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Published on Web 03/26/2003

Highly Regio- and Stereoselective Halohydroxylation Reaction of 1,2-Allenyl Phenyl Sulfoxides. Reaction Scope, Mechanism, and the Corresponding Pd- or Ni-Catalyzed Selective Coupling Reactions

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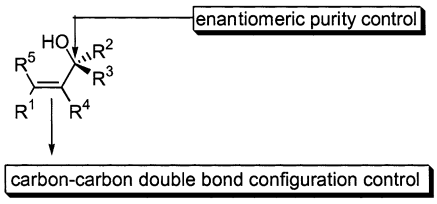
Abstract: A highly regio- and stereoselective halohydroxylation of 1,2-allenyl sulfoxides with X^+ and water was developed. The reaction shows *E*-stereoselectivity. In the iodohydroxylation reaction, I_2 was used to introduce the iodine atom. For bromohalohydroxylation, $CuBr_2$, NBS, or Br_2 can be used. When using I_2, NBS, or Br_2, the addition of $LiOAc\cdot 2H_2O$ is necessary for high yields of the halohydroxylation products. The chlorohydroxylation reaction was preformed by milling 1,2-allenyl sulfoxides and $CuCl_2\cdot 2H_2O$ with silica gel. Under the catalysis of a Pd(0) complex, the halohydroxylation products, that is, *E*-2-halo-1-phenylsulfinyl-1-alken-3-ols, can undergo Sonogashira, Suzuki, and Negishi cross-coupling reactions leading to *Z*-2-substituted-1-phenylsulfonyl-1-alken-3-ols. The C−S bond of the coupling product may undergo a further coupling reaction with organozincs under the catalysis of an Ni catalyst. Here, the presence of a hydroxyl group is important for a smooth coupling involving the C−S bond. Thus, optically active stereodefined multisubstituted allylic alcohols can be prepared by the reaction of the easily available optically active propargylic alcohols with sulfinyl chloride followed by *E*-halohydroxylation and a selective Pd- or Ni-coupling reaction.

Introduction

Stereodefined allylic alcohols are a class of compounds with important synthetic potentials due to the presence of the hydroxy group and carbon−carbon double bond. For their synthesis, there are two challenges: (1) the control of the configuration of the carbon−carbon double bonds and (2) the highly stereoselective establishment of the chiral centers adjacent to the hydroxy group (Scheme 1).[1] Here, stereoselective halohydroxylation[2] of 1,2-allenyl sulfoxides was applied for such a purpose.

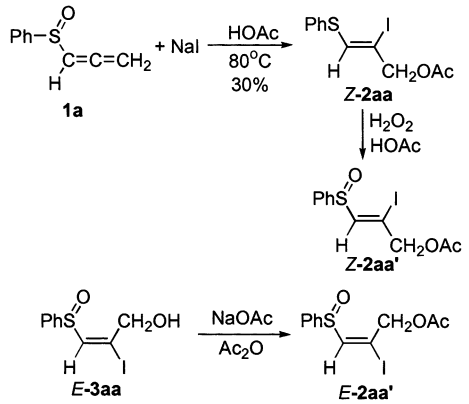
Recently, during the course of our systematic study of allene chemistry,[3] we observed that the hydrohalogenation[4] of 1,2-allenyl sulfones[5] occurred smoothly with metallic halides, while the corresponding reaction of 1,2-allenyl sulfoxides must be mediated by certain Al(III) species.[6] The simple reaction of 1,2-propadienyl phenyl sulfoxide (**1a**) with NaI in HOAc at 80 °C afforded 3-thiophenyl-2-iodo-2(*Z*)-propenyl acetate in 30% yield, which can be further oxidized with H_2O_2/HOAc to afford the corresponding sulfoxide *Z*-**2aa′**. The stereoselectivity was established by the NOE study and the comparison with its *E*-isomer, which was synthesized via the esterification of corresponding *E*-**3aa** (Scheme 2).

Scheme 1

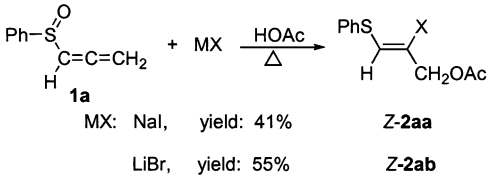


(1) Bianchini, J.-P.; Cocordano, M. *Tetrahedron* **1970**, *26*, 3401.
(2) (a) Cabanal-Duvillard, I.; Berrien, J.; Royer, J.; Husson, H. *Tetrahedron Lett.* **1998**, *39*, 5181. (b) Rossen, K.; Reamer, R. A.; Volante, R. P.; Reider, P. J. *Tetrahedron Lett.* **1996**, *37*, 6843. (c) Mevellec, L.; Evers, M.; Huet, F. *Tetrahedron* **1996**, *52*, 15103. (d) Crossley, M. J.; Davies, S. R.; Hambley, T. W. *Aust. J. Chem.* **1994**, *47*, 2221. (e) Sawyer, D. T.; Hage, J. P.; Sobkowiak, A. *J. Am. Chem. Soc.* **1995**, *117*, 106. (f) Hirosato, H.; Kondo, F.; Ichikawa, Y.; Look, G. C.; Wong, C. *J. Org. Chem.* **1992**, *57*, 7265. (g) Lai, J.; Wang, F.; Guo, G.; Dai, L. *J. Org. Chem.* **1993**, *58*, 6944. (h) Rodebaugh, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1994**, *116*, 3155. (i) Yamashita, M.; Iída, A.; Ikai, K.; Oshikawa, T.; Hanaya, T.; Yamamoto, H. *Chem. Lett.* **1992**, 407. (j) Miljkovic, D.; Djurendic, E.; Vukojevic, N.; Gasi, K.; Csanadi, J. *Carbohydr. Res.* **1992**, *233*, 251. (k) Kato, T.; Hirukawa, T.; Namiki, K. *Tetrahedron Lett.* **1992**, *33*, 1475.
(3) (a) Ma, S.; Shi, Z. *J. Org. Chem.* **1998**, *63*, 6387. (b) Ma, S.; Duan, D.; Shi, Z. *Org. Lett.* **2000**, *2*, 1419. (c) Ma, S.; Zhao, S. *J. Am. Chem. Soc.* **1999**, *121*, 7943. (d) Ma, S.; Shi, Z.; Yu, Z. *Tetrahedron Lett.* **1999**, *40*, 2393. (e) Ma, S.; Wu, S. *J. Org. Chem.* **1999**, *64*, 9314. (f) Ma, S.; Zhang, J. *Chem. Commun.* **2000**, 117. (g) Ma, S.; Li, L. *Org. Lett.* **2000**, *2*, 941. (h) Ma, S.; Wu, S. *Tetrahedron Lett.* **2001**, *42*, 4075. (i) Ma, S.; Shi, Z.; Wu, S. *Tetrahedron*: *Asymmetry* **2001**, *12*, 193. (j) Ma, S.; Zhao, S. *J. Am. Chem. Soc.* **2001**, *123*, 5578. (k) Ma, S.; Li, L. *Synlett* **2001**, 1206. (l) Ma, S.; Shi, Z. *Chem. Commun.* **2002**, 540. (m) Ma, S.; Yin, S.; Tan, F. *Org. Lett.* **2002**, *4*, 505. (n) Ma, S.; Jiao, N.; Zhao, S.; Hou, H. *J. Org. Chem.* **2002**, *67*, 2837. (o) Ma, S.; Duan, D.; Wang, Y. *J. Comb. Chem.* **2002**, *4*, 239−247. (p) Ma, S.; Yu, Z. *Angew. Chem., Int. Ed.* **2002**, 1775−1778.
(4) (a) Ma, S.; Li, L.; Xie, H. *J. Org. Chem.* **1999**, *64*, 5325. (b) Ma, S.; Shi, Z.; Li, L. *J. Org. Chem.* **1998**, *63*, 4522. (c) Ma, S.; Wang, G. *Chin. J. Chem.* **1999**, *17*, 545. (d) Ma, S.; Li, L.; Xie, H.; Wei, Q.; Wang, G.; Shi, Z.; Zhang, Z. *Pure Appl. Chem.* **2000**, *72*, 1739. (e) Ma, S.; Xie, H.; Wang, G.; Zhang, J.; Shi, Z. *Synthesis* **2001**, *5*, 713.
(5) Ma, S.; Wei, Q. *J. Org. Chem.* **1999**, *64*, 1026.
(6) Ma, S.; Wei, Q. *Eur. J. Org. Chem.* **2000**, 1939.

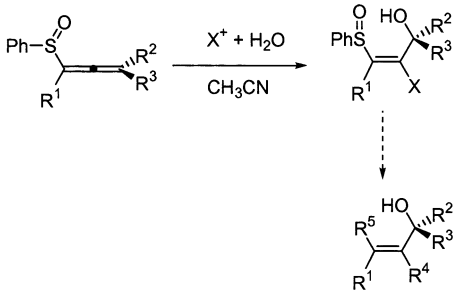
Scheme 2



Scheme 3



Scheme 4

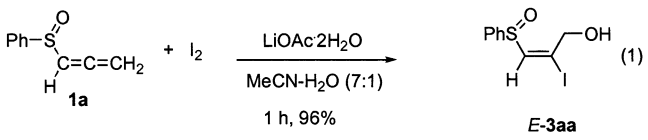


With anhydrous HOAc, the reaction of **1a** with NaI and LiBr afforded *Z*-**2aa** and *Z*-**2ab** exclusively in relatively higher yields, respectively (Scheme 3).

Furthermore, it is interesting to observe that the reaction of 1,2-allenyl phenyl sulfoxides with I_2 and H_2O in the presence of LiOAc·$2H_2O$ afforded the iodohydroxylation product *E*-2-iodo-3-(phenylsulfinyl)-2-propen-1-ols (Scheme 4).[7] We reasoned that this reaction may open up a new pathway for the highly stereoselective synthesis of substituted allylic alcohols (Scheme 4). In this paper, we wish to disclose our recent results on the scope, mechanism, and synthetic application of this reaction.

Results and Discussion

The iodohydroxylation reaction of 1,2-allenyl phenyl sulfoxide **1a** with I_2 and H_2O was carried out in MeCN−H_2O (7:1) to afford *E*-2-iodo-3-(phenylsulfinyl)-2-propen-1-ol (*E*-**3aa**) in high yield and stereoselectivity (eq 1).



The results in Table 1 show that the iodohydroxylation reactions of 1,2-allenyl phenyl sulfoxides with I_2 and H_2O was carried out in MeCN−H_2O (7:1) at room temperature affording *E*-iodo-3-(phenylsulfinyl)-2-alkenols in high yields and *E*-stereoselectivity. The stereoselectivity of the product was established by the X-ray diffraction study of *E*-**3aa** (Figure 1).[8] The iodohydroxylation reactions of aryl or alkyl substituted 1,2-allenic sulfoxides were faster than that of the unsubstituted **1a**, and the reactions finished in from 0.3 to 3.2 h at room temperature to give the corresponding products *E*-**3a** in high yields and excellent stereoselectivity (compare eq 1 with entries 1−11 of Table 1). Especially when the carbon atom of the 3-position of 1,2-allenic sulfoxides is substituted with two alkyl groups, the reaction is the quickest and requires only 0.3−0.5 h at room temperature (entries 5, 6, and 9, Table 1). The butyl and phenyl groups at the carbon atom of the 1-position of 1,2-allenic sulfoxides can also accelerate the reaction (entries 8−9, Table 1). When the carbon atom of the 3-position of 1,2-allenic sulfoxides is substituted with allyl or homoallylic groups, the iodohydroxylation occurs still in the β,γ-carbon−carbon double bond of the allene moiety (entries 10 and 11, Table 1, and Scheme 5), indicating a high chemoselectivity.

Generally speaking, the direct iodohydroxylation of carbon−

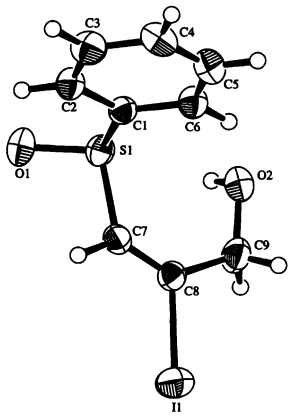
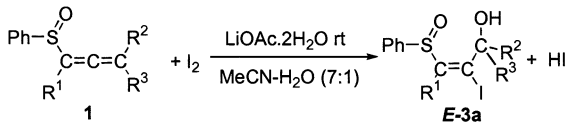


Figure 1. ORTEP representation of *E*-**3aa**.

Table 1. Reaction of 1,2-Allenic Sulfoxides with I_2/H_2O in Aqueous MeCN

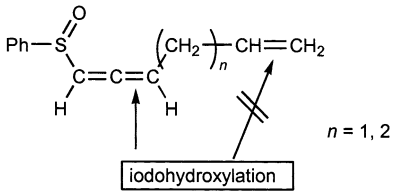


	1					
entry	R^1	R^2	R^3	I_2 (equiv)	time (h)	yield (%)
1	H	H	CH_3 (**1b**)	1.6	1.5	87 (*E*-**3ab**)
2	H	H	*n*-C_4H_9 (**1c**)	1.6	2	89 (*E*-**3ac**)
3	H	H	*n*-C_8H_{17} (**1d**)	1.6	1	89 (*E*-**3ad**)
4	H	H	*t*-C_4H_9 (**1e**)	1.2	3.2	87 (*E*-**3ae**)
5	H	CH_3	CH_3 (**1f**)	1.2	0.5	87 (*E*-**3af**)
6	H		$(CH_2)_5$ (**1g**)	1.2	0.3	74 (*E*-**3ag**)
7	*n*-C_4H_9	H	H (**1h**)	1.6	1.5	82 (*E*-**3ah**)
8	Ph	H	H (**1i**)	1.6	2.2	79 (*E*-**3ai**)
9	*n*-C_4H_9	CH_3	CH_3 (**1j**)	1.2	1.3	88 (*E*-**3aj**)
10	H	H	CH_2=$CHCH_2CH_2$ (**1k**)	1.6	1	82 (*E*-**3ak**)
11	H	H	CH_2=$CHCH_2$ (**1l**)	1.6	1	92 (*E*-**3al**)

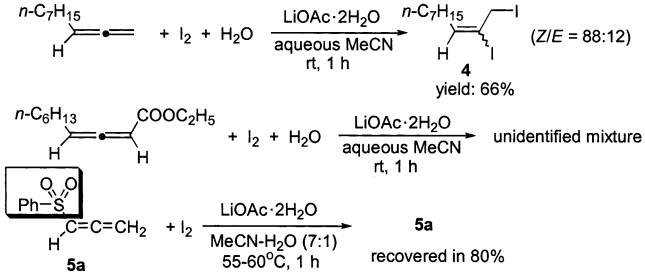
(7) Ma, S.; Wei, Q.; Wang, H. *Org. Lett.* **2000**, *2*, 3893.

(8) Crystal data of *E*-**3aa**: $C_9H_9IO_2S$, $M = 308.13$, colorless, prismatic, triclinic, space group *P*1 (#2), μ(Mo Kα) = 32.19 cm^{-1}, $R = 0.035$, $Rw = 0.049$, $a = 9.102(1)$, $b = 15.105(2)$, $c = 8.811(2)$ Å, $V = 1048.5(3)$ Å^3, $T = 20.0$ °C, $Z = 4$; no. of reflections measured, total 3875; no. observations ($I > 3.00\sigma(I)$), 3141; no. variables, 236. CCDC 192876.

Scheme 5

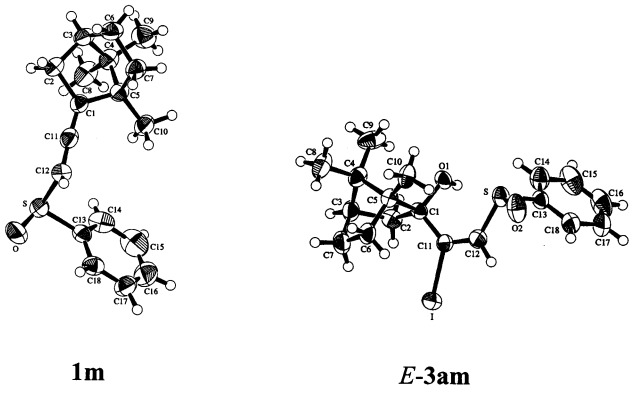


Scheme 6



carbon double bonds using I_2 and H_2O is difficult.[9] The reaction of alkyl substituted allenes or 2,3-allenoates with halogens was known to form dihalogenation products.[10] Even under the current reaction conditions for a halohydroxylation reaction, iodination product 1,2-diiodo-2-decene (**4**) with a *Z*/*E* ratio of 88:12 was formed (Scheme 6). It is interesting to observe that when 1,2-allenic sulfone **5a** was treated with iodine under the same conditions, no reaction was observed and 80% of the starting material was recovered, while under the same reaction conditions, 96% of iodohydroxylation product ***E*-3aa** from 1,2-allenic sulfoxide **1a** was obtained. The introduction of the sulfinyl group must be the key for the control of regio- and stereoselectivities.

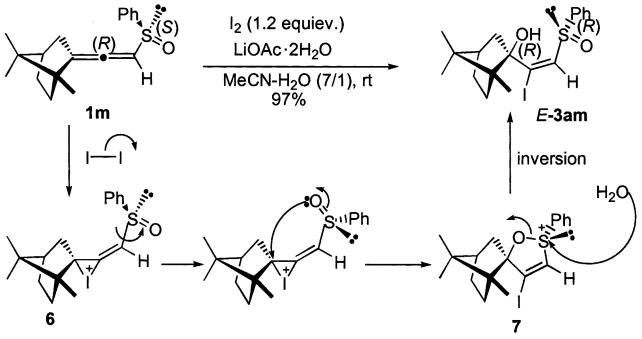
To study the mechanism of the iodohydroxylation reaction of 1,2-allenic sulfoxides, diastereoisomerically pure allenic sulfoxide (**1m**) was synthesized.[11] The structures of the optically active 1,2-allenyl sulfoxide **1m** and the corresponding iodohydroxylation product *E*-**3am** were identified respectively by means of X-ray diffraction studies, which showed that the configuration of the chiral sulfur centers in two compounds are just the opposite. The absolute configurations of **1m** and *E*-**3am** were determined based on the stereochemistry of the (+)-camphor part (Figure 2).[12]



1m *E*-**3am**

Figure 2.

Scheme 7



Based on these results, a mechanism involving the participation of the sulfinyl group is proposed. First, the reaction of the electron-rich carbon−carbon double bonds with I^+ forms iodonium intermediate **6**. Intramolecular attack of the sulfinyl oxygen at the 3-position affording a five-membered cyclic intermediate **7** accounts for the stereospecificity of this reaction. Subsequent hydrolysis of **7** afforded the product *E*-**3am** stereospecifically with the inversion of the chiral sulfur center (Scheme 7).

2,3-Allenic alcohols and 2,3-allenoic acid esters can react individually with halogens, and the hydroxyl group and carbonyl group participates the reactions as an intramolecular nucleophile.[13] To compare the participation ability of the sulfinyl group with that of these groups, we synthesized 1-hydroxymethyl-1,2-propadienyl sulfoxide **1n** and 1-(methoxycarbonyl)-3-methyl-1,2-butadienyl sulfoxide **1o**. The control experiment shows that the hydroxyl or carbonyl group did not participate in the iodohydroxylation reaction. The products of iodohydroxylation of the allene moiety were formed exclusively in high yields (Scheme 8), indicating that the sulfinyl group has a much stronger participation ability in these electrophilic addition reactions.

Bromohydroxylations of 1,2-Allenyl Sulfoxides.[14] When NBS was chosen as the halogen source, the bromohydroxylation reactions also proceeded smoothly at room temperature with good to excellent yields (entries 2, 3, and 5 of Table 2).

Recently, our group also developed a CuX_2-mediated halolactonization of 2,3-allenoic acids.[15] We tested the reaction of 1,2-

(9) (a) Asensio, G.; Andreu, C.; Boix-Bernardini, C.; Mello, R.; González-Nuñez, M. E. *Org. Lett.* **1999**, *1*, 2125. (b) Masuda, H.; Takase, K.; Nishio, M.; Hasegawa, A.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1994**, *59*, 5550. (c) Friesen, R. W.; Giroux, A. *Tetrahedron Lett.* **1993**, *34*, 1867. (d) Cambie, R. C.; Noall, W. I.; Potter, G. J.; Rutledge, P. S.; Woodgate, P. D. *J. Chem. Soc., Perkin Trans. 1* **1977**, 226. (e) Maligres, P. E.; Upadhyay, V.; Rossen, K.; Cianciosi, S. J.; Purick, R. M.; Eng, K. K.; Reamer, R. A.; Askin, D.; Volante, R. P.; Reider, P. J. *Tetrahedron Lett.* **1995**, *36*, 2195. (f) Dolenc, D. *Synlett* **2000**, 544.

(10) (a) Tendil, J.; Verny, M.; Vessiere, R. *Bull. Soc. Chim. Fr.* **1972**, 4027. (b) Natsias, K.; Hopf, H. *Tetrahedron Lett.* **1982**, *23*, 3673. (c) Georgoulis, C.; Smadja, W.; Valery, J. M. *Synthesis* **1981**, 572. (d) Coulomb, F.; Roumestant, M.; Gore, J. *Bull. Soc. Chim. Fr.* **1973**, 3352.

(11) Mattay, J.; Conrads, M.; Runsink, J. *Synthesis* **1988**, 595.

(12) Crystal data of **1m**: $C_{18}H_{22}OS$, M = 286.43, orthorhombic, space group $P2_12_12_1$ (#19), μ(MoKα) = 2.14 cm^{-1}, R = 0.044, Rw = 0.047, a = 10.705(4), b = 21.283(3), c = 6.981(3) Å, V = 1590(1) Å^3, T = 20.0 °C, Z = 4; no. of reflections measured, total 2122; no. observations ($I > 2.00\sigma(I)$), 1479; no. variables, 182. CCDC 192 875. Crystal data of ***E*-3am**: $C_{18}H_{23}OSI$, M = 430.34, prismatic, space group $P2_12_12_1$ (#19), μ(MoKα) = 18.70 cm^{-1}, R = 0.041, Rw = 0.049, a = 7.576(4), b = 37.003(7), c = 6.523(4) Å, V = 1828(1) Å^3, T = 20.0 °C, Z = 4; no. of reflections measured, total 2487; no. observations ($I > 2.00\sigma(I)$), 1953; no. variables, 200. CCDC 192 877. The supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1Ez, UK; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

(13) (a) Marshall, J. A.; Wang, X.-J. *J. Org. Chem.* **1990**, *55*, 2995. (b). Marshall, J. A.; Wang, X.-J. *J. Org. Chem.* **1991**, *56*, 4913. (b) Florio, S.; Ronzini, L.; Epifani, E.; Sgarra, R. *Tetrahedron* **1993**, *49*, 10413. (c) Gill, G. B.; Idris, M. S. H. *Tetrahedron Lett.* **1985**, *26*, 4811. (d) Marshall, J. A.; Wolf, M. A.; Wallace, E. M. *J. Org. Chem.* **1997**, *62*, 367.

(14) For a brief study of bromohydroxylation of 1,2-allenyl sulfoxides with Br_2, see: Horner, L.; Binder, V. *Liebigs Ann. Chem.* **1972**, *757*, 33.

Scheme 8

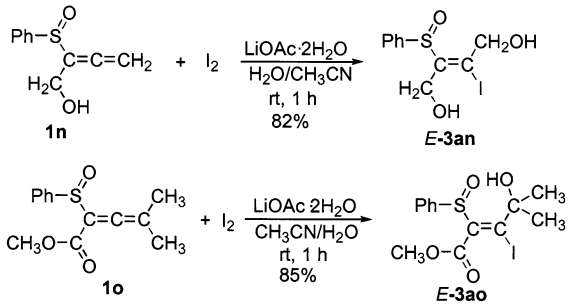
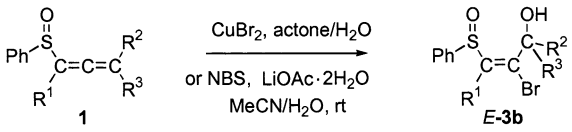
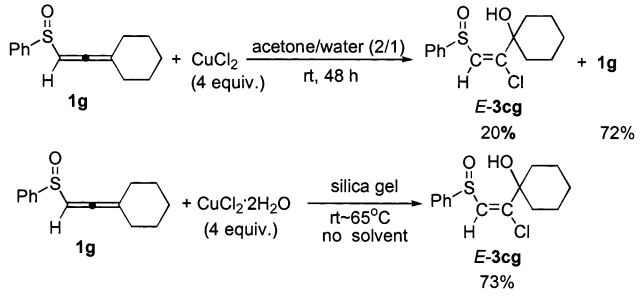


Table 2. Bromohydroxylation of 1,2-Allenic Sulfoxides with $CuBr_2$ or NBS



	1					
entry	R^1	R^2	R^3	reagent	time/temp (h/°C)	yield of *E*-**3b** (%)
1	H	H	H (**1a**)	$CuBr_2$	1.5/40−45	88 (*E*-**3ba**)
2	H	H	*n*-C_4H_9 (**1c**)	NBS	2	90 (*E*-**3bc**)
3	H	H	*n*-C_8H_{17} (**1d**)	NBS	2	98 (*E*-**3bd**)
4	H	H	*t*-C_4H_9 (**1e**)	$CuBr_2$	2.5	87 (*E*-**3be**)
5	H	CH_3	CH_3 (**1f**)	NBS	0.5	68 (*E*-**3bf**)
6	*n*-C_4H_9	H	H (**1h**)	$CuBr_2$	3.5	86 (*E*-**3bh**)
7	*n*-C_4H_9	CH_3	CH_3 (**1j**)	$CuBr_2$	1	92 (*E*-**3bj**)
8		**1m**		$CuBr_2$	1.5	95 (*E*-**3bm**)

Scheme 9

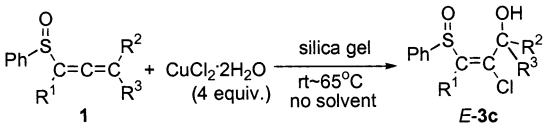


allenic sulfoxides with $CuBr_2$ in acetone/water and successfully obtained the bromohydroxylation products of 1,2-allenic sulfoxides with good yields and excellent stereoselectivity (entries 1, 4, and 6−8 of Table 2). The reaction can also proceed with NBS.

Chlorohydroxylation of 1,2-Allenyl Sulfoxides. At the beginning, the chlorohydroxylation met some difficulty. Cl_2/H_2O was a strong oxidant and, thus, cannot be used directly. NCS did not give a chlorohydroxylation product. When 1,2-allenic sulfoxides reacted with $CuCl_2 \cdot 2H_2O$ in acetone/water, the reaction proceeded extremely slowly to afford the product with only 20% yield of *E*-**3cg** after 48 h at room temperature (Scheme 9). At a higher reaction temperature, no chlorohydroxylation product could be isolated.

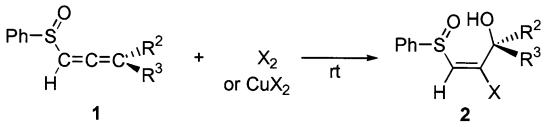
Recently, solvent-free reactions were developed rapidly.[16] As they occur on the surface of crystals of reactants, solvent-free reactions sometimes are clean and the yields are high. To our surprise, when allenic sulfoxide **1g** was mixed and milled with $CuCl_2 \cdot 2H_2O$ together with some silica gel 4 times from room temperature to 65°C, the chlorohydroxylation reaction occurred smoothly to afford product *E*-**3cg** in 73% yield. Some typical results are listed in Table 3.

Table 3. Solventless Chlorohydroxylations of 1,2-Allenic Sulfoxides with $CuCl_2 \cdot 2H_2O$



	1,2-allenic sulfoxides **1**				
entry	R^1	R^2	R^3	product *E*-**3c**	yield (%)
1	H	H	H (**1a**)	*E*-**3ca**	49
2	H	H	*t*-Bu (**1e**)	*E*-**3ce**	84
3	H	CH_3	CH_3 (**1f**)	*E*-**3cf**	61
4	H		$(CH_2)_5$ (**1g**)	*E*-**3cg**	73
5	*n*-Bu	H	H (**1h**)	*E*-**3ch**	51

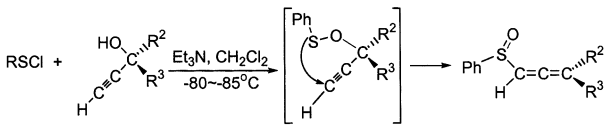
Table 4. Halohydroxylation of Optically Active 1,2-Allenic Sulfoxides



	1,2-allenic sulfoxides **1**						
entry	R^2	R^3	**1** (ee) (%)	halogen source	yield of **2**[a] (%)	**2** (ee) (%)
1	*n*-C_4H_9	H (*R*-**1c**)	96	I_2	98 (*R*-**3ac**)	95
2	*n*-C_4H_9	H (*R*-**1c**)	96	Br_2	96 (*R*-**3bc**)	96
3	*n*-C_4H_9	H (*R*-**1c**)	96	$CuBr_2$	92 (*R*-**3bc**)	97
4	H	*n*-C_8H_{17}(*S*-**1d**)	96	Br_2	99 (*S*-**3bd**)	97
5	H	*n*-C_8H_{17}(*S*-**1d**)	96	$CuBr_2$	97 (*S*-**3bd**)	96
6	H	*t*-C_4H_9 (*S*-**1e**)	>99	I_2	88 (*S*-**3ae**)	>99
7	H	*t*-C_4H_9 (*S*-**1e**)	>99	Br_2	85 (*S*-**3be**)	>99
8	H	*t*-C_4H_9 (*S*-**1e**)	>99	$CuBr_2$	69 (*S*-**3be**)	>99
9[b]	H	*t*-C_4H_9 (*S*-**1e**)	>99	$CuCl_2 \cdot 2H_2O$	82 (*S*-**3ce**)	>99

[a] Isolated yield. [b] Solventless reaction.

Scheme 10 [a]



(R)-**A**, R^2 = *n*-C_4H_9, R_3 = H, 96%ee
(S)-**B**, R^2 = H, R_3 = *n*-C_8H_{17}, 96%ee
(S)-**C**, R^2 = H, R_3 = *t*-C_4H_9, >99%ee

(R)-**1c**, 84% yield, 95.5% ee[a]
(S)-**1d**, 86% yield, 95.7% ee[a]
(S)-**1e**, 89% yield, >99% ee[a]

[a] Referred to the allene moiety.

Halohydroxylation Reaction of Optically Active 1,2-Allenyl Sulfoxides. Using optically active propargyl alcohols as starting materials, we obtained optically active 1,2-allenic sulfoxides whose configurations in the allene part are definite (Table 4). The chirality of the optically active propargylic alcohols were efficiently transferred to the allene moiety of sulfoxides, as determined by HPLC. The ratio of the two diastereoisomers of 1,2-allenic sulfoxides due to the presence of the sulfinyl group may change with time (Scheme 10). The absolute configurations of the allene moiety in **1c**, **1d**, and **1e** were assigned based on the mechanism.[17]

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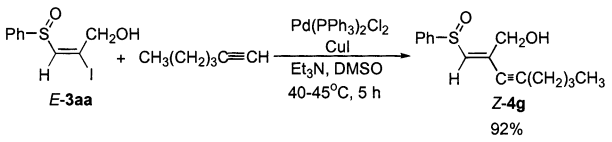
According to the halohydroxylation mechanism (Scheme 7), if the optically active 1,2-allenic sulfoxides with a definite configuration in the allene part react with halogen and H_2O, the chirality of the allene moiety can be transferred into the chiral center of the allylic alcohol. The absolute configurations of the chiral center connecting with the hydroxy group are assigned based on the halohydroxylation result of **1m**, and the ee value of halohydroxylation product is equal to that of the corresponding reactants (Table 4).

Synthetic Application of Pd- or Ni-Catalyzed Selective Coupling Reactions. Transition metal-catalyzed cross-coupling reaction has been becoming one of the most efficient methods for the formation of C−C bonds and C−X bonds.[18] The transformation of halohydroxylation products is challenging.[19] Generally, it is easy to convert the sulfinyl group to hydrogen[20] but difficult to convert it to useful organic functional groups.[21] Thus, various kinds of cross-coupling reactions of the iodohydroxylation products were studied.

1. Coupling Reactions of the C−I bond. 1.1. Sonogashira Coupling. Usually the coupling reaction of 1-alkenyl iodide with terminal alkyne was carried out in Et_3N under the catalysis of $Pd(PPh_3)_2Cl_2$ and CuI.[22] However, due to the low solubility of *E*-**3aa**, DMSO should be added as the cosolvent; the corresponding reaction afforded 1-en-3-ynyl sulfoxide *Z*-**4g** in 92% yield (eq 2).



1.2. Suzuki Coupling.[23] The Pd(0)-catalyzed coupling reaction of *E*-**3aa** with phenyl boronic acid using K_2CO_3 as the base in THF afforded **4a** in 70% yield with an *E*/*Z* ratio of 20:80, indicating the partial isomerization of the C═C bond, which makes it synthetically useless. However, with the addition of 10 mol % of TBAB, the reaction was finished within 3 h to afford **4a** in an *E*/*Z* ratio of 3:97. With *E*-1-hexenyl boronic acid, the reaction also afforded *Z*-**4h** in 90% yield highly stereoselectively (Scheme 11).

1.3. Negishi Coupling.[24] The Negishi coupling of *E*-**3aa** with phenyl zinc bromide in THF did not afford the corresponding coupling *Z*-**4a** (entry 1 of Table 5). When DMF was added as the cosolvent, the reaction afforded *Z*-**4a** in 94% yield stereospecifically. With ethyl zinc bromide, the reaction afforded *Z*-**4e** in 86% yield (entry 9 of Table 5). Similarly, the reaction with phenylacetylenic zinc bromide in THF did not work, while,

Scheme 11

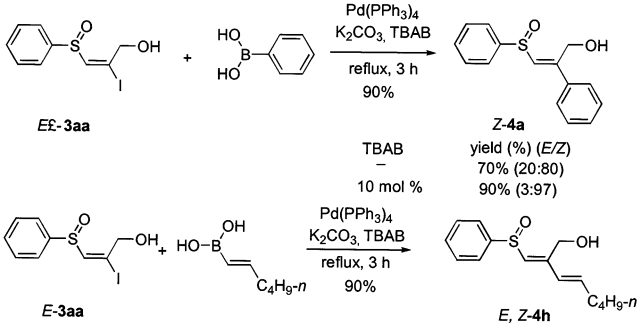
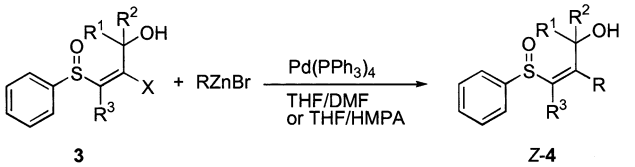


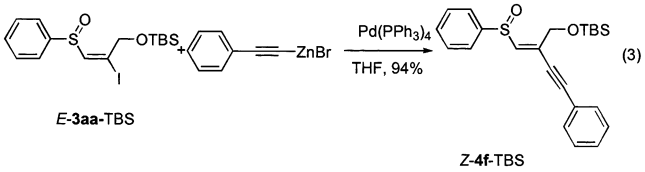
Table 5. Pd(0)-Catalyzed Mono Coupling Reaction of the C−X Bond of 4-Phenylsulfinyl-2-iodo-2(*E*)-alkenols with Organic Zincs



	3						
entry	R^1	R^2	R^3	RZnX	solvent	temp/ time (h)	yield (%)
1	H	H	H (*E*-**3aa**)	PhZnBr	THF	rt/3	0 (*Z*-**4a**)
2	H	H	H (*E*-**3aa**)	PhZnBr	THF/DMF	rt/1	94 (*Z*-**4a**)
3	H	H	^{n}Bu (*E*-**3ah**)	PhZnBr	THF/DMF	rt/2	82 (*Z*-**4b**)
4	H	*n*-Bu	H (*E*-**3ac**)	PhZnBr	THF/DMF	rt/1	71 (*Z*-**4c**)
5[a]	H	*n*-Bu	H (*E*-**3ac**)	PhZnBr	THF/DMF	rt/1	74 (*Z*-**4c**)
6	H	*n*-Oct	H (*E*-**3ad**)	PhZnBr	THF/DMF	rt/2	76 (*Z*-**4d**)
7[b]	H	*n*-Oct	H (*E*-**3ad**)	PhZnBr	THF/DMF	rt/2	78 (*Z*-**4d**)
8[c]	H	*n*-Oct	H (*E*-**3ad**)	PhZnBr	THF/DMF	rt/2	77 (*Z*-**4d**)
9	H	H	H (*E*-**3aa**)	EtZnBr	THF/DMF	rt/1	86 (*Z*-**4e**)
10	H	H	H (*E*-**3aa**)	PhC_2ZnBr	THF/DMF	rt/7	0 (*Z*-**4f**)
11	H	H	H (*E*-**3aa**)	PhC_2ZnBr	THF/HMPA	rt/1.5	94 (*Z*-**4f**)
12	H	H	H (*E*-**3ba**)	PhC_2ZnBr	THF/HMPA	rt/1.5	92 (*Z*-**4f**)

[a] (*R*)-*E*-**3ac** (97.1% ee); (*R*)-*Z*-**4c** (99.1% ee). [b] The starting (*R*)-propargylic alcohol (94.0% ee), (*R*)-*Z*-**4d** (98.1% ee). [c] The starting (*S*)-propargylic alcohol (95.7% ee), (*S*)-*Z*-**4d** (94.7% ee).

with the addition of HMPA as the cosolvent, the reaction went smoothly to afford *Z*-**4f** in high yields (compare entry 10 with entry 11 of Table 5). The reaction of *E*-**3aa**-TBS, in which the hydroxyl group was protected, in THF can afford the coupling product *Z*-**4f**-TBS in 94% yield (eq 3).



2. Coupling Reaction of the C−I Bond and the C−S Bond. Under the catalysis of $Pd(PPh_3)_4$, the coupling reaction stopped at the stage of iodide coupling affording *Z*-**4a**. However, when a Ni complex was added after the first coupling with the C−I bond, the C−S bond was reacted further to produce *Z*-2,3-diphenyl-2-propenyl alcohol (*Z*-**5c**) (Scheme 12). Among the catalysts tested, $Ni(acac)_2$ gave the best results (entry 3 of Table 6). *Z*-**5e** was formed in 54% yield at 40 °C (entry 6 of Table 6).

Under the catalysis of $Ni(acac)_2$ alone, the reaction of *E*-**3aa** and excess amount of phenyl zinc bromide in THF/DMF afforded a mixture of *Z*-**4a** and *Z*-**5c** together with some byproducts (Scheme 13).

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(24) (a) King, A. O.; Okukado, N.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1977**, 683. (b) Pour, M.; Negishi, E. *Tetrahedron Lett.* **1996**, *37*, 4679. (c) Pour, M.; Negishi, E. *Tetrahedron Lett.* **1997**, *38*, 525.

Scheme 12

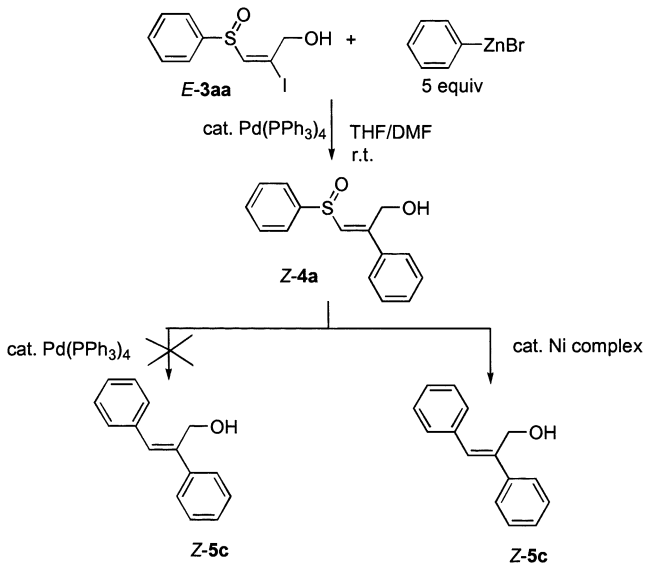
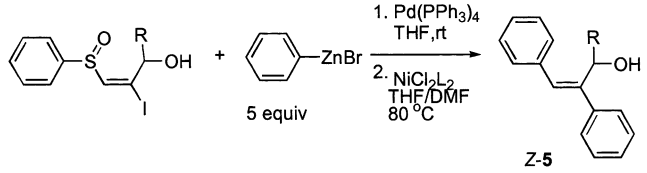


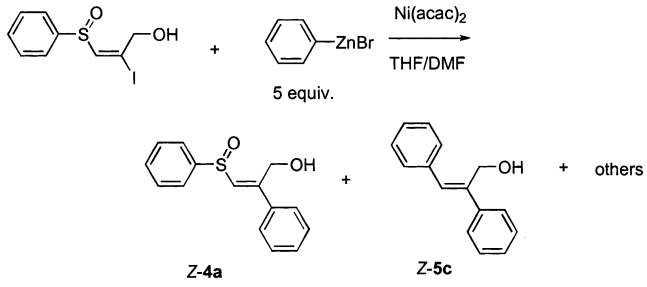
Table 6. Pd(0)- and Ni-Catalyzed Double Coupling Reaction of 4-Phenylsulfinyl-2-iodo-2(*E*)-alkenols with Organic Zincs



entry	$NiCl_2L_2$	R	step one time (h)	step two time (h)	yield (%)
1	$NiCl_2(PPh_3)_2$	H (*E*-**3aa**)	1	1.3	77 (*Z*-**5c**)
2	$NiCl_2$ (dppe)	H (*E*-**3aa**)	1	2	40 (*Z*-**5c**)
3	$Ni(acac)_2$	H (*E*-**3aa**)	1	4.5	84 (*Z*-**5c**)
4	$Ni(acac)_2$	*n*-C_8H_{17} (*E*-**3ad**)	1.2	11	44 (*Z*-**5e**)
5[a]	$Ni(acac)_2$	*n*-C_8H_{17} (*E*-**3ad**)	1	4	34 (*Z*-**5e**)
6[b]	$Ni(acac)_2$	*n*-C_8H_{17} (*E*-**3ad**)	1.6	12	54 (*Z*-**5e**)

[a] The starting (*S*)-propargylic alcohol (95.7% ee); (*S*)-*Z*-**5e** (95.4% ee). [b] The Ni-catalyzed second coupling reaction was carried out at 40 °C.

Scheme 13



A control experiment showed that the hydroxy group in *E*-**3aa** played an important role in the coupling reaction, since the coupling reaction of a 1:1 mixture of *E*-**3aa** and 2-phenylethenyl phenylsulfoxide with PhZnBr afforded *Z*-**5c** in 85% yield and stilbene in only 24% yield (eq 4).

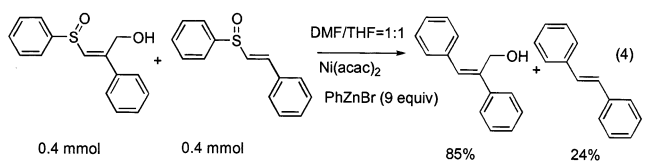
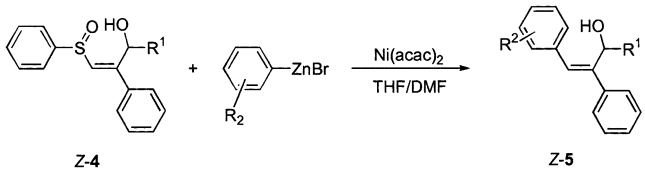


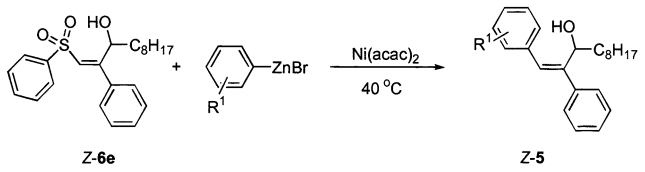
Table 7. Ni(0)-Catalyzed Coupling Reaction of C−S(O)Ph Bond with Aryl Zincs



entry	*Z*-**4** R^1	ArZnBr R^2	temp (°C)	time (h)	yield (%)
1	H (*Z*-**4a**)	*p*-Cl	80	1.5	68 (*Z*-**5a**)
2	H (*Z*-**4a**)	*p*-OMe	80	3	73 (*Z*-**5b**)
3	H (*Z*-**4a**)	H	40	15.5	84 (*Z*-**5c**)
4	H (*Z*-**4a**)	*o*-OMe	40	15	68 (*Z*-**5d**)
5	*n*-C_8H_{17} (*Z*-**4d**)	H	40	15	69 (*Z*-**5e**)
6[a]	*n*-C_8H_{17} (*Z*-**4d**)	H	40	12	64 (*Z*-**5e**)
7	*n*-C_8H_{17} (*Z*-**4d**)	*p*-OMe	40	19	60 (*Z*-**5f**)
8[b]	*n*-C_8H_{17} (*Z*-**4d**)	*p*-OMe	40	19	57 (*Z*-**5f**)
9	*n*-C_4H_9 (*Z*-**4c**)	*p*-$N(CH_3)_2$	40	12	76 (*Z*-**5g**)
10[c]	*n*-C_4H_9 (*Z*-**4c**)	*p*-$N(CH_3)_2$	40	12	73 (*Z*-**5g**)

[a] (*S*)-*Z*-**4d** (94.7% ee); (*S*)-*Z*-**5e** (95.6% ee). [b] (*S*)-*Z*-**4d** (94.7% ee); (*S*)-*Z*-**5f** (95.8% ee). [c] (*R*)-*Z*-**4c** (99.1% ee); (*R*)-*Z*-**5g** (94.0% ee).

Table 8. Ni(0)-Catalyzed Couling Reaction of C−SO_2Ph Bond with Aryl Zincs

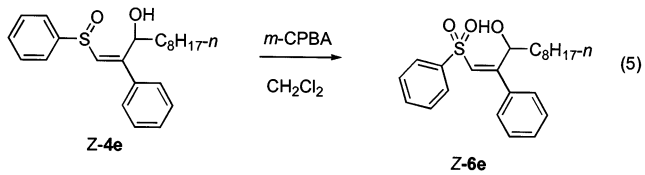


entry	R^1	time (h)	yield (%)
1	*m*-Me	19	63 (*Z*-**5h**)
2[a]	*m*-Me	19	57 (*Z*-**5h**)
3	*p*-Me	12	66 (*Z*-**5i**)
4[b]	*p*-Me	12	65 (*Z*-**5i**)
5	*p*-OMe	11	60 (*Z*-**5f**)
6	*p*-$N(CH_3)_2$	12	70 (*Z*-**5j**)

[a] (*S*)-*Z*-**6e** (96.0% ee); (*S*)-*Z*-**5h** (94.5% ee). [b] (*S*)-*Z*-**6e** (96.0% ee), (*S*)-*Z*-**5i** (96.6% ee).

Some typical examples of this coupling reaction are listed in Table 7. With optically active *Z*-**4c** and *Z*-**4d**, the reaction gave the corresponding products without loss of enantiopurity (entries 6, 8, and 10 of Table 7).

Sulfoxide *Z*-**4e** can be easily oxidized to the corresponding sulfone *Z*-**6e** (eq 5). Under the catalysis of $Ni(acac)_2$, its coupling reaction with aryl zinc bromide afforded *Z*-**5** with reasonable yield (Table 8). With optically active starting compounds, the loss of enantiopurity was not observed.



In conclusion, we have observed the unique regio- and stereoselectivity in the halohydroxylation reaction of 1,2-allenic sulfoxides, which provides an efficient entry to (*E*)-2-halo-3-hydroxy-1-alkenyl sulfoxides. With optically active 1,2-allenic sulfoxides, the efficiency for the chirality transfer is excellent.

Based on the reaction of **1m**, it was found that the absolute configuration of the sulfur center is inverted after the halohydroxylation reaction. Due to the easy availability of the starting materials, simple/convenient operation, and the ready elaboration of the functional groups in the products, the reaction will show its broad utility in organic synthesis. In addition, with different nucleophiles and the search for different groups, which are capable of controlling the pertinent selectivities, this protocol will open up a new area for the highly selective synthesis of stereodefined alkenes with functionality. Further study in this area is being carried out in our laboratory.

Experimental Section

Synthesis of Starting Materials. General Procedure for the Synthesis of Sulfinyl Allene Preparation: An oven-dried three-neck round-bottom flask was charged with propargyl alcohol in methylene chloride. After the mixture was cooled to −85 °C, 1 equiv of triethylamine was added. After 10 min with stirring, a solution of sulfenyl chloride (1 equiv) in methylene chloride was added dropwise. After the reaction was stirred at −85 °C for another 10 min, it was allowed to warm to room temperature following quenching with water. The organic layer was separated, and the aqueous layer was extracted with methylene chloride. The combined organic extracts were washed with water and brine and dried over anhydrous magnesium sulfate. The concentration of the solution reduced under pressure and afforded the appropriate allene.

(a) 1,2-Propadienyl Phenyl Sulfoxide (1a):[25] The reaction of propargyl alcohol (3.08 g, 55 mmol), Et_3N (5.05 g, 55 mmol), and sulfenyl chloride (7.23 g, 50 mmol) afforded 6.75 g (82%) of the product as oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.60−7.71 (m, 2H), 7.43−7.58 (m, 3H), 6.09 (t, J = 9 Hz, 1H), 5.23−5.42 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 206.96, 144.09, 130.65, 128.80, 123.66, 101.67, 81.96; IR (neat) 1937 cm^{-1}.

(b) 1,2-Butadienyl Phenyl Sulfoxide (1b):[26] The reaction of but-3-yn-2-ol (4.97 g, 71 mmol), Et_3N (7.2 g, 71 mmol), sulfenyl chloride (9.35 g, 64.6 mmol) afforded 8.684 g (76%) of the product as oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.58−7.75 (m, 2H), 7.40−7.58 (m, 3H), 5.93−6.08 (m, 1H), 5.58−5.80 (m, 1H), 1.70−1.90 (m, 3H).

(c) 1,2-Heptadienyl Phenyl Sulfoxide (1c): The reaction of hept-1-yn-3-ol (6.09 g, 54 mmol), Et_3N (5.05 g, 50 mmol), and sulfenyl chloride (7.23 g, 50 mmol) afforded 8.08 g (73%) of the product as an oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.60−7.72 (m, 2H), 7.40−7.60 (m, 3H), 5.96−6.08 (m, 1H), 5.65 (m, 1H), 2.00−2.23 (m, 2H), 1.22−1.52 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H); IR (neat) 1946, 1046 cm^{-1}; MS m/z 221 (M^+ + 1, 100). HRMS calcd for $C_{13}H_{16}OS$: 220.0918. Found: 220.0890.

(d) (*R*)-1,2-Heptadienyl Phenyl Sulfoxide ((*R*)-1c): The reaction of (*R*)-hept-1-yn-3-ol (240 mg, 2 mmol, 96% ee), 0.27 mL Et_3N (200 mg, 2 mmol), and sulfenyl chloride (290 mg, 2 mmol) afforded (*R*)-**1c**, 370 mg (84%), ee% = 95.5%, dr = 70:30 (HPLC conditions: Chiralcel OD column (0.46 cm ϕ × 25 cm); λ 254 nm; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 95:5). ^1H NMR (300 MHz, $CDCl_3$) δ 7.56−7.73 (m, 2H), 7.40−7.56 (m, 3H), 5.93−6.06 (m, 1H), 5.60−5.77 (m, 1H), 2.00−2.23 (m, 2H), 1.20−1.52 (m, 4H), 0.84−1.00 (m, 3H).

(e) 1,2-Undecadienyl Phenyl Sulfoxide (1d): The reaction of undec-1-yn-3-ol (5.04 g, 30 mmol), Et_3N (3.34 g, 33 mmol), and sulfenyl chloride (4.77 g, 33 mmol) afforded 7.03 g (85%) of the product. ^1H NMR (300 MHz, $CDCl_3$) δ 7.52−7.64 (m, 2H), 7.47−7.52 (m, 3H), 5.92−6.00 (m, 1H), 5.58−5.73 (m, 1H), 1.98−2.15 (m, 2H), 1.12−1.50 (m, 12H), 0.80 (t, J = 6.71 Hz, 3H); IR (neat) 1941, 1051 cm^{-1}; MS m/z 277 (M^+ + 1, 65.27), 126 (100). HRMS calcd for $C_{17}H_{24}OS$: 276.1548. Found: 276.1543.

(f) (*S*)-1,2-Undecadienyl Phenyl Sulfoxide ((*S*)-1d): The reaction of (*S*)-undec-1-yn-3-ol (840 mg, 5 mmol, 95.7% ee), Et_3N (505 mg, 5 mmol), and sulfenyl chloride (723 mg, 5 mmol) afforded 1.18 g (86%) of (*S*)-**1d**, ee% = 95.7%, dr = 61:39 (HPLC conditions: Chiralcel OD column (0.46 cm ϕ × 25 cm); λ 254 nm; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 95:5). ^1H NMR (300 MHz, $CDCl_3$) δ 7.57−7.70 (m, 2H), 7.38−7.57 (m, 3H), 5.96−6.07 (m, 1H), 5.63−5.70 (m, 1H), 2.00−2.20 (m, 2H), 1.12−1.50 (m, 12H), 0.86 (t, J = 6.2 Hz, 3H).

(g) 4,4-Dimethylpenta-1,2-dienyl Phenyl Sulfoxide (1e): The reaction of 4,4-dimethylpent-1-yn-3-ol (2.24 g, 20 mmol), Et_3N (2.22 g, 22 mmol), and sulfenyl chloride (3.18 g, 22 mmol) afforded 3.68 g (84%) of the product as solid, mp 48−50 °C (CH_2Cl_2/*n*-hexane). ^1H NMR (300 MHz, $CDCl_3$) δ 7.33−7.50 (m, 2H), 7.15−7.33 (m, 3H), 5.85 (d, J = 5.82 Hz, 1H), 5.46 (d, J = 5.82 Hz, 1H), 0.78 (s, 9H); IR (KBr) 1942, 1050 cm^{-1}; MS m/z 221 (M^+ + 1, 100). Anal. Calcd for $C_{13}H_{16}OS$: C, 70.90%; H, 7.30%. Found: C, 71.15%; H, 7.50%.

(h) 4,4-Dimethylpenta-1,2-dienyl Phenyl Sulfoxide ((*S*)-1e): The reaction of (*S*)-4,4-dimethyl-pent-1-yn-3-ol (448 mg, 4 mmol, >99% ee), Et_3N (400 mg, 4 mmol), and sulfenyl chloride (578 mg, 4 mmol) afforded 787 mg (89%) of (*S*)-**1e**, ee% > 99%, dr = 92:8 (HPLC conditions: Chiralcel OD column (0.46 cm ϕ × 25 cm); λ 254 nm; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 100:2). ^1H NMR (300 MHz, $CDCl_3$) δ 7.55−7.78 (m, 2H), 7.42−7.55 (m, 3H), 6.12 (d, J = 5.88 Hz, 1H), 5.70 (d, J = 5.88 Hz, 1H), 0.78 (s, 9H).

(i) 3-Methylbuta-1,2-dienyl Phenyl Sulfoxide (1f):[14] The reaction of 2-methyl-but-3-yn-2-ol (2.10 g, 25 mmol), Et_3N (2.53 g, 25 mmol), and sulfenyl chloride (3.62 g, 25 mmol) afforded 3.50 g (73%) of the product. ^1H NMR (300 MHz, $CDCl_3$) δ 7.56−7.60 (m, 2H), 7.42−7.49 (m, 3H), 5.84−5.88 (m, 1H), 1.76 (d, J = 2.40 Hz, 3H), 1.72 (d, J = 2.10 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 201.61, 144.83, 130.59, 128.94, 124.02, 104.65, 100.47, 19.89, 19.74.

(j) 2-(Cyclohexylideneethenyl)phenyl Sulfoxide (1g):[14] The reaction of 1-ethynylcyclohexanol (4.10 g, 33 mmol), Et_3N (3.34 g, 33 mmol), and sulfenyl chloride (4.77 g, 33 mmol) afforded 6.72 g (88%) of the product. ^1H NMR (300 MHz, $CDCl_3$) δ 7.36−7.83 (m, 5H), 5.95 (s, 1H), 2.10−2.40 (m, 4H), 1.40−1.90 (m, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 201.50, 145.14, 130.67, 129.05, 124.13, 113.62, 102.99, 34.39, 34.34, 20.56, 20.54, 13.73; MS, m/z 215 (M^+ -OH, 0.22), 79 (100).

(k) 1,2-heptadien-3-yl Phenyl Sulfoxide (1h): The reaction of hept-2-yn-1-ol (5.68 g, 51 mmol), Et_3N (5.13 g, 51 mmol), and sulfenyl chloride (7.33 g, 51 mmol) afforded 9.42 g (85%) of the product. ^1H NMR (300 MHz, $CDCl_3$) δ 7.58−7.61 (m, 2H), 7.44−7.51 (m, 3H), 5.18−5.29 (m, 2H), 2.11−2.16 (m, 1H), 1.77−1.81 (m, 1H), 1.17−1.40 (m, 4H), 0.77 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 205.38, 143.37, 130.68, 128.86, 124.36, 113.01, 82.05, 29.26, 22.15, 21.88, 13.57; IR (neat) 1946, 1443 cm^{-1}; MS m/z 220 (M^+, 16.88), 126 (100). HRMS calcd for $C_{13}H_{16}OS$: 220.0918. Found: 220.0942.

(l) 1-Phenylpropadienyl Phenyl Sulfoxide (1i): The reaction of 3-phenylprop-2-yn-1-ol (3.68 g, 28 mmol), Et_3N (2.83 g, 28 mmol), and sulfenyl chloride (4.05 g, 28 mmol) afforded 5.76g (86%) of the product. ^1H NMR (300 MHz, $CDCl_3$) δ 7.18−7.62 (m, 10H), 5.55 (d, J = 9 Hz, 1H), 5.47 (d, J = 9 Hz, 1H); IR (neat) 1931, 1050 cm^{-1}; MS m/z 240 (M^+, 13.74), 115 (100). HRMS calcd for $C_{15}H_{12}OS$: 240.0606. Found: 240.0602.

(m) 2-Methylocta-2,3-dien-4-yl Phenyl Sulfoxide (1j): The reaction of 2-methyl-oct-3-yn-2-ol (2.53 g, 18 mmol), Et_3N (1.99 g, 20 mmol), and sulfenyl chloride (2.86 g, 20 mmol) afforded 4.04 g (90%) of the product. ^1H NMR (300 MHz, $CDCl_3$) δ 7.57−7.63 (m, 2H), 7.43−7.57 (m, 3H), 2.18−2.30 (m, 1H), 1.75−1.92 (m, 1H), 1.82 (s, 3H), 1.80 (s, 3H), 1.17−1.40 (m, 4H), 0.81 (t, J = 7.21 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 199.21, 143.82, 130.10, 128.52, 124.09, 111.17, 104.18, 29.35, 22.55, 21.66, 20.14, 19.95, 13.48; IR (neat) 1959, 1048

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cm^{-1}; MS *m*/*z* 248 (M^+, 21.50), 81 (100). HRMS calcd for $C_{15}H_{20}OS$: 248.1230. Found: 248.1209.

(n) Hepta-1,2,6-trien-1-yl Phenyl Sulfoxide (1k): The reaction of hept-6-en-1-yn-3-ol (2.59 g, 23 mmol), Et_3N (2.29 g, 23 mmol), and sulfenyl chloride (3.28 g, 23 mmol) afforded 3.13 g (63%) of the product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58−7.73 (m, 2H), 7.45−7.58 (m, 3H), 6.00−6.07 (m, 1H), 5.64−5.88 (m, 2H), 4.95−5.11 (m, 2H), 2.07−2.33 (m, 4H); IR (neat) 1949, 1641, 1047 cm^{-1}; MS *m*/*z* 218 (M^+, 3.24), 126 (100). HRMS calcd for $C_{13}H_{14}OS$: 218.0762. Found: 218.0767.

(o) Hexa-1,2,5-trien-1-yl Phenyl Sulfoxide (1l): The reaction of hex-5-en-1-yn-3-ol (2.88 g, 30 mmol), Et_3N (3.0 g, 30 mmol), and sulfenyl chloride (4.34 g, 30 mmol) afforded 3.54 g (58%) of the product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56−7.70 (m, 2H), 7.40−7.56 (m, 3H), 6.00−6.12 (m, 1H), 5.63−5.86 (m, 2H), 5.00−5.18 (m, 2H), 2.74−2.96 (m, 2H); IR (neat) 1948, 1638, 1082 cm^{-1}; MS *m*/*z* 204 (M^+, 1.66), 77 (100). HRMS calcd for $C_{12}H_{12}OS$: 204.0606. Found: 204.0612.

(p) 2-(Benzenesulfinylvinylidene)-1,7,7-trimethylbicyclo[2.2.1]-heptane (1m): The reaction of (1*R*,2*S*,4*R*)-2-ethynyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (1.4 g, 7.9 mmol), Et_3N (0.8 g, 7.9 mmol), and sulfenyl chloride (1.14 g, 7.9 mmol) afforded 1.35 g (60%) of the product as solid, mp 89−90 °C (*n*-hexane), $[\alpha]_D^{25} = -54.9°$ (*C* = 1.0, EtOH). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58−7.69 (m, 2H), 7.42−7.58 (m, 3H), 6.06 (t, *J* = 3.5 Hz, 1H), 2.63−2.76 (m, 1H), 2.10−2.21 (m, 1H), 1.63−1.88 (m, 3H), 1.37−1.48 (m, 1H), 1.20−1.31 (m, 1H), 0.90 (s, 6H), 0.86 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 197.09, 144.85, 130.40, 128.82, 124.25, 120.31, 104.48, 53.11, 48.35, 44.51, 35.09, 34.41, 27.25, 19.46, 18.31, 13.11; IR (KBr) 1937, 1044 cm^{-1}; MS *m*/*z* 262 (M^+, 1.39), 105 (100).

(q) 2-Benzenesulfinylbuta-2,3-dien-1-ol (1n): The reaction of but-2-yn-1,4-diol (5.16 g, 60 mmol), Et_3N (3.01g, 30 mmol), and sulfenyl chloride (4.34 g, 30 mmol) afforded 1.52 g (26%) of the product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57−7.75 (m, 2H), 7.40−7.57 (m, 3H), 5.41 (d, *J* = 7.77 Hz, 1H), 5.24 (d, *J* = 7.77 Hz, 1H), 4.10−4.40 (m, 1H), 4.40−4.50 (m, 1H), 3.12 (t, *J* = 5.02 Hz, 1H); IR (neat) 1944, 1042 cm^{-1}; MS *m*/*z* 194 (M^+, 15.74), 147 (100). HRMS calcd for $C_{10}H_{10}O_2S$: 194.0399. Found: 194.0412

(r) 2-Benzenesulfinyl-4-methylpenta-2,3-dienoic Acid (1o):[27] The reaction of 4-hydroxy-4-methyl-but-2-ynoic acid methyl ester (2.84 g, 20 mmol), Et_3N (2.02 g, 20 mmol), and sulfenyl chloride (2.89 g, 20 mmol) afforded 3.66 g (72%) of the product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63−7.82 (m, 2H), 7.42−7.60 (m, 3H), 3.81 (s, 3H), 1.89 (s, 3H), 1.76 (s, 3H).

(*Z*)-2-Iodo-3-(thiophenyl)-2-propenyl Acetate (*Z*-2aa). A solution of NaI (300 mg, 2 mmol) and **1a** (82 mg, 0.5 mmol) in HOAc (1.5 mL) was heated at 80 °C with stirring for 5 h. When the reaction was complete, 2 mL of water was added, and the reaction mixture was extracted with ether (2 × 10 mL). The combined organic layer was washed with saturated $NaHCO_3$ until pH = 7 and dried over $MgSO_4$. Filtration, evaporation, and chromatography on silica gel (*n*-hexane/ethyl acetate (20:1)) afforded 69 mg (41%) of *Z*-**2aa** as oil.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.49 (m, 2H), 7.28−7.40 (m, 3H), 7.12 (s, 1H), 4.80 (s, 2H), 2.11 (s, 3H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ 170.13, 139.09, 133.25, 131.04, 129.39, 128.02, 92.66, 71.40, 20.94; MS *m*/*z* 334 (M^+, 1.69), 207 (100); IR (neat) 1737, 1650, 1232 cm^{-1}. HRMS calcd for $C_{11}H_{11}IO_2S$: 333.9521. Found: 333.9510.

(*Z*)-2-Iodo-3-(phenylsulfinyl)-2-propenyl Acetate (*Z*-2aa′). A solution of *Z*-**2aa** (40 mg, 0.14 mmol), HOAc (0.5 mL), and H_2O_2 (30%, 0.05 mL, 0.44 mmol) was stirred at room temperature for 18 h. When the reaction was over, 2 mL of water was added, and reaction mixture was extracted with ether (2 × 10 mL). The combined organic layer was washed with saturated $NaHCO_3$ until pH = 7 and dried over $MgSO_4$. Filtration, evaporation, and chromatography on silica gel (hexane/ethyl acetate (2:1)) afforded 42 mg (86%) of *Z*-**2aa′** as oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75−7.77 (m, 2H), 7.53−7.55 (m, 3H), 6.97 (s, 1H), 4.85 (dd, J_1 = 15.60 Hz, J_2 = 1.5 Hz, 1H), 4.75 (dd, J_1 = 15.60 Hz, J_2 = 1.5 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 169.22, 143.40, 142.65, 131.42, 129.51, 124.20, 107.59, 70.05, 20.55; MS *m*/*z* 351 ($M^+ + 1$, 75.08), 43 (100); IR (neat) 1743, 1223, 1041 cm^{-1}. HRMS calcd for $C_{11}H_{11}O_3S$ ($M^+ - I$): 223.0426. Found: 223.0414.

(*E*)-2-Iodo-3-(phenylsulfinyl)-2-propenyl Acetate (*E*-2aa′). To a dried reaction tube were added anhydrous NaOAc (82 mg, 1 mmol), (*E*)-**3aa** (154 mg, 0.5 mmol), Ac_2O (0.1 mL), and THF (1 mL) under N_2, and then the mixture was stirred at room temperature for 6 h. After the reaction was complete, 1 mL of water and 10 mL of ethyl acetate were added and the reaction mixture was neutralized with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate. The combined organic layer was dried over $MgSO_4$ and purified by chromatography on silica gel (hexane/ethyl acetate (4:1 to 2:1)) to afford 151 mg (86%) of *E*-**2aa′**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65−7.72 (m, 2H), 7.50−7.60 (m, 3H), 7.03 (s, 1H), 5.33 (d, *J* = 13.5 Hz, 1H), 5.02 (d, *J* = 13.5 Hz, 1H), 2.19 (s, 3H); IR (neat) 1739, 1669, 1220, 1021 cm^{-1}; MS *m*/*z* 351 ($M^+ + 1$, 49.05), 43 (100). HRMS calcd for $C_{11}H_{11}O_3S$ ($M^+ - I$): 223.0426. Found: 223.0429.

Typical Procedure for Iodohydroxylation of 1,2-Alkadienyl Phenyl Sulfoxides. (a) (*E*)-2-Iodo-3-(phenylsulfinyl)-2-propen-1-ol (*E*-3aa): A solution of LiOAc·$2H_2O$ (102 mg, 1.0 mmol), water (0.3 mL), and 1,2-propadienyl phenylsulfoxide **1a** (82 mg, 0.5 mmol) in MeCN (2 mL) was treated at 55 °C with I_2 (305 mg, 1.2 mmol) with stirring for 1 h. When the reaction was complete, it was quenched with water (2 mL), neutralized with saturated $NaHCO_3$ and washed with saturated sodium thiosulfate to remove the excess I_2. Then the mixture was extracted with CH_2Cl_2 (2 × 10 mL), and the organic layer was dried over $MgSO_4$. Filtration, evaporation, and flash chromatography on silica gel afforded 147 mg (96%) of *E*-**3aa** as solid, mp 115.5−116.5 °C (dichloromethane/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60−7.74 (m, 2H), 7.44−7.60 (m, 3H), 6.89 (s, 1H), 4.56 (d, *J* = 14.97 Hz, 1H), 4.69 (d, *J* = 15.21 Hz, 1H), 3.98 (bs, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 143.60, 142.51, 131.46, 129.70, 124.54, 115.79, 68.22; IR (KBr) 3219, 1589, 1473, 1012 cm^{-1}; MS *m*/*z* 308 (M^+, 100).

(b) (*E*)-3-Iodo-4-(phenylsulfinyl)-3-buten-2-ol (*E*-3ab): The reaction of **1b** (89 mg, 0.5 mmol), I_2 (203 mg, 0.8 mmol), and LiOAc·$2H_2O$ (102 mg, 1.0 mmol) afforded 140 mg (87%) of *E*-**3ab** as solid, mp 118−119 °C (dichloromethane/*n*-hexane), dr = 66:34. Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.73 (m, 5H), 6.89 (s, 1H), 4.60−4.66 (m, 1H), 4.10 (bs, 1H), 1.28 (d, *J* = 6.20 Hz, 3H). Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.73 (m, 5H), 6.85 (s, 1H), 4.66−4.73 (m, 1H), 4.10 (bs, 1H), 1.38 (d, *J* = 6.33 Hz, 3H); IR (KBr) 3392, 1646, 1580, 1009 cm^{-1}; MS *m*/*z* 322 (M^+, 5.61), 43 (100). Anal. Calcd. for $C_{10}H_{11}IO_2S$: C, 37.28%; H, 3.44%. Found: C, 37.22%; H, 3.41%.

(c) (*E*)-2-Iodo-1-(phenylsulfinyl)-1-hepten-3-ol (*E*-3ac): The reaction of **1c** (110 mg, 0.5 mmol), I_2 (203 mg, 0.8 mmol), and LiOAc·$2H_2O$ (102 mg, 1.0 mmol) afforded 161 mg (89%) of *E*-**3ac** as solid, mp 107−108 °C (dichloromethane/*n*-hexane), dr = 63:37. IR (KBr) 3285, 1578 cm^{-1}; MS *m*/*z* 365 ($M^+ + 1$, 29.7), 109 (100). Anal. Calcd for $C_{13}H_{17}IO_2S$: C, 42.87%; H, 4.70%. Found: C, 42.70%; H, 4.59%. The two isomers can be separated by repeated chromatography on silica gel. Less polar isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63−7.67 (m, 2H), 7.49−7.53 (m, 3H), 6.92 (s, 1H), 4.42 (dd, J_1 = 12.9 Hz, J_2 = 6.3 Hz, 1H), 3.31−4.33 (bs, 1H), 1.64 (q, *J* = 6.9 Hz, 2H), 1.31−1.46 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 143.83, 143.22, 131.26, 129.51, 125.15, 124.25, 73.18, 37.26, 27.01, 22.43, 13.89. More polar isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58−7.62 (m, 2H), 7.51−7.58 (m, 3H), 6.98 (s, 1H), 5.07 (d, *J* = 3.3 Hz, 1H), 4.36−4.42 (m, 1H), 1.69−1.73 (m, 1H), 1.21−1.46 (m, 5H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 142.46, 142.08, 131.49, 129.61, 128.89, 124.34, 71.33, 36.46, 27.27, 22.46, 13.91.

(27) Conrads, M.; Mattay, J. *Synthesis* **1991**, 11.

(d) (*E*)-2-Iodo-1-(phenylsulfinyl)-1-undecen-3-ol (*E*-3ad): The reaction of **1d** (110 mg, 0.4 mmol), I_2 (163 mg, 0.64 mmol), and LiOAc·$2H_2O$ (60 mg, 0.60 mmol) afforded 150 mg (89%) of *E*-**3ad**, dr = 72:28. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59−7.70 (m, 2H), 7.48−7.59 (m, 3H), 6.97 (s, 1H), 4.38−4.48 (m, 1H), 2.66 (bs, 1H), 1.62−1.80 (m, 2H), 1.14−1.62 (m, 12H), 0.81−0.96 (m, 3H). The following signal is discernible for the minor isomer: 6.90 (s, 1H); IR (KBr) 3330, 1582, 1034 cm^{-1}; MS *m*/*z* 421 ($M^+ + 1$, 37.29), 403 (100); HRMS calcd for $C_{17}H_{26}IO_2S$ ($M^+ + 1$): 421.0691. Found: 421.0722.

(e) (*E*)-2-Iodo-4,4-dimethyl-1-(phenylsulfinyl)-1-penten-3-ol (*E*-3ae): The reaction of **1e** (110 mg, 0.4 mmol), I_2 (153 mg, 0.60 mmol), and LiOAc·$2H_2O$ (102 mg, 1.0 mmol) afforded 158 mg (87%) of *E*-**3ae** as solid, mp 163.5−164.5 °C (dichloromethane/*n*-hexane), dr = 92:8. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65−7.73 (m, 2H), 7.47−7.59 (m, 3H), 7.21 (s, 1H), 4.36 (s, 1H), 3.70−4.20 (s, 1H), 1.07 (s, 9H). The following signal is discernible for the minor isomer: 7.10 (s, 1H), 4.40 (s, 1H); IR (KBr) 3422, 1626, 1032 cm^{-1}; MS *m*/*z* 365 ($M^+ + 1$, 11.7), 57 (100). Anal. Calcd for $C_{13}H_{17}IO_2S$: C, 42.87%; H, 4.70%. Found: C, 42.72%; H, 4.82%.

(f) (*E*)-3-Iodo-2-methyl-4-(phenylsulfinyl)-3-buten-2-ol (*E*-3af): The reaction of **1f** (96 mg, 0.5 mmol), I_2 (152 mg, 0.60 mmol), and LiOAc·$2H_2O$ (102 mg, 1.0 mmol) afforded 146 mg (87%) of *E*-**3af** as solid, mp 147.5−148.5 °C (ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73−7.87 (m, 2H), 7.42−7.60 (m, 3H), 6.73 (s, 1H), 3.40−2.50 (bs, 1H), 1.66 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 144.31, 143.90, 130.99, 129.26, 125.03, 120.99, 77.78, 30.16, 29.62; IR (KBr) 3262, 1626, 1576 cm^{-1}; MS *m*/*z* 336 (M^+, 0.71), 43 (100). Anal. Calcd for $C_{11}H_{13}IO_2S$: C, 39.30%; H, 3.90%. Found: C, 39.69%; H, 3.63%.

(g) 1-[(*E*)-1′-Iodo-2′-(phenylsulfinyl)ethenyl]-1-cyclohaxanol (*E*-3ag): The reaction of **1g** (232 mg, 1.0 mmol), I_2 (304 mg, 1.2 mmol), and LiOAc·$2H_2O$ (204 mg, 2.0 mmol) afforded 277 mg (74%) of *E*-**3ag** as solid, mp 173−174 °C (dichloromethane/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72−7.87 (m, 2H), 7.42−7.58 (m, 3H), 6.77 (s, 1H), 4.12−4.31 (bs, 1H), 2.03−2.20 (m, 2H), 1.85−2.03 (m, 2H), 1.37−1.85 (m, 4H), 1.13−1.23 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 144.48, 144.14, 130.81, 129.15, 124.98, 123.66, 78.52, 36.25, 35.73, 24.84, 21.50, 21.04; MS *m*/*z* 377 ($M^+ + 1$, 11.12), 359 (100); IR (KBr) 3235, 1591, 1029 cm^{-1}. Anal. Calcd for $C_{14}H_{17}IO_2S$: C, 44.69%; H, 4.55%. Found: C, 44.45%; H, 4.36%.

(h) (*E*)-2-Iodo-3-(phenylsulfinyl)-2-hepten-1-ol (*E*-3ah): The reaction of **1h** (110 mg, 0.50 mmol), I_2 (203 mg, 0.8 mmol), and LiOAc·$2H_2O$ (102 mg, 1.0 mmol) afforded 149 mg (82%) of *E*-**3ah**: solid, mp 83−84 °C (dichloromethane/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.53 (m, 2H), 7.53−7.68 (m, 3H), 4.94 (d, J = 13.4 Hz, 1H), 4.86 (d, J = 13.4 Hz, 1H), 2.80−3.03 (bs, 1H), 2.37−2.52 (m, 1H), 2.08−2.22 (m, 1H), 1.33−1.53 (m, 1H), 1.09−1.33 (m, 3H), 0.77 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 150.81, 141.55, 130.77, 129.19, 124.33, 117.55, 67.20, 32.05, 30.51, 22.74, 13.47; MS *m*/*z* 365 ($M^+ + 1$, 100); IR (KBr) 3324, 1615, 1042 cm^{-1}. Anal. Calcd for $C_{13}H_{17}IO_2S$: C, 42.87%; H, 4.70%. Found: C, 43.00%; H, 4.68%.

(i) (*E*)-2-Iodo-3-phenyl-3-(phenylsulfinyl)-2-propen-1-ol (*E*-3ai): The reaction of **1i** (120 mg, 0.50 mmol), I_2 (203 mg, 0.8 mmol), and LiOAc·$2H_2O$ (102 mg, 1.0 mmol) afforded 151 mg (79%) of *E*-**3ai** as solid, mp 147−148 °C (dichloromethane-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89−7.56 (m, 8H), 6.49−6.89 (bs, 2H), 5.13 (d, J = 13.59 Hz, 1H), 5.02 (d, J = 13.64 Hz, 1H), 3.22−3.55 (bs, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 151.39, 140.95, 134.27, 130.94, 129.76, 128.81, 128.78, 127.60, 124.57, 120.00, 67.03; MS *m*/*z* 385 ($M^+ + 1$, 56.04), 131 (100); IR (KBr) 3356, 1616, 1017 cm^{-1}. Anal. Calcd for $C_{15}H_{13}IO_2S$: C, 46.89%; H, 3.41%. Found: C, 46.71%; H, 3.27%.

(j) (*E*)-3-Iodo-2-methyl-4-(phenylsulfinyl)-3-octen-2-ol (*E*-3aj): The reaction of **1j** (248 mg, 1.0 mmol), I_2 (305 mg, 1.20 mmol), and LiOAc·$2H_2O$ (204 mg, 2.0 mmol) afforded 345 mg (88%) of *E*-**3aj** as solid, mp 150−152 °C (dichloromethane/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84−7.87 (m, 2H), 7.74−7.50 (m, 3H), 3.8−4.2 (bs, 1H), 2.55−2.65 (m, 1H), 2.38−2.48 (m, 1H), 1.81 (s, 3H), 1.71 (s, 3H), 1.43−1.54 (m, 1H), 1.20−1.34 (m, 2H), 0.94−1.03 (m, 1H), 0.83 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 146.85, 143.78, 130.63, 129.09, 125.71, 123.72, 79.16, 34.35, 33.18, 31.87, 31.36, 23.05, 13.90; MS, *m*/*z* 393 ($M^+ + 1$, 27.84), 375 (100); IR (KBr) 3218, 1673, 1029 cm^{-1}; Anal. Calcd for $C_{15}H_{21}IO_2S$: C, 45.93%; H, 5.40%. Found: C, 45.81%; H, 5. 23%.

(k) (*E*)-2-Iodo-1-(phenylsulfinyl)-1,6-heptadien-3-ol (*E*-3ak): The reaction of **1k** (436 mg, 1.0 mmol), I_2 (305 mg, 1.20 mmol), and LiOAc·$2H_2O$ (408 mg, 4.0 mmol) afforded 594 mg (82%) of *E*-**3ak** as solid, mp 86−94 °C (dichloromethane/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.83 (m, 5H), 6.93 (s, 1H), 5.75−5.95 (m, 1H), 4.96−5.23 (m, 2H), 4.35−4.60 (m, 1H), 3.37 (bs, 1H), 2.05−2.40 (m, 2H), 1.71−2.01 (m, 2H). The following signal is discernible for the minor isomer: 6.97 (s, 1H); IR (KBr) 3402, 1635, 1016 cm^{-1}; MS *m*/*z* 345 ($M^+ - 17$, 40.7), 109 (100). HRMS calcd for $C_{13}H_{14}IOS$ ($M^+ - OH$): 344.9806. Found: 344.9824.

(l) (*E*)-2-Iodo-1-(phenylsulfinyl)-1,5-hexadien-3-ol (*E*-3al): The reaction of **1l** (102 mg, 0.5 mmol), I_2 (203 mg, 0.80 mmol), and LiOAc·$2H_2O$ (102 mg, 1.0 mmol) afforded 160 mg (92%) of *E*-**3al** as solid, mp 92−95 °C (dichloromethane/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60−7.78 (m, 2H), 7.42−7.60 (m, 3H), 6.99 (s, 1H), 5.65−5.95 (m, 1H), 5.08−5.31 (m, 2H), 4.45−4.64 (m, 1H), 2.40−2.60 (m, 2H), 2.24−2.40 (m, 1H). The following signal is discernible for the minor isomer: 6.94 (s, 1H); IR (KBr): 3350, 1637, 1028 cm^{-1}; MS *m*/*z* 348 (M^+, 12.04), 109 (100). Anal. Calcd. for $C_{12}H_{13}IO_2S$: C, 41.39%; H, 3.76%. Found: C, 41.37%; H, 3.64%.

(m) (1*R*,2*R*,4*R*)-2-Hydroxyl-2-[(*E*)-1′-iodo-2′-(phenylsulfinyl)ethenyl]-1,7,7-trimethylbicyclo[2.2.1]heptane (*E*-**3am**): The reaction of 1m (72 mg, 0.25 mmol), I_2 (77 mg, 0.30 mmol), and LiOAc·$2H_2O$ (51 mg, 0.50 mmol) afforded 105 mg (98%) of *E*-**3am** as solid, mp 141−143 °C (dichloromethane/*n*-hexane), $[\alpha]_{20}^{D} = -142.3°$ (C = 1, ethanol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82−7.88 (m, 2H), 7.56−7.63 (m, 3H), 7.36 (s, 1H), 2.75 (d, J = 14 Hz, 1H), 2.42−2.65 (s, 1H), 2.26−2.37 (m, 1H), 1.99 (t, J = 4 Hz, 1H), 1.57−1.95 (m, 4H), 1.36 (s, 3H), 1.24 (s, 3H), 1.01 (s, 3H); MS *m*/*z* 431 ($M^+ + 1$, 0.57), 413 (100); IR (KBr) 3394, 1626, 1220, 999 cm^{-1}.

(n) (*E*)-3-Iodo-2-(phenylsulfinyl)-2-buten-1,4-diol (*E*-3an): The reaction of **1n** (97 mg, 0.50 mmol), I_2 (203 mg, 0.80 mmol), and LiOAc·$2H_2O$ (102 mg, 1.0 mmol) afforded 137 mg (81%) of *E*-**3an** as solid, mp 97−98 °C (dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60−7.71 (m, 2H), 7.48−7.60 (m, 3H), 4.93 (d, J = 14.97 Hz, 1H), 4.75 (d, J = 13.95 Hz, 1H), 4.47 (d, J = 13.21 Hz, 1H), 4.37 (d, J = 13.21 Hz, 1H), 2.85 (bs, 2H); IR (KBr) 3378, 1604, 1030 cm^{-1}; MS *m*/*z* 338 (M^+, 5.64), 127 (100). Anal. Calcd for $C_{10}H_{11}IO_3S$: C, 35.52%; H, 3.28%. Found: C, 35.43%; H, 3.19%.

(o) Methyl (*E*)-4-Methyl-3-iodo-3-hydroxy-2-(phenylsulfinyl)-2-pentenoate (*E*-3ao): The reaction of **1o** (100 mg, 0.40 mmol), I_2 (127 mg, 0.50 mmol), and LiOAc·$2H_2O$ (102 mg, 1.0 mmol) afforded 134 mg (85%) of *E*-**3ao** as solid, mp 161−163 °C (dichloromethane/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87−8.00 (m, 2H), 7.35−7.50 (m, 3H), 4.15−4.65 (bs, 1H), 3.76 (s, 3H), 1.62 (s, 3H), 1.17 (s, 3H); MS *m*/*z* 395 ($M^+ + 1$, 100); IR (KBr) 3237, 1730, 1593, 1241, 1018 cm^{-1}; Anal. Calcd for $C_{13}H_{15}IO_4S$: C, 39.61%; H, 3.84; Found: C, 39.32%; H, 3.84%.

Bromohydroxylation of 1,2-Alkadienyl Phenyl Sulfoxides. (a) (*E*)-2-Bromo-3-(phenylsulfinyl)-2-propen-1-ol (*E*-3ba): The reaction of $CuBr_2$ (892 mg, 4.0 mmol), **1a** (164 mg, 1.0 mmol), and water/acetone (1:2 (v/v), 8 mL) was stirred at 40−45 °C for 1.5 h. After the reaction was complete as monitored by TLC, it was extracted with CH_2Cl_2 (3 × 10 mL) and the combined layer was washed subsequently with saturated aqueous $NaHCO_3$ and distilled water and dried over $MgSO_4$. Filtration, evaporation, and flash chromatography on silica gel (eluent: hexane/ethyl acetate (2:1)) afforded 230 mg (88%) of **3ba** as solid, mp 87−88 °C (dichloromethane/*n*-hexane). ^{1}H NMR (300 MHz,

$CDCl_3$) δ 7.67−7.70 (m, 2H), 7.52−7.57 (m, 3H), 6.67 (s, 1H), 4.70 (d, J = 15.2 Hz, 1H), 4.64 (d, J = 15.2 Hz, 1H), 4.41 (bs, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 142.77, 137.39, 137.21, 131.42, 129.60, 124.38, 65.13; IR (KBr) 3278, 1607, 1027 cm^{-1}; MS *m*/*z* 263 (M^+ + 1 (^{81}Br), 4.66), 261 (M^+ + 1 (^{79}Br), 4.62), 77 (100). Anal. Calcd for $C_9H_9BrO_2S$: C, 41.40%; H, 3.47%. Found: C, 41.42%; H, 3.44%.

(b) (*E*)-2-Bromo-4,4-dimethyl-1-(phenylsulfinyl)-1-penten-3-ol (*E*-3be): The reaction of **1e** (55 mg, 0.25 mmol), $CuBr_2$ (223 mg, 1.00 mmol), and H_2O/acetone (1:2, 3 mL) afforded 69 mg (87%) of *E*-**3be** as solid, mp 144 °C−145 °C (dichloromethane/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63−7.76 (m, 2H), 7.51−7.63 (m, 3H), 6.89 (s, 1H), 4.85 (m, 1H), 2.97 (m, 1H), 1.12 (s, 9H). The following signal is discernible for the minor isomer: 6.80 (s, 1H), 1.19 (s, 9H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 142.75, 142.53, 137.65, 131.68, 129.66, 124.87, 77.51, 36.33, 27.06; MS *m*/*z* 319 (M^+ + 1 (^{81}Br), 31.46), 317 (M^+ + 1 (^{79}Br), 31.11), 243 (100); IR (KBr) 3362, 1578, 1034 cm^{-1}. Anal. Calcd for $C_{13}H_{17}BrO_2S$: C, 49.22%; H, 5.40%. Found: C, 49.02%; H, 5.35%.

(c) (*E*)-2-Bromo-3-(phenylsulfinyl)-2-hepten-1-ol (*E*-3bh): The reaction of **1h** (55 mg, 0.25 mmol), $CuBr_2$ (223 mg, 1.00 mmol), and H_2O/acetone (1:2, 3 mL) afforded 68 mg (86%) of *E*-**3bh** as solid, mp 71 °C−72 °C (dichloromethane/*n*-hexane).^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61−7.64 (m, 2H), 7.26−7.53 (m, 3H), 4.87−4.93 (m, 2H), 3.08 (t, J = 6.60 Hz, 1H), 2.33−2.38 (m, 1H), 2.14−2.18 (m, 1H), 1.25−1.50 (m, 1H), 1.15−1.25 (m, 2H), 0.70−0.90 (m, 1H), 0.76 (t, J = 6.90 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 146.95, 141.35, 135.52, 130.80, 129.14, 124.38, 64.40, 30.28, 27.62, 22.72, 13.41; IR (KBr) 3348, 1616, 1030 cm^{-1}; MS *m*/*z* 319 (M^+ + 1 (^{81}Br), 80.63), 317 (M^+ + 1 (^{79}Br), 79.39), 299 (100). Anal. Calcd for $C_{13}H_{17}BrO_2S$: C, 49.22%; H, 5.40%. Found: C, 49.27%; H, 5.30%.

(d) (*E*)-3-Bromo-2-methyl-4-(phenylsulfinyl)-3-octen-2-ol (*E*-3bj): The reaction of **1j** (62 mg, 0.25 mmol), $CuBr_2$ (223 mg, 1.00 mmol), and H_2O/acetone (1:2, 3 mL) afforded 79 mg (92%) of *E*-**3bj** as solid, mp 126−127 °C (dichloromethane/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.88 (m, 2H), 7.47−7.50 (m, 3H), 3.60−4.80 (bs, 1H), 2.36−2.50 (m, 2H), 1.77 (s, 3H), 1.63 (s, 3H), 1.37−1.56 (m, 1H), 1.21−1.31 (m, 2H), 0.91−1.03 (m, 1H), 0.82 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 143.66, 142.78, 140.85, 130.62, 129.07, 125.60, 78.28, 31.30, 31.26, 30.74, 28.98, 23.12, 13.93; IR (KBr) 3241, 1593, 1032 cm^{-1}; MS *m*/*z* 347 (M^+ + 1 (^{81}Br), 23.39), 345 (M^+ + 1 (^{79}Br), 23.79), 329 (100); Anal. Calcd for $C_{15}H_{21}BrO_2S$: C, 52.18%; H, 6.13%. Found: C, 52.39%; H, 5.98%.

(e) (1*R*,2*R*,4*R*)-2-hydroxy-2-[(*E*)-1′-bromo-2′-(phenylsulfinylethenyl)]-1,7,7-trimethylbicyclo[2.2.1]heptane (*E*-**3bm**): The reaction of **1m** (72 mg, 0.25 mmol), $CuBr_2$ (223 mg, 1.00 mmol), and H_2O/acetone (1:2, 3 mL) afforded 38 mg of *E*-**3bm** (94.5%) as solids, mp 170 −172 °C (dichloromethane/*n*-hexane), $[\alpha]^{20}_D$ = −208.1° (*C* = 1.0, alcohol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70−7.73 (m, 2H), 7.42−7.45 (m, 3H), 6.72 (s, 1H), 3.02 (s, 1H), 2.62 (d, J = 14.10 Hz, 1H), 2.02−2.09 (m, 1H), 1.85 (t, J = 4.20 Hz, 1H), 1.60−1.70 (m, 2H),1.40−1.52 (m, 2H), 1.21 (s, 3H), 1.15 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 144.52, 142.69, 140.06, 130.82, 129.18, 125.12, 87.49, 56.43, 50.33, 46.57, 45.56, 30.84, 25.57, 21.10, 20.63, 11.26. IR (KBr) 3394, 1626, 1021 cm^{-1}; MS *m*/*z* 385 (M^+ + 1 (^{81}Br), 10.46), 383 (M^+ + 1 (^{79}Br), 10.37), 367 (100), 365 (96.16). Anal. Calcd for $C_{18}H_{23}BrO_2S$: C, 56.40%; H, 6.05%. Found: C, 56.34%; H, 6.02%. In this reaction, 42 mg of the starting material was recovered.

(f) (*E*)-2-Bromo-1-(phenylsulfinyl)-1-hepten-3-ol (*E*-3bc): The reaction of **1c** (110 mg, 0.50 mmol), NBS (110 mg, 0.60 mmol), $LiOAc\cdot 2H_2O$ (60 mg, 0.60 mmol), and H_2O/CH_3CN (1:7, 2.5 mL) was stirred at room temperature for 2 h. After the reaction was complete as monitored by TLC, it was subsequently extracted with CH_2Cl_2 (3 × 10 mL) and the combined layer was washed with brine and dried over $MgSO_4$. Filtration, evaporation, and flash chromatography on silica gel afforded 143 mg (90%) of *E*-**3bc** as solid, mp 70−71 °C (dichloromethane/*n*-hexane). Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60−7.69 (m, 2H), 7.47−7.59 (m, 3H), 6.70 (s, 1H), 4.94−5.04 (m, 1H), 4.08−4.12 (m, 1H), 1.71−1.92 (m, 2H), 1.31−1.55 (m, 4H), 0.83−1.05 (m, 3H). Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60−7.69 (m, 2H), 7.47−7.59 (m, 3H), 6.67 (s, 1H), 4.90−5.00 (m, 1H), 3.10 (d, J = 7.23 Hz, 1H), 1.71−1.92 (m, 2H), 1.31−1.55 (m, 4H), 0.83−1.05 (m, 3H); IR (KBr) 3378, 1694, 1601, 1046 cm^{-1}; MS *m*/*z* 319 (M^+ + 1 (^{81}Br), 3.35), 317 (M^+ + 1 (^{79}Br), 3.71), 77 (100). Anal. Calcd for $C_{13}H_{17}BrO_2S$: C, 49.22%; H, 5.40%. Found: C, 49.07%; H, 5.40%.

(g) (*E*)-2-Bromo-1-(phenylsulfinyl)-1-undec-3-ol (*E*-3bd): The reaction of **1d** (138 mg, 0.50 mmol), NBS (110 mg, 0.60 mmol), and $LiOAc\cdot 2H_2O$ (60 mg, 0.60 mmol) afforded 182 mg (98%) of *E*-**3bd** as solid, mp 84−85 °C (dichloromethane/*n*-hexane). Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61−7.69 (m, 2H), 7.52−7.55 (m, 3H), 6.70 (s, 1H), 4.91−5.06 (m, 1H), 4.06 (d, J = 4.71 Hz, 1H), 1.70−1.86 (m, 2H), 1.10−1.55 (m, 12H), 0.88 (t, J = 6.64 Hz, 3H). Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61−7.69 (m, 2H), 7.52−7.55 (m, 3H), 4.85−5.05 (m, 1H), 3.02 (d, J = 7.46 Hz, 1H), 1.70−1.86 (m, 2H), 1.10−1.55 (m, 12H), 0.88 (t, J = 6.64 Hz, 3H); IR (KBr) 3394, 1595, 1034 cm^{-1}; MS *m*/*z* 375 (M^+ + 1 (^{81}Br), 19.20), 373 (M^+ + 1 (^{79}Br), 19.11), 357 (100). HRMS calcd for $C_{17}H_{26}{}^{81}BrO_2S$ (M^+ + 1): 375.0810. Found: 375.0815. HRMS calcd for $C_{17}H_{26}{}^{79}BrO_2S$ (M^+ + 1): 373.0830. Found: 373.0825.

(h) (*E*)-3-Bromo-2-methyl-4-(phenylsulfinyl)-3-buten-2-ol (*E*-3bf): The reaction of **1f** (96 mg, 0.50 mmol), NBS (110 mg, 0.60 mmol), and $LiOAc\cdot 2H_2O$ (60 mg, 0.60 mmol) afforded 98 mg (68%) of *E*-**3bf** as solid, mp 112.5−113.5 °C (dichloromethane/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79−7.81 (m, 2H), 7.48−7.50 (m, 3H), 6.47 (s, 1H), 1.63 (s, 3H), 1.40−1.60 (bs, 1H), 1.41 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 144.22, 141.73, 136.93, 130.95, 129.21, 124.88, 77.45, 29.00, 28.93; IR (KBr) 3265, 1628, 1591, 1023 cm^{-1}; MS *m*/*z* 290 (M^+ (^{81}Br), 1.22), 288 (M^+ (^{79}Br), 1.09), 43 (100). Anal. Calcd for $C_{11}H_{13}BrO_2S$: C, 45.69%; H, 4.53%. Found: C, 45.44%; H, 4.45%.

Chlorohydroxylation of 1,2-Alkadienyl Phenyl Sulfoxides. (a) (*E*)-2-Chloro-3-(phenylsulfinyl)-2-propen-1-ol (*E*-3ca): To a pestle were added 400 mg of silica gel (200 mesh) and **1a** (180 mg, 1.1 mmol). After these were mixed thoroughly, $CuCl_2\cdot 2H_2O$ (748 mg, 4.4 mmol) was added and the mixture was milled for a couple of minutes followed by heating at 65 °C (under an IR lamp) for 5 min. This process was repeated 4 times until the complete disappearance of the starting sulfoxide. Chromatography on silica gel (eluent: petroleum ether/ethyl acetate (1:1 to 1:2)) afforded 105 mg (49%) of **3ca** as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.69 (m, 2H), 7.48−7.55 (m, 3H), 6.47 (s, 1H), 4.80−5.40 (bs, 1H), 4.69 (d, J = 14.90 Hz, 1H), 4.59 (d, J = 14.90 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 146.27, 142.76, 134.18, 131.36, 129.54, 124.29, 63.38; IR (neat) 3338, 1614, 1030 cm^{-1}; MS *m*/*z* 219 (M^+ + 1 (^{37}Cl), 16.90, 217 (M^+ + 1 (^{35}Cl), 42.64)), 77 (100). HRMS calcd for C_9H_8ClOS (M^+ − OH): 198.9980. Found: 198.9977.

(b) (*E*)-2-Chloro-4,4-dimethyl-1-(phenylsulfinyl)-1-penten-3-ol (*E*-3ce): The reaction of 200 mg of silica gel (200 mesh), **1e** (110 mg, 0.50 mmol), and $CuCl_2\cdot 2H_2O$ (340 mg, 2.0 mmol) afforded 114 mg (84%) of *E*-**3ce** as solid, mp 146−148°C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68−7.71 (m, 2H), 7.52−7.56 (m, 3H), 6.60 (s, 1H), 4.88 (d, J = 5.4 Hz, 1H), 3.60 (d, J = 6.0 Hz, 1H), 1.08 (s, 9H). The following signal is discernible for the minor isomer: 6.56 (s, 1H), 1.17 (s, 3H). MS *m*/*z* 254 (M^+ − H_2O (^{35}Cl), 31.93), 199 (100); IR (KBr) 3387, 1623, 1576, 1036 cm^{-1}; Anal. Calcd for $C_{13}H_{17}ClO_2S$: C, 57.24%; H, 6.28%. Found: C, 57.15%; H, 6.11%.

(c) (*E*)-3-Chloro-2-methyl-4-(phenylsulfinyl)-3-buten-2-ol (*E*-3cf): The reaction of 400 mg of silica gel (200 mesh), **1f** (96 mg, 0.50 mmol), and $CuCl_2\cdot 2H_2O$ (340 mg, 2.0 mmol) afforded 74 mg (61%) of *E*-**3cf** with the recovery of 11 mg (12%) of **1f**. *E*-**3cf**: solid, mp 133−134 °C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.65−7.78 (m, 2H), 7.40−7.50 (m, 3H), 6.23 (s, 1H), 1.56 (s, 3H), 1.39 (s, 3H); IR (KBr) 3235, 1600, 1020 cm^{-1}; ^{13}C NMR (75.4 MHz,

$CDCl_3$) δ 150.06, 144.39, 133.74, 130.94, 129.23, 124.79, 76.15, 28.53, 28.47; MS *m*/*z* 247 ($M^+ + 1(^{37}Cl)$, 245 ($M^+ + 1(^{35}Cl)$, 12.82), 4.78), 43 (100). Anal. Calcd for $C_{11}H_{13}ClO_2S$: C, 53.98%; H, 5.35%. Found: C, 54.01%; H, 5.34%.

(d) 1-[(*E*)-1′-Chloro-2′-(phenylsulfinylethenyl)]-1-cyclohexanol (*E*-3cg): The reaction of 200 mg of silica gel (200 mesh), **1g** (58 mg, 0.25 mmol), and $CuCl_2 \cdot 2H_2O$ (170 mg, 1.0 mmol) afforded 52 mg (73%) of *E*-**3cg** as solid, mp 142 °C−143 °C(CH_2Cl_2/hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66−7.80 (m, 2H), 7.40−7.55 (m, 3H), 6.29 (s, 1H), 3.74−3.85 (s, 1H), 1.47−2.18 (m, 8H), 1.07−1.27 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 150.95, 144.53, 134.03, 130.80, 129.17, 124.77, 77.58, 34.68, 34.54, 24.86, 21.03, 20.69; IR (KBr) 3429, 3226, 1594, 1023 cm^{-1}; MS *m*/*z* 286 (M^+ (^{37}Cl), 2.08), 284 (M^+ (^{35}Cl), 3.56), 110 (100). Anal. Calcd for $C_{14}H_{17}ClO_2S$: C, 59.04%; H, 6.02%. Found: C, 58.99%; H, 5.88%.

(e) (*E*)-2-Chloro-3-(phenylsulfinyl)-2-hepten-1-ol (*E*-3ch): The reaction of 200 mg of silica gel (200 mesh), **1h** (55 mg, 0.25 mmol), and $CuCl_2 \cdot 2H_2O$ (170 mg, 1.0 mmol) afforded 35 mg (51%) of *E*-**3ch** as solid, mp 74 −75 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50−7.60 (m, 2H), 7.35−7.50 (m, 3H), 4.63−4.82 (m, 2H), 2.80−3.10 (s, 1H), 2.20−2.32 (m, 1H), 1.95−2.15 (m, 1H), 1.20−1.28 (m, 1H), 1.00−1.10 (m, 2H), 0.70−0.85 (m, 1H), 0.67 (t, J = 7.31 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 144.89, 142.12, 141.33, 130.80, 129.12, 124.40, 62.83, 30.27, 25.16, 22.73, 13.42; IR (KBr) 3343, 1622, 1030 cm^{-1}; MS *m*/*z* 257 ($M^+ - OH$ (^{37}Cl), 0.05), 255 ($M^+ - OH$ (^{35}Cl), 0.94), 121 (100). Anal. Calcd for $C_{13}H_{17}ClO_2S$: C, 57.24%; H, 6.28%. Found: C, 57.25%; H, 6.22%.

Halohydroxylation of Optically Active 1,2-Alkadienyl Phenyl Sulfoxides. (a) 2-Iodo-1-(phenylsulfinyl)-1(*E*)-hepten-(*R*)-3-ol ((*R*)-*E*-3ac): The reaction of (*R*)-**1c** (110 mg, 0.5 mmol), I_2(153 mg, 0.6 mmol), and $LiOAc \cdot 2H_2O$ (102 mg, 1.0 mmol) afforded 179 mg (98%) of (*R*)-*E*-**3ac**, ee% = 95%, dr = 73:27 (HPLC conditions: Chiralpak AS column (0.46 cm $\phi \times$ 25 cm); λ 254 nm; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 65:35). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60−7.75 (m, 2H), 7.46−7.60 (m, 3H), 6.98 (s, 1H), 4.40−4.51 (m, 1H), 2.50−3.20 (bs, 1H), 1.59−1.80 (m, 2H), 1.15−1.59 (m, 4H), 0.74−1.06 (m, 3H). The following signal is discernible for the minor isomer: 6.93 (s, 1H).

(b) 2-Bromo-1-(phenylsulfinyl)-1(*E*) -hepten-3(*R*)-ol ((*R*)-*E*-3bc). Method A: The reaction of (*R*)-**1c** (55 mg, 0.25 mmol), Br_2 (0.5 M in MeCN, 0.6 mL, 0.3 mmol), and $LiOAc \cdot 2H_2O$ (60 mg, 0.6 mmol) afforded 76 mg (96%) of (*R*)-*E*-**3bc**, ee% = 96%, dr = 50:50 (HPLC conditions: Chiralcel OJ column (0.46 cm $\phi \times$ 25 cm); λ 254 nm; rate, 0.7 mL/min; eluent: hexane/*i*-PrOH = 90:10). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.71 (m, 5H), 6.69 (s, 1H), 4.91−5.01 (m, 1H), 2.80 (d, J = 7.05 Hz, 1H), 1.62−1.88 (m, 2H), 1.23−1.62 (m, 4H), 0.83−1.05 (m, 3H). The following signal is discernible for the minor isomer: 6.66 (s, 1H), 4.91−5.01 (m, 1H), 3.75 (bs, 1H).

Method B: The reaction of $CuBr_2$ (223 mg, 1 mmol), (*R*)-**1c** (55 mg, 0.25 mmol), and water/acetone (1:2, 2 mL) at room temperature afforded 73 mg (92%) of (*R*)-*E*-**3bc**, ee% = 97%, dr = 51:49.

(c) 2-Bromo-1-(phenylsulfinyl)-1(*E*)-undecen-3(*S*)-ol ((*S*)-*E*-3bd). Method A: The reaction of (*S*)-**1d** (69 mg, 0.25 mmol), Br_2 (0.5 M in MeCN, 0.7 mL, 0.35 mmol), and $LiOAc \cdot 2H_2O$ (60 mg, 0.6 mmol) afforded 92 mg (99%) of (*S*)-*E*-**3bd**, ee% = 97%, dr = 53:47 (HPLC conditions: Chiralcel OD column (0.46 cm $\phi \times$ 25 cm); λ 254 nm; rate, 0.8 mL/min; eluent, hexane/*i*-PrOH = 97:3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.70 (m, 5H), 6.68 (s, 1H), 4.90−5.05 (m, 1H), 3.30−4.20 (bs, 1H), 1.53−1.87 (m, 2H), 1.14−1.53 (m, 12H), 0.73−0.94 (m, 3H). The following signal is discernible for the minor isomer: 6.66 (s, 1H).

Method B: The reaction of (*S*)-**1d** (69 mg, 0.25 mmol), $CuBr_2$ (223 mg, 1 mmol), and water/acetone (1:2, 2 mL) afforded 90 mg (97%) of (*S*)-*E*-**3bd**, ee% = 96%, dr = 51:49.

(d) 2-Iodo-4,4-dimethyl-1-(phenylsulfinyl)-1(*E*)-penten-3(*S*)-ol ((*S*)-*E*-3ae): The reaction of (*S*)-**1e** (110 mg, 0.50 mmol), I_2 (153 mg, 0.60 mmol), and $LiOAc \cdot 2H_2O$ (102 mg, 1.0 mmol) afforded 160 mg (88%) of (*S*)-*E*-**3ae**, ee% > 99%, dr = 99:1(HPLC conditions: Chiralcel OD column (0.46 cm $\phi \times$ 25 cm); λ 254 nm; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 95:5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65−7.73 (m, 2H), 7.47−7.59 (m, 3H), 7.20 (s, 1H), 4.36 (s, 1H), 1.50−1.85 (s, 1H), 1.06 (s, 9H).

(e) 2-Bromo-4,4-dimethyl-1-(phenylsulfinyl)-1(*E*)-penten-3(S)-ol ((*S*)-*E*-3be). Method A: The reaction of (*S*)-**1e** (110 mg, 0.50 mmol), Br_2 (0.50 M in MeCN, 1.2 mL, 0.6 mmol), and $LiOAc \cdot 2H_2O$ (102 mg, 1.0 mmol) afforded 135 mg (85%) of (*S*)-*E*-**3be**, ee > 99%, dr = 92:8 (HPLC conditions: Chiralcel OD column (0.46 cm $\phi \times$ 25 cm); λ 254 nm; rate, 0.9 mL/min; eluent, hexane/*i*-PrOH = 100:1.5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60−7.73 (m, 2H), 7.48−7.60 (m, 3H), 6.84 (s, 1H), 4.80 (d, J = 5.7 Hz, 1H), 3.16 (d, J = 5.8 Hz, 1H), 1.08 (s, 9H). The following signal is discernible for the minor isomer: 6.80 (s, 1H), 1.18 (s, 3H).

Method B: The reaction of (*S*)-**1e** (110 mg, 0.5 mmol), $CuBr_2$ (446 mg, 2 mmol), and water/acetone (1:2, 2 mL) at room temperature afforded 109 mg (69%) of (*S*)-*E*-**3be**, ee% > 99%, dr = 98:2 (HPLC conditions: Chiralcel OD column (0.46 cm $\phi \times$ 25 cm); λ 254 nm; rate, 0.8 mL/min; eluent, hexane/*i*-PrOH = 97:3.

(f) 2-Chloro-4,4-dimethyl-1-(phenylsulfinyl)-1(*E*)-penten-3(*S*)-ol ((*S*)-*E*-3ce). Method C: The reaction of 245 mg of silica gel, (*S*)-**1e** (67 mg, 0.3 mmol), and $CuCl_2 \cdot 2H_2O$ (204 mg, 1.2 mmol) afforded 67 mg (82%) of (*S*)-*E*-**3ce**, ee% > 99%, dr = 89:11 (HPLC conditionss: Chiralcel OD column (0.46 cm $\phi \times$ 25 cm); λ 254 nm; rate, 0.9 mL/min; eluent, hexane/*i*-PrOH = 100:1.5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60−7.68 (m, 2H), 7.41−7.55 (m, 3H), 6.52 (s, 1H), 4.81 (s, 1H), 1.50−1.70 (s, 1H), 1.02 (s, 9H).

Coupling Reaction of the Carbon−Halogen Bond. (a) *Z*-2-(Benzenesulfinylmethylene)oct-3-yn-1-ol (*Z*-4g): A mixture of *E*-**3aa** (77 mg, 0.25 mmol), Et_3N (1 mL), 1-hexyne (41 mg, 0.5 mmol), Pd-$(PPh_3)_2Cl_2$ (0.9 mg, 0.001 25 mmol), CuI (0.5 mg, 0.0026 mmol), and DMSO (1 mL) were heated at 40−45 °C over a period of 5 h under nitrogen. After the reaction mixture was cooled to room temperature, 1 mL of water was added. The organic layer was separated. The aqueous layer was extracted with three 5 mL portions of ether. The combined organic layer was dried over $MgSO_4$. Evaporation and column chromatography on silica gel (eluent: hexane/ethyl acetate = 2:1) gave *Z*-**4g** (60 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64−7.67 (m, 2H), 7.44−7.51 (m, 3H), 6.37 (s, 1H), 4.54 (dd, J_1 = 14.10 Hz, J_2 = 6.30 Hz, 1H), 4.45 (ddd, J_1 = 14.10 Hz, J_2 = 6.60 Hz, J_3 = 0.90 Hz, 1H), 4.26 (t, J = 6.90 Hz, 1H), 2.29 (t, J = 6.90 Hz, 2H), 1.30−1.48 (m, 4H), 0.84 (t, J = 7.50 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 143.41, 139.52, 135.16, 130.89, 129.32, 124.46, 98.55, 77.53, 62.17, 30.18, 21.85, 19.16, 13.45; IR (neat) 1612, 1039 cm^{-1}; MS *m*/*z* 263 ($M^+ + 1$, 100). HRMS calcd for $C_{15}H_{18}O_2S$: 262.1023. Found: 262.1005.

(b) *Z*-2-(Benzenesulfinylmethylene)oct-3(*E*)-en-1-ol (*Z*-4h): A mixture of *E*-**3aa** (27.2 mg, 0.09 mmol), *E*-1-hexenyl boronic acid (12.6 mg, 0.1 mmol), $Pd(PPh_3)_4$ (5.8 mg, 5% mmol), *n*-Bu_4NBr (1.6 mg, 5mol %), K_2CO_3 (2 M in water, 0.15 mL, 0.3 mmol), and THF (1 mL) was refluxed under nitrogen for 3 h. After the reaction mixture was cooled to room temperature, 1 mL of water was added. The organic layer was separated. The aqueous layer was extracted with three 5 mL portions of CH_2Cl_2. The combined organic layer was dried over $MgSO_4$. Evaporation and column chromatography on silia gel (eluent: hexane/ethyl acetate = 2:1) gave *Z*-**4h** (21 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58−7. 61 (m, 2H), 7.38−7.45 (m, 3H), 6.16 (dt, J_1 = 15.90 Hz, J_2 = 7.20 Hz, 1H), 6.04 (s, 1H), 5.86 (d, J = 15.90 Hz, 1H), 4.68 (d, J = 13.20 Hz, 1H), 4.54 (d, J = 12.90 Hz, 1H), 3.89 (bs, 1H), 2.05 (q, J = 6.90 Hz, 2H), 1.18−1.32 (m, 4H), 0.80 (t, J = 6.90 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 148.17, 144.00, 138.57, 133.82, 130.67, 129.26, 128.10, 124.41, 58.66, 32.83, 30.82, 22.20, 13.82; IR (neat) 3330, 1634, 1022 cm^{-1}; MS *m*/*z* 265 ($M^+ + 1$, 100). HRMS calcd for $C_{15}H_{20}OS$ ($M^+ + 1 - OH$): 248.1230. Found: 248.1268.

(c) *Z*-3-Benzenesulfinyl-2-phenylprop-2-en-1-ol (*Z*-4a):[28] *E*-**3aa** (154 mg, 0.5 mmol), phenylboronic acid (91.5 mg, 0.75 mmol), Pd(PPh_3)$_4$ (29 mg, 5% mmol), *n*-Bu_4NBr (15.7 mg, 10%), K_2CO_3 (2 M in water, 0.75 mL, 1.5 mmol), and THF (4 mL) gave *E*-**4a** (116.1 mg, 90%), *E*/*Z* = 3:97.

(d) *Z*-3-Benzenesulfinyl-2-phenylprop-2-en-1-ol (*Z*-4a):[28] To a solution of anhydrous $ZnBr_2$ (1.35 g, 2.0 mmol) in dry THF (10 mL) was added PhMgBr (1.1084 M, 5.4 mL, 2.0 mmol) at 0 °C. The reaction mixture was stirred for 1 h at room temperature. After removing THF by vacuum, a solution of *E*-**3aa** (616 mg, 2.0 mmol) in anhydrous DMF (10 mL) and Pd(PPh_3)$_4$ (115 mg, 5 mol %) were added to the reaction mixture. After the mixture was stirred for 1 h under N_2 at ambient temperature, saturated of NH_4Cl (5 mL) was added. The mixture was extracted with ether (3 × 30 mL), washed with brine (3 × 30 mL), and dried over $MgSO_4$. Filtration, evaporation, and flash chromatography on silica gel (ethyl acetate/*n*-hexane = 1:2) afforded *Z*-**4a (**484 mg, 94%) as solid, mp 95.5−96 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70−7.73 (m, 2H), 7.41−7.54 (m, 5H), 7.25−7.39 (m, 3H), 6.47 (s, 1H), 4.04 (d, J = 13.80 Hz, 1H), 4.86 (d, J = 13.50 Hz, 1H), 3.67 (bs, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 150.92, 144.09, 137.48, 134.81, 131.18, 129.71, 129.68, 128.99, 127.15, 124.79, 61.18; MS *m*/*z* 259 (M^+ + 1, 3.99), 103 (100); IR (KBr) 3380, 2915, 1598, 1442, 1037, 737 cm^{-1}.

(e) *Z*-3-(Benzenesulfinyl)-2-phenylhept-2-en-1-ol (*Z*-4b): The reaction of anhydrous $ZnBr_2$ (203 mg, 0.9 mmol), PhMgBr (0.7656 M, 1.2 mL, 0.9 mmol), *E*-**3ah** (109.2 mg, 0.3 mmol), and Pd(PPh_3)$_4$ (17 mg, 5 mol %) afforded *E*-**4b** (77.2 mg, 82%) as white needle solid, mp 94−95 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.39−7.49 (m, 3H), 7.26−7.30 (m, 3H), 7.16 (d, J = 8.1 Hz, 2H), 4.79 (m, 2H), 3.78 (bs, 1H), 2.09−2.19 (m, 1H), 1.89−1.99 (m, 1H), 0.98−1.05 (m, 1H), 0.78−0.87 (m, 2H), 0.55−0.62 (m, 1H), 0.44 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 147.84, 145.06, 142.44, 138.32, 129.95, 128.71, 128.16, 127.54, 127.46, 124.37, 62.34, 31.52, 23.95, 22.24, 12.95; MS *m*/*z* 314 (M^+, 1.05), 91 (100); IR (KBr) 3442, 2955, 1600, 1443, 1041, 749 cm^{-1}; Anal. Calcd for $C_{19}H_{22}O_2S$: C, 72.57; H, 7.05; Found: C, 72.61; H, 7.05.

(f) *Z*-1-(Benzenesulfinyl)-2-phenylhept-1-en-3-ol (*Z*-4c): The reaction of anhydrous $ZnCl_2$ (2.04 g, 15.0 mmol), PhMgBr (0.8275 M, 18.0 mL, 15.0 mmol), *E*-**3ac** (1.82 g, 5.0 mmol), and Pd(PPh_3)$_4$ (145 mg, 2.5 mol %) afforded 1.1073 g (71%) of *Z*-**4c**. The two isomers can be separated by repeated chromatography on silica gel. Less polar isomer: solid, mp 124−125 °C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69−7.73 (m, 2H), 7.44−7.53 (m, 3H), 7.35−7.38 (m, 2H), 7.20−7.30 (m, 3H), 6.25 (s, 1H), 5.18−5.24 (m, 1H), 4.62 (d, J = 4.8 Hz, 1H), 1.72−1.78 (m, 1H), 1.41−1.58 (m, 2H), 1.20−1.29 (m, 3H), 0.81 (t, J = 7.05 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 155.22, 144.52, 137.79, 135.08, 131.10, 129.63, 129.02, 128.52, 128.05, 124.90, 72.06, 35.79, 28.34, 22.68, 14.21; MS *m*/*z* 314 (M^+, 0.61), 241 (100); IR (KBr) 3271, 2938, 1580, 1442, 1078, 1036 cm^{-1}. Anal. Calcd for $C_{19}H_{22}O_2S$: C, 72.57; H, 7.05. Found: C, 72.54; H, 7.02. More polar isomer:^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67−7.70 (m, 2H), 7.41−7.49 (m, 3H), 7.24−7.33 (m, 5H), 6.18 (s, 1H), 5.05−5.08 (m, 1H), 3.04 (m, 1H), 1.59−1.63 (m, 1H), 1.39−1.43 (m, 1H), 1.18−1.29 (m, 4H), 0.79 (t, J = 7.20 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 154.91, 144.31, 137.98, 134.81, 130.88, 129.35, 128.77, 128.39, 127.58, 124.65, 72.85, 36.12, 27.89, 22.35, 13.88; MS *m*/*z* 314 (M^+, 1.02), 298 (100). HRMS calcd for $C_{19}H_{22}O_2S$: 314.1341. Found: 314.3332.

(g) (*R*)-*Z*-1-(benzenesulfinyl)-2-phenyl-hept-1-en-3-ol ((*R*)-*Z*-4c): The reaction of anhydrous $ZnCl_2$ (1.54 g, 11.3 mmol), PhMgBr (0.8275 M, 13.7 mL, 11.3 mmol), *E*-(*R*)-**3ac** (1.37 g, 3.76 mmol), and Pd(PPh_3)$_4$ (108 mg, 2.5 mol %) afforded 869 mg (74%) of (*R*)-*Z*-**4c**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71−7.78 (m, 2H), 7.48−7.55 (m, 3H), 7.26−7.40 (m, 5H), 6.26 (s, 1H), 5.14−5.20 (m, 1H), 2.60 (bs, 1H), 1.76−1.79 (m, 1H), 1.55−1.65 (m, 2H), 1.25−1.34 (m, 3H), 0.84 (t, J = 6.90 Hz, 3H). The following signal is discernible for the minor isomer: 6.24 (s, 1H), 5.10−5.16 (m, 1H); ee% = 99.1% (HPLC conditions: Chiralpak AS column (0.46 cm ϕ × 25 cm); λ 254 nm; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 80:20).

(h) *Z*-1-(Benzenesulfinyl)-2-phenylundec-1-en-3-ol (*Z*-4d): The reaction of anhydrous $ZnBr_2$ (5.06 g, 22.5 mmol), 0.79 M PhMgBr (28.5 mL, 22.5 mmol), *E*-**3ad** (3.15 g, 7.5 mmol), and Pd(PPh_3)$_4$ (433 mg, 5 mol %) afforded 2.0959 g (76%) of *Z*-**4d**. The two isomers can be separated by repeated chromatography on silica gel. Less polar isomer: solid, mp 85−85.5 °C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71−7.75 (m, 2H), 7.45−7.54 (m, 3H), 7.23−7.40 (m, 5H), 6.26 (s, 1H), 5.17−5.21 (m, 1H), 3.99 (bs, 1H), 1.72−1.82 (m, 1H), 1.41−1.60 (m, 2H), 1.20−1.25 (m, 11H), 0.85 (t, J = 6.90 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 154.84, 144.20, 137.48, 134.89, 130.76, 129.26, 128.69, 128.21, 127.63, 124.54, 72.03, 35.92, 31.69, 29.29, 29.18, 29.03, 25.81, 22.52, 14.00; MS *m*/*z* 353 (M^+ − H_2O, 100); IR (KBr) 3276, 2928, 1597, 1579, 1442, 1079, 1037 cm^{-1}; Anal. Calcd for $C_{23}H_{30}O_2S$: C, 74.55; H, 8.16. Found: C, 74.81; H, 8.00. More polar isomer: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69−7.72 (m, 2H), 7.37−7.45 (m, 3H), 7.19−7.28 (m, 5H), 6.16 (s, 1H), 5.04 (bs, 1H), 4.33 (bs, 1H), 1.47−1.52 (m, 2H), 1.12−1.19 (m, 12H), 0.78 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 155.52, 144.69, 138.12, 134.72, 130.74, 129.28, 128.72, 128.35, 127.54, 124.77, 72.79, 36.40, 31.79, 29.38, 29.32, 29.16, 25.74, 22.61, 14.10; MS *m*/*z* 369 (M^+ − H, 1.59); IR (neat) 3300, 2922, 1444, 1004, 989, 747, 690 cm^{-1}. HRMS calcd for $C_{23}H_{29}OS$ (M^+ − OH): 353.1939. Found: 353.1905.

(i) (*R*)-*Z*-1-(Benzenesulfinyl)-2-phenylundec-1-en-3-ol ((*R*)-*Z*-4d): The reaction of anhydrous $ZnBr_2$ (193 mg, 0.86 mmol), 0.98 M PhMgBr (0.87 mL, 0.86 mmol), (*R*)-*E*-**3ad** (120 mg, 0.29 mmol), and Pd(PPh_3)$_4$ (17 mg, 5 mol %) afforded 105.7 mg (78%) of (*R*)-*Z*-**4d**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47−7.55 (m, 2H), 7.21−7.30 (m, 3H), 6.97−7.14 (m, 5H), 6.00 (s, 1H), 4.95−4.99 (m, 1H), 1.50−1.54 (m, 1H), 1.19−1.36 (m, 2H), 0.96 (m, 11H), 0.62 (t, J = 6.90 Hz, 3H); ee% = 98.1% (HPLC conditions: Chiralcel OD column (0.46 cm ϕ × 25 cm); λ 254 nm; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 92:8).

(j) (*S*)-*Z*-1-(Benzenesulfinyl)-2-phenyl-undec-1-en-3-ol ((*S*)-*Z*-4d): The reaction of anhydrous $ZnBr_2$ (0.97 g, 4.30 mmol), 1.00 M PhMgBr (4.30 mL, 4.30 mmol), (*R*)-*E*-**3ad** (600 mg, 1.43 mmol), and Pd(PPh_3)$_4$ (80 mg, 5 mol %) afforded 408.1 mg (77%) of (*S*)-*Z*-**4d**. ^{1}H NMR (300 MHz,$CDCl_3$) δ 7.72−7.77 (m, 2H), 7.49−7.55 (m, 3H), 7.26−7.40 (m, 5H), 6.24 (s, 1H), 5.14−5.17 (m, 1H), 3.22 (br, 1H), 1.61−1.65 (m, 1H), 1.43−1.48 (m, 2H), 1.18−1.27 (m, 11H), 0.86 (t, J = 6.90 Hz, 3H), dr = 37:63, ee% = 94.7% (HPLC conditions: Chiralcel OD column (0.46 cm ϕ × 25 cm); λ 254 nm; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 92:8).

(k) *Z*-3-(Benzenesulfinyl)-2-ethylprop-2-en-1-ol (*Z*-4e):[28] The reaction of anhydrous $ZnBr_2$ (225 mg, 0.4 mmol), EtMgBr (0.7721 M in THF, 1.3 mL, 1.0 mmol), *E*-**3aa** (123.2 mg in 4 mL of DMF, 0.4 mmol), and Pd(PPh_3)$_4$ (23 mg, 5 mol %) afforded *Z*-**4e (**72.3 mg, 86%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61−7.65 (m, 2H), 7.43−7.54 (m, 3H), 6.02 (s, 1H), 4.65 (d, J = 13.5 Hz, 1H), 4.42 (d, J = 13.8 Hz, 1H), 3.83 (bs, 1H), 2.30 (q, J = 7.80 Hz, 2H), 1.04 (t, J = 7.35 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 156.73, 144.36, 131.15, 130.89, 129.52, 124.60, 61.51, 27.72, 11.77; MS *m*/*z* 193 (M^+ + 1 − H_2O, 62.04), 51 (100); IR (neat) 3341, 2935, 1610, 1443, 1016, 746 cm^{-1}.

(l) *Z*-3-(Benzenesulfinyl)-2-(phenylacetylenyl)-2-en-1-ol (*Z*-4f): After the flask was purged with nitrogen, a mixture of phenylacetylene (122.4 mg, 1.2 mmol) and 3 mL of THF was treated with a solution of *n*-BuLi (1.52 M in *n*-hexane, 0.8 mL, 1.2 mmol), which was added over 10 min at −70 °C, and stirred for 15 min. Subsequently, a solution of anhydrous $ZnBr_2$ (270 mg, 1.2 mmol) in 2 mL of THF was added over a few minutes with vigorous stirring at room temperature for another 30 min followed by the subsequent addition of 1 mL of HMPA, *E*-**3aa** (123 mg, 0.4 mmol), and Pd(PPh_3)$_4$ (23 mg, 5 mol %). After

(28) Dubouclin, J. G.; Jousseaume, B.; Thoumazeau, E. *Bull. Soc. Chim. Fr. II* **1983**, 105.

1.5 h at ambient temperature with stirring, the mixture was quenched with 2 mL of saturated aqueous solution of ammonium chloride. The aqueous layer was extracted with ether, and the combined organic layer was washed 4 times with brine and subsequently dried over $MgSO_4$. Filtration, evaporation, and flash chromatography on silica gel afforded *Z*-**4f** (105.9 mg, 94%) as white solids: mp 104.5−105 °C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70−7.73 (m, 2H), 7.51−7.53 (m, 3H), 7.26−7.43 (m, 5H), 6.58 (s, 1H), 4.70 (d, J = 14.10 Hz, 1H), 4.58 (d, J = 13.80 Hz, 1H), 3.82 (bs, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 143.30, 140.69, 134.42, 131.94, 131.19, 129.54, 129.32, 128.42, 124.67, 121.74, 96.16, 86.07, 62.19; MS *m*/*z* 282 (M^+, 2.71), 105 (100); IR (KBr) 3204, 2206, 2178, 1570, 1440, 1010, 748; Anal. Calcd for $C_{17}H_{14}O_2S$: C, 72.31; H, 5.00. Found: C, 72.25; H, 5.16.

***Z*-1-(Benzenesulfonyl)-2-phenylundec-1-en-3-ol (*Z*-6e):** A solution of *m*-CPBA (85%, 91.4 mg, 0.45 mmol) in CH_2Cl_2 (3 mL) was added to a solution of *Z*-**4d** (111 mg, 0.3 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred vigorously at 25 °C. After 30 min, saturated Na_2SO_3 (2 mL) and saturated $NaHCO_3$ (2 mL) were added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried ($MgSO_4$) followed by evaporation of the solvent. The residue was purified by flash chromatography (*n*-hexane/ethyl acetate = 5:1) to give *Z*-**6e** (100.4 mg, 87%) as white solids: mp 44−45 °C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99−8.02 (m, 2H), 7.54−7.67 (m, 3H), 7.31−7.43 (m, 5H), 6.36 (s, 1H), 5.25−5.29 (m, 1H), 3.46−3.48 (m, 1H), 1.67−1.72 (m, 1H), 1.36−1.53 (m, 2H), 1.18−1.29 (m, 11H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 160.51, 141.73, 137.92, 133.82, 129.62, 129.58, 129.56, 128.66, 128.09, 127.59, 70.94, 36.10, 32.04, 29.59, 29.46, 29.36, 25.97, 22.87, 14.35; MS *m*/*z* 386 (M^+, 0.31), 103 (100); IR (KBr) 3864, 2920, 1612, 1282, 1294, 1145. Anal. Calcd for $C_{23}H_{30}O_3S$: C, 71.46; H, 7.82. Found: C, 71.64; H, 7.73.

***(S)*-*Z*-1-(Benzenesulfonyl)-2-phenylundec-1-en-3-ol ((*S*)-*Z*-6e):** The reaction of *m*-CPBA (85%, 244 mg, 1.2 mmol) and (*S*)-*Z*-**4d** (420 mg, 1.0 mmol) gave (*S*)-*Z*-**6e** (348.9 mg, 80%) as oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99−8.01 (m, 2H), 7.55−7.65 (m, 3H), 7.33−7.41 (m, 5H), 6.35 (s, 1H), 5.22 (m, 1H), 3.30 (d, J = 7.5 Hz, 1H), 1.67−1.72 (m, 1H), 1.36−1.54 (m, 2H), 1.18−1.25 (m, 11H), 0.86 (t, J = 6.9 Hz, 3H); ee% = 96.0% (HPLC conditions: Chiralcel AD column (0.46 cm ϕ × 25 cm); λ 254 nm; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 95:5).

Coupling Reaction of C−S Bond. A. Coupling Reaction of Carbon−Sulfinyl Bond. (a) *Z*-3-(4′-Chlorophenyl)-2-phenylprop-2-en-1-ol (*Z*-5a): A three necked flask equipped with a thermometer, a gas inlet, and an addition funnel was charged under N_2 with 1-chloro-4-iodobenzene (477 mg, 2.0 mmol) in 2 mL of THF and cooled to −78 °C followed by the addition of *n*-BuLi (2.5 M in *n*-hexane, 0.8 mL, 2.0 mmol) over 5 min. The resulting solution was stirred for another 5 min followed by the addition of a THF (2 mL) solution of $ZnBr_2$ (450 mg, 2.0 mmol). After an additional 30 min, a DMF (4 mL) solution of *Z*-**4a** (103.2 mg, 0.4 mmol) and $Ni(acac)_2$ (5 mg, 5mol %) was added, and then the reaction mixture was stirred for 1.5 h at 80 °C. The mixture was quenched by pouring it into a saturated aqueous NH_4Cl solution (2 mL) and was extracted with diethyl ether. The combined organic layer was dried over anhydrous $MgSO_4$. The resulting crude product was purified by chromatography on silica gel to afford the pure product *Z*-**5a** (66.9 mg, 68%) as solid: mp 70−71 °C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56−7.59 (m, 2H), 7.34−7.44 (m, 7H), 6.90 (s, 1H), 4.67 (s, 2H), 1.57 (bs, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 140.85, 140.59, 135.55, 133.49, 130.53, 130.38, 128.99, 128.82, 128.17, 126.81, 60.48; MS *m*/*z* 246 (M^+(^{37}Cl), 14.87), 244 (M^+(^{35}Cl), 48.19), 105 (100); IR (KBr) 3262, 1595, 1489, 1464, 1094, 1037, 697 cm^{-1}. Anal. Calcd for $C_{15}H_{13}ClO$: C, 73.62; H, 5.35. Found: C, 73.75; H, 5.51.

(b) *Z*-3-(4-Methoxyphenyl)-2-phenylprop-2-en-1-ol (*Z*-5b):[29] The reaction of 4-iodoanisole (468 mg, 2.0 mmol), *n*-BuLi (2.5 M in *n*-hexane, 0.8 mL, 2.0 mmol), $ZnBr_2$ (450 mg, 2.0 mmol), *Z*-**4a** (103.2 mg, 0.4 mmol), and $Ni(acac)_2$ (5 mg, 5 mol %) afforded the pure product *Z*-**5b** (70.4 mg, 73%) as white solids, mp 99−100 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56−7.60 (m, 2H), 7.31−7.43 (m, 5H), 6.92−6.95 (m, 3H), 4.72 (s, 2H), 3.84 (s, 3H), 1.58 (bs, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 159.18, 141.15, 138.74, 131.38, 130.57, 129.71, 128.91, 127.74, 126.71, 114.07, 60.68, 55.54; MS *m*/*z* 240 (M^+, 55.16), 121 (100); IR (KBr) 3530, 1601, 1507, 1243, 1178 cm^{-1}.

General Procedure for the Synthesis of *Z*-5c−j: A solution of dry zinc bromide in dry THF was added to a Grignard reagent at ambient temperature. The thick white mixture was then stirred for 0.5−1 h at ambient temperature. The reaction mixture was cooled to 0 °C, and a solution of benzenesulfinyl alcohol (*Z*-**4a**, *Z*-**4c**, and *Z*-**4d**) or benzenesulfonyl alcohol (*Z*-**6e**) in DMF was added via a syringe followed by the addition of $Ni(acac)_2$. The mixture was stirred at 40 °C for 12−24 h. When the benzenesulfinyl alcohol disappeared, the mixture was worked up with a saturated aqueous NH_4Cl solution and extracted with diethyl ether. The combined organic layer was dried over anhydrous $MgSO_4$. The resulting crude product was purified by chromatography on silica gel to afford the pure product.

(c) *Z*-2,3-Diphenyl-2-propen-1-ol (*Z*-5c):[30] The reaction of anhydrous $ZnBr_2$ (450 mg, 2.0 mmol), PhMgBr (0.7905 M, 2.53 mL, 2.0 mmol), *Z*-**4a** (103.2 mg, 0.4 mmol, in 4 mL of DMF), and $Ni(acac)_2$ (5 mg, 5 mol %) afforded *Z*-**5c** (70.5 mg, 84%) as solids, mp 78−79 °C (*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51−7.53 (d, J = 6.72 Hz, 2H), 7.18−7.36 (m, 8H), 6.91 (s, 1H), 4.65 (s, 2H), 1.52 (bs, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 140.85, 140.38, 137.17, 131.56, 129.21, 128.95, 128.67, 128.00, 127.65, 126.87, 60.57; MS *m*/*z* 210 (M^+, 48.8), 105 (100); IR (KBr) 3265, 1600, 1490, 1450, 1080, 1035, 774 cm^{-1}.

(d) *Z*-3-(2-Methoxyphenyl)-2-phenylprop-2-en-1-ol (*Z*-5d): The reaction of anhydrous $ZnBr_2$ (450 mg, 2.0 mmol, in 2.2 mL THF), *o*-$CH_3OC_6H_4MgBr$ (0.53 M, 3.8 mL, 2.5 mmol), *Z*-**4a** (129 mg, 0.5 mmol, in 6 mL of DMF), and $Ni(acac)_2$ (12.8 mg, 10 mol %) afforded *Z*-**5d** (81.5 mg, 68%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62−7.66 (m, 2H), 7.26−7.43 (m, 5H), 6.92−7.03 (m, 3H), 4.63 (s, 2H), 3.85 (s, 3H), 1.79 (bs, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 157.05, 140.29, 139.88, 130.14, 128.82, 128.45, 127.46, 126.53, 126.50, 125.85, 120.39, 110.43, 60.47, 55.40; MS *m*/*z* 240 (M^+, 38.96), 108 (100); IR (neat) 3396, 2940, 1597, 1577, 1245, 1111 cm^{-1}. HRMS calcd for $C_{16}H_{16}O_2$: 240.1150. Found: 240.1192.

(e) *Z*-1,2-(Diphenyl)undec-1-en-3-ol (*Z*-5e): The reaction of anhydrous $ZnBr_2$ (450 mg, 2.0 mmol), PhMgBr (1.0 M, 2.0 mL, 2.0 mmol), *Z*-**4d** (148 mg, 0.4 mmol, in 4 mL of DMF), and $Ni(acac)_2$ (10 mg, 10 mol %) afforded *Z*-**5e** (88.3 mg, 68.6%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56−7.59 (m, 2H), 7.26−7.42 (m, 8H), 6.73 (s, 1H), 4.90 (t, J = 7.03 Hz, 1H), 1.70 (bs, 1H), 1.52−1.63 (m, 2H), 1.18−1.33 (m, 12H), 0.87 (t, J = 7.03 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 144.75, 140.85, 137.15, 132.18, 129.14, 128.88, 128.54, 128.24, 127.47, 127.30, 70.50, 36.00, 32.04, 29.66, 29.61, 29.40, 26.03, 22.89, 14.37; MS *m*/*z* 322 (M^+, 2.12), 209 (100); IR (neat) 3389, 2925, 1600, 1493, 772 cm^{-1}. HRMS calcd for $C_{23}H_{30}O$: 322.2297. Found: 322.2292.

(f) (*S*)-*Z*-1,2-(Diphenyl)undec-1-en-3-ol ((*S*)-*Z*-5e): The reaction of anhydrous $ZnBr_2$ (450 mg, 2.0 mmol), PhMgBr (0.7905 M, 2.5 mL, 2.0 mmol), (*S*)-*Z*-**4d** (148 mg, 0.4 mmol, in 4 mL of DMF), and $Ni(acac)_2$ (10 mg, 10 mol %) afforded (*S*)-*Z*-**5e** (82.2 mg, 64%) as oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56−7.59 (m, 2H), 7.26−7.44 (m, 8H), 6.72 (s, 1H), 4.86−4.92 (m, 1H), 1.69 (bs, 1H), 1.47−1.64 (m, 2H), 1.17−1.37 (m, 12H), 0.87 (t, J = 6.9 Hz, 3H); ee% = 95.6% (HPLC conditions: Chiralcel OD column (0.46 cm ϕ × 25 cm); λ 254 nm; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 85:15).

(g) *Z*-1-(4′-Methoxyphenyl)-2-phenylundec-1-en-3-ol (*Z*-5f): The

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(30) Nalesnik, T. E.; Fish, J. G.; Horgan, S. W.; Orchin, M. *J. Org Chem.* **1981**, *46*, 1987.

reaction of anhydrous $ZnBr_2$ (450 mg, 2.0 mmol), *p*-$MeOC_6H_4MgBr$ (0.55 M, 3.6 mL, 2.0 mmol), *Z*-**4d** (148 mg, 0.4 mmol, in 5 mL of DMF), and $Ni(acac)_2$ (10 mg, 10 mol %) afforded *Z*-**5f** (84.6 mg, 60%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47−7.50 (m, 2H), 7.19−7.32 (m, 5H), 6.85 (d, J = 8.7 Hz, 2H), 6.59 (s, 1H), 4.85 (t, J = 6.30 Hz, 1H), 3.77 (s, 3H), 1.71 (bs, 1H), 1.47−1.54 (m, 2H), 1.11−1.25 (m, 12H), 0.80 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 158.90, 143.62, 141.13, 131.87, 130.43, 129.58, 128.85, 128.20, 127.30, 113.95, 70.54, 55.48, 36.00, 32.06, 29.67, 29.64, 29.41, 26.09, 22.89, 14.35; MS *m*/*z* 352 (M^+, 13.92), 121 (100); IR (neat) 3408, 2926, 1607, 1510, 1249, 1178 cm^{-1}. HRMS calcd for $C_{24}H_{32}O_2$: 352.2402. Found: 352.2359.

(h) (*S*)-*Z*-1-(4-Methoxyphenyl)-2-phenylundec-1-en-3-ol ((*S*)-*Z*-5f): The reaction of anhydrous $ZnBr_2$ (450 mg, 2.0 mmol), *p*-$MeOC_6H_4$-MgBr (0.55 M, 3.6 mL, 2.0 mmol), (*S*)-*Z*-**4d** (148 mg, 0.4 mmol, in 5 mL of DMF), and $Ni(acac)_2$ (10 mg, 10 mol %) afforded (*S*)-*Z*-**5f** (75 mg, 57%) as oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55−7.70 (m, 2H), 7.27−7.40 (m, 5H), 6.95 (d, J = 6.9 Hz, 2H), 6.67 (s, 1H), 4.92 (t, J = 6.6 Hz, 1H), 3.85 (s, 3H), 1.74 (bs, 1H), 1.53−1.60 (m, 2H), 1.12−1.32 (m, 12H), 0.87 (t, J = 6.9 Hz, 3H); ee% = 95.8% (HPLC conditions: Chiralcel OD column (0.46 cm ϕ × 25 cm); λ 254 nm; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 85:15).

(i) *Z*-1-(4′-Dimethylaminophenyl)-2-phenylhept-1-en-3-ol (*Z*-5 g): The reaction of anhydrous $ZnBr_2$ (360 mg, 1.6 mmol), *p*-$N(CH_3)_2C_6H_4$-MgBr (0.85 M, 1.9 mL, 1.6 mmol), *Z*-**4c** (125.6 mg, 0.4 mmol, in 4 mL of DMF), and $Ni(acac)_2$ (10.28 mg, 10 mol %) afforded *Z*-**5 g** (93.6 mg, 76%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60−7.62 (m, 2H), 7.28−7.41 (m, 5H), 6.75 (d, J = 8.40 Hz, 2H), 6.67 (s, 1H), 5.04 (t, J = 7.2 Hz, 1H), 3.01 (s, 6H), 1.97 (bs, 1H), 1.57−1.68 (m, 2H), 1.19−1.31 (m, 4H), 0.85 (t, J = 6.90 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 149.77, 141.97, 141.66, 132.59, 130.34, 128.90, 128.18, 127.09, 125.16, 112.39, 70.65, 40.78, 35.69, 28.46, 22.90, 14.37; MS *m*/*z* 309 (M^+, 61.81), 252 (100); IR (neat) 3419, 2953, 1609, 1520, 1355 cm^{-1}. HRMS calcd for $C_{21}H_{27}NO$: 309.2093. Found: 309.2125.

(j) (*R*)-*Z*-1-(4-Dimethylamino-phenyl)-2-phenylhept-1-en-3-ol ((*R*)-*Z*-5g): The reaction of anhydrous $ZnBr_2$ (360 mg, 1.6 mmol), *p*-$N(CH_3)_2C_6H_4MgBr$ (0.85 M, 1.9 mL, 1.6 mmol), (*R*)-*Z*-**4c** (125.6 mg, 0.4 mmol, in 4 mL of DMF), and $Ni(acac)_2$ (10.28 mg, 10 mol %) afforded (*R*)-*Z*-**5 g** (89.7 mg, 73%) as oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57−7.60 (m, 2H), 7.26−7.40 (m, 5H), 6.75 (d, J = 9 Hz, 2H), 6.66 (s, 1H), 5.03 (t, J = 7.2 Hz, 1H), 3.00 (s, 6H), 1.87 (bs, 1H), 1.56−1.68 (m, 2H), 1.18−1.41 (m, 4H), 0.85 (t, J = 6.90 Hz, 3H); ee% = 94.0% (HPLC conditions: Chiralpak AD column (0.46 cm ϕ × 25 cm); λ 254 nm; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 90:10).

B. Coupling Reaction of Carbon−Sulfonyl Bond. (k) *Z*-2-Phenyl-1-(*m*-methylphenyl)undec-1-en-3-ol (*Z*-5h): The reaction of anhydrous $ZnBr_2$ (450 mg, 2.0 mmol), *m*-MeC_6H_4MgBr (0.8675 M, 2.30 mL, 2.0 mmol), *Z*-**6e** (193 mg, 0.5 mmol, in 5 mL of DMF), and $Ni(acac)_2$ (12.85 mg, 10 mol %) afforded *Z*-**5h** (106.2 mg, 63.2%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53−7.57 (m, 2H), 7.26−7.38 (m, 4H), 7.08−7.14 (m, 3H), 6.68 (s, 1H), 4.89 (t, J = 6.00 Hz, 1H), 2.37 (s, 3H), 1.70 (bs, 1H), 1.51−1.63 (m, 2H), 1.17−1.29 (m, 12H), 0.85 (t, J = 6.75 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 144.65, 140.95, 138.10, 137.11, 132.26, 129.87, 128.90, 128.43, 128.23, 128.06, 127.43, 126.19, 70.50, 35.97, 32.07, 29.69, 29.63, 29.42, 26.03, 22.91, 21.73, 14.37; MS *m*/*z* 336 (M^+, 5.71), 224 (100); IR (neat) 3393, 2925, 1601, 1492, 1464 cm^{-1}. HRMS calcd for $C_{24}H_{32}O$: 336.24532. Found: 336.24254.

(l) *Z*-2-Phenyl-1-(*m*-methylphenyl)undec-1-en-3-ol ((*S*)-*Z*-5h): The reaction of anhydrous $ZnBr_2$ (315 mg, 1.4 mmol), *m*-MeC_6H_4MgBr (0.8675 M, 1.6 mL, 1.4 mmol), (*S*)-*Z*-**6e** (135 mg, 0.35 mmol, in 3.5 mL of DMF), and $Ni(acac)_2$ (9.0 mg, 10 mol %) afforded (*S*)-*Z*-**5h** (66.4 mg, 57%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53−7.56 (m, 2H), 7.22−7.38 (m, 4H), 7.08−7.14 (m, 3H), 6.67 (s, 1H), 4.89 (t, J = 6.00 Hz, 1H), 2.37 (s, 3H), 1.70 (bs, 1H), 1.53−1.58 (m, 2H), 1.17−1.28 (m, 12H), 0.85 (t, J = 6.60 Hz, 3H); ee% = 94.5% (HPLC conditions: Chiralcel OD column (0.46 cm ϕ × 25 cm); λ 254 nm, rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 90:10).

(m) *Z*-2-Phenyl-1-(*p*-methylphenyl)undec-1-en-3-ol (*Z*-5i): The reaction of anhydrous $ZnBr_2$ (450 mg, 2.0 mmol), *p*-MeC_6H_4MgBr (0.85 M, 2.35 mL, 2.0 mmol), *Z*-**6e** (193 mg, 0.5 mmol, in 5 mL of DMF), and $Ni(acac)_2$ (12.85 mg, 10 mol %) afforded *Z*-**5i** (110 mg, 66%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57−7.60 (m, 2H), 7.19−7.41 (m, 7H), 6.71 (s, 1H), 4.93 (t, J = 6.75 Hz, 1H), 2.40 (s, 3H), 1.78 (bs, 1H), 1.54−1.62 (m, 2H), 1.20−1.35 (m, 12H), 0.89 (t, J = 7.20 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 144.25, 141.06, 137.06, 134.23, 132.20, 129.27, 129.10, 128.89, 128.23, 127.38, 70.55, 35.97, 32.09, 29.69, 29.65, 29.44, 26.07, 22.93, 21.47, 14.40; MS *m*/*z* 336 (M^+, 5.44), 223 (100); IR (neat) 3395, 2925, 1600, 1510, 1465 cm^{-1}; HRMS calcd for $C_{24}H_{32}O$: 336.24 532. Found: 336.246 92.

(n) *Z*-2-Phenyl-1-(*p*-methylphenyl)undec-1-en-3-ol ((*S*)-*Z*-5i): The reaction of anhydrous $ZnBr_2$ (450 mg, 2.0 mmol), *p*-MeC_6H_4MgBr (0.85 M, 2.35 mL, 2.0 mmol), (*S*)-*Z*-**6e** (193 mg, 0.5 mmol, in 5 mL of DMF), and $Ni(acac)_2$ (12.85 mg, 10 mol %) afforded *Z*-**5i** (108.5 mg, 65%) as oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.49 (m, 2H), 7.21−7.29 (m, 3H), 7.07−7.21 (m, 4H), 6.59 (s, 1H), 4.81 (t, J = 7.2 Hz, 1H), 2.28 (s, 3H), 1.67 (s,1H), 1.44−1.50 (m, 2H), 1.08−1.23 (m, 12H), 0.77 (t, J = 6.9 Hz, 3H); ee% = 96.6% (HPLC conditions: Chiralcel OD column (0.46 cmϕ × 25 cm); λ 254 nm; rate, 0.7 mL/min; eluent, hexane/*i*-PrOH = 90:10).

(o) *Z*-1-(4′-Methoxyphenyl)-2-phenylundec-1-en-3-ol (*Z*-5f): The reaction of anhydrous $ZnBr_2$ (225 mg, 1.0 mmol), *p*-$CH_3OC_6H_4MgBr$ (1.00 M, 1.00 mL, 1.0 mmol), *Z*-**6e** (96.5 mg, 0.25 mmol, in 2.5 mL of DMF), and $Ni(acac)_2$ (6.4 mg, 10 mol %) afforded *Z*-**5f** (52.8 mg, 60%) as oil.

(p) *Z*-1-(4′-Dimethylaminophenyl)-2-phenylundec-1-en-3-ol (*Z*-5j): The reaction of anhydrous $ZnBr_2$ (225 mg, 1.0 mmol), *p*-$N(CH_3)_2$-C_6H_4MgBr (0.80 M, 1.25 mL, 1.0 mmol), *Z*-**6e** (96.5 mg, 0.25 mmol, in 2.5 mL of DMF), and $Ni(acac)_2$ (6.4 mg, 10 mol %) afforded *Z*-**5j** (64 mg, 70%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53−7.60 (m, 2H), 7.24−7.37 (m, 5H), 6.72−6.76 (m, 2H), 6.63 (s, 1H), 4.99 (t, J = 6.90 Hz, 1H), 2.98 (s, 6H), 1.55−1.67 (m, 3H), 1.18−1.25 (m, 12H), 0.85 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 149.48, 141.71, 141.32, 132.26, 130.01, 128.58, 127.88, 126.78, 124.84, 112.05, 70.42, 40.45, 35.70, 31.81, 29.45, 29.43, 29.17, 25.92, 22.65, 14.12; MS *m*/*z* 365 (M^+, 4.87), 248 (100); IR (neat) 3410, 2855, 1610, 1521, 1355, 1166, 815, 701 cm^{-1}. HRMS calcd for $C_{25}H_{35}NO$: 365.2719. Found: 365.2687.

Acknowledgment. We are grateful to the Major State Basic Research Development Program (Grant No. G2000077500) and the National Natural Science Foundation of China. S.M. is the recipient of the 1999 Qiu Shi Award for Young Scientific Workers issued by the Hong Kong Qiu Shi Foundation of Science and Technology (1999−2003).

JA034039Q