Selective Oxidation of Allylic Sulfides by Hydrogen Peroxide with the Trirutile-type Solid Oxide Catalyst $LiNbMoO_6$

Soojin Choi,[†,§] Jae-Deuk Yang,[‡] Minkoo Ji,[‡] Hojin Choi,[‡] Minyong Kee,[‡] Kwang-Hyun Ahn,[†]
Song-Ho Byeon,[†] Woonphil Baik,[‡] and Sangho Koo*[,‡]

Department of Chemistry, Kyung Hee University, Yongin, Kyunggi-Do, 449-701, Korea, and
Department of Chemistry, Myong Ji University, Yongin, Kyunggi-Do, 449-728, Korea

sangkoo@mju.ac.kr

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Chemoselective sulfur oxidation of allylic sulfides containing double bonds of high electron density due to multiple alkyl substituents or extended conjugation was developed using the composite metal oxide catalyst, $LiNbMoO_6$, without any epoxidation of the electron-rich double bond(s). Selective oxidation to either the corresponding sulfoxides or the sulfones was realized by controlling the stoichiometry of the quantitative oxidant, H_2O_2. This new oxidant system had general applicability for chemoselective oxidation of various allylic, benzylic, or propargylic sulfides containing unsaturated carbon−carbon bonds with different electron properties. Various functional groups including hydroxy, formyl, and ethers of THP or TBDMS are compatible under this mild oxidation reaction condition.

Introduction

Organosulfur compounds are useful intermediates for constructing highly functionalized biologically and medicinally important natural products.[1] Among the various transformations of organic sulfides, chemoselective oxidation to sulfoxides or to sulfones has been widely studied with regard to extending the carbon skeleton[2] and/or double bond formation[3] using the resulting sulfoxides or sulfones. There is much room for improvement, however, in the chemoselectivity of this oxidation reaction.

Electrophilic oxidants are useful for the selective oxidation of sulfide to sulfoxide because the initial oxidation of a highly nucleophilic sulfide to a sulfoxide is an easier process than the second oxidation of the resulting much less nucleophilic sulfoxide to sulfone.[4] Thus, selective oxidation of sulfides to sulfoxides or to sulfones can be realized based on the stoichiometry of the electrophilic oxidant used under carefully controlled reaction conditions. The use of reactive electrophilic oxidants, however, might interfere with chemoselectivity, especially with sulfides containing nucleophilic functional groups.[5]

We studied the oxidation reactions of allylic sulfides comprising double bonds of high electron density due to multiple alkyl substituents or extended conjugation. We were unable to selectively convert these allylic sulfides to the corresponding sulfoxides or to the sulfones using well-known conventional oxidants such as *m*-chloroperbenzoic acid (MCPBA),[6] $NaIO_4$,[7] SeO_2,[8] Oxone,[5] the $AcOH-H_2O_2$ system,[9] etc., because the electron-rich double bonds interfered with the selective oxidation of sulfur in the allylic sulfides. It is critical to use a much less electrophilic but still reactive oxidant system to selectively convert these allylic sulfides to the corresponding sulfoxides or to the sulfones. We then reviewed various metal oxide catalyst−H_2O_2 oxidant systems,[10] which are efficient oxidants rendering both selectivity (due to low electrophilicity) and reactivity to organosulfides. Though somewhat satisfactory results were obtained for allylic sulfides with electron-rich double bonds due to alkyl substituents, chemoselective oxidation of an allylic sulfide comprising conjugated polyenes was still problematic.

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* To whom correspondence should be addressed: Professor Sangho Koo, Department of Chemistry, Myong Ji University, San 38-2, Nam-Dong, Yongin, Kyunggi-Do, 449-728, South Korea. Phone: +82-31-330-6185. Fax no. 82-31-335-7248.

[†] Kyung Hee University.

[‡] Myong Ji University.

[§] Current address: R&D Center, Daewoong Pharm. Co., Ltd., Seongnam, Kyunggi-do, 462-120, Korea.

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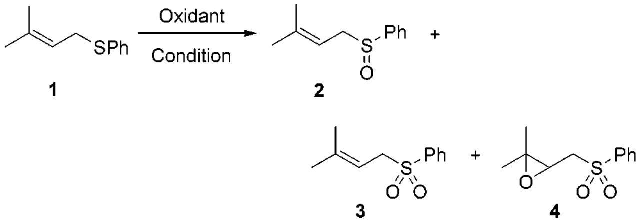
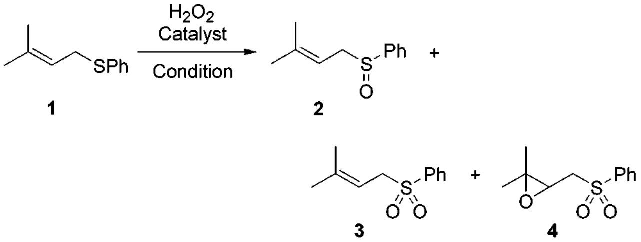
Table 1. Oxidation of Allylic Sulfide 1 by Conventional Oxidants



entry	oxidant (equiv)	solvent	reaction condition, temperature (time)	yields (%)		
				2	3	4
1	H_2O_2 (3)	AcOH	rt (24 h)	90	−	−
2	H_2O_2 (3)	AcOH	70 °C (3 h)	5	5	12
3	Oxone (1)	MeOH	0 °C (1 h)	54	15	−
4	Oxone (3)	MeOH	rt (6 h)	40	32	−
5	$NaIO_4$ (1)	MeOH	0 °C (4 h) to rt (4 h)	66	−	−
6	$NaIO_4$ (3)	MeOH	rt (6 h)	82	2	−
7	MCPBA (1)	CH_2Cl_2	0 °C (4 h) to rt (4 h)	75	2	−
8	MCPBA (3)	CH_2Cl_2	rt (4 h)	−	22	62

Table 2. Oxidation of Allylic Sulfide 1 by Metal Oxide Catalyst−H_2O_2 Oxidant



entry	catalyst	equiv of H_2O_2	reaction condition, temperature (time)	yields (%)		
				2	3	4
1	MoO_3	1	rt (24 h)	64	20	−
2	MoO_3	3	rt (24 h)	62	26	−
3	$MeReO_3$	1	0 °C (1 h)	70	14	−
4	$MeReO_3$	3	rt (2 h)	−	28	41
5	V_2O_5	1	0 °C (1 h)	74	13	−
6	V_2O_5	3	rt (3 h)	−	82	−
7	Na_2WO_4	1	0 °C (4 h) to rt (1 h)	64	23	−
8	Na_2WO_4	3	rt (1 h)	−	85	−

The trirutile-type solid oxide, $LiNbMoO_6$, is a stable metal oxide that has been known for several decades. Previous reports have described the crystallographic structure[11] and preparation method[12] of $LiNbMoO_6$. Although to our knowledge this composite metal oxide has never been used as a catalyst of sulfur oxidation, we examined whether it might confer both selectivity and reactivity to the oxidant system allowing chemoselective oxidation of allylic sulfides with electron-rich double bond(s). Indeed, $LiNbMoO_6$ effectively catalyzed the chemoselective oxidation of allylic sulfides with electron-rich double bond(s) due to extended conjugation as well as alkyl substitutions by hydrogen peroxide. Herein, we report a study of chemoselective oxidation of allylic sulfides with electron-rich double bond(s).

Results and Discussion

Oxidation of Allylic Sulfide with Electron-Rich Double Bond Due To Alkyl Substituents. As a model compound of an allylic sulfide possessing an electron-rich double bond due to alkyl substituents, we chose phenyl prenyl sulfide (**1**) and attempted oxidation reactions using the various oxidants mentioned above. Hydrogen peroxide is a nucleophilic oxidant which is believed to become electrophilic in acetic acid solvent, presumably by forming peracetic acid in situ. With an excess of this oxidant system (3 equiv of H_2O_2), only the corresponding sulfoxide **2** was produced in 90% yield at ambient temperature even after a prolonged reaction time of 24 h without producing any sulfone **3**. Under more vigorous conditions (heating the reaction mixture to 70 °C for 3 h), sulfoxide **2**, sulfone **3**, and epoxysulfone **4** were obtained in 5%, 5%, and 12% yield, respectively (entries 1 and 2, Table 1). The formation of epoxysulfone **4** is noteworthy in that the electron-rich double bonds also attack the electrophilic oxidant under more vigorous conditions to give epoxidation as well as sulfur oxidation. The overall yield was low in this case, presumably due to the instability of the allylic sulfur compounds under acidic conditions with heating. The identification of the oxidation products, sulfoxide **2**, sulfone **3**, and epoxysulfone **4**, is straightforward by comparing infrared spectra[13] and by ^{1}H NMR analyses of each compound.

Potassium hydrogen persulfate ($KHSO_5$), commercially available as Oxone, selectively oxidizes sulfides to sulfoxides or to sulfones.[5] Even under the carefully controlled reaction conditions of slowly adding 1 equiv of Oxone at 0 °C, however, an appreciable amount of sulfone **3** (15%) was also obtained. Furthermore, excess Oxone (3 equiv) did not produce complete oxidation of sulfide **1** to sulfone **3** (entries 3 and 4, Table 1). Sodium periodate ($NaIO_4$) was very effective in the selective oxidation of sulfide **1** to sulfoxide **2**,[7] even with excessive use of the oxidant (entries 5 and 6, Table 1). As was expected based on the electrophilic nature of the oxidant, 3 equiv of MCPBA produced epoxysulfone **4** as a major oxidation product (62%), though selective formation of sulfoxide **2** was observed with 1 equiv of the oxidant at 0 °C (entries 7 and 8, Table 1). Overall, selective oxidation of the allylic sulfide **1** to sulfoxide **2** was feasible using the above conventional oxidants under carefully controlled reaction conditions. Selective oxidation of allylic sulfide **1** to sulfone **3**, however, was not possible due to either too low or too high reactivity of the above oxidants.

To achieve selective oxidation of allylic sulfide **1** to the corresponding sulfone **3**, it was necessary to use a less electrophilic but still reactive oxidant to avoid epoxidation of the electron-rich double bond. Thus, an oxidant system consisting of a metal oxide catalyst and H_2O_2 as a quantitative oxidizing agent was used. Selective oxidation of phenyl prenyl sulfide (**1**) was attempted using either 1 or 3 equiv of H_2O_2 with MoO_3, $MeReO_3$, V_2O_5, and Na_2WO_4 as representative metal oxide catalysts.[10] MoO_3 was not an efficient oxidation catalyst, providing sulfoxide **2** as the major product with low chemoselectivity regardless of the amount of H_2O_2 used (entries 1 and 2, Table 2). The formation of epoxysulfone **4** (41%) with 3 equiv of H_2O_2 indicates that $MeReO_3$−H_2O_2[14] forms a highly electrophilic oxidant system, as is the case with MCPBA. Thus, selective oxidation to sulfoxide **2** was attempted at 0 °C with 1 equiv of H_2O_2, but the formation of sulfone

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[11] Nam, H.-J.; Kim, H.; Chang, S. H.; Kang, S.-G.; Byeon, S.-H. *Solid State Ionics* **1999**, *120*, 189−195.

[12] Bhuvanesh, N. S. P.; Gopalakrishnan, J. *Inorg. Chem.* **1995**, *34*, 4, 3760−3764. (b) Kar, T.; Choudhary, R. N. P. *Mater. Lett.* **1997**, *32*, 109−113.

[13] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds,* 5th ed.; Wiley: New York, 1991; p 129.

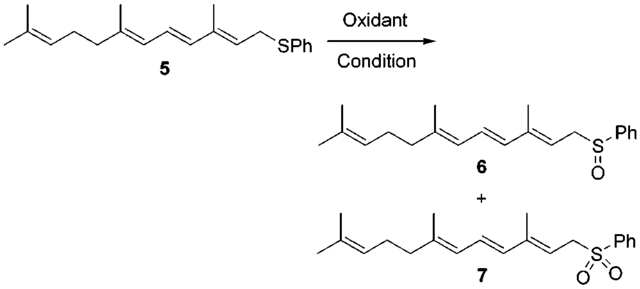
3 (14%) could not be prevented (entries 3 and 4, Table 2). On the other hand, highly chemoselective oxidation of sulfide **1** to sulfone **3** was realized in good yields with V_2O_5 and Na_2WO_4 catalysts with 3 equiv of H_2O_2. The selective oxidation to sulfoxide **2** with 1 equiv of H_2O_2 at 0 °C was, however, problematic due to the formation of an appreciable amount of sulfone **3** (entries 5–8, Table 2).

Thus, certain metal oxides are appropriately selective and reactive to induce chemoselective oxidation of allylic sulfide with electron-rich double bonds due to alkyl substituents to the corresponding allylic sulfone without epoxidation. The possibility of chemoselective oxidation of allylic sulfides composed of conjugated polyenes was then studied with these metal oxides.

Oxidation of Allylic Sulfide with Electron-Rich Double Bonds Due To Conjugation. We also examined the oxidation reaction of allylic sulfides composed of conjugated polyene chains to the corresponding sulfoxides or sulfones, which can be used in retinoid and carotenoid syntheses.[15] It is critical to use an appropriate oxidant to selectively oxidize the sulfur moiety without inducing epoxidation of the conjugated polyenes. The oxidant for this purpose should be less electrophilic but still require high reactivity to convert sulfide to sulfone. We utilized phenyl 3,7,11-trimethyl-2,4,6,10-dodecatetraenyl sulfide (**5**) as the allylic sulfide containing conjugated polyene and evaluated whether various oxidants, including a metal oxide catalyst–H_2O_2, could selectively oxidize the sulfide **5** to either sulfoxide **6** or sulfone **7** by controlling the stoichiometry of the oxidants. The reaction condition was carefully controlled, especially for the oxidation to sulfone **7** where 2 equiv of oxidant were used, by maintaining the reaction temperature at 0 °C during and after the addition of the oxidant.

Differently from allylic sulfide **1**, which has only one electron-rich double bond, selective oxidation of allylic sulfide **5** containing the conjugated triene moiety to the corresponding sulfoxide **6** or to the sulfone **7** were poor. In contrast to the composite metal oxide, $LiNbMoO_6$, which successfully catalyzed the selective oxidation of allylic sulfide **5** to sulfoxide **6** or sulfone **7** by H_2O_2 (vide infra), niobium(V) oxide or molybdenum(VI) oxide alone were not good catalysts for selective oxidation (entries 1–4, Table 3). Other metal oxide catalysts, such as $MeReO_3$, Na_2WO_4, and V_2O_5 with H_2O_2 as a quantitative oxidant did not produce either sulfoxide **6** or sulfone **7** in a chemoselective manner (entries 5–10, Table 3). The oxidation of sulfide **5** by *N*-methylmorpholine *N*-oxide (NMO) with tetrapropylammonium perruthenate (TPAP) catalyst[16] was very sluggish, and poor yields as well as no chemoselectivity have been observed with this oxidant system (entries 11 and 12, Table 3). The oxidation reaction was then attempted with a nonmetal oxide catalyst, the SeO_2–H_2O_2 oxidant system, and MCPBA. With these oxidants, selective formation of sulfoxide **6** was possible, though the product yield was low for SeO_2–H_2O_2. Chemoselective oxidation to sulfone **7** was, however, still problematic with those oxidants (entries 13–16, Table 3).

Table 3. Oxidation of Allylic Sulfide 5 by Various Oxidants



entry	catalyst[a]	oxidant[b] (equiv)	reaction condition, temperature (time)	yields[c] (%)	
				6	**7**
1	Nb_2O_5	H_2O_2 (1)	rt (4 h)	30	14
2	Nb_2O_5	H_2O_2 (2)	0 °C (2 h) to rt (22 h)	17	23
3	MoO_3	H_2O_2 (1)	rt (18 h)	25	6
4	MoO_3	H_2O_2 (2)	0 °C (2 h) to rt (22 h)	9	15
5	$MeReO_3$	H_2O_2 (1)	rt (0.5 h)	26	10
6	$MeReO_3$	H_2O_2 (2)	0 °C (0.5 h) to rt (0.5 h)	14	15
7	Na_2WO_4	H_2O_2 (1)	rt (0.5 h)	43	27
8	Na_2WO_4	H_2O_2 (2)	0 °C (1 h) to rt (1 h)	30	50
9	V_2O_5	H_2O_2 (1)	rt (1 h)	56	4
10	V_2O_5	H_2O_2 (2)	0 °C (2 h) to rt (2 h)	11	9
11	*n*-Pr_4NRuO_4	NMO (1)	40 °C (22 h)	4	7
12	*n*-Pr_4NRuO_4	NMO (2)	40 °C (22 h)	10	12
13	SeO_2	H_2O_2 (1)	rt (18 h)	26	0
14	SeO_2	H_2O_2 (1)	0 °C (2 h) to rt (22 h)	10	12
15	–	MCPBA (1)	rt (1 h)	79	2
16	–	MCPBA (2)	0 °C (0.5 h) to rt (0.5 h)	21	35

[a] Five mol % of catalyst was used based on sulfide **5**. [b] MeOH was used as solvent for H_2O_2 oxidant, CH_3CN for NMO, and CH_2Cl_2 for MCPBA oxidation. [c] An appreciable amount of side products were obtained that were presumed to be epoxysulfones, but the structures were not identified.

The product yields were generally low in the above process, presumably due to the generation of side-products such as epoxysulfones. Thus, a more efficient metal oxide catalyst was developed to achieve selective oxidation of allylic sulfides composed of conjugated polyenes, and not only the allylic sulfides having double bonds of increased electron density due to alkyl substituents, to the corresponding sulfoxides or sulfones.

Chemoselective Oxidation of Various Allylic Sulfides by the $LiNbMoO_6$–H_2O_2 Oxidant System. Fine-tuning the reactivity of oxidants is essential for the selective oxidation of the sulfur moiety of allylic sulfides containing conjugated polyenes without inducing oxidation of the double bonds. We hypothesized that a composite metal oxide might have quite different reactivity than that of each metal oxide in the catalysis of those selective oxidation reactions with H_2O_2 as a quantitative oxidant. The air-stable and easy to handle trirutile-type solid oxide, $LiNbMoO_6$, was prepared as previously described,[12] and selective oxidation reactions were attempted for allylic sulfides **1** and **5**. By controlling the stoichiometry of the quantitative oxidant, H_2O_2, remarkable selectivity as well as reactivity in the oxidation of a sulfur moiety without any epoxidation was observed. Sulfoxide **2** was obtained in good yield (77%) when 1 equiv of H_2O_2 was utilized at 0 °C, although it was contaminated by the further oxidation product, sulfone **3**, in 14% yield. Complete chemoselectivity, however, was observed in the oxidation to sulfones **3** by using 3 equiv of H_2O_2 at ambient temperature, and no epoxidation product was obtained (entry 1, Table 4). The chemoselectivity of the $LiNbMoO_6$ catalyst was even better for

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(14) Yamazaki, S. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2955–2959.

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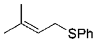
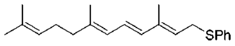
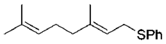
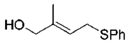
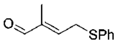
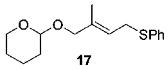
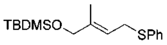
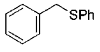
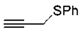
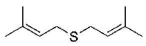
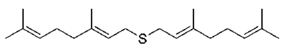
(16) Guertin, K. R.; Kende, A. S. *Tetrahedron Lett.* **1993**, *34*, 5369–5372.

Table 4. Oxidation of Various Sulfides by $LiNbMoO_6$ Catalyst−H_2O_2 Oxidant

Entry	Allylic sulfide	Yield of sulfoxide (sulfone)[a] (%)	Yield of sulfone[b] (%)
1	 **1**	**2** (**3**) 77 (14)	**3** 82
2	 **5**	**6** (**7**) 80 (4)	**7** 77
3	 **8**	**9** (**10**) 78 (14)	**10** 85
4	 **11**	**12** (**13**) 75 (12)	**13** 95
5	 **14**	**15** (**16**) 84 (10)	**16** 82
6	 **17**	**18** (**19**) 82 (12)	**19** 85
7	 **20**	**21** (**22**) 80 (9)	**22** 80
8	 **23**	**24** (**25**) 94 (3)	**25** 98
9	 **26**	**27** (**28**) 93 (6)	**28** 84
10	 **29**	**30** (**31**) 54 (6)	**31** 71
11	 **32**	**33** (**34**) 48 (7)	**34** 72

[a] The yields of sulfoxide and sulfone when 1 equiv of H_2O_2 was used at 0 °C. [b] The yield of sulfone when 3 equiv (2.5 equiv for entry 2) of H_2O_2 was used at room temperature.

allylic sulfide **5** containing conjugated triene, which had problems of low selectivity and low yield presumably due to epoxidation with the other oxidants (Table 3). Selective oxidations to sulfoxide **6** (80%) and to sulfone **7** (77%) were achieved by using either 1 or 2.5 equiv of H_2O_2 at 0 °C or at room temperature, respectively. Once again, the oxidation to sulfoxide **6** (80%) was accompanied by further oxidation to sulfone **7** (4%) (entry 2, Table 4).

To establish the general applicability of $LiNbMoO_6$ catalyst in chemoselective sulfur oxidation by H_2O_2, various allylic sulfides with electron-rich double bonds, together with benzylic and propargylic sulfides, were used for the oxidation (Table 4). Thus, highly efficient sulfur oxidations to sulfones were observed with $LiNbMoO_6$ (0.05 mol %)−H_2O_2 (3 equiv) oxidant for phenyl sulfides of allylic, benzyl, and propargyl groups. High chemoselectivity was also observed for the oxidation to sulfoxides, but formation of small amounts of sulfones was unavoidable, even under carefully controlled reaction conditions using 1 equiv of H_2O_2 at 0 °C. This chemoselective oxidation reaction was not hindered by the presence of various functional groups including hydroxy, formyl, and ethers of tetrahydropyranyl (THP) or *tert*-butyldimethylsilyl (TBDMS) groups (entries 4−7, Table 4). Yields of the oxidation products, however, dropped significantly for diallylic sulfides **29** and **32** of prenyl and geranyl, even though the chemoselectivity was still maintained. This phenomenon was more prominent for the oxidation to sulfoxide, which might be explained by the possible rearrangements (either Pummerer[17] or 2,3-sigmatropic[18]) of the resulting allylic sulfoxides.

The role of the $LiNbMoO_6$ catalyst in these highly chemoselective oxidation reactions is not clear at this point; however, it presumably forms a somewhat reactive metal−hydroperoxide intermediate with H_2O_2, which can selectively oxidize only the sulfur moiety. For the oxidation to occur chemoselectively, the allylic sulfides must be highly soluble in methanol. In the case of sulfides with low solubility, some benzene is added to the sulfide solution to obtain complete dissolution. To improve the selectivity of the oxidation to sulfoxide, the reaction temperature is preferably maintained at 0 °C. The oxidation is generally completed within approximately 1 h at 0 °C in the case of sulfoxides, or approximately 4 h at room temperature in the case of oxidation to sulfones using 0.05 equiv of the catalyst, $LiNbMoO_6$.

Conclusion

Oxidation of allylic sulfides comprising double bond(s) with high electron density due to many alkyl substituents or conjugation often accompanies epoxidation of the electron-rich double bond(s) as well as sulfur-oxidation, especially with electrophilic oxidants. We have developed a highly chemoselective oxidant system for sulfur-oxidation consisting of the new composite metal oxide catalyst, $LiNbMoO_6$, and H_2O_2 as a quantitative oxidant. With this less electrophilic but still reactive oxidant system, a highly chemoselective oxidation of allylic sulfides containing electron-rich double bonds to the corresponding sulfoxides or sulfones in high yields has been achieved by controlling the stoichiometry of the quantitative oxidant, H_2O_2, without inducing epoxidation.

Experimental Section

General Experimental. ^1H (300 MHz) and ^{13}C NMR (75.5 MHz) spectra were recorded in deuterated chloroform ($CDCl_3$). Solvents for oxidation reactions, extraction, and chromatography were reagent grade and used as received. Phenyl sulfide compounds were prepared by the reaction of the corresponding halides (either bromide or chloride) with benzenethiol in THF in the presence of Et_3N. Diallylic sulfide compounds were prepared by the reaction of the corresponding allylic bromides with $Na_2S·9H_2O$ in CH_3OH. Column chromatography was performed by the method of Still with silica gel 60, 230−400 mesh ASTM supplied by Merck. All reactions were performed in an open system under air.

Oxidation of Phenyl Prenyl Sulfide (1):[19] Preparation of Sulfoxide 2,[20] Sulfone 3,[21] and Epoxysulfone 4.[22]

By H_2O_2−AcOH Oxidant at Room Temperature. To a stirred solution of phenyl prenyl sulfide (**1**) (524 mg, 2.94 mmol) in AcOH (15 mL) at room temperature was added 30% aqueous solution of H_2O_2 (1.00 g, 8.82 mmol). The mixture was stirred vigorously at that temperature for 24 h and diluted with ether (30 mL) and then with H_2O (15 mL). The mixture was washed with 1 M NaOH solution (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash column

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chromatography to give rise to phenyl prenyl sulfoxide (**2**) (516 g, 2.65 mmol) in 90% yield as the sole product.

By H_2O_2−AcOH Oxidant at 70 °C. The mixture of sulfide **1** (637 mg, 3.57 mmol) and 30% H_2O_2 solution (1.10 g, 10.7 mmol) in AcOH (18 mL) was heated to 70 °C for 3 h and then cooled to room temperature. The resulting mixture was worked up and purified as above to provide sulfoxide **2** (40 mg, 0.19 mmol), sulfone **3** (34 mg, 0.17 mmol), and epoxysulfone **4** (88 mg, 0.42 mmol) in 5%, 5%, and 12% yield, respectively.

General Oxidation Procedure of Phenyl Prenyl Sulfide (1) by Other Electrophilic Oxidants. To a stirred solution of sulfide **1** in the selected solvent was added each oxidant at 0 °C. After certain reaction time, the mixture was diluted with $CHCl_3$, washed with H_2O, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Sulfoxide **2** or sulfone **3** was obtained after purification by SiO_2 flash chromatography.

By Oxone. The reaction of sulfide **1** (178 mg, 1.00 mmol) in CH_3OH (5 mL) with Oxone (615 mg, 1.00 mmol) at room temperature for 1 h gave sulfoxide **2** (104 mg, 0.54 mmol) and sulfone **3** (32 mg, 0.15 mmol) in 54% and 15% yield, respectively. When 3 equiv of Oxone (1.85 g, 3.00 mmol) was used for the oxidation of sulfide **1** (178 mg, 1.00 mmol) at room temperature for 6 h, sulfoxide **2** (78 mg, 0.40 mmol) and sulfone **3** (68 mg, 0.32 mmol) were obtained in 40% and 32% yield, respectively.

By $NaIO_4$. The reaction of sulfide **1** (178 mg, 1.00 mmol) in CH_3OH (5 mL) with $NaIO_4$ (214 mg, 1.00 mmol) at 0 °C for 4 h and then at room temperature for another 4 h gave sulfoxide **2** (129 mg, 0.66 mmol) in 66% yield as a single product. When 3 equiv of $NaIO_4$ (642 mg, 3.00 mmol) was used for the oxidation of sulfide **1** (178 mg, 1.00 mmol) at room temperature for 6 h, sulfoxide **2** (159 mg, 0.82 mmol) and sulfone **3** (5 mg, 0.02 mmol) were obtained in 82% and 2% yield, respectively.

By MCPBA. The reaction of sulfide **1** (178 mg, 1.00 mmol) in CH_2Cl_2 (5 mL) with ~70% MCPBA (247 mg, 1.00 mmol) at 0 °C for 4 h and then at room temperature for another 4 h gave sulfoxide **2** (145 mg, 0.75 mmol) and sulfone **3** (4 mg, 0.04 mmol) in 75% and 4% yield, respectively. When 3 equiv of ~70% MCPBA (741 mg, 3.00 mmol) was used for the oxidation of sulfide **1** (178 mg, 1.00 mmol) at room temperature for 4 h, sulfone **3** (46 mg, 0.22 mmol) and epoxysulfone **4** (141 mg, 0.67 mmol) were obtained in 22% and 67% yield, respectively.

General Procedure for Oxidation of Sulfide 1 by Metal Oxide Catalyst−H_2O_2 Oxidant. To a stirred solution of sulfide **1** (178 mg, 1.00 mmol) in CH_3OH (5 mL) were consecutively added metal oxide catalyst (0.05 mmol) and 30% aqueous solution of H_2O_2 (1.00 or 3.00 mmol) at 0 °C (or at room temperature). The reaction mixture was stirred at 0 °C or at room temperature for the specified amounts of time. The mixture was then concentrated under reduced pressure. The crude product was then purified by SiO_2 flash chromatography.

By MoO_3. The reaction using MoO_3 catalyst (7 mg, 0.05 mmol) and 1 equiv of 30% H_2O_2 (113 mg, 1.00 mmol) at room temperature for 24 h gave sulfoxide **2** (124 mg, 0.64 mmol) and sulfone **3** (41 mg, 0.20 mmol) in 64% and 20% yield, respectively. While, use of 3 equiv of 30% H_2O_2 (339 mg, 3.00 mmol) at room temperature for 24 h gave sulfoxide **2** (120 mg, 0.62 mmol) and sulfone **3** (54 mg, 0.26 mmol) in 62% and 26% yield, respectively.

By $MeReO_3$. The reaction using $MeReO_3$ catalyst (12 mg, 0.05 mmol) and 1 equiv of 30% H_2O_2 (113 mg, 1.00 mmol) at 0 °C for 1 h gave sulfoxide **2** (136 mg, 0.70 mmol) and sulfone **3** (29 mg, 0.14 mmol) in 70% and 14% yield, respectively. While, use of 3 equiv of 30% H_2O_2 (339 mg, 3.00 mmol) at room temperature for 2 h gave sulfone **3** (59 mg, 0.28 mmol) and epoxysulfone **4** (92 mg, 0.41 mmol) in 28% and 41% yield, respectively.

By V_2O_5. The reaction using V_2O_5 catalyst (9 mg, 0.05 mmol) and 1 equiv of 30% H_2O_2 (113 mg, 1.00 mmol) at 0 °C for 1 h gave sulfoxide **2** (144 mg, 0.74 mmol) and sulfone **3** (27 mg, 0.13 mmol) in 74% and 13% yield, respectively. While, use of 3 equiv of 30% H_2O_2 (339 mg, 3.00 mmol) at room temperature for 3 h gave sulfone **3** (172 mg, 0.82 mmol) in 82% yield as a single product.

By Na_2WO_4. The reaction using Na_2WO_4 catalyst (17 mg, 0.05 mmol) and 1 equiv of 30% H_2O_2 (113 mg, 1.00 mmol) at 0 °C for 4 h and then room temperature for 1 h gave sulfoxide **2** (124 mg, 0.64 mmol) and sulfone **3** (48 mg, 0.23 mmol) in 64% and 23% yield, respectively. While, use of 3 equiv of 30% H_2O_2 (339 mg, 3.00 mmol) at room temperature for 1 h gave sulfone **3** (179 mg, 0.85 mmol) in 85% yield as a single product.

Oxidation of Phenyl 3,7,11-Trimethyl-2,4,6,10-dodecatetraenyl Sulfide (5): Preparation of Sulfide 6 or Sulfone 7. General Procedure for Oxidation of Sulfide 5 by Metal or Nonmetal Oxide Catalyst−H_2O_2 Oxidant. To a stirred solution of sulfide **5** (67 mg, 0.20 mmol), a mixture of stereoisomers (2.5:1, trans:cis at C-2) in CH_3OH (1.5 mL) and benzene (0.5 mL) were consecutively added the catalyst (0.05 equiv, 0.01 mmol) and 1 equiv or 2 equiv of 30% aqueous solution of H_2O_2 (0.20 or 0.40 mmol) at 0 °C or at room temperature. The reaction mixture was stirred at 0 °C or at room temperature for the specified amounts of time. The mixture was then concentrated under reduced pressure. The crude product was purified by SiO_2 flash chromatography to give sulfoxide **6** or sulfone **7**. The stereoisomers (2.5:1, trans:cis at C-2) were separable after oxidation to sulfone **7**. In all of the cases, an appreciable amount of side products that are believed to be epoxidation products was obtained. These side products were hardly separable and were not identified.

By Nb_2O_5. The reaction using Nb_2O_5 catalyst (3 mg, 0.01 mmol) and 1 equiv of 30% H_2O_2 (23 mg, 0.20 mmol) at room temperature for 4 h gave sulfoxide **6** (21 mg, 0.06 mmol) and sulfone **7** (10 mg, 0.028 mmol) in 30% and 14% yield, respectively. While, use of 2 equiv of 30% H_2O_2 (46 mg, 0.40 mmol) at 0 °C for 2 h and then at room temperature for 22 h gave sulfoxide **6** (12 mg, 0.034 mmol) and sulfone **7** (16 mg, 0.046 mmol) in 17% and 23% yield, respectively. Data for **6** (major trans isomer): ^{1}H NMR δ 1.59 (3H, s), 1.63 (3H, s), 1.70 (3H, s), 1.81 (3H, s), 2.12 (4H, br s), 3.71 (1H, d of A of ABq, $J_{\mathrm{d}} = 8.6$, $J_{\mathrm{AB}} = 12.8$ Hz), 3.78 (1H, d of B of ABq, $J_{\mathrm{d}} = 8.2$, $J_{\mathrm{AB}} = 12.8$ Hz), 5.13 (1H, br s), 5.29 (1H, t, $J = 8.4$ Hz), 5.90 (1H, d, $J = 10.9$ Hz), 6.14 (1H, d, $J = 15.2$ Hz), 6.44 (1H, dd, $J = 15.2$, 10.9 Hz), 7.47−7.55 (3H, m), 7.57−7.65 (2H, m) ppm; ^{13}C NMR δ 12.5, 16.8, 17.6, 25.6, 26.5, 40.0, 57.2, 115.8, 123.7, 124.3, 124.8, 125.9, 128.0, 128.9, 131.0, 131.7, 133.5, 140.6, 142.5 ppm; IR (KBr) 1444, 1047 cm^{-1}; HRMS (CI^{+}) calcd for $C_{21}H_{29}OS$ 329.1939, found 329.1949. Data for **7** (trans at C-2): ^{1}H NMR δ 1.60 (3H, s), 1.68 (3H, s), 1.71 (3H, s), 1.78 (3H, s), 2.09 (4H, br s), 3.67 (2H, d, $J = 8.0$ Hz), 5.10 (1H, br s), 5.57 (1H, t, $J = 8.0$ Hz), 5.89 (1H, d, $J = 11.0$ Hz), 6.16 (1H, d, $J = 15.2$ Hz), 6.40 (1H, dd, $J = 15.2$, 11.0 Hz), 7.12−7.44 (5H, m); ^{13}C NMR δ 12.2, 16.8, 17.5, 25.5, 26.4, 39.9, 56.5, 114.7, 123.6, 124.7, 126.4, 128.3, 128.9, 131.6, 133.1, 133.5, 138.5, 140.9, 142.7 ppm; IR (KBr) 1307, 1151 cm^{-1}; HRMS (FAB^{+}) calcd for $C_{21}H_{29}O_2S$ 345.1888, found 345.1893. Data for **7** (cis at C-2) ^{1}H NMR δ 1.60 (3H, s), 1.68 (3H, s), 1.79 (3H, s), 1.88 (3H, s), 2.10 (4H, br s), 3.73 (2H, d, $J = 7.9$ Hz), 5.10 (1H, br s), 5.44 (1H, t, $J = 7.9$ Hz), 5.93 (1H, d, $J = 11.5$ Hz), 6.16 (1H, d, $J = 15.2$ Hz), 6.47 (1H, dd, $J = 15.2$, 11.0 Hz), 7.12−7.44 (5H, m) ppm; ^{13}C NMR d16.9, 17.7, 20.6, 25.7, 26.5, 40.1, 55.5, 112.8, 123.7, 124.9, 125.1, 128.4, 128.9, 129.2, 131.7, 133.6, 138.6, 141.4, 141.6 ppm; IR (KBr) 1307, 1151 cm^{-1}; HRMS (FAB^{+}) calcd for $C_{21}H_{29}O_2S$ 345.1888, found 345.1893.

By MoO_3. The reaction using MoO_3 catalyst (1.4 mg, 0.01 mmol) and 1 equiv of 30% H_2O_2 (23 mg, 0.20 mmol) at room temperature for 18 h gave sulfoxide **6** (18 mg, 0.05 mmol) and sulfone **7** (4.3 mg, 0.012 mmol) in 25% and 6% yield, respectively. While, use of 2 equiv of 30% H_2O_2 (46 mg, 0.40 mmol) at 0 °C for 2 h and then at room temperature for 22 h gave sulfoxide **6** (6.4 mg, 0.019 mmol) and sulfone **7** (10.4 mg, 0.030 mmol) in 9% and 15% yield, respectively.

By $MeReO_3$. The reaction using $MeReO_3$ catalyst (2.4 mg, 0.0096 mmol) and 1 equiv of 30% H_2O_2 (23 mg, 0.20 mmol) at room temperature for 0.5 h gave sulfoxide **6** (19 mg, 0.056 mmol) and sulfone **7** (7.2 mg, 0.020 mmol) in 26% and 10%

yield, respectively. While, use of 2 equiv of 30% H_2O_2 (46 mg, 0.40 mmol) at 0 °C for 0.5 h and then at room temperature for 0.5 h gave sulfoxide **6** (9.5 mg, 0.028 mmol) and sulfone **7** (10.4 mg, 0.030 mmol) in 14% and 15% yield, respectively.

By Na_2WO_4. The reaction using Na_2WO_4 catalyst (3.4 mg, 0.010 mmol) and 1 equiv of 30% H_2O_2 (23 mg, 0.20 mmol) at room temperature for 0.5 h gave sulfoxide **6** (30 mg, 0.09 mmol) and sulfone **7** (19.3 mg, 0.055 mmol) in 43% and 27% yield, respectively. While, use of 2 equiv of 30% H_2O_2 (46 mg, 0.40 mmol) at 0 °C for 1 h and then at room temperature for 1 h gave sulfoxide **6** (21 mg, 0.063 mmol) and sulfone **7** (35 mg, 0.01 mmol) in 30% and 50% yield, respectively.

By V_2O_5. The reaction using V_2O_5 catalyst (2 mg, 0.01 mmol) and 1 equiv of 30% H_2O_2 (23 mg, 0.20 mmol) at room temperature for 1 h gave sulfoxide **6** (39 mg, 0.12 mmol) and sulfone **7** (3 mg, 0.01 mmol) in 56% and 4% yield, respectively. While, use of 2 equiv of 30% H_2O_2 (46 mg, 0.40 mmol) at 0 °C for 2 h and then at room temperature for 2 h gave sulfoxide **6** (8 mg, 0.023 mmol) and sulfone **7** (6 mg, 0.02 mmol) in 11% and 9% yield, respectively.

By SeO_2. The reaction using SeO_2 catalyst (1 mg, 0.01 mmol) and 1 equiv of 30% H_2O_2 (23 mg, 0.20 mmol) at room temperature for 18 h gave sulfoxide **6** (18 mg, 0.054 mmol) in 26% yield. While, use of 2 equiv of 30% H_2O_2 (46 mg, 0.40 mmol) at 0 °C for 2 h and then at room temperature for 22 h gave sulfoxide **6** (7 mg, 0.021 mmol) and sulfone **7** (8 mg, 0.024 mmol) in 10% and 12% yield, respectively.

By TPAP/NMO. The oxidation of sulfide **5** (156 mg, 0.50 mmol) using TPAP catalyst (9 mg, 0.025 mmol) and 1 equiv of NMO (59 mg, 0.50 mmol) oxidant in CH_3CN (2.5 mL) with 4 Å molecular sieve (50 mg) at 40 °C for 22 h gave sulfoxide **6** (7 mg, 0.02 mmol) and sulfone **7** (12 mg, 0.035 mmol) in 4% and 7% yield, respectively, while use of 2 equiv of NMO (117 mg, 1.00 mmol) oxidant at 40 °C for 22 h gave sulfoxide **6** (17 mg, 0.05 mmol) and sulfone **7** (20 mg, 0.06 mmol) in 10% and 12% yield, respectively.

By MCPBA. The reaction of sulfide **5** (67 mg, 0.20 mmol) in CH_2Cl_2 (2 mL) with ~70% MCPBA (49 mg, 0.20 mmol) at room temperature for 1 h gave sulfoxide **6** (56 mg, 0.17 mmol) and sulfone **7** (1.4 mg, 0.004 mmol) in 79% and 2% yield, respectively, while use of 2 equiv of ~70% MCPBA (98 mg, 0.40 mmol) at 0 °C for 0.5 h and then room temperature for 0.5 h gave sulfoxide **6** (15 mg, 0.044 mmol) and sulfone **7** (25 mg, 0.07 mmol) in 21% and 35% yield, respectively.

General Procedure for Chemoselective Oxidation of Various Sulfides by $LiNbMoO_6$ Catalyst−H_2O_2 Oxidant: To Sulfoxides. To a stirred solution of allylic sulfide (1 equiv) in methanol (and benzene in some cases) at 0 °C were added $LiNbMoO_6$ (0.05 equiv) and ~30% aqueous solution of hydrogen peroxide (1 equiv). After stirring the resultant mixture at 0 °C for a specified amount of time, the solvent was removed by evaporation under reduced pressure. Thus obtained crude product was purified by silica gel column chromatography to give allylic sulfoxide. Small amount of allylic sulfone was also obtained. **To Sulfones.** To a stirred solution of allylic sulfide (1 equiv) in methanol (and benzene in some cases) at 0 °C were added $LiNbMoO_6$ (0.05 equiv) and ~30% aqueous solution of hydrogen peroxide (3 equiv). After stirring the resultant mixture at room temperature for a specified duration, chloroform was added, and the mixture was well washed with distilled water, dried over anhydrous Na_2SO_4, and filtered. After removing the solvent under reduced pressure, the crude product was purified by silica gel column chromatography to give allylic sulfones.

Oxidation of Phenyl Prenyl Sulfide (1): Preparation of Sulfoxide 2. Phenyl prenyl sulfide (**1**) (0.71 g, 4.00 mmol) was reacted with $LiNbMoO_6$ (58 mg, 0.20 mmol) and 30% aqueous H_2O_2 solution (454 mg, 4.00 mmol) in CH_3OH (20 mL) at 0 °C for 4 h to give sulfoxide **2** (0.60 g, 3.10 mmol, yield: 77%). Sulfone **3** (0.12 g, yield: 14%) was also obtained. **Preparation of Sulfone 3.** Phenyl prenyl sulfide (**1**) (0.60 g, 3.30 mmol) was reacted with $LiNbMoO_6$ (49 mg, 0.20 mmol) and 30% aqueous H_2O_2 solution (1.13 g, 10.0 mmol) in CH_3OH (20 mL) at room temperature for 4 h to give sulfone **3** (0.56 g, 2.70 mmol, yield: 82%).

Oxidation of Phenyl 3,7,11-Trimethyl-2,4,6,10-dodecatetraenyl Sulfide (5): Preparation of Sulfoxide 6. Phenyl 3,7,11-trimethyl-2,4,6,10-dodecatetraenyl sulfide (**5**) having trans/cis ratio (on the double bond of C-2) of about 2.5:1 (156 mg, 0.50 mmol) was reacted with $LiNbMoO_6$ (7 mg, 0.025 mmol) and 34% aqueous H_2O_2 solution (50 μL, 0.50 mmol) in a mixture of methanol (2.0 mL) and benzene (0.5 mL) at 0 °C to room temperature for 2.5 h to give sulfoxide **6** having trans/cis ratio (on the double bond of C-2) of about 2.5:1 (131 mg, 0.40 mmol, yield: 80%). Sulfone **7** (7 mg, 0.02 mmol, yield: 4%) was also obtained. **Preparation of Sulfone 7.** Phenyl 3,7,11-trimethyl-2,4,6,10-dodecatetraenyl sulfide (**5**) having trans/cis ratio (on the double bond of C-2) of about 2.5:1 (16 g, 51.5 mmol) was reacted with $LiNbMoO_6$ (301 mg, 1.03 mmol) and 35% aqueous H_2O_2 solution (12.5 g, 0.13 mol) in a mixture of benzene (30 mL) and methanol (70 mL) at 0 °C to 25 °C for 6 h to give sulfone **7** (13.7 g, 39.8 mmol, yield: 77%). The sulfone had trans/cis ratio (on the double bond of C-2) of about 2.5:1, and the trans- and cis-isomers were separated by column chromatography.

Oxidation of Geranyl Phenyl Sulfide (8):[23] Preparation of Sulfoxide 9.[24] Geranyl phenyl sulfide (**8**) (123 mg, 0.50 mmol) was reacted with $LiNbMoO_6$ (7 mg, 0.05 mmol) and 34% aqueous H_2O_2 solution (50 mg, 0.50 mmol) in methanol (2.5 mL) at 0 °C for 1 h to give sulfoxide **9** (102 mg, 0.39 mmol, yield: 78%). Sulfone **10** (19 mg, 0.07 mmol, yield: 14%) was also obtained. **Preparation of Sulfone 10.[25]** Geranyl phenyl sulfide (**8**) (2.80 g, 11.4 mmol) was reacted with $LiNbMoO_6$ (0.17 g, 0.60 mmol) and 30% aqueous H_2O_2 solution (3.86 g, 34.1 mmol) in methanol (45 mL) at room temperature for 4 h to give sulfone **10** (2.68 g, 9.60 mmol, yield: 85%).

Oxidation of 4-Hydroxy-3-methyl-2-butenyl Phenyl Sulfide (11):[26] Preparation of Sulfoxide 12.[27] 4-Hydroxyprenyl phenyl sulfide (**11**) (97 mg, 0.50 mmol) was reacted with $LiNbMoO_6$ (7 mg, 0.05 mmol) and 34% aqueous H_2O_2 solution (50 mg, 0.50 mmol) in methanol (2.5 mL) at 0 °C for 1 h to give sulfoxide **12** (79 mg, 0.38 mmol, yield: 75%). At the same time, sulfone **13** (14 mg, 0.06 mmol, yield: 12%) was also obtained. **Preparation of Sulfone 13.** 4-Hydroxyprenyl phenyl sulfide (**11**) (600 mg, 3.20 mmol) was reacted with $LiNbMoO_6$ (46 mg, 0.20 mmol) and 30% aqueous H_2O_2 solution (960 mg, 9.50 mmol) in methanol (15 mL) at room temperature for 4 h to give sulfone **13** (670 mg, 3.00 mmol, yield: 95%). Data for **13**: ^1H NMR δ 1.34 (3H, s), 2.92 (1H, br s), 3.86 (2H, d, $J = 8.1$ Hz), 3.96 (2H, s), 5.52 (1H, t, $J = 8.1$ Hz), 7.31−7.89 (5H, m) ppm; ^{13}C NMR δ 13.4, 55.4, 66.9, 109.5, 128.1, 129.6, 133.7, 138.2, 145.6 ppm; IR (KBr) 3511, 1447, 1304, 1149 cm^{-1}; HRMS (CI$^+$) calcd for $C_{11}H_{15}O_3S$ 227.0743, found 227.0749.

Oxidation of 4-Formyl-3-methyl-2-butenyl Phenyl Sulfide (14):[28] Preparation of Sulfoxide 15. Formylprenyl phenyl sulfide **14** (192 mg, 1.00 mmol) was reacted with $LiNbMoO_6$ (15 mg, 0.10 mmol) and 35% aqueous H_2O_2 solution (98 mg, 1.00 mmol) in methanol (5 mL) at 0 °C for 5 h to give sulfoxide **15** (175 mg, 0.84 mmol, yield: 84%). At the same time, sulfone **16** (23 mg, 0.10 mmol, yield: 10%) was also obtained. **Preparation of Sulfone 16.[29]** Formylprenyl phenyl sulfide **14** (192 mg, 1.00 mmol) was reacted with $LiNbMoO_6$ (15 mg, 0.10 mmol) and 35% aqueous H_2O_2 solution (294 mg, 3.00 mmol) in methanol (5 mL) at room temperature for 18 h to give sulfone **16** (184 mg, 0.82 mmol, yield: 82%). In these

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cases, acid workup was required to convert some acetal formed by the reaction with MeOH into the formyl group again. Data for **15**: ^{1}H NMR δ 1.39 (3H, s), 3.65 (1H, d of A of ABq, $J_d = 8.4$, $J_{AB} = 13.1$ Hz), 3.87 (1H, d of B of ABq, $J_d = 7.7$, $J_{AB} = 13.1$ Hz), 6.28 (1H, dd, $J = 7.7$, 8.4 Hz), 7.38–7.50 (5H, m), 9.26 (1H, s) ppm; ^{13}C NMR δ 9.1, 55.2, 123.6, 128.9, 131.1, 138.0, 142.0, 144.7, 193.3 ppm; IR (KBr) 1688, 1443, 1307 cm^{-1}; HRMS (CI$^+$) calcd for $C_{11}H_{13}O_2S$ 209.0636, found 209.0635.

Oxidation of 4-Hydroxy-3-methyl-2-butenyl Phenyl Sulfide, Tetrahydropyranyl Ether (17). Preparation of Sulfoxide 18. THP ether of hydroxyprenyl phenyl sulfide **17** (278 mg, 1.00 mmol) was reacted with $LiNbMoO_6$ (15 mg, 0.10 mmol) and 35% aqueous H_2O_2 solution (98 mg, 1.00 mmol) in methanol (5 mL) at 0 °C for 3 h to give sulfoxide **18** (241 mg, 0.82 mmol, yield: 82%). At the same time, sulfone **19** (37 mg, 0.12 mmol, yield: 12%) was also obtained. **Preparation of Sulfone 19.** THP ether of hydroxyprenyl phenyl sulfide **17** (278 mg, 1.00 mmol) was reacted with $LiNbMoO_6$ (15 mg, 0.10 mmol) and 35% aqueous H_2O_2 solution (294 mg, 3.00 mmol) in methanol (5 mL) at room temperature for 18 h to give sulfone **19** (264 mg, 0.85 mmol, yield: 85%). Data for **18**: ^{1}H NMR δ 1.45 (3H, s), 1.44–1.86 (6H, m), 3.43–3.54 (1H, m), 3.62 (2H, d, $J = 8.1$ Hz), 3.75–3.89 (1H, m), 3.84 (1H, A of ABq, $J_{AB} = 13.0$ Hz), 4.07 (1H, B of ABq, $J_{AB} = 13.0$ Hz), 4.55 (1H, dt, $J_d = 3.5$, $J_t = 3.4$ Hz), 5.39 (1H, t, $J = 8.1$ Hz), 7.39–7.86 (5H, m) ppm; ^{13}C NMR δ 13.8, 18.9, 25.0, 30.1, 55.5, 61.6, 70.9, 97.2, 112.1, 124.0, 128.5, 130.6, 141.6, 142.9 ppm; IR (KBr) 1443, 1037 cm^{-1}; HRMS (CI$^+$) calcd for $C_{16}H_{23}O_3S$ 295.1368, found 295.1371. Data for **19**: ^{1}H NMR δ 1.36 (3H, s), 1.45–1.86 (6H, m), 3.45–3.55 (1H, m), 3.70–3.84 (1H, m), 3.83 (1H, A of ABq, $J_{AB} = 13.6$ Hz), 3.87 (2H, d, $J = 8.0$ Hz), 4.06 (1H, B of ABq, $J_{AB} = 13.6$ Hz), 4.54 (1H, dd, $J = 3.5$, 3.1 Hz), 5.50 (1H, t, $J = 8.0$ Hz), 7.48–7.89 (5H, m) ppm; ^{13}C NMR δ 13.7, 19.1, 25.2, 30.3, 55.5, 61.9, 70.8, 97.5, 111.6, 128.2, 128.9, 133.5, 138.4, 142.5 ppm; IR (KBr) 1447, 1307, 1152 cm^{-1}; HRMS (CI$^+$) calcd for $C_{16}H_{23}O_4S$ 311.1317, found 311.1317.

Oxidation of 4-Hydroxy-3-methyl-2-butenyl Phenyl Sulfide, *tert*-Butyldimethylsilyl Ether (20): Preparation of Sulfoxide 21. TBDMS ether of hydroxyprenyl phenyl sulfide **20** (309 mg, 1.00 mmol) was reacted with $LiNbMoO_6$ (15 mg, 0.10 mmol) and 35% aqueous H_2O_2 solution (98 mg, 1.00 mmol) in methanol (5 mL) at 0 °C for 3 h to give sulfoxide **21** (260 mg, 0.80 mmol, yield: 80%). At the same time, sulfone **22** (31 mg, 0.09 mmol, yield: 9%) was also obtained. **Preparation of Sulfone 22.** TBDMS ether of hydroxyprenyl phenyl sulfide **20** (309 mg, 1.00 mmol) was reacted with $LiNbMoO_6$ (15 mg, 0.10 mmol) and 35% aqueous H_2O_2 solution (294 mg, 3.00 mmol) in methanol (5 mL) at room temperature for 18 h to give sulfone **22** (272 mg, 0.80 mmol, yield: 80%). Data for **21**: ^{1}H NMR δ 0.03 (6H, s), 0.89 (9H, s), 1.42 (3H, s), 3.58 (1H, d of A of ABq, $J_d = 8.4$, $J_{AB} = 12.5$ Hz), 3.66 (1H, d of B of ABq, $J_d = 8.4$, $J_{AB} = 12.5$ Hz), 3.99 (2H, s), 5.35 (1H, t, $J = 8.4$ Hz), 7.47–7.63 (5H, m) ppm; ^{13}C NMR δ −5.6, 13.5, 18.1, 25.7, 55.8, 67.0, 109.5, 124.3, 128.7, 130.8, 143.1, 144.1 ppm; IR (KBr) 1443, 1048 cm^{-1}; HRMS (CI$^+$) calcd for $C_{17}H_{29}O_2SSi$ 325.1657, found 325.1662. Data for **22**: ^{1}H NMR δ 0.04 (6H, s), 0.89 (9H, s), 1.56 (3H, s), 3.85 (2H, d, $J = 8.2$ Hz), 3.96 (2H, s), 5.35 (1H, t, $J = 8.2$ Hz), 7.43–7.93 (5H, m) ppm; ^{13}C NMR δ −5.6, 13.2, 18.1, 25.7, 55.4, 66.8, 109.0, 128.3, 128.8, 133.4, 138.5, 144.7 ppm; IR (KBr) 1447, 1307, 1152 cm^{-1}; HRMS (CI$^+$) calcd for $C_{17}H_{29}O_4SSi$ 341.1606, found 341.1607.

Oxidation of Benzyl Phenyl Sulfide (23):[30] **Preparation of Sulfoxide 24.**[31] Benzyl phenyl sulfide (**23**) (100 mg, 0.50 mmol) was reacted with $LiNbMoO_6$ (7.3 mg, 0.05 mmol) and 34% aqueous H_2O_2 solution (50 mg, 0.50 mmol) in methanol (2.5 mL) at 0 °C for 1 h to give sulfoxide **24** (102 mg, 0.47 mmol, yield: 94%). Sulfone **25** (3 mg, 0.01 mmol, yield: 3%) was also obtained. **Preparation of Sulfone 25.**[32] Benzyl phenyl sulfide (**23**) (2.00 g, 10.0 mmol) was reacted with $LiNbMoO_6$ (0.15 mg, 0.50 mmol) and 30% aqueous H_2O_2 solution (3.40 g, 30.0 mmol) in methanol (50 mL) at room temperature for 4 h to give sulfone **25** (2.27 g, 9.80 mmol, yield: 98%).

Oxidation of Phenyl Propargyl Sulfide (26): [33] **Preparation of Sulfoxide 27.**[34] Phenyl propargyl sulfide (**26**) (74 mg, 0.50 mmol) was reacted with $LiNbMoO_6$ (7.3 mg, 0.05 mmol) and 34% aqueous H_2O_2 solution (50 mg, 0.50 mmol) in methanol (2.5 mL) at 0 °C for 1 h to give sulfoxide **27** (76 mg, 0.46 mmol, yield: 93%). Sulfone **28** (5 mg, 0.03 mmol, yield: 6%) was also obtained. **Preparation of Sulfone 28.**[35] Phenyl propargyl sulfide (**26**) (1.58 g, 10.7 mmol) was reacted with $LiNbMoO_6$ (0.16 g, 0.50 mmol) and 30% aqueous H_2O_2 solution (3.60 g, 32.0 mmol) in methanol (50 mL) at room temperature for 4 h to give sulfone **28** (1.62 g, 9.00 mmol, yield: 84%).

Oxidation of Diprenyl Sulfide (29):[36] **Preparation of Sulfoxide 30.**[37] Diprenyl sulfide (**29**) (85 mg, 0.50 mmol) was reacted with $LiNbMoO_6$ (7.3 mg, 0.05 mmol) and 34% aqueous H_2O_2 solution (50 mg, 0.50 mmol) in methanol (2.5 mL) at 0 °C for 1 h to give sulfoxide **30** (50 mg, 0.27 mmol, yield: 54%). Sulfone **31** (108 mg, 0.53 mmol, yield: 6%) was also obtained. **Preparation of Sulfone 31.**[38] Diprenyl sulfide (**29**) (0.60 g, 3.50 mmol) was reacted with $LiNbMoO_6$ (51 mg, 0.20 mmol) and 30% aqueous H_2O_2 solution (1.00 g, 10.1 mmol) in methanol (18 mL) at room temperature for 4 h to give sulfone **31** (0.43 g, 2.10 mmol, yield: 71%).

Oxidation of Digeranyl Sulfide (32):[39] **Preparation of Sulfoxide 33.**[40] Digeranyl sulfide (**32**) (153 mg, 0.50 mmol) was reacted with $LiNbMoO_6$ (7.3 mg, 0.05 mmol) and 34% aqueous H_2O_2 solution (50 mg, 0.50 mmol) in methanol (2.5 mL) at 0 °C for 1 h to give sulfoxide **33** (77 mg, 0.24 mmol, yield: 48%). Sulfone **34** (12 mg, 0.04 mmol, yield: 7%) was also obtained. **Preparation of Sulfone 34.**[38] Digeranyl sulfide (**32**) (3.57 g, 11.7 mmol) was reacted with $LiNbMoO_6$ (0.17 g, 0.60 mmol) and 30% aqueous H_2O_2 solution (3.96 g, 35.0 mmol) in methanol (40 mL) at room temperature for 4 h to give sulfone **34** (2.84 g, 8.40 mmol, yield: 72%).

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