H), 7.19-7.59 (m, 7H). *Anal.* Calcd for $C_{14}H_{14}O_2S$: C, 68.27; H, 5.73. Found: C, 68.07; H, 5.67.

2-(2-Ethylsulfinylphenyl)-2-propanol (1c): Colorless oil. IR ($CHCl_3$) cm^{-1}: 3300, 2970, 1000. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.26 (t, 3H, *J* = 7.5), 1.66 (s, 3H), 1.68 (s, 3H), 2.75 (dq, 1H, *J* = 14.8, 7.5), 3.19 (dq, *J* = 14.8, 7.5), 7.27 (dd, 1H, *J* = 7.0, 1.0), 7.38-7.45 (m, 2H), 8.12 (d, 1H, *J* = 7.5). HRMS (FAB) calcd for $C_{11}H_{16}O_2S$: 212.0871. Found: 212.0863. Calcd for $C_{11}H_{17}O_2S$: 213.0949. Found: 213.0975.

2-(2-Phenacylsulfinylphenyl)-2-propanol (1d): Colorless prisms, mp 165.5-166.5 °C (CH_2Cl_2). IR (KBr) cm^{-1}: 3330, 1690 1285, 1020, 735. ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 1.50 (s, 3H), 1.59 (s, 3H), 4.13 (d, 1H, *J* = 14.5), 4.93 (d, 1H, *J* = 14.5), 5.87 (br s, 1H, exchangeable with D_2O), 7.36-7.69 (m, 6H), 7.99-8.11 (m, 3H). *Anal.* Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00. Found: C, 67.55; H, 5.98.

2-(2-Methylsulfinylphenyl)-2-propanol (1e): Colorless needles, mp 97-98 °C (Et_2O). IR (KBr) cm^{-1}: 3400, 3030, 1060, 1020, 970. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.68 (s, 6H), 2.77 (br s, 1H, exchangeable with D_2O), 2.81 (s, 3H), 7.26 (m, 1H), 7.37-7.52 (m, 2H), 8.23 (dd, 1H, *J* = 7.4, 1.4). *Anal.* Calcd for $C_{10}H_{14}O_2S$: C, 60.57; H, 7.12. Found: C, 60.58; H, 7.11.

2-[2-(2-Hydroxyethyl)sulfinylphenyl]-2-propanol (1f): Colorless prisms, mp 131-133 °C (ethyl acetate). IR (KBr) cm^{-1}: 3380, 3220, 1055, 990. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.64 (s, 3H), 1.66 (s, 3H), 2.85 (ddd, 1H, *J* = 13.5, 5.5, 3.0), 3.58 (ddd, 1H, *J* = 13.5, 9.0, 3.5), 4.03 (m, 1H), 4.17 (m, 1H), 4.32 (t, 1H, *J* = 5.5), 7.26 (d, 1H, *J* = 8.0), 7.42 (t, 1H, *J* = 8.0), 7.47 (t, 1H, *J* = 8.0), 8.20 (d, 1H, *J* = 8.0) . *Anal.* Calcd for $C_{11}H_{16}O_3S$: C, 57.87; H, 7.06. Found: C, 57.66; H, 7.04.

2-[2-(1,3-Dioxolan-2-yl)methylsulfinylphenyl]-2-propanol (1g): Colorless oil. IR ($CHCl_3$) cm^{-1}: 3400, 3020, 1740, 1480, 1440, 1410, 1370, 1240, 1180, 1130, 1020, 970. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.66 (s, 3H), 1.68 (s, 3H), 2.84 (br s, 1H), 2.97 (dd, 1H, *J* = 13.0, 3.6), 3.50 (dd, 1H, *J* = 13.0, 6.2), 3.87-4.06 (m, 4H), 5.38 (dd, 1H, *J* = 6.2, 3.6), 7.26 (dd, 1H, *J* = 7.2, 2.0), 7.37-7.52 (m, 2H), 8.24 (dd, 1H, *J* = 7.6, 1.8) . *Anal.* Calcd for $C_{13}H_{18}O_4S$: C, 57.76; H, 6.71. Found: C, 57.47; H, 6.54.

Typical procedure for intramolecular Pummerer reaction of sulfoxide (1)

A mixture of **1a** (56.9 mg, 0.207 mmol), molecular sieves 3A (576 mg), anhydrous *p*-toluenesulfonic acid (37.5 mg, 0.218 mmol), and dry toluene (18 mL) was stirred for 1 h at rt, and then filtered. The filtrate was poured into a saturated sodium bicarbonate aqueous solution and extracted with CH_2Cl_2. The extract was washed with brine and dried over $MgSO_4$. Evaporation of the solvent gave a residue, which was purified by silica gel chromatography with hexane - ethyl acetate (4:1) to give **2a** (48.5 mg, 91%). The analytical sample was obtained by recrystallization or further purification with preparative TLC.

4,4-Dimethyl-2-phenyl-3,1-benzoxathiin (2a): Colorless plates, mp 95-96 °C (hexane). IR (KBr) cm^{-1}: 3020, 1255, 1070, 1050, 720. ^{1}H-NMR (60 MHz, $CDCl_3$) δ: 1.68 (s, 3H), 1.70 (s, 3H), 6.17 (s, 1H), 7.14-7.54 (m, 9H). *Anal.* Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29. Found: C, 75.28; H, 6.49.

2-Phenyl-4*H*-3,1-benzoxathiin (2b)[7]: Colorless plates, mp 114.5-116 °C (hexane - ethyl acetate). IR (KBr) cm^{-1}: 1445, 1235, 1095, 750, 705. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 5.12 (s, 2H), 6.13 (s, 1H), 7.05-7.57 (m, 9H). *Anal.* Calcd for $C_{14}H_{12}OS$: C, 73.65; H, 5.30. Found: C, 73.77; H, 5.49.

2,4,4-Trimethyl-3,1-benzoxathiin (2c): Spectral data of this compound were identical with those of an authentic sample.[5b]

2-Benzoyl-4,4-dimethyl-3,1-benzoxathiin (2d): Pale yellow oil. IR ($CHCl_3$) cm^{-1}: 3020, 1700, 1610, 1460, 1280, 1250, 1175, 1100, 995. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.70 (s, 3H), 1.77 (s, 3H), 6.45 (s, 1H), 7.11-7.26 (m, 4H), 7.44-7.65 (m, 3H), 8.09-8.13 (m, 2H). *Anal.* Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67. Found: C, 71.52; H, 5.85.

4,4-Dimethyl-3,1-benzoxathiin (2e): Pale yellow oil. IR ($CHCl_3$) cm^{-1}: 3030, 1485, 1440, 1395, 1375, 1315, 1245, 1090. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.59 (s, 6H), 5.04 (s, 2H), 7.06-7.17 (m, 4H). *Anal.* Calcd for $C_{10}H_{12}OS$: C, 66.63; H, 6.71. Found: C, 66.46; H, 6.55.

4,4-Dimethyl-2-hydroxymethyl-3,1-benzoxathiin (2f): Colorless prisms, mp 69-69.5 °C (hexane). IR ($CHCl_3$) cm^{-1}: 3500, 3020, 1480, 1440, 1395, 1375, 1280, 1255, 1175, 1105, 1070, 1040, 970. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.61 (s, 3H), 1.63 (s, 3H), 2.27 (br s, 1H), 3.89 (m, 2H), 5.34 (dd, 1H, J = 6.0, 4.0), 7.08-7.18 (m, 4H). *Anal.* Calcd for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71. Found: C, 62.80; H, 6.61.

4,4-Dimethyl-2-(1,3-dioxolan-2-yl)-3,1-benzoxathiin (2g): Pale yellow oil. IR ($CHCl_3$) cm^{-1}: 3040, 1490, 1440, 1395, 1380, 1280, 1060, 1100, 1040, 950. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.62 (s, 3H), 1.63 (s, 3H), 3.99-4.01 (m, 2H), 4.09-4.11 (m, 2H), 5.19 (d, 2H, J = 4.5), 5.28 (d, J = 4.5), 7.05-7.11 (m, 2H), 7.13-7.16 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 28.38, 30.51, 65.63, 65.78, 77.50, 103.43, 124.80, 126.04, 126.68, 128.33, 130.06, 139.19. HRMS (FAB) calcd for $C_{13}H_{16}O_3S$: 252.0820. Found: 252.0845.

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