DOI: 10.1002/adsc.201000973

Highly Regio- and Stereoselective Iodohydroxylation of 1,2-Allenylic Sulfoxides in the Presence of Benzyl Thiol

Minyan Wang,[a] Chunling Fu,[a,*] and Shengming Ma[a,*]

[a] Laboratory of Molecular Recognition and Synthesis, Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China
Fax: (+86)-21-6260-9305; e-mail: fucl@zju.edu.cn or masm@sioc.ac.cn

Received: December 27, 2010; Revised: April 22, 2011; Published online: June 30, 2011

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adcs.201000973.

Abstract: The iodohydroxylation of 1,2-allenyl sulfoxides with iodine in the presence of benzyl thiol afforded 3-hydroxy-2-iodo-2(*E*)-alkenyl sulfides in good yields and high regio- and stereoselectivities. In this reaction it was observed that the sulfoxide functionality was reduced to sulfide and the water in the reaction mixture plays an important role for the stereoselectivity observed. A mechanism involving the attack of benzyl thiol at the positively charged sulfur atom in the five-membered intermediate **2** has been proposed.

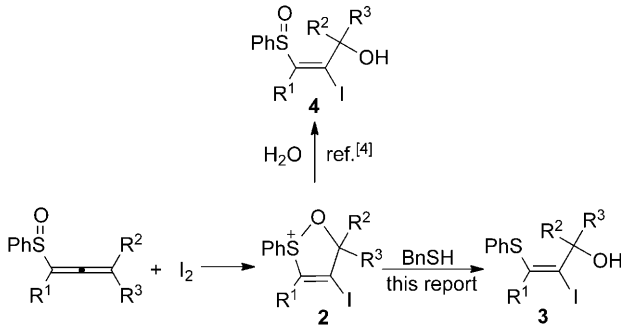
Keywords: allenes; iodohydroxylation; reduction; sulfoxides

Introduction

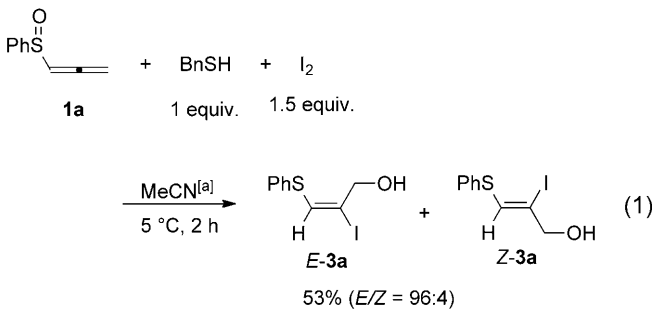
During the last 10–15 years, the reactions of allenes have been shown to be very powerful in organic synthesis,[1] especially much attention has been paid to the transition metal-catalyzed or -mediated transformation of allenes.[2] In addition, much interest has been shown to the regio- and stereoselective electrophilic addition of allenes.[3–5] In one such study, we observed that the halohydroxylation of 1,2-allenyl sulfoxides afforded 3-phenylsulfinyl-2-halo-2(*E*)-alkenols *via* the participation of the sulfinyl group forming a 5-membered intermediate **2** (Scheme 1), which accounts for the *E*-selectivity.[4] In a preliminary communication, we have also reported the iodohydroxylation of 1,2-allenyl sulfoxides in the presence of BnSH affording 3-phenylthio-2-iodo-2(*E*)-alkenols **3**.[5] In this paper, we wish to disclose our recent studies on the details of this reaction including the scope, the factors controlling the stereoselectivity, and the mechanism.

Results and Discussion

According to our previous results,[5] MeCN was used as the solvent for this type of reaction. When the reaction of 1,2-propadienyl phenyl sulfoxide **1a** was conducted with 1.5 equivalents of I_2 in the commercial MeCN in the presence of 1 equivalent of BnSH at 5 °C, a 53% yield of thioether *E*-**3a** was obtained with an *E*/*Z* ratio of 96/4 [Eq. (1)]. The stereochemistry was determined by the NOE study of *E*-**3a**.

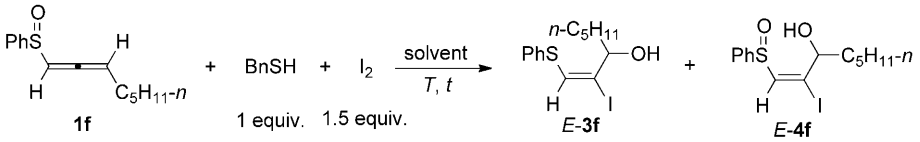


Scheme 1.



[a] Commercially available MeCN was used without additional treatment.

Table 1. The reaction of octa-1,2-dienyl phenyl sulfoxide **1f** with I_2 in the presence of BnSH.[a]



Entry	Conditions	Solvent	T [°C]	Time t [min]	Yield of **3f** [%][b]	E/Z of **3f**[b]	Yield of E-**4f** [%][b]
1	A	MeCN	5	60	10	30/70	3
2	B	MeCN	5	10	31	61/39	3
3	B	MeCN	−10	30	45	76/24	11
4	B	MeCN	−20	42	58	91/9	13
5[c]	B	MeCN	−20	42	4	>99/1	63
6	B	MeCN	−40	60	47	96/4	33
7	B	CH_2Cl_2	−20	60	35	–	–
8	B	toluene	−20	60	72	89/11	6
9	B	acetone	−20	30	57	81/19	9
10	B	CH_3NO_2	−20	30	71	92/8	17
11	B	dioxane	r.t.	42	62	97/3	10
12	B	DMF	−20	90	0	0	0
13[d]	B	MeCN/H_2O	−20	42	72	>99/1	16

[a] *Conditions A:* a solution of **1f** (0.4 mmol) in commercial MeCN (4 mL) was treated with I_2 (0.6 mmol) for 5 min followed by the addition of a solution of BnSH (0.4 mmol) in commercial MeCN (2 mL) with stirring at 5 °C. After the reaction was complete, the mixture was quenched with 6 mL of water followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$. *Conditions B:* to a flask containing a solution **1f** (0.4 mmol) and BnSH (0.4 mmol) in the indicated solvent (3 mL) was added a solution of I_2 (0.6 mmol) in the indicated solvent (3 mL) with stirring. When the reaction was complete as monitored by TLC, the reaction was quenched with H_2O (6 mL), which was followed by the treatment with a saturated aqueous solution of $Na_2S_2O_3$ at 0 °C.

[b] NMR yield with CH_2Br_2 as the internal standard.

[c] The reaction was conducted in the absence of BnSH.

[d] Anhydrous MeCN and 2.0 equiv. H_2O were used.

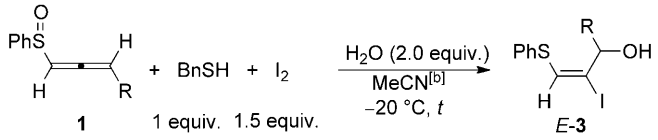
However, when we tried to extend this reaction to 3-monosubstituted 1,2-allenyl sulfoxides, i.e., octa-1,2-dienyl phenyl sulfoxide **1f**, the yield of 2-iodo-1-phenylthio-1-octen-3-ol **3f** was only 10% with an *E/Z* ratio of 30/70 (entry 1, Table 1). The reaction at 5 °C afforded **3f** with 31% yield and 61/39 *E/Z* stereoselectivity under conditions B (entry 2, Table 1). By comparing entry 4 with entry 5, it should be noted that BnSH is important for the formation of **3f**. Without BnSH the major product was sulfoxide *E*-**4f** in 63% yield (entry 5, Table 1). According to the study on the effect of temperature on the selectivity of the reaction, we observed that **3f** was formed in 58% yield with 91/9 *E/Z* stereoselectivity when the reaction was conducted at −20 °C (entry 4, Table 1). Then we screened the most commonly used solvents, such as CH_2Cl_2, toluene, $MeNO_2$, acetone, and 1,4-dioxane: the iodohydroxylation of **1f** in these solvents afforded **3f** in moderate yields (35–72%) (entries 7–11, Table 1). However, DMF is poor for this type of reaction. To our surprise, when 2.0 equivalents of H_2O in MeCN was used as solvent, the reaction afforded **3f** in 72% yield together with >99/1 *E/Z* stereoselectivity (entry 13, Table 1).

When anhydrous MeCN (distilled from CaH_2 after refluxing over CaH_2 for 5 h) was employed, the *E/Z* ratio dropped from 91/9 to 77/23. Thus, it is obvious that water has an impact on the stereoselectivity. Then the effect of H_2O on the stereoselectivity was carefully studied. The reaction with 2.0 equivalents of H_2O afforded *E*-**3f** in 72% yield with the stereoselectivity being >99/1. On increasing the loading of water to 10.0 equivalents, the reaction did not proceed and 73% of **1f** was recovered.

With this set of optimized reaction conditions, we studied the scope of the iodohydroxylation of propadienyl phenyl sulfoxide **1a** and the 3-monosubstituted 1,2-allenyl sulfoxide **1b–k** with 1.0 equivalent of BnSH and 2.0 equivalents of H_2O (Table 2). In all these cases, the stereoselectivity was ≥95/5 with good yields.

However, the current reaction conditions are not suitable for 3,3-disubstituted 1,2-allenyl sulfoxides since the reaction of **1l** formed a mixture of sulfides *E*-**3l** and *Z*-**3l** with a very lower *E/Z* selectivity under the above optimized reaction conditions (entry 1, Table 3). Further screening led us to observe that when the reaction was conducted at −40 °C, the *E/Z* ratio was improved to 94/6 (entry 2, Table 3). Interest-

Table 2. Iodohydroxylation of 3-monosubstituted 1,2-allenyl sulfoxides in the presence of BnSH.[a]



1 E-3

Entry	R	Time *t* [min]	Yield of *E*-**3** [%][c]	*E*/*Z* of **3**[d]
1[e]	H (**1a**)	120	47 (*E*-**3a**)	>99/1
2	CH_3 (**1b**)	34	70 (*E*-**3b**)	96/4
3	C_2H_5 (**1c**)	44	77 (*E*-**3c**)	97/3
4	*i*-C_3H_7 (**1d**)	33	75 (*E*-**3d**)	97/3
5	*n*-C_4H_9 (**1e**)	31	67 (*E*-**3e**)	99/1
6	*n*-C_5H_{11} (**1f**)	44	72 (*E*-**3f**)	> 99/1
7	*n*-C_6H_{13} (**1g**)	49	81 (*E*-**3g**)	99/1
8	*n*-C_7H_{15} (**1h**)	91	65 (*E*-**3h**)	> 99/1
9	*n*-C_8H_{17} (**1i**)	61	71 (*E*-**3i**)	95/5
10	*n*-C_9H_{19} (**1j**)	52	77 (*E*-**3j**)	96/4
11	Ph (**1k**)	45	74 (*E*-**3k**)	>99/1

[a] *Conditions B:* to a solution of **1** (0.4 mmol), BnSH (0.4 mmol), and H_2O (0.8 mmol, 14.4 μL) in anhydrous MeCN (3 mL) was added a solution of I_2 (0.6 mmol) in anhydrous MeCN (3 mL) with stirring at −20 °C. The reaction was quenched with H_2O (6 mL) at −20 °C, which was followed by the treatment with a saturated aqueous solution $Na_2S_2O_3$ at 0 °C.
[b] Anhydrous MeCN (distilled from CaH_2 after refluxing over CaH_2 for 5 h) was used.
[c] Isolated yield.
[d] Determined by ^1H NMR analysis using CH_2Br_2 as internal standard.
[e] The reaction was conducted under conditions A and anhydrous MeCN was used.

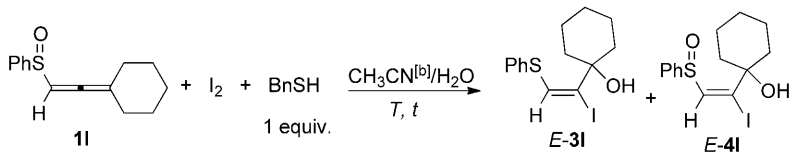
ingly, by increasing the loading of the water to 10.0 equivalents, the stereoselectivity was improved dramatically to >99/1 with 59% yield (entry 4, Table 3). Decreasing the amount of I_2 did not affect the stereoselectivity (entry 5, Table 3). We also tried the different types of quenching method, the reaction afforded the best results when the resulting mixture was quenched with water at −40 °C, then warmed up to 0 °C, which was followed by treatment with a saturated aqueous solution of $Na_2S_2O_3$ (entry 5, Table 3).

Thus, the reactions of polysubstituted 1,2-allenyl sulfoxides **1m**–**1t** were conducted at −40 °C to afford the sulfides **3m**–**3t** with a highly stereoselectivity and good yields (Table 4).

It has been reported that thiols or thiophenols may reduce the sulfoxides to sulfides upon heating.[6] Thus, in order to see the possibility for the formation of sulfide *E*-**3a** from the *in situ* reduction of *E*-**4a** with BnSH, the normal iodohydroxylation product *E*-**4a** was treated with I_2 in MeCN or only BnSH in MeCN at 5 °C, no reaction was observed. Then *E*-**4a** was treated with I_2 in the presence of BnSH in MeCN, the reduction did occur with 18% yield of *E*-**3a** (Scheme 2). Based on this, it is concluded that although it is possible that the sulfide *E*-**3** may be formed partially *via* the reduction of the normal iodohydroxylation product *E*-**4** with BnSH and I_2, there must exist a major alternative pathway for the formation of the sulfide *E*-**3**.

Thus, the reaction of **1a** in the presence of BnSSBn and I_2 was also conducted with *E*-**3a** whereby *E*-**4a** was isolated in 13% and 57% yields, respectively, in-

Table 3. The reaction of 3,3-pentamethylenepropadienyl phenyl sulfoxide **1l** with I_2 in the presence of BnSH.[a]

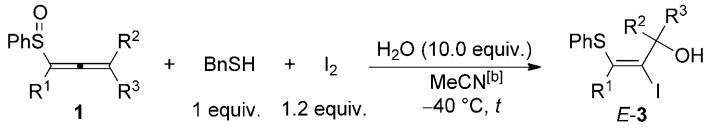


1l E-3l E-4l

Entry	I_2 (equiv.)	*T* [°C]	H_2O (equiv)	Time *t* [min]	Yield of *E*-**3l** [%][b]	*E*/*Z* of **3l**[c]	Yield of *E*-**4l** [%][c]
1	1.5	−20	2.0	17	34	43/57	25
2	1.5	−40	2.0	17	64	94/6	34
3	1.5	−40	5.0	17	52	>99/1	30
4	1.5	−40	10.0	11	59	>99/1	34
5	1.2	−40	10.0	46	65 (67[d])	>99/1	28 (24[d])
6[e)]	1.2	−40	10.0	21	66	97/3	15
7[f)]	1.2	−40	10.0	41	42	>99/1	0

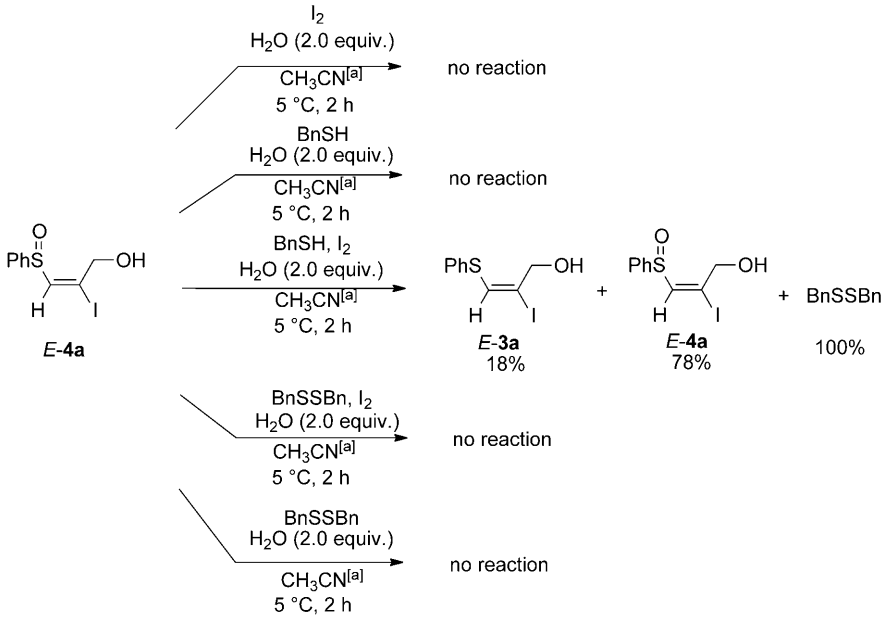
[a] To a solution of **1l** (0.4 mmol), BnSH (0.4 mmol) and H_2O in anhydrous MeCN (4.2 mL) was added a solution of I_2 in anhydrous MeCN (1.8 mL) with stirring. The reaction was quenched with H_2O (6 mL), which was followed by the treatment with a saturated solution of $Na_2S_2O_3$ at 0 °C.
[b] Anhydrous MeCN (distilled from CaH_2 after refluxing over CaH_2 for 5 h) was used.
[c] NMR yield with CH_2Br_2 as the internal standard.
[d] Isolated yield.
[e] The reaction was quenched with H_2O at 0 °C.
[f] The reaction was quenched with a saturated aqueous solution $Na_2S_2O_3$ at −40 °C, 42% of **1l** was recovered.

Table 4. Iodohydroxylation of poly-substituted 1,2-allenyl sulfoxides in the presence of BnSH.[a]



Entry	R^1	R^2	R^3	Time *t* [min]	Yield of *E*-**3** [%][c]	*E*/*Z* of **3**[d]
1	H	CH_3	CH_3 (**1m**)	15	60 (*E*-**3m**)	>99/1
2	H	C_2H_5	C_2H_5 (**1n**)	20	71 (*E*-**3n**)	>99/1
3[e)]	H	C_2H_5	Ph (**1o**)	30	64 (*E*-**3o**)	>99/1
4	H	CH_3	*i*-C_4H_9 (**1p**)	20	67 (*E*-**3p**)	>99/1
5	H	CH_3	C_2H_5 (**1q**)	20	63 (*E*-**3q**)	>99/1
6	H	CH_3	*n*-C_3H_7 (**1r**)	21	69 (*E*-**3r**)	>99/1
7	H	CH_3	Ph (**1s**)	21	62 (*E*-**3s**)	>99/1
8	*n*-C_4H_9	CH_3	CH_3 (**1t**)	19	66 (*E*-**3t**)	>99/1

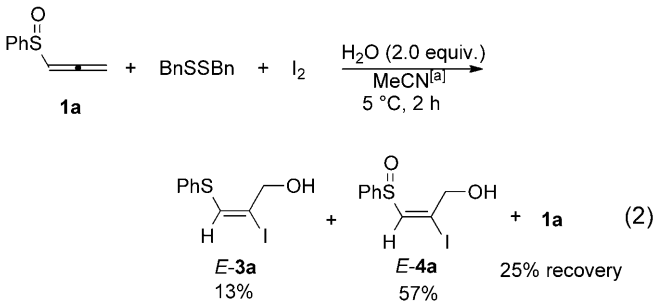
[a] *Conditions C:* to a solution of **1** (0.4 mmol), BnSH (0.4 mmol), and H_2O (4 mmol, 72 μL) in anhydrous MeCN (4.2 mL) was added a solution of I_2 (0.48 mmol) in anhydrous MeCN (1.8 mL) with stirring at −40 °C. After the reaction was complete as monitored by TLC, the reaction was quenched with H_2O (6 mL) at −40 °C, which was followed by the treatment with a saturated aqueous solution of $Na_2S_2O_3$ at 0 °C.
[b] Anhydrous MeCN (distilled from CaH_2 after refluxing over CaH_2 for 5 h) was used.
[c] Isolated yield.
[d] Determined by ^1H NMR analysis using CH_2Br_2 as internal standard.
[e] 1.5 equiv. I_2 were added.



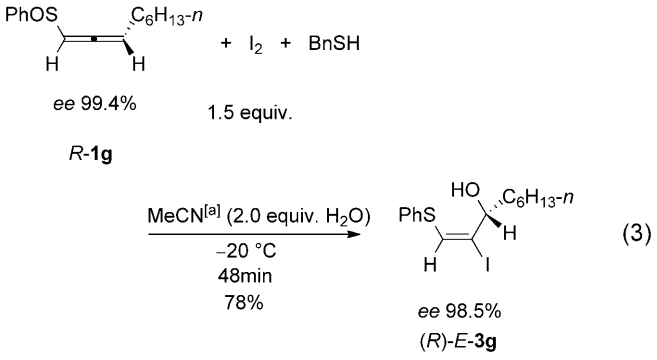
Scheme 2.

dicating that BnSSBn may also be partially responsible for the formation of sulfide *E*-**3a** [Eq. (2)]. However, no reduction of *E*-**4a** was observed with BnSSBn in the absence or presence of I_2 in MeCN (Scheme 2).

Based on these studies, we proposed a mechanistic rationale for the formation of sulfide *E*-**3**, which is shown in Scheme 3. The highly selective reaction of the electron-rich carbon-carbon double bond with I^+ forms the iodonium intermediate. The sulfinyl oxygen effects an intramolecular attack on the iodonium intermediate at the 3-position affording the five-membered charged intermediate **2**,[7] which accounts for the stereoselectivity of this reaction. The reaction of



[a] Anhydrous MeCN (distilled from CaH_2 after refluxing over CaH_2 for 5 hours) was used.

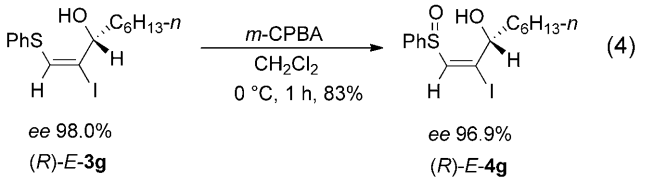


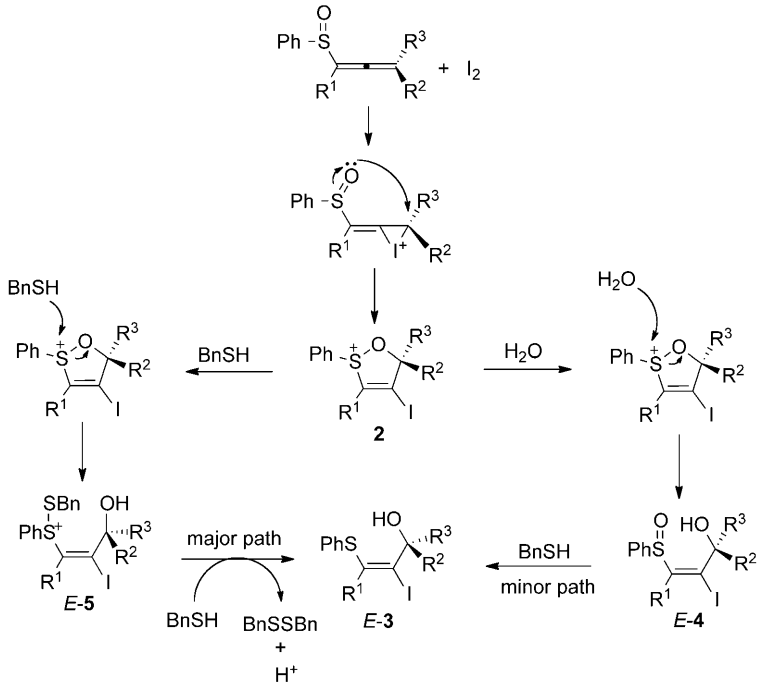
[a] Anhydrous MeCN (distilled from CaH_2 after refluxing over CaH_2 for 5 hours) was used.

the positively charged intermediate **2** with BnSH would afford intermediate *E*-**5**, which could be attacked by a molecule of BnSH to afford BnSSBn. The transformation from *E*-**5** to *E*-**3** is the major pathway. The minor pathway is the reaction of intermediate **2** with H_2O affording *E*-**4**, which may be reduced to form *E*-**3**.

According to the mechanism presented in Scheme 3, if an optically active 1,2-alleylic sulfoxide with a defined axial chirality in the allene moiety were allowed to react with I_2 in the presence of BnSH, the chirality of the allene moiety would be transferred into the chiral center of the allylic alcohol. In fact, it was observed that the *ee* value of halohydroxylation product *E*-**3g** is essentially equal to that of the corresponding reactant **1g** [Eq. (3)].[8] The absolute configuration of the product *E*-**3g** was established by the X-ray diffraction study of its oxidized product *E*-**4g** [Eq. (4) and Figure 1].[9] The result further supports our proposed mechanism shown in Scheme 3.

Furthermore, it is quite interesting to observe that *E*-**3a** would isomerize to *Z*-**3a** in the presence of I_2:





Scheme 3.

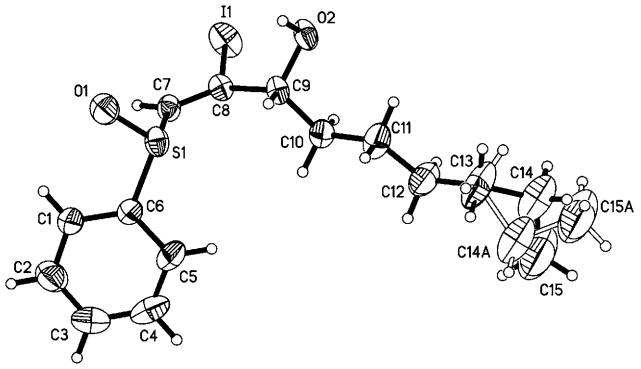
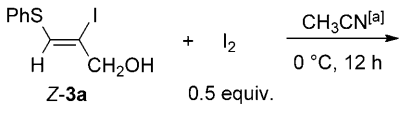
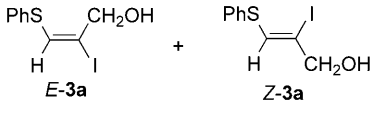


Figure 1. ORTEP representation of (*R*)-*E*-**4g**.

With 0.5 equivalents of I_2 after 13 h at 0 °C, the reaction of *E*-**3a** afforded an *E/Z* mixture of **3a** (entry 1, Table 5). When 1.5 equivalents of I_2 were applied, the reaction afforded **3a** in 91% yield with a *Z/E* ratio of 95/5 (entry 3, Table 5). With 2.0 equivalents of I_2 and a longer reaction time, the yield dropped to 83% (entry 4, Table 5).

As expected, the corresponding *Z* isomer is much more stable, which may be explained by the interaction of the lone electron pair of the sulfur atom with the empty orbital of I,[10] thus, a mixture of *E/Z*-**3a** in a final ratio of 4/96 was formed after being treated with 0.5 equivalents of I_2 for 12 h [Eq. (5)], which is in consistent with the results shown in entries 3 and 4 in Table 5.



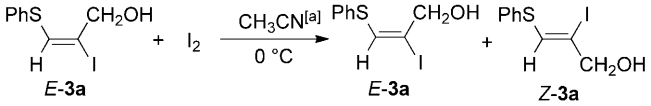


(5)

[a] Anhydrous MeCN (distilled from CaH2 after refluxing over CaH2 for 5 hours) was used.

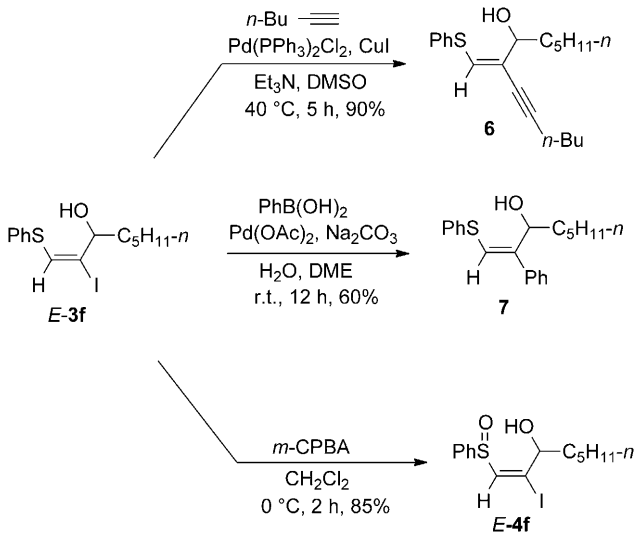
3-Phenylthio-2-iodo-2(*E*)-alkenols are very useful building blocks in organic synthesis due to the existence of the C–I bond, the C–S bond and the OH function. The Sonogashira coupling of *E*-**3f** with a terminal alkyne was carried out in Et_3N and DMSO under the catalysis of $Pd(PPh_3)_2Cl_2$ and CuI to afford **6** in 90% yield; the Suzuki coupling of *E*-**3f** with phenylboronic acid using Na_2CO_3 as the base in DME and H_2O (1:1) afforded **7** in 60% yield; when *E*-**3f** was added to *m*-CPBA in CH_2Cl_2 at 0 °C, the sulfoxide product *E*-**4f** was formed in 85% yield after 2 h (Scheme 4).

Table 5. The isomerization of *E*-2-iodo-3-phenylthio-2-propen-1-ol.



Entry	I_2 (equiv.)	Time *t* [h]	Yield of **3a**[b] [%]	*E/Z* of **3a**[c]
1	0.5	13	83	62/38
2	1.0	15	90	11/89
3	1.5	15	91	5/95
4	2.0	24	83	5/95

[a] Anhydrous MeCN (distilled from CaH_2 after refluxing over CaH_2 for 5 h) was used.
[b] Isolated yield.
[c] Determined by ^1H NMR analysis.



Scheme 4.

Conclusions

We have described the highly stereoselective iodohydroxylation of 1,2-allenylic sulfoxides in the presence of BnSH affording 3-hydroxy-2-iodo-2(*E*)-alkenyl sulfides in detail. The C=C bond configuration in the products is opposite to what was synthesized *via* the iodohydroxylation of 1,2-allenyl sulfides.[4] The stereoselectivity depends on the amount of H_2O in MeCN. Based on careful control experiments and a mechanistic study, a rationale has been proposed. It is also observed that 3-phenylthio-2-iodo-2(*E*)-alkenols are more stable and may be converted to 3-phenylthio-2-iodo-2(*Z*)-alkenols in the presence of I_2 in MeCN. Further studies in this area are being conducted in our laboratory.

Experimental Section

Anhydrous MeCN was distilled from CaH_2 after refluxing over CaH_2 for 5 h.

Synthesis of the Starting Materials

Compounds **1a–h**, **1k–q**, **1s** and **1t** were prepared according to the known procedures.[7a] Compounds **1i**, **1j**, and **1r** were prepared as follows.

1,2-Undecadienyl Phenyl Sulfoxide (1i); Typical Procedure[7a]

To a dried three-neck round-bottom flask were added undec-1-yn-3-ol (1.69 g, 10 mmol), triethylamine (1.70 mL, $d=0.72$ g/mL, 12 mmol, 1.22 g), and CH_2Cl_2 (20 mL) sequentially. After the mixture had beens cooled to −70 °C, a solution of sulfenyl chloride (1.74 g, 12 mmol) was added dropwise in 5 min. After being stirred at −70 °C for 10 min, methyl iodide (0.1 mL, $d=2.28$ g/mL, 1.6 mmol, 0.23 g) was added and the mixture was allowed to warm up naturally to room temperature followed by quenching with water (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. Filtration, evaporation and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8/1) of the crude product afforded **1i** as an oil; yield: 1.68 g (61%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.67$–7.60 (m, 2H, ArH), 7.60–7.44 (m, 3H, ArH), 6.06–6.00 (m, 1H, =CH), 5.80–5.65 (m, 1H, =CH), 2.20–2.04 (m, 2H, CH_2), 1.52–1.18 (m, 12H, 6 × CH_2), 0.88 (t, $J=6.6$ Hz, 3H, CH_3); IR (neat): $\nu=2926$, 2854, 1947, 1464, 1443, 1084, 1049 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 276 (M^+, 11.69), 163 (100); HR-MS: *m/z* = 276.1555, calcd. for $C_{17}H_{24}OS$ (M^+): 276.1548.

1,2-Dodecadienyl phenyl sulfoxide (1j): The reaction of dodeca-1-yn-3-ol (1.41 g, 7.7 mmol), triethylamine (1.10 mL, $d=0.72$ g/mL, 7.8 mmol, 0.79 g), sulfenyl chloride (0.92 g, 7.7 mmol), and methyl iodide (0.4 mL, $d=2.28$ g/mL, 6.4 mmol, 0.91 g) in CH_2Cl_2 (20 mL) at −65 °C afforded **1j** as an oil (eluent: petroleum ether/ethyl acetate = 4/1); yield: 1.29 g (57%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.64$–7.56 (m, 2H, ArH), 7.52–7.42 (m, 3H, ArH), 6.02–5.96 (m, 1H, = CH), 5.74–5.62 (m, 1H, =CH), 2.14–2.02 (m, 2H, CH_2), 1.44–1.14 (m, 14H, 7 × CH_2), 0.84 (t, $J=6.6$ Hz, 3H, CH_3); IR (neat): $\nu=2925$, 2854, 1948, 1582, 1466, 1443, 1377, 1304, 1084, 1049 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 291 (M^++1, 1.59), 290 (M^+, 0.69), 126 (100); HR-MS: *m/z* = 291.1789, calcd. for $C_{18}H_{27}OS$ (M^++1): 291.1777.

3-Methylhexa-1,2-dienyl phenyl sulfoxide (1r): The reaction of 3-methylhex-1-yn-3-ol (3.73 g, 33 mmol), Et_3N (4.2 mL, $d=0.72$ g/mL, 33 mmol, 3.02 g), sulfenyl chloride (4.44 g, 30 mmol), and methyl iodide (0.68 mL, $d=2.28$ g/mL, 10.9 mmol, 1.55 g) afforded **1r** as an oil (eluent: petroleum ether/ethyl acetate = 4/1); yield: 3.10 g (47%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.68$–7.58 (m, 2H, ArH), 7.58–7.42 (m, 3H, ArH), 6.02–5.94 (m, 1H, =CH), 2.08–1.90 (m, 2H, $=CCH_2$), 1.88–1.72 (m, 3H, $=CCH_3$), 1.54–1.36 (m, 2H, CH_2), 0.97–0.88 (m, 3H, CH_3); IR(neat): $\nu=2967$, 2928, 2873, 1949, 1580, 1443, 1374, 1341, 1164, 1083, 1039 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 220 (M^+, 3.42), 126 (100); HR-MS: *m/z* = 243.0832, calcd. for $C_{13}H_{16}OSNa$ (M^++Na): 243.0814.

Iodohydroxylation of 1,2-Allenylic Sulfoxides in the Prescence of BnSH

(*E*)-2-Iodo-3-phenylthio-2-propen-1-ol (*E*-3a): A solution of **1a** (82.3 mg, 0.5 mmol) in commercial MeCN (4 mL) was treated with I_2 (195.1 mg, 0.77 mmol) for 5 min followed by the addition of a solution of BnSH (63.1 mg, 0.5 mmol) in commercial MeCN (2 mL) with stirring. After being stirred at 5 °C for 2 h, the mixture was quenched with 6 mL of water followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$. The mixture was extracted with dichloromethane (25 mL × 3) and dried over anhydrous $MgSO_4$. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 ~ 2/1 afforded *E*-**3a** (yield: 74.0 mg, 51%) and *Z*-**3a**[10a] (yield: 3.3 mg, 2%).

E-**3a**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.38$–7.18 (m, 5H, ArH), 6.94 (s, 1H, =CH), 4.37 (d, $J=3.6$ Hz, 2H, CH_2), 2.33 (bs, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=134.2$, 132.5, 129.7, 129.2, 127.4, 99.2, 65.6; IR (neat) $\nu=3383$, 1666, 1580, 1528, 1478, 1439 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 292 (M^+, 92.72), 111 (100); anal. calcd. for C_9H_9SOI: C 37.00, H 3.11; found: C 37.24, H 3.17.

Z-**3a**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.48$–7.40 (m, 2H, ArH), 7.40–7.24 (m, 3H, ArH), 7.07 (t, $J=0.9$ Hz, 1H, =CH), 4.30 (s, 2H, CH_2), 2.00 (bs, 1H, OH).

***E*-2-Iodo-1-phenylthio-1-buten-3-ol (*E*-3b):** To a solution of **1b** (70.6 mg, 0.4 mmol), BnSH (50.8 mg, 0.4 mmol), and H_2O (14.5 μL, 0.8 mmol) in anhydrous MeCN (3 mL) was added a solution of I_2 (3.0 mL, 0.2 M in anhydrous MeCN, 0.6 mmol) within 4 min at −20 °C with stirring. After being stirred at −20 °C for 30 min, the mixture was quenched subsequently with 6 mL of water at −20 °C and a saturated aqueous solution of $Na_2S_2O_3$ at 0 °C. The mixture was extracted with dichloromethane (20 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1–2/1) afforded *E*-**3b** (yield: 84.7 mg, 70%), *Z*-**3b**[10b] (yield: 3.4 mg, 3%), and *E*-**4b**[7a] (yield: 16.8 mg, 13%).

E-**3b**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.30$–7.16 (m, 5H, ArH), 6.78 (d, $J=0.6$ Hz, 1H, =CH), 4.26–4.16 (m, 1H, CH), 2.06 (bs, 1H, OH), 1.18 (d, $J=6.3$ Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=134.3$, 130.0, 129.6, 129.2, 127.3, 109.0, 67.6, 22.9; IR (neat): $\nu=3385$, 2974, 1580, 1479, 1439, 1369, 1116, 1067, 1024, 1000 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 306 (M^+, 13.05), 69 (100); HR-MS (EI): *m/z* = 305.9586, calcd. for $C_{10}H_{11}SOI$ (M^+): 305.9575.

Z-**3b**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.42$–7.34 (m, 2H, ArH), 7.32–7.20 (m, 3H, ArH), 7.02 (d, $J=0.6$ Hz, 1H, =CH), 4.02–3.94 (m, 1H, CH), 1.79 (bs, 1H, OH), 1.28 (d, $J=6.3$ Hz, 3H, CH_3).

The following compounds were prepared according to this procedure.

***E*-2-Iodo-1-phenylthio-1-penten-3-ol (*E*-3c):** The reaction of **1c** (76.7 mg, 0.4 mmol), 49.3 mg (0.4 mmol) of BnSH, 14.5 μL (0.8 mmol) of H_2O, and I_2 (3.0 mL, 0.2 M in MeCN) at −20 °C afforded *E*-**3c** (yield: 98.9 mg, 77%), *Z*-**3c**[10b] (yield: 5.7 mg, 4%), and *E*-**4c** (yield: 16.7 mg, 12%).

E-**3c**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.16 (m, 5H, ArH), 6.88 (s, 1H, =CH), 3.91 (t, J = 7.1 Hz, 1H, CH), 1.95 (bs, 1H, OH), 1.68–1.40 (m, 2H, CH_2), 0.87 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.5, 131.7, 129.7, 129.2, 127.4, 107.9, 72.8, 30.1, 9.3; IR (neat): ν = 3385, 3057, 2963, 2930, 2873, 1580, 1478, 1459, 1440, 1379, 1331, 1089, 1057, 1023 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 320 (M^+, 47.09), 291 (100); HR-MS (EI): *m/z* = 342.9616, calcd. for $C_{11}H_{13}SOINa$ (M^++Na): 342.9602.

Z-**3c**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.32 (m, 2H, ArH), 7.32–7.20 (m, 3H, ArH), 7.01 (d, J = 0.3 Hz, 1H, =CH), 3.58 (t, J = 6.9 Hz, 1H, CH), 1.79 (bs, 1H, OH), 1.68–1.42 (m, 2H, CH_2), 0.87 (t, J = 7.5 Hz, 3H, CH_3).

***E*-2-Iodo-4-methyl-1-phenylthio-1-penten-3-ol (*E*-3d):** The reaction of **1d** (81.5 mg, 0.4 mmol), 50.1 mg (0.4 mmol) of BnSH, 14.5 μL (0.8 mmol) of H_2O, and I_2 (3.0 mL, 0.2 M in MeCN) at −20 °C afforded *E*-**3d** (yield: 98.8 mg, 75%), *Z*-**3d**[10b] (yield: 3.1 mg, 2%), and *E*-**4d**[7b] (yield: 23.9 mg, 17%).

E-**3d**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.15 (m, 5H, ArH), 6.89 (d, J = 0.6 Hz, 1H, =CH), 3.52 (d, J = 9.0 Hz, 1H, CH), 1.96 (bs, 1H, OH), 1.78–1.65 (m, 1H, CH), 1.06 (d, J = 6.9 Hz, 3H, CH_3), 0.80 (d, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.5, 132.3, 129.7, 129.2, 127.4, 107.2, 77.9, 34.6, 18.34, 18.32; IR (neat): ν = 3380, 1650, 1381, 1042, 1022 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 334 (M^+, 18.91), 291 (100); anal. calcd. for $C_{12}H_{15}SOI$: C 43.12, H 4.52; found: C 43.24, H 4.86.

Z-**3d**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.35 (m, 2H, ArH), 7.36–7.20 (m, 3H, ArH), 6.98 (d, J = 0.9 Hz, 1H, =CH), 3.24–3.17 (m, 1H, CH), 1.84–1.78 (m, 1H, CH), 1.78–70 (m, 1H, OH), 0.99 (d, J = 6.9 Hz, 3H, CH_3), 0.78 (d, J = 6.6 Hz, 3H, CH_3).

***E*-2-Iodo-1-phenylthio-1-hepten-3-ol (*E*-3e):** The reaction of **1e** (88.8 mg, 0.4 mmol), 50.5 mg (0.4 mmol) of BnSH, 14.5 μL (0.8 mmol) of H_2O, and I_2 (3.0 mL, 0.2 M in MeCN) at −20 °C afforded *E*-**3e** (yield: 93.7 mg, 67%), *Z*-**3e**[10b] (yield: 2.0 mg, 1%), and *E*-**4e**[7a] (yield: 15.9 mg, 11%).

E-**3e**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.14 (m, 5H, ArH), 6.84 (s, 1H, =CH), 3.98 (bs, 1H, CH), 2.07 (m, 1H, OH), 1.62–1.38 (m, 2H, CH_2), 1.38–1.12 (m, 4H, 2 × CH_2), 0.85 (t, J = 6.9 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.5, 131.3, 129.7, 129.2, 127.4, 108.4, 71.4, 36.6, 26.9, 22.5, 14.0; IR (neat): ν = 3406, 1581, 1479, 1025 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 348 (M^+, 26.22), 331 (100); anal. cacld. for $C_{13}H_{17}SOI$: C 44.84, H 4.92; found: C 44.93, H 4.90.

Z-**3e**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.40 (m, 2H, ArH), 7.40–7.24 (m, 3H, ArH), 7.06 (s, 1H, =CH), 3.78–3.66 (m, 1H, CH), 1.83 (d, J = 5.4 Hz, 1H, OH), 1.66–1.52 (m, 2H, CH_2), 1.40–1.12 (m, 4H, 2 × CH_2), 0.91 (t, J = 6.9 Hz, 3H, CH_3).

***E*-2-Iodo-1-phenylthio-1-octen-3-ol (*E*-3f):** The reaction of **1f** (94.2 mg, 0.4 mmol), 50.7 mg (0.4 mmol) of BnSH, 14.5 μL (0.8 mmol) of H_2O, and I_2 (3.0 mL, 0.2 M in MeCN) at −20 °C afforded *E*-**3f** (yield: 104.9 mg, 72%) and *E*-**4f**[7a] (yield: 19.0 mg, 12%).

E-**3f**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.18 (m, 5H, ArH), 6.88 (s, 1H, =CH), 4.01 (t, J = 6.8 Hz, 1H, CH), 1.95 (bs, 1H, OH), 1.62–1.40 (m, 2H, CH_2), 1.40–1.20 (m, 6H, 3 × CH_2), 0.85 (t, J = 6.3 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.5, 131.4, 129.7, 129.3, 127.4, 108.4, 71.5, 37.0, 31.6, 24.5, 22.5, 14.0; IR (neat): ν = 3407, 3059, 2955, 2929, 2857, 1581, 1466, 1479, 1440, 1378, 1304, 1184, 1122, 1086, 1025, 1000 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 362 (M^+, 27.40), 41 (100); HR-MS (EI): *m/z* = 362.0178, calcd. for $C_{14}H_{19}SOI$ (M^+): 362.0201.

***E*-2-Iodo-4-methyl-1-phenylthio-1-nonen-3-ol (*E*-3g):** The reaction of **1g** (98.6 mg, 0.4 mmol), 49.7 mg (0.4 mmol) of BnSH, 14.5 μL (0.8 mmol) of H_2O, and I_2 (3.0 mL, 0.2 M in anhydrous MeCN) at −20 °C afforded *E*-**3g** (yield: 121.3 mg, 81%) and *E*-**4g** (yield: 27.1 mg, 17%).

E-**3g**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.20 (m, 5H, ArH), 6.92 (d, 1H, J = 0.3 Hz ,=CH), 4.10–4.00 (m, 1H, CH), 2.17 (d, 1H, J = 5.1 Hz, OH), 1.65–1.48 (m, 2H, CH_2), 1.48–1.15 (m, 8H, 4×CH_2), 0.89 (t, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.4, 131.2, 129.6, 129.2, 127.3, 108.5, 71.3, 36.9, 31.6, 29.0, 24.8, 22.5, 14.0; IR (neat): ν = 3384, 2926, 2855, 1581, 1477, 1440, 1377, 1045, 1025 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 376 (M^+, 32.90), 291 (100); HR-MS (EI): *m/z* = 376.0360, calcd. for $C_{15}H_{21}SOI$ (M^+): 376.0358.

***E*-2-Iodo-1-phenylthio-1-decen-3-ol (*E*-3h):** The reaction of **1h** (104.6 mg, 0.4 mmol), 50.3 mg (0.4 mmol) of BnSH, 14.5 μL (0.8 mmol) of H_2O, and I_2 (3.0 mL, 0.2 M in MeCN) at −20 °C afforded *E*-**3h**[10b] (yield: 101.8 mg, 65%) and *E*-**4h**[7a] (yield: 16.2 mg, 10%).

E-**3h**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.22 (m, 5H, ArH), 6.92 (s, 1H, =CH), 4.10–4.01 (m, 1H, CH), 2.15 (d, J = 5.7 Hz, 1H, OH), 1.68–1.45 (m, 2H, CH_2), 1.42–1.20 (m, 10H, 5 × CH_2), 0.88 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.5, 131.3, 129.7, 129.2, 127.4, 108.4, 71.4, 37.0, 31.7, 29.4, 29.2, 24.8, 22.6, 14.1; IR (neat): ν = 3386, 3058, 2925, 2855, 1581, 1479, 1465, 1440, 1377 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 390 (M^+, 34.45), 373 (100); anal. calcd. for $C_{16}H_{23}SOI$: C 49.23, H 5.94; found: C 49.27, H 5.99.

***E*-2-Iodo-1-phenylthio-1-undecen-3-ol (*E*-3i):** The reaction of **1i** (109.6 mg, 0.4 mmol), 50.4 mg (0.4 mmol) of BnSH, 14.5 μL (0.8 mmol) of H_2O, and I_2 (3.0 mL, 0.2 M in MeCN) at −20 °C afforded *E*-**3i** (yield: 114.6 mg, 71%), *Z*-**3i** (yield: 2.1 mg, 1%), and *E*-**4i**[7a] (yield: 9.4 mg, 6%).

E-**3i**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.20 (m, 5H, ArH), 6.92 (d, J = 0.6 Hz, 1H, =CH), 4.12–4.00 (m, 1H, CH), 2.11 (d, J = 4.5 Hz, 1H, OH), 1.66–1.42 (m, 2H, CH_2), 1.40–1.08 (m, 12H, 6 × CH_2), 0.88 (t, J = 6.9 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.5, 131.2, 129.6, 129.2, 127.3, 108.5, 71.4, 36.9, 31.8, 29.42, 29.37, 29.2, 24.8, 22.6, 14.1; IR (neat): ν = 3387, 2925, 2854, 1581, 1478, 1440, 1377, 1025 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 404 (M^+, 24.82), 291 (100); HR-MS (EI): *m/z* = 404.0688, calcd. for $C_{17}H_{25}SOI$ (M^+): 404.0671.

Z-**3i**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.40 (m, 2H, ArH), 7.40–7.30 (m, 3H, ArH), 7.06 (s, 1H, =CH), 3.78–3.66 (m, 1H, CH), 1.81 (d, J = 5.1 Hz, 1H, OH), 1.68–1.46 (m, 2H, CH_2), 1.40–1.16 (m, 12H, 6 × CH_2), 0.89 (t, J = 3.3 Hz, 3H, CH_3).

***E*-2-Iodo-1-phenylthio-1-dodecen-3-ol (*E*-3j):** The reaction of **1j** (115.5 mg, 0.4 mmol), 49.3 mg (0.4 mmol) of BnSH, 14.5 μL (0.8 mmol) of H_2O, and I_2 (3.0 mL, 0.2 M in MeCN) at −20 °C afforded *E*-**3j** (yield: 127.5 mg, 77%), *Z*-**3j** (yield: 4.8 mg, 3%), and *E*-**4j** (yield: 27.1 mg, 16%).

E-**3j**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.14 (m, 5H, ArH), 6.84 (s, 1H, =CH), 3.98 (t, J = 6.6 Hz, 1H, CH),

2.05 (bs, 1H, OH), 1.60–1.36 (m, 2H, CH_2), 1.34–1.12 (m, 14H, 7 × CH_2), 0.80 (t, J=6.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=134.5, 131.3, 129.6, 129.2, 127.4, 108.5, 71.4, 37.0, 31.8, 29.5, 29.4, 29.2, 24.8, 22.6, 14.1; IR (neat): ν=3406, 2924, 2854, 1581, 1479, 1465, 1440, 1377, 1119, 1024 cm^{-1}; MS (70 eV, EI): m/z (%)=418 (M^+, 13.93), 41 (100); HR-MS (EI): m/z=418.0792, calcd. for $C_{18}H_{27}SOI$ (M^+): 418.0827.

Z-**3j**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.40–7.35 (m, 2H, ArH), 7.35–7.22 (m, 3H, ArH), 6.99 (d, J=0.6 Hz, 1H, =CH), 3.65 (t, J=6.9 Hz, 1H, CH), 1.73 (bs, 1H, OH), 1.60–1.40 (m, 2H, CH_2), 1.36–1.08 (m, 14H, 7×CH_2), 0.81 (t, J=6.9 Hz, 3H, CH_3).

***E*-2-Iodo-1-phenyl-3-phenylthio-2-propen-3-ol (*E*-3k):** The reaction of **1k** (96.5 mg, 0.4 mmol), 50.2 mg (0.4 mmol) of BnSH, 14.5 μL (0.8 mmol) of H_2O, and I_2 (3.0 mL, 0.2 M in MeCN) at −20 °C afforded *E*-**3k** (yield: 109.3 mg, 74%) and *E*-**4k** (yield: 13.6 mg, 9%).

E-**3k**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.52–7.44 (m, 2H, ArH), 7.42–7.24 (m, 8H, ArH), 7.01 (s, 1H, =CH), 5.44 (d, J=5.7 Hz, 1H, CH), 2.56 (d, J=5.7 Hz, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=140.6, 134.2, 132.1, 129.9, 129.4, 128.5, 128.0, 127.6, 125.8, 106.4, 72.6; IR (neat): ν=3449, 3059, 3028, 2854, 1686, 1581, 1492, 1478, 1449, 1440, 1376, 1225, 1187, 1086, 1051, 1025, 1006 cm^{-1}; MS (70 eV, EI): m/z (%)=368 (M^+, 5.61), 131 (100); HR-MS (EI): m/z=367.9719, calcd. for $C_{15}H_{13}SOI$ (M^+): 367.9732.

E-(1-Iodo-2-phenylthio)ethenyl cyclohexanol (*E*-3l)

To a solution of **1l** (92.1 mg, 0.4 mmol), BnSH (50.4 mg, 0.4 mmol), and H_2O (72 μL, 4 mmol) in anhydrous MeCN (4.2 mL) was added a solution of I_2 (1.8 mL, 0.267 M in anhydrous MeCN, 0.48 mmol) in 1 min at −40 °C with stirring. After being stirred at −40 °C for 45 min, the mixture was quenched sequentially with 6 mL of water at −40 °C and a saturated aqueous solution of $Na_2S_2O_3$ at 0 °C. The mixture was extracted with dichloromethane (20 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate=40/1~3/1) afforded *E*-**3l** (yield: 95.3 mg, 67%) and *E*-**4l**[7a] (yield: 35.6 mg, 24%).

E-**3l**: Oil, ^{1}H NMR (300 Hz, $CDCl_3$): δ=7.43–7.21 (m, 5H, ArH), 6.92 (s, 1H, =CH), 2.13 (s, 1H, OH), 2.10–1.96 (m, 2H, CH_2), 1.80–1.70 (m, 2H, CH_2), 1.70–1.52 (m, 5H, 2×CH_2 and one proton in CH_2), 1.42–1.14 (m, 1H, one proton in CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ=136.4, 132.0, 130.4, 129.2, 127.5, 105.0, 77.3, 36.5, 25.0, 21.8; IR (neat): ν=3396, 2955, 2930, 2856, 1581, 1479, 1440 cm^{-1}; MS (70 eV, EI): m/z (%)=360 (M^+, 41.47), 110 (100); HR-MS (EI): m/z=360.0094, calcd. for $C_{14}H_{17}SOI$ (M^+): 360.0045.

The following compounds were prepared according to this procedure.

***E*-3-Iodo-2-methyl-4-phenylthio-3-buten-2-ol (*E*-3m):** The reaction of **1m** (77.0 mg, 0.4 mmol), 50.0 mg (0.4 mmol) of BnSH, 72 μL (4 mmol) of H_2O, and I_2 (1.8 mL, 0.267 M in MeCN) at −40 °C afforded *E*-**3m** (yield: 76.6 mg, 60%) and *E*-**4m**[7a] (yield: 27.2 mg, 20%).

E-**3m**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.44–7.23 (m, 5H, ArH), 6.88 (s, 1H, =CH), 2.40 (d, J=11.4 Hz, 1H, OH), 1.61 (s, 6H, 2×CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=136.1, 131.8, 130.4, 129.2, 127.6, 103.0, 76.8, 29.8; IR (neat): ν=3416, 1637, 1617, 1581, 1475, 1439 cm^{-1}; MS (70 eV, EI): m/z (%)=320 (M^+, 56.43), 43 (100); anal. calcd. for $C_{11}H_{13}SOI$: C 41.26, H 4.00; found: C 41.37, H 4.37.

***E*-3-Ethyl-2-iodo-1-phenylthio-1-penten-3-ol (*E*-3n):** The reaction of **1n** (88.6 mg, 0.4 mmol), 49.6 mg (0.4 mmol) of BnSH, 72 μL (4 mmol) of H_2O, and I_2 (1.8 mL, 0.267 M in MeCN) at −40 °C afforded *E*-**3n** (yield: 99.9 mg, 71%) and *E*-**4n**[7a] (yield: 15.1 mg, 10%).

E-**3n**: Oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.34–7.15 (m, 5H, ArH), 6.95 (s, 1H, =CH), 2.31 (bs, 1H, OH), 2.01–1.87 (m, 2H, CH_2), 1.65–1.51 (m, 2H, CH_2), 0.92 (t, J=7.5 Hz, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=136.5, 134.3, 130.3, 129.2, 127.5, 100.3, 82.1, 33.4, 7.3; IR (neat): ν=3374, 1654, 1381, 1089, 1049 cm^{-1}; MS (70 eV, EI): m/z (%)=348 (M^+, 40.04), 331 (100); HR-MS (EI): m/z=348.0014, calcd. for $C_{13}H_{17}SOI$ (M^+): 348.0045.

***E*-2-Iodo-3-phenyl-1-phenylthio-1-penten-3-ol (*E*-3o):** The reaction of **1o** (107.8 mg, 0.4 mmol), 50.5 mg (0.4 mmol) of BnSH, 72 μL (4 mmol) of H_2O, and I_2 (3.0 mL, 0.2 M in MeCN) at −40 °C afforded *E*-**3o** (yield: 101.9 mg, 64%), and *E*-**4o**[11] (yield: 43.4 mg, 26%).

E-**3o**: Oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.61–7.52 (m, 2H, ArH), 7.43–7.20 (m, 8H, ArH), 7.06 (s, 1H, =CH), 2.69 (s, 1H, OH), 2.56–2.40 (m, 1H, one proton in CH_2), 2.28–2.13 (m, 1H, one proton in CH_2), 1.05 (t, J=7.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=144.0, 136.1, 134.1, 130.5, 129.2, 128.3, 127.8, 127.6, 126.0, 102.5, 81.7, 33.8, 8.0; IR (neat): ν=3378, 1650, 1381, 1089, 1049 cm^{-1}; MS (70 eV, EI): m/z (%)=396 (M^+, 26.33), 367 (100); HR-MS (EI): m/z=396.0064, Calcd. for $C_{17}H_{17}SOI$ (M^+): 396.0045.

***E*-2-Iodo-3,5-dimethyl-1-phenylthio-1-hexen-3-ol (*E*-3p):** The reaction of **1p** (92.6 mg, 0.4 mmol), 50.7 mg (0.4 mmol) of BnSH, 72 μL (4 mmol) of H_2O, and I_2 (1.8 mL, 0.267 M in MeCN) at −40 °C afforded *E*-**3p** (yield: 96.4 mg, 67%) and *E*-**4p**[11] (yield: 42.5 mg, 28%).

E-**3p**: Oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.43–7.24 (m, 5H, ArH), 6.91 (s, 1H, =CH), 2.25 (s, 1H, OH), 2.02–1.84 (m, 2H, CH_2), 1.63–1.51 (m, 4H, CH_3 and CH), 1.10–0.98 (m, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=136.5, 132.4, 130.4, 129.2, 127.5, 102.9, 79.7, 49.4, 29.9, 29.7, 24.7, 24.41, 24.36; IR (neat): ν=3257, 1634, 1578, 1445, 1369, 1011 cm^{-1}; MS (70 eV, EI): m/z (%)=362 (M^+, 6.96), 43 (100); HR-MS (EI): m/z=362.0184, calcd. for $C_{14}H_{19}SOI$ (M^+): 362.0201.

***E*-2-Iodo-3-methyl-1-phenylthio-1-penten-3-ol (*E*-3q):** The reaction of **1q** (82.7 mg, 0.4 mmol), 50.3 mg (0.4 mmol) of BnSH, 72 μL (4 mmol) of H_2O, and I_2 (1.8 mL, 0.267 M in MeCN) at −40 °C afforded *E*-**3q** (yield: 84.1 mg, 63%) and *E*-**4q**[11] (yield: 35.8 mg, 25%).

E-**3q**: Oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.35–7.16 (m, 5H, ArH), 6.86 (s, 1H, =CH), 2.27 (bs, 1H, OH), 2.00–1.86 (m, 1H, one proton in CH_2), 1.73–1.59 (m, 1H, one proton in CH_2), 1.49 (s, 3H, CH_3), 0.92 (t, J=7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=136.3, 132.8, 130.4, 129.2, 127.5, 101.9, 79.2, 34.3, 28.3, 7.7; IR (neat): ν=3463, 2969, 2932, 2876, 1581, 1477, 1455, 1440, 1374, 1348, 1289, 1160, 1091, 1025 cm^{-1}; MS (70 eV, EI): m/z (%)=334 (M^+, 6.66), 43 (100); HR-MS (EI): m/z=333.9917, calcd. for $C_{12}H_{15}SOI$ (M^+): 333.9888.

***E*-2-Iodo-3-methyl-1-phenylthio-1-hexen-3-ol (*E*-3r):** The reaction of **1r** (89.0 mg, 0.4 mmol), 50.2 mg (0.4 mmol) of BnSH, 72 μL (4 mmol) of H_2O, and I_2 (1.8 mL, 0.267 M in

MeCN) at −40 °C afforded *E*-**3r** (yield: 96.5 mg, 69%) and *E*-**4r**[11] (yield: 41.0 mg, 28%).

E-**3r**: Oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.23 (m, 5H, ArH), 6.91 (s, 1H, =CH), 2.37 (s, 1H, OH), 2.02–1.87 (m, 1H, one proton in CH_2), 1.76–1.61 (m, 1H, one proton in CH_2), 1.57 (s, 3H, CH_3), 1.52–1.38 (m, 2H, CH_2), 0.97 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.4, 132.6, 130.4, 129.2, 127.5, 102.2, 79.1, 43.8, 28.7, 16.8, 14.3; IR (neat): ν = 3453, 3058, 2959, 2930, 2870, 1581, 1476, 1439, 1373, 1324, 1159, 1025 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 348 (M^+, 22.95), 43 (100); HR-MS (EI): *m/z* = 348.0086, calcd. for $C_{13}H_{17}SOI$ (M^+): 348.0045.

***E*-3-Iodo-2-phenyl-4-phenylthio-3-buten-2-ol (*E*-3s):** The reaction of **1s** (101.4 mg, 0.4 mmol), 50.4 mg (0.4 mmol) of BnSH, 72 μL (4 mmol) of H_2O, and I_2 (1.8 mL, 0.267 M in MeCN) at −40 °C afforded *E*-**3s** (yield: 95.1 mg, 62%) and *E*-**4s**[11] (yield: 42.8 mg, 27%).

E-**3s**: Oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.52 (m, 2H, ArH), 7.42–7.20 (m, 8H, ArH), 7.04 (s, 1H, =CH), 2.94 (s, 1H, OH), 1.97 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 135.7, 133.5, 130.5, 129.2, 128.4, 127.9, 127.7, 125.7, 103.8, 79.2, 29.9; IR (neat): ν = 3458, 3058, 3026, 2980, 2931, 1599, 1581, 1492, 1477, 1440, 1372, 1184, 1091, 1068, 1026, 1001 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 382 (M^+, 39.37), 43 (100); HR-MS (EI): *m/z* = 381.9859, calcd. for $C_{16}H_{15}SOI$ (M^+): 381.9888.

***E*-3-Iodo-2-methyl-4-phenylthio-3-octen-2-ol (*E*-3t):** The reaction of **1t** (99.4 mg, 0.4 mmol), 50.2 mg (0.4 mmol) of BnSH, 72 μL (4 mmol) of H_2O, and I_2 (1.8 mL, 0.267 M in MeCN) at −40 °C afforded *E*-**3t** (yield: 99.7 mg, 66%) and *E*-**4t**[7a] (yield: 28.7 mg, 18%).

E-**3t** (Eluent: petroleum ether/ethyl ether = 40/1–1/1): oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.24 (m, 5H, ArH), 4.90 (s, 1H, OH), 2.48–2.40 (m, 2H, CH_2), 1.67 (s, 6H, 2 × CH_3), 1.58–1.48 (m, 2H, CH_2), 1.33–1.20 (m, 2H, CH_2), 0.86 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.4, 133.7, 130.1, 129.2, 127.3, 122.5, 76.8, 44.5, 32.8, 29.6, 22.2, 13.9; IR (neat): ν = 3380, 1650, 1381, 1089, 1049 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 376 (M^+, 9.07), 43 (100); HR-MS (EI): *m/z* = 376.0390, calcd. for $C_{15}H_{21}SOI$ (M^+): 376.0358.

(3*R*,*E*)-2-Iodo-4-methyl-1-phenylthio-1-nonen-3-ol [(*R*)-*E*-3g]: The reaction of *R*-**1g** (99.5 mg, 99.4% *ee*, 0.4 mmol), 48.8 mg (0.4 mmol) of BnSH, 14.5 μL (0.8 mmol) of H_2O, and I_2 (3.0 mL, 0.2 M in anhydrous MeCN) after 48 min at −20 °C afforded (*R*)-*E*-**3g** as an oil; yield: 117.4 mg (98.5% *ee*, 78%). HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95/5, 0.8 mL min^{-1}, λ = 254 nm): t_r = 10.9 (major), 19.3 (minor); $[\alpha]_D^{20}$: +117.8 (*c* 0.82, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.22 (m, 5H, ArH), 6.92 (s, 1H, =CH), 4.10–4.00 (m, 1H, CH), 2.07 (d, 1H, J = 5.4 Hz, OH), 1.66–1.48 (m, 2H, CH_2), 1.48–1.10 (m, 8H, 4 × CH_2), 0.89 (t, J = 6.5 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.5, 131.2, 129.6, 129.2, 127.3, 108.5, 71.4, 36.9, 31.7, 29.0, 24.8, 22.5, 14.1; IR (neat): ν = 3367, 3058, 2953, 2927, 2855, 1581, 1479, 1466, 1439, 1045, 1024 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 376 (M^+, 35.19), 291 (100); HR-MS (EI): *m/z* = 376.0363, calcd. for $C_{15}H_{21}SOI$ (M^+): 376.0358.

E-2-Iodo-1-phenylsulfinyl-1-octen-3-ol (*E*-4f)

A solution of *m*-CPBA (52.2 mg, 0.3 mmol) in CH_2Cl_2 (1 mL) was added to a solution of *E*-**3f** (73.3 mg, 0.2 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred at 0 °C. After 2 h, a saturated aqueous solution of $NaHCO_3$ (2 mL) was added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was dried over Na_2SO_4, Filtration, evaporation and flash chromatography (eluent: petroleum ether/ethyl acetate = 4:1) afforded *E*-**4f** as a white solid; yield: 64.8 mg (85%); mp 89.2–91.0 °C (Et_2O/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.48 (m, 5H, ArH), [7.00 (s, 0.69H), 6.94 (s, 0.30H), =CH], [4.61 (bs, 0.50H), 3.29 (bs, 0.26H), OH], 4.55–4.38 (m, 1H, CH), 1.82–1.60 (m, 1H, one proton in CH_2), 1.60–1.18 (m, 7H, one proton in CH_2 + 3 × CH_2), 1.02–0.82 (m, 3H, CH_3); IR (KBr): ν = 3349, 3058, 2950, 2929, 2857, 1582, 1443, 1302, 1082, 1034 cm^{-1}; MS (70 eV, EI): *m/z* = 378 (M^++1, 0.32), 361 (M^+−OH), 125 (100); anal. calcd. for $C_{14}H_{19}SO_2I$: C 44.45, H 5.06; found: C 44.55, H 5.05.

The following compounds were prepared according to this procedure.

***E*-2-Iodo-4-methyl-1-phenylsulfinyl-1-nonen-3-ol (*E*-4g):** The reaction of *E*-**3g** (75.6 mg, 0.2 mmol) and *m*-CPBA (51.9 mg, 0.3 mmol) in CH_2Cl_2 (2 mL) at 0 °C for 1 h afforded *E*-**4g** as a white solid; yield: 67.4 mg (86%); mp 96.1–96.7 °C (Et_2O/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.59 (m, 2H, ArH), 7.59–7.46 (m, 3H, ArH), [7.00 (s, 0.63H), 6.93 (s, 0.36H), =CH], [4.87 (d, J = 3.6 Hz, 0.61H), 3.81 (d, J = 6.0 Hz, 0.34H), OH], 4.52–4.35 (m, 1H, CH), 1.80–1.58 (m, 1H, one proton in CH_2), 1.56–1.13 (m, 9H, one proton in CH_2 + 4 × CH_2), 0.96–0.80 (m, 3H, CH_3); IR (KBr): ν = 3358, 3060, 2953, 2926, 2855, 1582, 1443, 1082, 1033 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 393 (M^++1, 0.05), 375 (M^+−OH), 217 (100); anal. calcd. for $C_{15}H_{21}SO_2I$: C 45.92, H 5.40; found: C 46.09, H 5.39.

(3*R*,*E*)-2-Iodo-4-methyl-1-phenylsulfinyl-1-nonen-3-ol [(*R*)-*E*-4g]: The reaction of (*R*)-*E*-**1g** (75.9 mg, 98.0% *ee*, 0.2 mmol), *m*-CPBA (52.2 mg, 0.3 mmol) in CH_2Cl_2 at 0 °C for 1 h afforded (*R*)-*E*-**4g** as a white solid; yield: 65.8 mg (96.9% *ee*, 83%); mp 123.8–124.6 °C (Et_2O/*n*-hexane). HPLC (Chiralcel; AD-H, hexane/*i*-PrOH = 95/5, 0.7 mL min^{-1}, λ = 254 nm): t_r = 19.0 (minor), 20.7 (major), 22.7 (major), 29.5 (minor); $[\alpha]_D^{20}$: −37.1 (*c* 0.97, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.60 (m, 2H, ArH), 7.60–7.51 (m, 3H, ArH), [6.99 (s, 0.64H), 6.95 (s, 0.36H), =CH], 4.49–4.38 (m, 1H, CH), [3.72 (d, J = 4.5 Hz, 0.63H), 2.62 (d, J = 7.2 Hz, 0.35H), OH], 1.80–1.62 (m, 1H, one proton in CH_2), 1.60–1.18 (m, 9H, one proton in CH_2 + 4 × CH_2), 0.96–0.84 (m, 3H, CH_3); IR (KBr): ν = 3303, 3008, 2924, 2855, 1581, 1442, 1318, 1077, 1036 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 393 (M^++1, 0.09), 375 (M^+−OH), 217 (100); anal. calcd. for $C_{15}H_{21}SO_2I$: C 45.92, H 5.40; found: C 46.23, H 5.42.

Z-7-Phenylthiomethylene-8-tridecyn-6-ol (6)

A mixture of *E*-**3f** (73.0 mg, 0.2 mmol), Et_3N (0.8 mL), 1-hexyne (33.2 mg, 0.4 mmol), $Pd(PPh_3)_2Cl_2$ (7.1 mg, 0.01 mmol), CuI (7.6 mg, 0.4 mmol), and DMSO (0.8 mL) was heated at 40 °C over a period of 5 h under nitrogen and monitored by TLC. After the reaction mixture had been cooled to room temperature, 10 mL of ethyl ether was added. Filtration, evaporation and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40:1)

gave **6**; yield: 57.2 mg (90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.20 (m, 5H, ArH), 6.57 (s, 1H, =CH), 4.57 (t, J = 6.8 Hz, 1H, CH), 2.35 (t, J = 6.9 Hz, 2H, CH_2) 1.94 (bs, 1H, OH), 1.80–1.22 (m, 12H, 6 × CH_2), 1.00–0.84 (m, 6H, 2 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.0, 130.6, 129.6, 129.1, 127.13, 127.08, 93.0, 77.1, 70.0, 36.1, 31.7, 30.8, 25.0, 22.6, 22.0, 19.1, 14.0, 13.6; IR (neat): ν = 3440, 2956, 2931, 2859, 2212, 1583, 1479, 1466, 1440, 1379, 1089, 1025 cm^{-1}; MS (70 eV, EI): m/z (%) = 316 (M^+, 100); HR-MS (EI): m/z = 316.1867, calcd. for $C_{20}H_{28}SO$ (M^+): 316.1861.

Z-2-Phenyl-1-phenylthio-1-octen-3-ol (7)

A mixture of *E*-**3f** (73.1 mg, 0.2 mmol), 1,2-dimethoxyethane (1 mL), Na_2CO_3 (64.3 mg, 0.6 mmol), H_2O (1 mL), phenylboronic acid (27.2 mg, 0.22 mmol), and $Pd(OAc)_2$ (2.4 mg, 0.01 mmol) was heated at 30 °C under nitrogen for 12 h. After the reaction was complete as monitored by TLC, 5 mL of ethyl ehter were added. Filtration and evaporation, and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) gave **7**; yield: 37.6 mg (60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.18 (m, 10H, ArH), 6.42 (s, 1H, =CH), 5.06–4.92 (m, 1H, CH), 2.15 (d, J = 4.2 Hz, OH), 1.82–1.68 (m, 1H, one proton in CH_2), 1.68–1.54 (m, 1H, one proton in CH_2), 1.54–1.38 (m, 1H, one proton in CH_2), 1.38–1.20 (m, 5H, one proton in CH_2 + 2 × CH_2), 0.86 (t, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.2, 139.5, 135.9, 129.3, 129.1, 128.1, 127.9, 127.4, 126.8, 124.5, 72.2, 35.6, 31.6, 25.5, 22.5, 14.0; IR (neat): ν = 3417, 3057, 3019, 2954, 2929, 2857, 1582, 1491, 1479, 1440, 1378, 1088, 1025 cm^{-1}; MS (70 eV, EI): m/z (%) = 312 (M^+, 29.56), 241 (100); HR-MS (EI): m/z = 312.1550, calcd for $C_{20}H_{24}SO$ (M^+): 312.1548.

Typical procedure for the Isomerization of *Z*-2-Iodo-3-phenylthio-2-propen-1-ol (*Z*-3a)

To a solution of *E*-**3a** (61.8 mg, 0.21 mmol) in anhydrous MeCN (3 mL) was added I_2 (82.4 mg, 0.32 mmol) at 0 °C. After 15 h with stirring, the mixture was quenched with 6 mL of water followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$. The mixture was extracted with dichloromethane (25 mL × 3), washed with brine, and dried over anhydrous $MgSO_4$. After evaporation, the ratio of *E*-**3a**/*Z*-**3a** (5/95) was determined by NMR analysis. Column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) afforded *Z*-**3a** as an oil; yield: 56.4 mg (91%).

Acknowledgements

*Financial support from the National Natural Science Foundation of China (No. 20732005, 20972135) and Zhejiang Provincial Natural Science Foundation of China (No. Y4090217) is greatly appreciated. We thank Mr. B. Wan in this group for reproducing the preparation of E-**3d** in Table 3 and E-**3n** and **E-3t** in Table 5, Shengming Ma is a Qiu Shi Adjunct Professor at Zhejiang University.*

References

[1] a) *Allenes in Organic Synthesis*, (Eds.: H. F. Schuster; G. M. Coppola), John Wiley & Sons, New York, **1984**; b) *The Chemistry of Ketenes, Allenes, and Related Compounds, Part 1*, (Ed.: S. Patai), John Wiley & Sons, New York, **1980**; c) *Modern Allene Chemistry*, (Eds.: N. Krause; A. S. K. Hashmi), Wiley-VCH, Weinheim, **2004**; d) *Cumulenes and Allenes*, in: *Science of Synthesis*, Georg. Thieme Verlag, Vol. 44, **2008**; e) S. Ma, *Chem. Rev.* **2005**, *105*, 2829; f) S. Ma, *Acc. Chem. Res.* **2003**, *36*, 701; g) L. K. Sydnes, *Chem. Rev.* **2003**, *103*, 1133.

[2] a) S. Ma, *Handbook of Organic Synthesis*, (Ed.: E. Negishi), John Wiley and Sons, New York, **2002**, p 1491; b) M. A. Tius, *Acc. Chem. Res.* **2003**, *36*, 284; c) L. L. Wie, H. Xiong, R. P. Hsung, *Acc. Chem. Res.* **2003**, *36*, 773; d) R. Zimmer, C. U. Dinesh, E. Nadanan, F. A. Khan, *Chem. Rev.* **2000**, *100*, 3067; e) A. S. K. Hashmi, *Angew. Chem.* **2000**, *112*, 3737; *Angew. Chem. Int. Ed.* **2000**, *39*, 3590; f) S. Ma, *Pd-Catalyzed two- or three-component cyclization of functionalized allenes*, in: *Topics in Organometallic Chemisty*, (Ed.: J. Tsuji) Springer-Verlag, Heidelberg, **2005**, p 187; g) L. Brandsma, N. A. Nedolya, *Synthesis* **2004**, 735.

[3] For a recent review, see: S. Ma, *Ionic Additions to Allenes*, in: *Topics in Modern Allene Chemistry 2*, (Eds.: N. Krause; A. S. K. Hashmi), Wiley-VCH, Weinheim, **2004**.

[4] For an account, see: S. Ma, *Acc. Chem. Res.* **2009**, *42*, 1679.

[5] C. Fu; X. Huang, S. Ma, *Tetrahedron Lett.* **2004**, *45*, 6063.

[6] a) T. J. Wallace, *J. Am. Chem. Soc.* **1964**, *86*, 2018; b) T. J. Wallace, J. J. Mahon, *J. Am. Chem. Soc.* **1964**, *86*, 4099.

[7] a) S. Ma, H. Ren, Q. Wei, *J. Am. Chem. Soc.* **2003**, *125*, 4817. For isolation of the five-membered intermediates, see: b) C. Zhou, C. Fu, S. Ma, *Angew. Chem.* **2007**, *119*, 4457; *Angew. Chem. Int. Ed.* **2007**, *46*, 4379; c) C. Zhou, C. Fu, S. Ma, *Tetrahedron* **2007**, *63*, 7612. For a similar effect of sulfoxide on such electrophilic addition reactions, see: d) J. L. G. Ruano, V. Marcos, J. Alemán, *Angew. Chem.* **2009**, *121*, 3201; *Angew. Chem. Int. Ed.* **2009**, *48*, 3155.

[8] a) J. L. García Ruano, J. Alemán, M. B. Cid, M. Á. Fernández- Ibáñez, M. C. Maestro, M. R. Mart, A. M. Martín-Castro, *Asymmetric Transformation Mediated by Sulfinyl Groups*, in: *Organosulfur Chemistry in Asymmetric Synthesis*, (Eds.: T. Toru, C. Bolm), Wiley-VCH, Weinheim, pp 55–159; b) M. C. Carreño, G. Hernández-Torres, M. Ribagorda, A. Urbano, *Chem. Commun.* **2009**, *41*, 6129.

[9] Crystal data for compound *E*-**4g**: $C_{15}H_{21}SO_2I$, MW = 392.28, orthorhombic, space group P 21, final R indices [I > 2σ(I)], $R1$ = 0.0325, $wR2$ = 0.0680; R indices (all data), $R1$ = 0.0433, $wR2$ = 0.0726; a = 6.4601(4) Å, b = 14.3005(6) Å, c = 18.8441(8) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 1740.87(14) Å3, T = 293(2) K, Z = 4, reflections collected/unique 15480/3184 (R_{int} = 0.0312), number of observations [$>2\sigma(I)$] 2678, parameters: 186. Supplementary crystallographic data have been

deposited at the Cambridge Crystallographic Data Centre, CCDC 822024. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[10] a) S. Ma, X. Hao, X. Huang, *Org. Lett.* **2003**, *5*, 1217; b) S. Ma, X. Hao, X. Meng, X. Huang, *J. Org. Chem.* **2004**, *69*, 5720.
[11] C. Fu, G. Chen, Y. Deng, X. Huang, S. Ma, *Chin. J. Chem.* **2004**, *22*, 990.

