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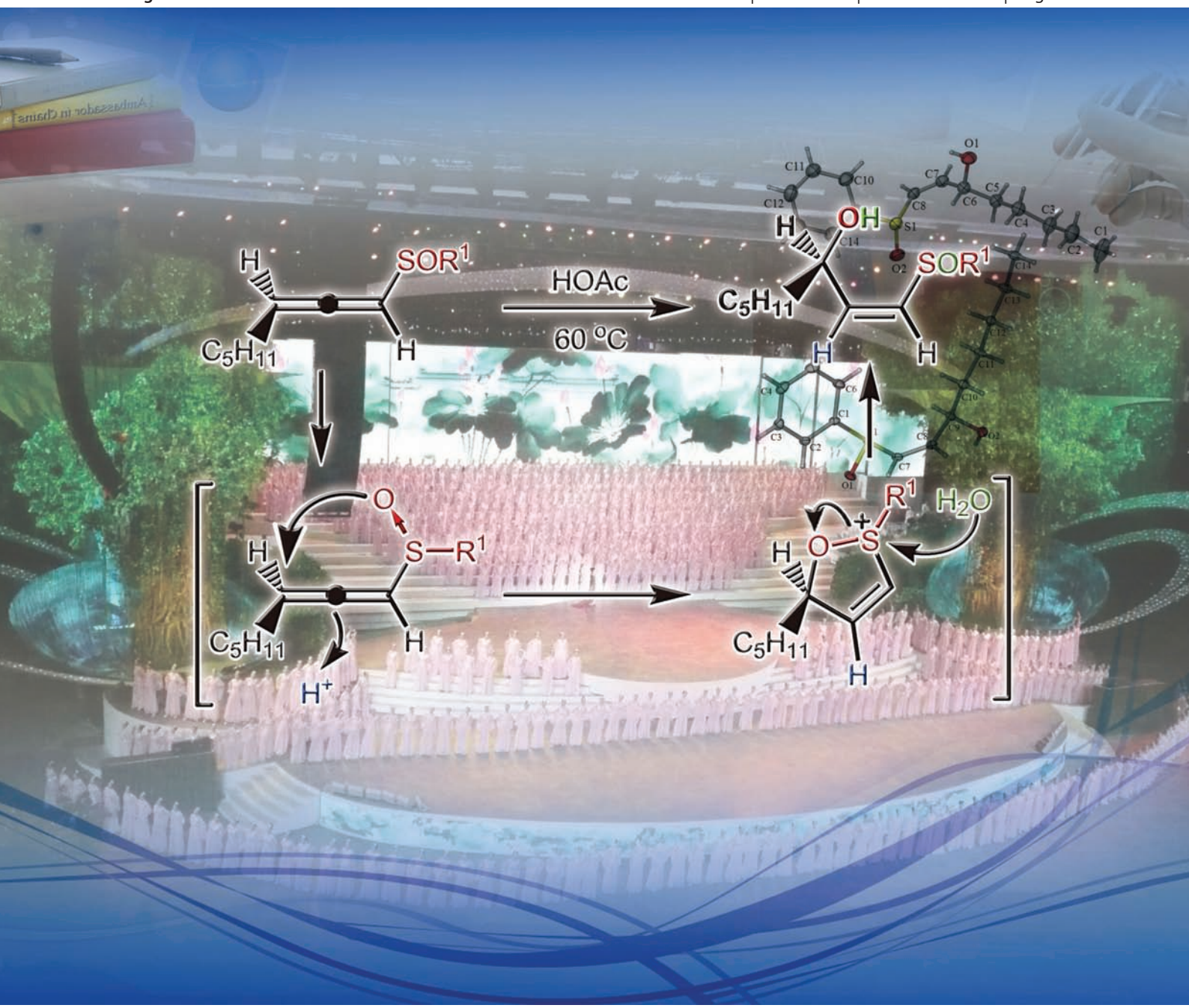

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FULL PAPER
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PERSPECTIVE
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Regioselective syntheses of fully-substituted 1,2,3-triazoles: the CuAAC/C–H bond functionalization nexus

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Studies on highly regio- and stereoselective hydration of 1,2-allenylic sulfoxides†

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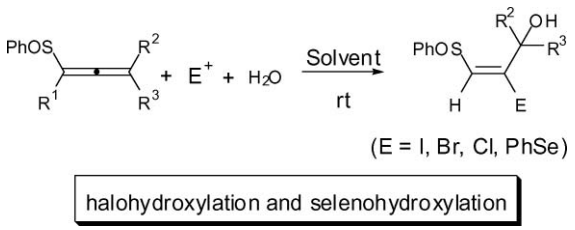
A highly regio- and stereoselective hydration of 1,2-allenylic sulfoxides in which proton served as the electrophile was reported. Through the X-ray diffraction study, it was concluded that the reaction may proceed *via* a 5-membered cyclic intermediate following by attack of the $^{-}$OH at the sulfur atom.

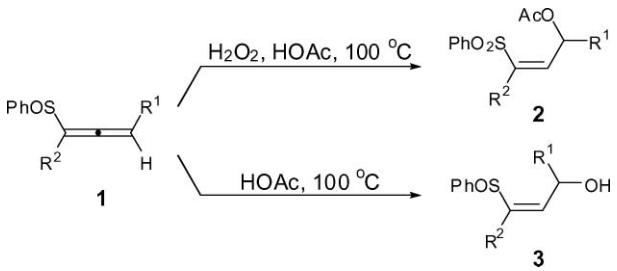
Introduction

1,2-Allenylic sulfoxides are important building blocks and structural units in organic synthesis due to the high reactivity of the allene moiety and the electron-withdrawing effect of the sulfoxide functionality.[1] Cycloaddition reactions of 1,2-allenylic sulfoxides such as vinylallenyl sulfoxides with other unsaturated bonds, such as alkenes, dienes and alkynes, either intermolecularly or intramolecularly form cyclic units.[2] Pd-catalyzed cross-coupling reaction of 1,2-allenylic sulfoxides with allyl bromide affording synthetically useful 2-allyl-1(*E*),3(*E*)-alkadienyl sulfoxides highly stereoselectively has also been reported by this group.[3] In addition, it was observed that nucleophilic addition of 1,2-allenylic sulfoxides with AlX_3 and H_2O or sodium phenyltellurolates afforded 2-haloallyl sulfoxides[4a] or (β-phenyltelluro)allyl phenyl sulfoxides,[4b] respectively. Recently, we have also reported the electrophilic addition reactions of different electrophiles, such as NXS (X = I, Br), halogen and PhSeCl, with 1,2-allenylic sulfoxides affording the *E*-halohydroxylation[5a,b] or *E*-selenohydroxylation[5c,d] products in which the X^{+} is connected to the center carbon atom of the allene while the OH group is linked to the carbon atom at the 3-position (Scheme 1).



Scheme 1 Halohydroxylation and selenohydroxylation of 1,2-allenylic sulfoxides.

In 2009, we have reported that the oxidative hydroacetoxylation reaction[6] of 1,2-allenylic sulfoxides with H_2O_2 in acetic acid at 100 °C for 17 h produced 3-sulfonyl-2(*Z*)-alkenyl acetates *via* a sulfoxide group-assisted formation of five-membered cyclic intermediate and S_N2-type attack of OAc^{-} at the tertiary carbon atom followed by oxidation of the sulfoxide functionality. As a consequence, we wondered if 3-sulfinyl-2(*Z*)-alkenyl acetates would be produced in the absence of H_2O_2. To our surprise, the reaction of 1,2-allenylic sulfoxides in acetic acid in the absence of H_2O_2 under the otherwise same reaction conditions afforded 3-sulfoxyl-2(*Z*)-alkenols **3** with exclusive *E*-selectivity, which is in accordance with our previous reports on halohydroxylation of sulfoxides and sulfones,[5] (Scheme 2). In this paper, we wish to report these observations.



Scheme 2 Oxidative hydroacetoxylation and halohydroxylation of 1,2-allenylic sulfoxides.

Results and discussion

We used 3,3-pentamethylenepropadienyl phenyl sulfoxide **1a** as the substrate to screen a series of different reaction conditions. Among various solvents tested, acetic acid gave the best result, while TFA gave the product in only moderate yield probably because of decomposition of the product under the relatively strong acidic conditions (entries 1 and 2, Table 1); addition of water led to a lower yield of the product **3a** (entry 3, Table 1); acetonitrile and nitromethane, which are commonly used in electrophilic additions of allenes,[5e] afforded **3a** in lower yields (entries 4 and 5, Table 1). When 1 equiv. of acetic acid was added, the substrate **1a** was recovered from the reaction in DMSO (entry 6, Table 1). The effect of temperature, reaction time, and concentration was also tested (entries 7–11, Table 1). Finally, it is observed that the best result was obtained when the reaction of **1a** was conducted in acetic acid at 60 °C for 24 h.

The reaction of different types of substrates proceeded smoothly under the optimized reaction conditions giving 3-sulfoxyl-2(*Z*)-alkenols in moderate to good yields: R^1 could be phenyl or a substituted phenyl ring while R^2, R^3 and R^4 could be H, alkyl, aryl or allyl groups. As expected, the electronic effect of substituent

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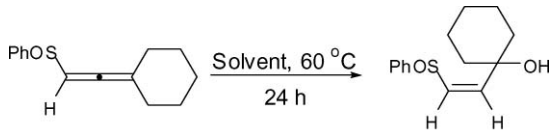
Table 1 Electrophilic hydration of 3,3-pentamethylenepropadienyl phenyl sulfoxide **1a**[a]

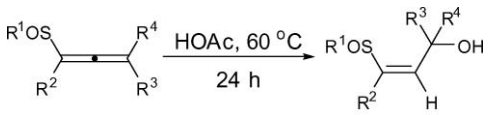


1a **Z-3a**

Entry	Solvent	[c]/mol L^{-1}	NMR yield of **3** (%)
1	HOAc	0.1	85(87)
2	TFA	0.1	46
3	HOAc–H_2O = 1 : 1	0.1	7
4[b]	CH_3CN	0.1	53
5[b]	CH_3NO_2	0.1	57
6[b]	DMSO	0.1	recovery
7[d]	HOAc	0.1	66
8[e]	HOAc	0.1	41
9[f]	HOAc	0.1	77
10	HOAc	0.05	86
11	HOAc	0.2	82

[a] The substrate **1a** (0.3 mmol) was dissolved in 3.0 mL of solvent and heated at 60 °C for 24 h. [b] 1 equiv. of HOAc was added. [c] 96% of **1a** was recovered. [d] The reaction proceeded at 40 °C for 24 h. [e] The reaction proceeded at 80 °C for 24 h. [f] The reaction proceeded at 60 °C for 12 h.

Table 2 Electrophilic hydration reaction of 1,2-allenylic sulfoxides **1** in HOAc[a]



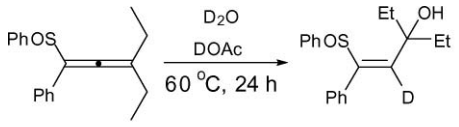
1 **Z-3**

Entry	**1** $R^1/R^2/R^3/R^4$	Isolated yield of *Z*-**3** (%) (*dr* value)
1	Ph/H/–$(CH_2)_5$– (**1a**)	87 (***Z*-3a**)
2	Ph/H/–$(CH_2)_4$– (**1b**)	53 (***Z*-3b**)
3	Ph/H/*n*-C_6H_{13}/H (**1c**)	65 (1.66/1)[c] (***Z*-3c**)
4	Ph/H/*n*-C_5H_{11}/H (**1d**)	66 (1.21 : 1)[c] (***Z*-3d**)
5	*p*-BrC_6H_4/H/*n*-C_5H_{11}/H (**1e**)	74 (2.06 : 1)[c] (***Z*-3e**)
6	*p*-$O_2NC_6H_4$/H/*n*-C_5H_{11}/H (**1f**)	70 (2.13 : 1)[c] (***Z*-3f**)
7[b]	Ph/*n*-C_4H_9/CH_3/CH_3 (**1g**)	87 (***Z*-3g**)
8[b]	Ph/Ph/C_2H_5/C_2H_5 (**1h**)	81 (***Z*-3h**)
9	*p*-BrC_6H_4/H/Me/H (**1i**)	76 (1.94 : 1)[d] (***Z*-3i**)
10	Ph/*n*-C_4H_9/H/H (**1j**)	58 (***Z*-3j**)
11	Ph/Ph/H/H (**1k**)	51 (***Z*-3k**)
12	Ph/allyl/H/H (**1l**)	64 (***Z*-3l**)
13	Ph/H/CH_3/CH_3 (**1m**)	58 (***Z*-3m**)
14	Ph/H/C_2H_5/C_2H_5 (**1n**)	76 (***Z*-3n**)
15	Ph/H/C_3H_7/C_3H_7 (**1o**)	71 (***Z*-3o**)
16	Ph/H/C_4H_9/C_4H_9 (**1p**)	69 (***Z*-3p**)
17	Ph/H/Ph/Me (**1q**)	48 (1.43 : 1)[c] (***Z*-3q**)
18	*p*-BrC_6H_4/Et/Me/H (**1r**)	68 (1.62 : 1)[c] (***Z*-3r**)

[a] The substrate **1** (0.3 mmol) was dissolved in 3 mL of HOAc and heated at 60 °C for 24 h. [b] The substrate was stirred at room temperature for 24 h. [c] The ratio was determined by isolated yield. [d] The ratio was determined by ^1H NMR analysis.

on the sulfoxide group shows no obvious impact on the reaction (entries 4–6 Table 2). Fully substituted 1,2-allenylic sulfoxides led to the desired products under relatively milder conditions (room temperature) (entries 7 and 8, Table 2). When R^3 is a phenyl group, the yield is low, probably due to the instability of the substrate (entry 17, Table 2). When $R^3 \neq R^4$, an extra chiral carbon center was formed from the axial chirality of the allene moiety in the reaction; thus, the products are a mixture of diastereoisomers (entries 3–6, 9, 17 and 18).

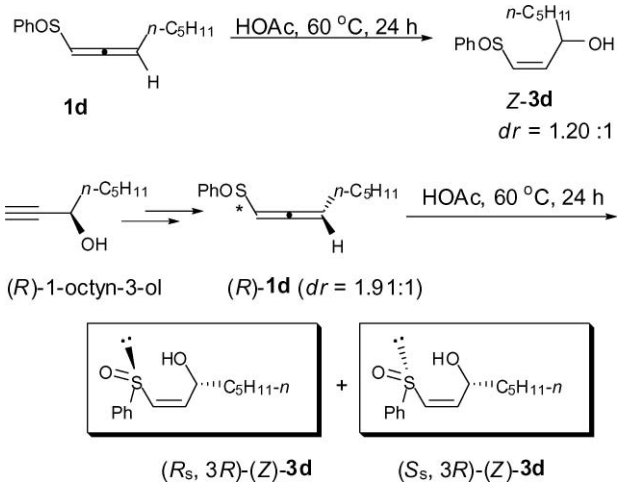
In order to study the mechanism, we used DOAc as the solvent and 1 equiv. of D_2O was added as the hydroxyl source. Under the typical conditions (60 °C, 24 h), the reaction proceeded smoothly affording the expected product *d*-(*Z*)-**3h** in 78% yield with 97% D-incorporation at the center carbon atom of the allene moiety (eqn 1).



1h *d*-(*Z*)-**3h** (1)

Yield = 78 %, 97% D

Further study on the stereoselectivity of this reaction provided more information for the mechanism. We synthesized optically active substrate (*R*)-**1d** from (*R*)-1-octyn-3-ol.[7] Under the standard conditions, the reaction afforded the desired solid products *Z*-**3d** in 68% combined yield as a pair of two diastereoisomers (Scheme 3). The absolute configurations of these two isomers were determined by an X-ray diffraction study[8,9] (Fig. 1 and 2). The axial chirality of the easily available optically active 1,2-allenylic sulfoxide was transformed efficiently into the center chirality affording (R_s,3*R*)-(*Z*)-**3d** and (S_s,3*R*)-(*Z*)-**3d**, which is different from what was observed in the oxidative hydroacetoxylation of 1,2-allenylic sulfoxide[6] but in accordance with the related halohydroxylation reaction.[5] Other optically active 1,2-allenylic



Scheme 3 Reaction of optically active substrate (*R*)-**1d**

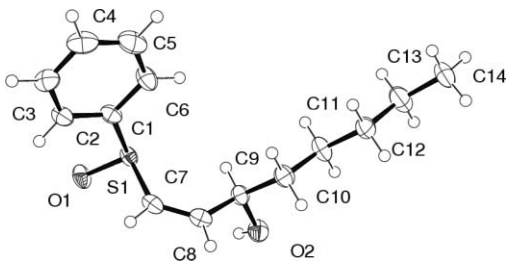
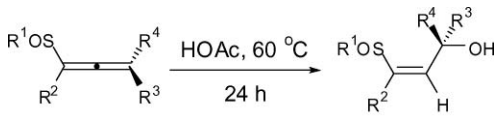


Fig. 1 ORTEP representation of (R_s,3*R*)-(*Z*)-**3d**.

Table 3 Hydration of optically active 1,2-allenylic sulfoxides[a]



1 **Z-3**

Entry	Optically active 1,2-allenylic sulfoxides **1** $R^1/R^2/R^3/R^4$	**1** (ee) %	Yield of *Z*-**3** (%)	*Z*-**3** (ee) (%)	
1	Ph/H/H/*n*-C_5H_{11}	98.5	68	97.6	96.5
2	Ph/H/H/*n*-C_6H_{13}	99.0	65	98.9	98.6
3	*p*-BrC_6H_4/Et/H/Me	95.1	74	95.5	94.1

[a] All the ee values in this part refer to the axial chirality of the allene or center chirality of carbon atom only.

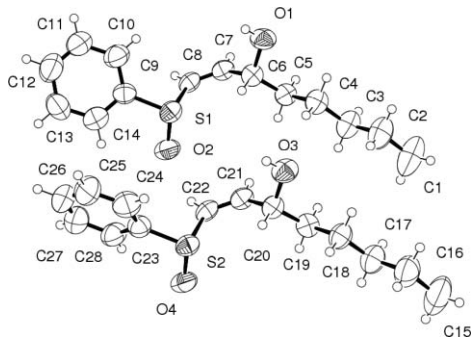
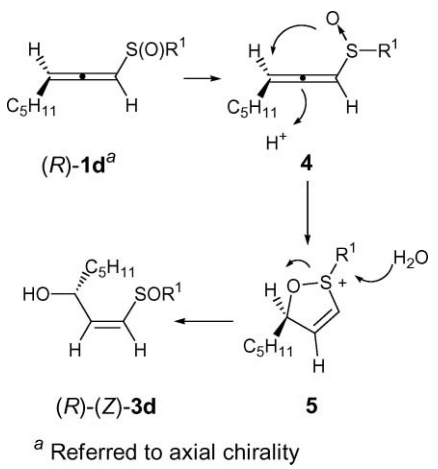


Fig. 2 ORTEP representation of (S_s,3*R*)-(*Z*)-**3d**.

sulfoxides had also been tested and the results are summarized in Table 3.

Based on these results, we proposed a possible mechanism (Scheme 4). Firstly, electrophilic addition of the proton with the relatively electron-rich carbon–carbon double bond and the subsequent intramolecular neighboring group participation of the sulfinyl oxygen atom forms the five-membered intermediate **5**. Subsequently, water in the solvent attacks the positively charged sulfur atom to cleave the S–O bond affording the final product (*R*)-(*Z*)-**3d**.[5]



Scheme 4 Mechanism of hydration of 1,2-allenylic sulfoxides

Conclusion

In conclusion, we have demonstrated a highly regio- and stereoselective hydration of 1,2-allenylic sulfoxide to afford 3-sulfinyl-2(*Z*)-alkenols in which the H^+ served as the electrophile while H_2O coming from the solvent attacked the sulfinyl group. The mechanism and stereochemistry are similar to those of the halohydroxylation but different from those of the oxidative hydroacetoxylation reaction of 1,2-allenylic sulfoxides **1**. The axial chirality of substrates was transferred efficiently to the center chirality of the carbon atom connected to the hydroxyl group in the final products. Considering the high loading of functionalities, easy availability of the optically active starting material, and simple/convenient operation, this transformation may be useful in organic synthesis and further extend the scope of electrophilic addition reactions of allenes by applying H^+ as the electrophile. Further studies in this area are being carried out in our laboratory.

Experimental section

Materials

Racemic starting materials **1a–1d**, **1g**, **1i–1r**[5] and optically active starting materials (*R*)-(−)-**1c** and (*R*)-(−)-**1r**[6] were prepared according to known procedures.

All the ee values refer to the axial chirality of allene moiety or the center chiral carbon atom only.

1. Synthesis of (*R*)-1,2-octadienyl phenyl sulfoxide ((*R*)-(−)-1d). *Typical Procedure.* In a dried three-necked round-bottom flask, a solution of (*R*)-oct-1-yn-3-ol (0.4586 g, 3.6 mmol) and Et_3N (0.5 mL, d = 0.726 g mL^{-1}, 0.363 g, 3.6 mmol) in 15 mL of methylene chloride was cooled to −67 °C under the protection of N_2. Then a solution of phenylsulfenyl chloride (0.6093 g, 4.2 mmol) in 3 mL of methylene chloride was added dropwise to the mixture within 20 min. After being stirred at −67 °C for another 15 min as monitored by TLC, it was quenched with methyl iodide (0.05 mL, d = 2.28 g mL^{-1}, 0.1140 g, 0.8 mmol) and allowed to warm up to room temperature followed by the addition of 20 mL of water. Then the organic layer was separated and the aqueous layer was extracted with diethyl ether (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4. After filtration and evaporation, column chromatography on silica gel (petroleum ether–ethyl acetate = 5 : 1) afforded (*R*)-(−)-**1d** (0.6764 g, 79%) with 98.5% ee as determined by HPLC analysis (Chiralcel OD–H, n-hexane–*i*-PrOH = 95 : 5, 0.7 mL min^{-1}, λ = 254 nm, t_R = 12.329 min (major), 15.634 min (minor), 17.430 min (major), 19.946 min (minor)): $[\alpha]_D^{20}$ = −62.2 (c = 1.33, $CHCl_3$); oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.49 (m, 2 H), 7.47-7.31 (m, 3 H), 5.99-5.89 (m, 1 H), 5.70-5.55 (m, 1 H), 2.09-1.87 (m, 2 H), 1.42-1.08 (m, 6 H), 0.86-0.72 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.7, 203.6, 144.8, 144.7, 130.8, 129.0, 124.1, 102.53, 102.46, 99.3, 99.1, 31.03, 30.98, 28.20, 28.17, 27.93, 27.90, 22.2, 13.9, 13.8; IR (neat) ν/cm^{-1} 3057, 2955, 2929, 2857, 1946, 1579, 1462, 1443, 1371, 1299, 1084, 1048; MS (70 eV, EI) m/z (%) 234 (M^+, 8.82), 173 (100); HRMS Calcd for $C_{14}H_{18}OS$ (M^+): 234.1078; Found: 234.1082.

The following compounds were prepared according to this procedure.

2. Synthesis of 1,2-octadienyl 4-bromophenyl sulfoxide (1e). The reaction of oct-1-yn-3-ol (0.5053 g, 4.0 mmol), Et_3N (0.56 mL, $d = 0.726$ g mL^{-1}, 0.4066 g, 4.0 mmol) and 4-bromophenylsulfenyl chloride (0.9465 g, 4.2 mmol) in 15 + 2 mL of methylene chloride quenched with CH_3I (0.05 mL, d = 2.280 g mL^{-1}, 0.1140 g, 0.80 mmol) afforded **1e** (0.7558 g, 60%) (petroleum ether–ethyl acetate = 5 : 1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.60 (m, 2 H), 7.54-7.44 (m, 2 H), 6.04-5.97 (m, 1 H), 5.80-5.67 (m, 1 H), 2.19-2.04 (m, 2 H), 1.52-1.20 (m, 6 H), 0.96-0.81 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.0, 203.9, 144.0, 132.4, 132.3, 125.8, 125.4, 102.4, 102.3, 99.7, 99.5, 31.2, 31.1, 28.3, 28.05, 28.02, 22.4, 14.0; IR (neat) ν/cm^{-1} 2961, 2928, 2857, 1946, 1570, 1468, 1384, 1172, 1081, 1051, 1007; MS (70 eV, EI) m/z (%) 314 (M$^+$(^{81}Br), 13.91), 312 (M$^+$(^{79}Br), 13.29), 134 (100); Elemental analysis calcd for $C_{14}H_{17}BrOS$: C, 53.68; H, 5.47; Found: C, 53.74; H, 5.32.

3. Synthesis of 1,2-octadienyl 4-nitrophenyl sulfoxide (1f). The reaction of oct-1-yn-3-ol (0.6298 g, 5.0 mmol), Et_3N (0.70 mL, $d = 0.726$ g mL^{-1}, 0.5082 g, 5.0 mmol) and 4-nitrophenylsulfenyl chloride (0.9944 g, 5.3 mmol) in 20 + 5 mL of methylene chloride quenched with CH_3I (0.07 mL, d = 2.280 g mL^{-1}, 0.1596 g, 1.1 mmol) afforded **1f** (0.8006 g, 57%) (petroleum ether–ethyl acetate = 5 : 1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43-8.29 (m, 2 H), 7.88-7.76 (m, 2 H), 6.10-5.98 (m, 1 H), 5.88-5.72 (m, 1 H), 2.23-2.05 (m, 2 H), 1.53-1.19 (m, 6 H), 0.95-0.78 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.4, 204.3, 152.5, 152.3, 149.2, 125.2, 124.20, 124.17, 101.8, 100.1, 100.0, 31.03, 31.00, 28.3, 28.2, 28.0, 27.8, 22.3, 22.2, 13.89, 13.87; IR (neat) ν/cm^{-1} 3097, 2956, 2929, 2858, 1946, 1603, 1582, 1526, 1467, 1345, 1315, 1082, 1053, 1011; MS (70 eV, EI) m/z (%) 279 (M$^+$, 100); Elemental analysis calcd for $C_{14}H_{17}NO_3S$: C, 60.19; H, 6.13; N, 5.01; Found: C, 60.21; H, 5.97; N, 5.13.

4. Synthesis of 1-phenyl-3-ethyl-1,2-pentadienyl phenyl sulfoxide (1h). The reaction of 3-ethyl-1-phenylpent-1-yn-3-ol (0.9432 g, 5.0 mmol), Et_3N (0.70 mL, $d = 0.726$ g mL^{-1}, 0.5082 g, 5.0 mmol) and phenylsulfenyl chloride (0.7634 g, 5.3 mmol) in 15 + 2 mL of methylene chloride quenched with CH_3I (0.07 mL, d = 2.280 g mL^{-1}, 0.1596 g, 1.1 mmol) afforded **1h** (0.7135 g, 48%) (petroleum ether–ethyl acetate = 7.5 : 1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58-7.48 (m, 2 H), 7.43-7.34 (m, 5 H), 7.33-7.18 (m, 3 H), 2.23-1.98 (m, 4 H), 1.08 (t, J = 7.4 Hz, 3 H), 0.95 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.2, 144.0, 131.9, 130.6, 128.6, 128.5, 128.0, 127.7, 124.7, 120.5, 118.2, 26.2, 26.0, 12.3, 12.0; IR (neat) ν/cm^{-1} 3058, 2968, 2932, 2901, 2877, 1938, 1747, 1596, 1580, 1493, 1445, 1375, 1323, 1176, 1147, 1086, 1049; MS (70 eV, EI) m/z (%) 296 (M$^+$, 68.52), 157 (100); Elemental analysis calcd for $C_{19}H_{20}OS$: C, 76.98; H, 6.80; Found: C, 76.89; H, 6.94.

Hydration of 1,2-allenylic sulfoxides.

1. Synthesis of 1-[(*Z*)-2′(phenylsulfinylethenyl)]-1-cyclohexanol (*Z*-3a). *Typical procedure.* A solution of **1a** (69.4 mg, 0.30 mmol) in HOAc (3.0 mL) was stirred vigorously at 60 °C for 24 h as monitored by TLC. The resulting mixture was quenched with 10 mL of an aqueous saturated solution of $NaHCO_3$, extracted with diethyl ether (15 mL × 3), washed with a saturated aqueous solution of $NaHCO_3$, and dried over anhydrous Na_2SO_4. After filtration and evaporation, column chromatography on silica gel (petroleum ether–ethyl acetate = 1 : 1) afforded *Z*-**3a** (64.9 mg, 87%): white solid; m.p. 147-149 °C (n-hexane–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86-7.70 (m, 2 H), 7.56-7.37 (m 3 H), 6.14 (d, J = 10.8 Hz 1 H), 5.97 (d, J = 10.8 Hz, 1 H), 4.19 (s, 1 H), 1.88-1.37 (m, 9 H), 1.34-1.14 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6, 144.5, 134.6, 130.7, 129.2, 124.9, 73.0, 38.4, 37.6, 25.1, 21.7, 21.4; IR (KBr) ν/cm^{-1} 3405, 3293, 2924, 2848, 1687, 1612, 1579, 1473, 1442, 1377, 1279, 1134, 1077, 1019; MS (70 eV, EI) m/z (%) 250 (M$^+$, 1.14), 205 (100); Elemental analysis calcd for $C_{14}H_{18}O_2S$: C, 67.16; H, 7.25; Found: C, 67.19; H, 7.29.

The following compounds were prepared according to this procedure.

2. Synthesis of 1-[(*Z*)-2′(phenylsulfinylethenyl)]-1-cyclopentanol (*Z*-3b). The reaction of **1b** (64.1 mg, 0.3 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded *Z*-**3b** (petroleum ether–ethyl acetate = 2 : 1) (37.4 mg, 53%): white solid; m.p. 163–164 °C (n-hexane–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.72 (m, 2 H), 7.55-7.42 (m, 3 H), 6.21 (d, J = 10.8 Hz, 1 H), 6.03 (d, J = 10.8 Hz, 1 H), 3.89 (s, 1 H), 2.04-1.62 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.9, 144.5, 134.9, 130.8, 129.2, 124.9, 82.1, 42.0, 41.0, 23.9, 23.8; IR (KBr) ν/cm^{-1} 3318, 3059, 3021, 2968, 2950, 2867, 1619, 1579, 1467, 1442, 1397, 1300, 1196, 1167, 1077, 1037, 1014; MS (70 eV, EI) m/z (%) 236 (M$^+$, 0.59), 219 (M$^+$–OH, 23.26), 191 (M$^+$–C_4H_9, 79.46), 81 (100); Elemental analysis calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82; Found: C, 66.09; H, 6.78.

3. Synthesis of 1-(phenylsulfinyl)non-1(*Z*)-en-3-ol (*Z*-3c). The reaction of **1c** (74.2 mg, 0.30 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded *Z*-**3c** (petroleum ether–ethyl acetate = 2 : 1) (19.3 mg (less polar isomer) and 32.1 mg (more polar isomer), 65%).

Less polar isomer: white solid; m.p. 60–62 °C (n-hexane–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.63 (m, 2 H), 7.55-7.41 (m, 3 H), 6.24-6.10 (m, 2 H), 4.97-4.77 (m, 1 H), 3.19 (d, J = 5.1 Hz, 1 H), 1.75-1.53 (m, 2 H), 1.53-1.17 (m, 8 H), 0.87 (t, J = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 142.9, 136.6, 130.8, 129.3, 124.4, 68.8, 37.3, 31.7, 29.1, 25.1, 22.5, 14.1; IR (KBr) ν/cm^{-1} 3358, 3052, 3034, 2953, 2922, 2866, 2849, 1618, 1467, 1443, 1316, 1122, 1069, 1046, 1004; MS (70 eV, EI) m/z (%) 267 (M$^+$+1, 0.04), 266 (M$^+$, 0.005), 249 (M$^+$–OH, 100.00); Elemental analysis calcd for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.32; Found: C, 67.72; H, 8.40.

More polar isomer: white solid; m.p. 71–73 °C (n-hexane–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.57 (m, 2 H), 7.56-7.44 (m, 3 H), 6.28-6.15 (m, 2 H), 4.99-4.85 (m, 1 H), 4.38 (d, J = 3.6 Hz, 1 H), 1.79-1.58 (m, 1 H), 1.58-1.39 (m, 2 H), 1.39-1.17 (m, 7 H), 0.87 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3, 143.4, 135.4, 131.1, 129.4, 124.4, 67.8, 36.5, 31.7, 29.1, 25.3, 22.5, 14.1; IR (KBr) ν/cm^{-1} 3374, 3057, 3033, 2953, 2924, 2854, 1624, 1576, 1469, 1444, 1371, 1311, 1296, 1257, 1084, 1071, 1041, 1023; MS (70 eV, EI) m/z (%) 267 (M$^+$+1, 0.13), 249 (M$^+$–OH, 100.00); Elemental analysis calcd for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.32; Found: C, 67.70; H, 8.40.

4. Synthesis of 1-(phenylsulfinyl)oct-1(*Z*)-en-3-ol (*Z*-3d). The reaction of **1d** (70.6 mg, 0.30 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded *Z*-**3d** (petroleum ether–ethyl acetate = 1 : 1)

(22.8 mg (less polar isomer) and 27.5 mg (more polar isomer), 66%).

Less polar isomer: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76-7.62 (m, 2 H), 7.53-7.41 (m, 3 H), 6.24-6.10 (m, 2 H), 4.91-4.78 (m, 1 H), 3.30 (bs, 1 H), 1.73-1.14 (m, 8 H), 0.88 (t, J = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 143.0, 136.6, 130.8, 129.3, 124.4, 68.8, 37.3, 31.6, 24.8, 22.5, 14.0; IR (KBr) ν/cm^{-1} 3362, 3058, 2929, 2858, 1739, 1617, 1581, 1462, 1444, 1379, 1304, 1177, 1082, 1020; MS (70 eV, EI) m/z (%) 235 (M$^+$–OH, 100.00); Elemental analysis calcd for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99; Found: C, 66.84; H, 8.00.

More polar isomer: yellow solid; m.p. 74–76 °C (n-hexane–diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73-7.57 (m, 2 H), 7.57-7.43 (m, 3 H), 6.25-6.12 (m, 2 H), 5.00-4.82 (m, 1 H), 4.17 (s, 1 H), 1.77-1.19 (m, 8 H), 0.88 (t, J = 5.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3, 143.5, 135.5, 131.1, 129.4, 124.4, 67.9, 36.6, 31.6, 25.0, 22.5, 14.0; IR (neat, cm^{-1}) 3374, 3059, 2929, 2858, 1741, 1652, 1619, 1582, 1467, 1444, 1378, 1305, 1232, 1123, 1083, 1026; MS (70 eV, EI) m/z (%) 235 (M$^+$–OH, 100.00); Elemental analysis calcd for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99; Found: C, 66.64; H, 8.15.

5. Synthesis of 1-(*p*-bromophenylsulfinyl)oct-1(*Z*)-en-3-ol (*Z*-3e). The reaction of **1e** (92.2 mg, 0.29 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded *Z*-**3e** (petroleum ether–ethyl acetate = 1 : 2) (23.5 mg (less polar isomer) and 48.4 mg (more polar isomer), 74%).

Less polar isomer: white solid; m.p. 86–88 °C (n-hexane–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.52 (m, 4 H), 6.20-6.10 (m, 2 H), 4.86-4.74 (m, 1 H), 3.22 (bs, 1 H), 1.71-1.20 (m, 8 H), 0.89 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 136.7, 132.4, 126.1, 125.3, 69.0, 37.3, 31.6, 24.8, 22.5, 14.0; IR (neat, cm^{-1}) 3376, 2956, 2930, 2856, 1636, 1572, 1470, 1411, 1388, 1309, 1065, 1015, 1000; MS (70 eV, EI) m/z (%) 315 (M$^+$–OH (^{81}Br), 100.00), 313 (M$^+$–OH (^{79}Br), 100.00); Elemental analysis calcd for $C_{14}H_{19}BrO_2S$: C, 50.76; H, 5.78; Found: C, 50.95; H, 6.09.

More polar isomer: white solid; m.p. 52–53 °C (n-hexane–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.56 (m, 2 H), 7.56-7.43 (m, 2 H), 6.26-6.12 (m, 2 H), 4.95-4.75 (m, 1 H), 4.20 (d, J = 1.5 Hz, 1 H), 1.77-1.17 (m, 8 H), 0.88 (t, J = 5.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.7, 142.7, 135.2, 132.6, 126.0, 125.6, 68.0, 36.5, 31.6, 25.0, 22.5, 14.0; IR (neat, cm^{-1}) 3364, 2929, 2857, 1618, 1571, 1469, 1386, 1296, 1123, 1080, 1066, 1033, 1006; MS (70 eV, EI) m/z (%) 315 (M$^+$–OH (^{81}Br), 100.00), 313 (M$^+$–OH (^{79}Br), 100.00); Elemental analysis calcd for $C_{14}H_{19}BrO_2S$: C, 50.76; H, 5.78; Found: C, 50.76; H, 5.79.

6. Synthesis of 1-(*p*-nitrophenylsulfinyl)oct-1(*Z*)-en-3-ol (*Z*-3f). The reaction of **1f** (88.0 mg, 0.32 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded *Z*-**3f** (petroleum ether–ethyl acetate = 1 : 2) (20.8 mg (less polar isomer) and 44.4 mg (more polar isomer), 70%).

Less polar isomer: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38-8.29 (m, 2 H), 7.98-7.89 (m, 2 H), 6.27-6.15 (m, 2 H), 4.86-4.77 (m, 1 H), 3.14 (d, J = 9 Hz, 1 H), 1.71-1.26 (m, 8 H), 0.89 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6, 149.2, 143.8, 136.3, 125.7, 124.2, 69.3, 37.4, 31.5, 24.8, 22.5, 13.9; IR (neat, cm^{-1}) 3379, 3099, 2928, 2858, 1603, 1582, 1528, 1466, 1347, 1106, 1080, 1028; MS (70 eV, EI) m/z (%) 280 (M$^+$–OH, 100.0); Elemental analysis calcd for $C_{14}H_{19}NO_4S$: C, 56.55; H, 6.44; N, 4.71; Found: C, 56.65; H, 6.49; N, 4.63.

More polar isomer: white solid; m.p. 76–77 °C (n-hexane–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40-8.30 (m, 2 H), 7.88-7.77 (m, 2 H), 6.30 (dd, J_1 = 7.5 Hz, J_2 = 9.9 Hz, 1 H), 6.18 (d, J = 9.9 Hz, 1 H), 4.95-4.86 (m, 1 H), 3.77 (d, J = 2.4 Hz, 1 H), 1.81-1.26 (m, 8 H), 0.90 (t, J = 6.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 149.3, 145.4, 134.6, 125.5, 124.4, 68.6, 36.6, 31.6, 25.1, 22.5, 14.0; IR (neat, cm^{-1}) 3389, 3007, 2955, 2911, 2859, 2843, 1605, 1583, 1529, 1459, 1416, 1399, 1364, 1344, 1315, 1287, 1103, 1083, 1069, 1036, 1010; MS (70 eV, EI) m/z (%) 280 (M$^+$–OH, 100.0); Elemental analysis calcd for $C_{14}H_{19}NO_4S$: C, 56.55; H, 6.44; N, 4.71; Found: C, 56.62; H, 6.49; N, 4.68.

7. Synthesis of 2-methyl-4-(phenylsulfinyl)oct-3(*Z*)-en-2-ol (*Z*-3g). The reaction of **1g** (49.6 mg, 0.20 mmol) in HOAc (2.0 mL) at room temperature for 24 h afforded *Z*-**3g** (petroleum ether–ethyl acetate = 2 : 1) (46.2 mg, 87%): solid; m.p. 63–65 °C (n-hexane–diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85-7.77 (m, 2 H), 7.53-7.42 (m, 3 H), 6.05 (t, J = 1.2 Hz, 1 H), 3.66 (bs, 1 H), 2.22-2.08 (m, 1 H), 1.94-1.77 (m, 1 H), 1.57 (s, 3 H), 1.50 (s, 3 H), 1.38-1.12 (m, 4 H), 0.78 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 142.9, 142.2, 130.2, 128.8, 125.6, 71.6, 31.53, 31.49, 31.0, 26.0, 22.0, 13.6; IR (KBr, cm^{-1}) 3346, 3060, 2963, 2930, 2871, 1582, 1476, 1466, 1443, 1375, 1360, 1306, 1221, 1179, 1077, 1018; MS (70 eV, EI) m/z (%) 266 (M$^+$, 0.26), 126 (100); Elemental analysis calcd for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.32; Found: C, 67.97; H, 8.31.

8. Synthesis of 3-ethyl-1-phenyl-1-(phenylsulfinyl)pent-1(*Z*)-en-3-ol (*Z*-3h). The reaction of **1h** (88.9 mg, 0.30 mmol) in HOAc (3.0 mL) at room temperature for 24 h afforded *Z*-**3h** (petroleum ether–ethyl acetate = 4 : 1) (76.4 mg, 81%): white solid; m.p. 134–135 °C (n-hexane–diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66-7.49 (m, 2 H), 7.43-7.18 (m, 6 H), 7.16-6.98 (m, 2 H), 6.10 (s, 1 H), 4.98 (s, 1 H), 1.88-1.66 (m, 4 H), 1.03 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.0, 144.8 142.1, 134.9, 130.7, 129.4, 128.7, 128.5, 128.1, 125.9, 76.9, 34.7, 34.1, 8.5, 8.4; IR (KBr, cm^{-1}) 3289, 3056, 2962, 2932, 2874, 2845, 1633, 1576, 1490, 1475, 1459, 1443, 1414, 1373, 1318, 1281, 1186, 1100, 1078, 1026, 1016; MS (70 eV, EI) m/z (%) 315 (M+H$^+$, 0.53), 87 (100); Elemental analysis calcd for $C_{19}H_{22}O_2S$: C, 72.57; H, 7.05; Found: C, 72.55; H, 7.02.

9. Synthesis of 4-(*p*-bromophenylsulfinyl)but-3(*Z*)-en-2-ol (*Z*-3i). The reaction of **1i** (77.6 mg, 0.30 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded *Z*-**3i** (petroleum ether–ethyl acetate = 1 : 1) (mixture, dr = 1.94 : 1, 62.7 mg, 76%): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.44 (m, 4 H), 6.28-6.08 (m, 2 H), 5.14-4.96 (m, 1 H), 3.94 (d, J = 3.3 Hz, 0.66 H), 3.41 (d, J = 4.8 Hz, 0.34 H), 1.42-1.32 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 144.1, 143.1, 142.5, 135.7, 134.5, 132.6, 132.4, 126.1, 125.9, 125.6, 125.3, 65.1, 64.2, 23.5, 22.8; IR (neat, cm^{-1}) 3377, 3080, 2972, 2926, 1729, 1645, 1618, 1570, 1470, 1385, 1288, 1113, 1065, 1032, 1005; MS (70 eV, EI) m/z (%) 276 (M$^+$ (^{81}Br), 0.08), 274 (M$^+$ (^{79}Br), 0.07), 259 (M$^+$–OH (^{81}Br), 100.00), 257 (M$^+$–OH (^{79}Br), 95.69); Elemental analysis calcd for $C_{10}H_{11}BrO_2S$: C, 43.65; H, 4.03; Found: C, 43.60; H, 4.16.

10. Synthesis of 3-(phenylsulfinyl)hept-2(*Z*)-en-1-ol (*Z*-3j). The reaction of **1j** (66.9 mg, 0.30 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded *Z*-**3j** (petroleum ether–ethyl acetate = 2/ : 1) (41.7 mg, 58%): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58-7.50 (m, 2 H), 7.50-7.39 (m, 3 H), 6.20-6.12 (m, 1 H), 4.89-4.75

(m, 1 H), 4.52-4.38 (m, 1 H), 3.82 (s, 1 H), 2.35-2.19 (m, 1 H), 1.94-1.79 (m, 1 H), 1.39-1.08 (m, 4 H), 0.74 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6, 141.9, 135.5, 130.4, 129.0, 124.3, 58.2, 30.0, 24.6, 22.1, 13.7; IR (neat, cm^{-1}) 3384, 3059, 2957, 2930, 2871, 1585, 1465, 1443, 1377, 1302, 1224, 1082, 1019; MS (70 eV, EI) m/z (%) 239 (M+H$^+$, 6.37), 238 (M$^+$, 0.20), 221 (100); HRMS Calcd for $C_{13}H_{18}O_2S$ (M$^+$): 238.1028, Found: 238.1025.

11. Synthesis of 3-phenyl-3-(phenylsulfinyl)prop-2(*Z*)-en-1-ol (*Z*-3k). The reaction of **1k** (72.4 mg, 0.30 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded *Z*-**3k** (petroleum ether–ethyl acetate = 1 : 1) (39.8 mg, 51%): white solid; m.p. 104–105 °C (n-hexane–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.08 (m, 10 H), 6.42 (t, J = 6.5 Hz, 1 H), 4.87-4.76 (m, 1 H), 4.70-4.59 (m, 1 H), 3.25-3.17 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.1, 141.6, 139.1, 133.2, 130.7, 129.0, 128.9, 128.6, 127.9, 124.8, 58.1; IR (KBr, cm^{-1}) 3304, 3060, 2923, 2874, 1484, 1442, 1084, 1013; MS (70 eV, EI) m/z (%) 241 (M$^+$–OH, 20.29), 103 (100); Elemental analysis calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46; Found: C, 69.84; H, 5.45.

12. Synthesis of 3-(phenylsulfinyl)hexa-2(*Z*)-5-dien-1-ol (*Z*-3l). The reaction of **1l** (61.7 mg, 0.30 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded *Z*-**3l** (petroleum ether–ethyl acetate = 1 : 1) (43.0 mg, 64%): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.51 (m, 2 H), 7.51-7.40 (m, 3 H), 6.22-6.13 (m, 1 H), 5.59-5.41 (m, 1 H), 5.04-4.88 (m, 2 H), 4.81 (dd, J_1 = 13.5 Hz, J_2 = 7.8 Hz, 1 H), 4.47 (dd, J_1 = 13.5 Hz, J_2 = 4.5 Hz, 1 H), 3.79 (s, 1 H), 3.07 (dd, J_1 = 17.0 Hz, J_2 = 6.5 Hz, 1 H), 2.54 (dd, J_1 = 16.8 Hz, J_2 = 7.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 141.5, 137.1, 133.6, 130.6, 129.1, 124.3, 118.4, 58.2, 29.0; IR (neat, cm^{-1}) 3383, 3075, 3060, 3008, 2979, 2921, 1639, 1581, 1477, 1443, 1426, 1364, 1305, 1228, 1080, 1018; MS (70 eV, EI) m/z (%) 222 (M$^+$, 0.36), 78 (100); Elemental analysis calcd for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35; Found: C, 64.74; H, 6.40;

13. Synthesis of 2-methyl-4-(phenylsulfinyl)but-3(*Z*)-en-2-ol (*Z*-3m). The reaction of **1m** (55.5 mg, 0.30 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded *Z*-**3m** (petroleum ether–ethyl acetate = 2 : 3) (35.4 mg, 58%): white solid; m.p. 100–102 °C (n-hexane–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82-7.73 (m, 2 H), 7.54-7.44 (m, 3 H) 6.16 (d, J = 10.8 Hz, 1 H), 5.97 (d, J = 10.8 Hz, 1 H), 4.15 (s, 1 H), 1.50 (s, 3 H), 1.38 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6, 144.5, 134.2, 130.7, 129.1, 124.9, 71.9, 30.6, 30.0; IR (KBr, cm^{-1}) 3306, 3057, 3014, 2987, 2975, 2934, 1653, 1579, 1540, 1467, 1443, 1375, 1358, 1252, 1195, 1148, 1129, 1075, 1015; MS (70 eV, EI) m/z (%) 210 (M$^+$, 18.94), 195 (100); Elemental analysis calcd for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71; Found: C, 62.82; H, 6.70.

14. Synthesis of 3-ethyl-1-(phenylsulfinyl)pent-1(*Z*)-en-3-ol (*Z*-3n). The reaction of **1n** (66.8 mg, 0.30 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded *Z*-**3n** (petroleum ether–ethyl acetate = 1/1) (54.9 mg, 76%): white solid; m.p. 113–115 °C (n-hexane–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.71 (m, 2 H), 7.54-7.40 (m, 3 H), 6.13 (d, J = 11.1 Hz, 1 H), 5.98 (d, J = 10.8 Hz, 1 H), 3.24 (s, 1 H), 1.81-1.49 (m, 4 H), 0.99 (t, J = 7.4 Hz, 3 H), 0.87 (t, J = 7.5 Hz, 3 H);^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 144.2, 136.8, 130.7, 129.1, 124.9, 77.6, 33.8, 33.6, 8.05, 8.03; IR (KBr, cm^{-1}) 3346, 2963, 2925, 2877, 1615, 1576, 1475, 1463, 1444, 1410, 1320, 1274, 1210, 1076, 1009; MS (70 eV, EI) m/z (%) 238 (M$^+$, 1.07), 209 (100); Elemental analysis calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61; Found: C, 65.46; H, 7.62.

15. Synthesis of 3-propyl-1-(phenylsulfinyl)hex-1(*Z*)-en-3-ol (*Z*-3o). The reaction of **1o** (75.2 mg, 0.30 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded *Z*-**3o** (petroleum ether–ethyl acetate = 3 : 1) (57.2 mg, 71%): white solid; m.p. 95–97 °C (n-hexane–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82-7.70 (m, 2 H), 7.54-7.37 (m, 3 H) 6.07 (d, J = 10.8 Hz, 1 H), 5.97 (d, J = 10.8 Hz, 1 H), 3.48 (s, 1 H), 1.71-1.10 (m, 8 H), 0..98-0.75 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 144.6 136.2, 130.5, 129.0, 124.9, 77.2, 43.8, 43.7, 17.0, 16.9, 14.4, 14.3; IR (KBr, cm^{-1}) 3332, 3060, 2958, 2932, 2872, 1621, 1582, 1475, 1466, 1444, 1379, 1305, 1262, 1207, 1143, 1078, 1014; MS (70 eV, EI) m/z (%) 267 (M+H$^+$, 0.44), 266 (M$^+$, 0.26), 223 (100); Elemental analysis calcd for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.32; Found: C, 67.70; H, 8.23.

16. Synthesis of 3-butyl-1-(phenylsulfinyl)sept-1(*Z*)-en-3-ol (*Z*-3p). The reaction of **1p** (107.0 mg, 0.39 mmol) in HOAc (4.0 mL) at 60 °C for 23.5 h afforded *Z*-**3p** (petroleum ether–ethyl acetate = 2.5 : 1) (78.1 mg, 69%): white solid; m.p. 47–49 °C (n-hexane–diethyl ether);^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.69 (m, 2 H), 7.55-7.36 (m, 3 H) 6.09 (d, J = 11.1 Hz, 1 H), 5.98 (d, J = 10.5 Hz, 1 H), 3.13 (s, 1 H), 1.75-1.59 (m, 2 H), 1.59-1.48 (m, 2 H), 1.48-1.02 (m, 8 H), 0.97-0.77 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.0, 144.5, 136.3, 130.5, 128.9, 124.9, 77.1, 41.3, 41.0, 25.82, 25.75, 22.94, 22.92, 13.9; IR (KBr, cm^{-1}) 3330, 3060, 2956, 2933, 2861, 1585, 1466, 1443, 1378, 1305, 1244, 1140, 1078, 1015; MS (70 eV, EI) m/z (%) 294 (M$^+$, 0.11), 237 (100); Elemental analysis calcd for $C_{17}H_{26}O_2S$: C, 69.34; H, 8.90; Found: C, 69.39; H, 8.71.

17. Synthesis of 2-phenyl-4-(phenylsulfinyl)but-3(*Z*)-en-2-ol (*Z*-3q). The reaction of **1q** (75.9 mg, 0.30 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded *Z*-**3q** (petroleum ether–ethyl acetate = 1 : 1) (23.0 mg (less polar isomer) and 16.1 mg (more polar isomer), 48%).

Less polar isomer: white solid; m.p. 116–118 °C (n-hexane–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.52 (m, 2 H), 7.45-7.34 (m, 5 H), 7.32-7.16 (m, 3 H), 6.46 (d, J = 10.5 Hz, 1 H), 5.99 (d, J = 10.5 Hz, 1 H), 3.28 (bs, 1 H), 1.75 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 145.3, 144.2, 134.5, 130.9, 129.2, 128.6, 127.6, 125.2, 125.0, 75.4, 30.2; IR (KBr, cm^{-1}) 3268, 3083, 3055, 3018, 2988, 2937, 1492, 1471, 1442, 1363, 1236, 1201, 1111, 1078, 1055, 1024, 1000; MS (70 eV, EI) m/z (%) 272 (M$^+$, 0.81), 229 (100); Elemental analysis calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92; Found: C, 70.51; H, 5.99.

More polar isomer: white solid; m.p. 122–124 °C (n-hexane–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.61 (m, 2 H), 7.56-7.41 (m, 5 H), 7.39-7.23 (m, 3 H), 6.51 (d, J = 11.1 Hz, 1 H), 6.07 (d, J = 10.5 Hz, 1 H), 4.71 (s, 1 H), 1.82 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.4, 146.1, 144.0, 134.7, 130.9, 129.2, 128.4, 127.2, 124.9, 74.9, 31.7; IR (KBr, cm^{-1}) 3284, 3057, 2976, 1493, 1475, 1449, 1406, 1369, 1231, 1192, 1106, 1075, 1015; MS (70 eV, EI) m/z (%) 272 (M$^+$, 1.36), 229 (100); Elemental analysis calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92; Found: C, 70.57; H, 6.06.

18. Synthesis of 4-(*p*-bromophenylsulfinyl)hex-3(*Z*)-en-2-ol (*Z*-3r). The reaction of **1r** (86.0 mg, 0.30 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded *Z*-**3r** (petroleum ether–ethyl acetate = 3 : 1) (23.9 mg (less polar isomer) and 38.7 mg (more polar isomer), 68%).

Less polar isomer: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.49 (m, 4 H), 5.92 (dt, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1 H), 5.26-5.12 (m, 1 H), 3.04 (s, 1 H), 2.42-2.24 (m, 1 H), 1.86-1.68 (m, 1 H), 1.42 (d, J = 6.0 Hz, 3 H), 0.91 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.4, 141.2, 138.7, 132.1, 126.1, 124.8, 63.5, 24.4, 17.8, 12.0; IR (neat, cm^{-1}) 3385, 2970, 2928, 1644, 1571, 1469, 1384, 1293, 1263, 1148, 1113, 1066, 1028, 1006; MS (70 eV, EI) m/z (%) 287 (M^+–OH (^{81}Br), 57.03), 285 (M^+–OH (^{79}Br), 55.09), 97 (100); Elemental analysis calcd for $C_{12}H_{15}BrO_2S$: C, 47.53; H, 4.99; Found: C, 47.53; H, 5.07.

More polar isomer: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65-7.58 (m, 2 H), 7.40-7.33 (m, 2 H), 5.99 (dt, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1 H), 5.38-5.25 (m, 1 H), 3.97 (d, J = 2.4 Hz, 1 H), 2.43-2.26 (m, 1 H), 1.85-1.64 (m, 1 H), 1.38 (d, J = 6.3 Hz, 3 H), 0.94 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.1, 141.1, 140.5, 132.3, 125.9, 125.0, 62.9, 23.0, 17.7, 12.1; IR (neat, cm^{-1}) 3388, 2971, 2929, 1643, 1571, 1468, 1384, 1289, 1152, 1112, 1066, 1041, 1006; MS (70 eV, EI) m/z (%) 287 (M^+–OH (^{81}Br), 43.08), 285 (M^+–OH (^{79}Br), 40.88), 43 (100); Elemental analysis calcd for $C_{12}H_{15}BrO_2S$: C, 47.53; H, 4.99; Found: C, 47.68; H, 5.14.

19. Synthesis of 1-(phenylsulfinyl)non-1(*Z*)-en-3(*R*)-ol ((*R*)-*Z*-3c). The reaction of (*R*)-**1c** (73.9 mg, 0.30 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded (*R*)-*Z*-**3c** (20.5 mg (less polar isomer) and 31.2 mg (more polar isomer), 65%).

Less polar isomer: 98.9% ee determined by HPLC analysis (Chiralcel OJ-H, n-hexane/–*i*-PrOH = 95 : 5, 0.5 mL min^{-1}, λ = 254 nm, t_R = 19.698 min (minor), 20.923 min (major)), $[\alpha]_D^{20}$ = +95.8 (c = 0.657, $CHCl_3$); white solid; m.p. 59–61 °C (n-hexane–methylene chloride). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.62 (m, 2 H), 7.54-7.42 (m, 3 H), 6.24-6.10 (m, 2 H), 4.93-4.80 (m, 1 H), 3.07 (d, J = 4.8 Hz, 1 H), 1.75-1.53 (m, 2 H), 1.53-1.17 (m, 8 H), 0.88 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 142.9, 136.7, 130.8, 129.3, 124.4, 68.8, 37.4, 31.7, 29.1, 25.1, 22.6, 14.1; IR (KBr) ν/cm^{-1} 3358, 3034, 2953, 2922, 2849, 2865, 1612, 1467, 1443, 1316, 1069, 1046, 1004; MS (70 eV, EI) m/z (%) 249 (M^+–OH, 100); Elemental analysis calcd for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.32; Found: C, 67.68; H, 8.31.

More polar isomer: 98.6% ee determined by HPLC analysis (Chiralcel OJ–H, n-hexane–*i*-PrOH = 95 : 5, 0.5 mL min^{-1}, λ = 254 nm, t_R = 13.848 min (major), 15.961 min (minor)), $[\alpha]_D^{20}$ = –98.0 (c = 1.013, $CHCl_3$); white solid; m.p. 52–54 °C (n-hexane–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.58 (m, 2 H), 7.56-7.44 (m, 3 H), 6.25-6.14 (m, 2 H), 4.99-4.86 (m, 1 H), 4.27 (d, J = 3.6 Hz, 1 H), 1.77-1.60 (m, 1 H), 1.60-1.39 (m, 2 H), 1.39-1.18 (m, 7 H), 0.87 (t, J = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 143.4, 135.5, 131.1, 129.4, 124.4, 67.8, 36.6, 31.7, 29.1, 25.3, 22.5, 14.1; IR (KBr) ν/cm^{-1} 3373, 3057, 3033, 2953, 2924, 2867, 2854, 1627, 1576, 1469, 1444, 1371, 1314, 1290, 1260, 1125, 1084, 1071, 1041, 1023; MS (70 eV, EI) m/z (%) 249 (M–OH$^-$, 100); Elemental analysis calcd for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.32; Found: C, 67.63; H, 8.49.

20. Synthesis of 1-(phenylsulfinyl)oct-1(*Z*)-en-3(*R*)-ol ((*R*)-*Z*-3d). The reaction of (*R*)-**1d** (118.2 mg, 0.50 mmol) in HOAc (5.0 mL) at 60 °C for 24 h afforded (*R*)-*Z*-**3d** (petroleum ether/ethyl acetate = 2/1) (38.7 mg (less polar isomer) and 46.6 mg (more polar isomer), 68%).

Less polar isomer: 97.7% ee determined by HPLC analysis (Chiralcel OJ–H, n-hexane/*i*-PrOH = 90/10, 0.5 mL min^{-1}, λ = 254 nm, t_R = 12.535 min (minor), 13.179 min (major)), $[\alpha]_D^{20}$ = +96.8 (c = 0.720, $CHCl_3$); solid; m.p. 38–40 °C (n-hexane–diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.62 (m, 2 H), 7.54-7.41 (m, 3 H), 6.23-6.08 (m, 2 H), 4.92-4.78 (m, 1 H), 3.04 (s, 1 H), 1.73-1.52 (m, 2 H), 1.52-1.19 (m, 6 H), 0.88 (t, J = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 142.9, 136.6, 130.8, 129.3, 124.4, 68.8, 37.3, 31.6, 24.8, 22.5, 14.0; IR (KBr) ν/cm^{-1} 3363, 3059, 2967, 2930, 2858, 1740, 1615, 1582, 1476, 1464, 1444, 1378, 1305, 1227, 1123, 1083, 1017; MS (70 eV, EI) m/z (%) 253 ($M+H^+$, 0.07), 252 (M^+, 0.03), 235 (M^+–OH), 100.00); Elemental analysis calcd for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99; Found: C, 66.84; H, 8.04.

More polar isomer: 96.5% ee determined by HPLC analysis (Chiralcel OJ–H, n-hexane–*i*-PrOH = 90 : 10, 0.5 mL min^{-1}, λ = 254 nm, t_R = 11.131 min (major), 12.092 min (minor)), $[\alpha]_D^{20}$ = –96.9 (c = 1.060, $CHCl_3$); solid; m.p. 78–80 °C (n-hexane–diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73-7.57 (m, 2 H), 7.57-7.44 (m, 3 H), 6.25-6.14 (m, 2 H), 5.00-4.85 (m, 1 H), 4.21 (d, J = 3.9 Hz, 1 H), 1.78-1.61 (m, 1 H), 1.57-1.40 (m, 2 H), 1.40-1.18 (m, 5 H), 0.88 (t, J = 5.9 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 143.5, 135.6, 131.1, 129.4, 124.4, 67.9, 36.6, 31.6, 25.0, 22.5, 14.0; IR (neat, cm^{-1}) 3374, 3056, 3031, 2955, 2925, 2905, 2870, 2856, 1467, 1442, 1422, 1384, 1320, 1304, 1126, 1084, 1069, 1042; MS (70 eV, EI) m/z (%) 253 ($M+H^+$, 0.11), 252 (M^+, 0.02), 235 (M^+–OH), 100.00); Elemental analysis calcd for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99; Found: C, 66.61; H, 7.94.

21. Synthesis of 4-(*p*-bromophenylsulfinyl)hex-3(*Z*)-en-2(*R*)-ol ((*R*)-*Z*-3r). The reaction of (*R*)-**1r** (84.4 mg, 0.30 mmol) in HOAc (3.0 mL) at 60 °C for 24 h afforded (petroleum–ethyl acetate = 2 : 1) (*R*)-*Z*-**3r** (26.3 mg (less polar isomer) and 40.1 mg (more polar isomer), 74%).

Less polar isomer: 95.5% ee determined by HPLC analysis (Chiralcel OJ–H, n-hexane–*i*-PrOH = 90 : 10, 0.5 mL min^{-1}, λ = 254 nm, t_R = 14.281 min (minor), 16.307 min (major)), $[\alpha]_D^{20}$ = +220.5 (c = 0.877, $CHCl_3$); oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.49 (m, 4 H), 5.92 (d, J = 8.7 Hz, 1 H), 5.26-5.14 (m, 1 H), 2.80 (bs, 1 H), 2.47-2.22 (m, 1 H), 1.86-1.66 (m, 1 H), 1.42 (d, J = 6.3 Hz, 3 H), 0.92 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.5, 141.2, 138.6, 132.1, 126.1, 124.8, 63.5, 24.5, 17.7, 12.0; IR (neat, cm^{-1}) 3382, 3079, 2969, 2928, 2877, 1666, 1645, 1571, 1471, 1385, 1294, 1149, 1113, 1066, 1027, 1006; MS (70 eV, EI) m/z (%) 287 (M^+–OH (^{81}Br), 94.92), 285 (M^+–OH (^{79}Br), 91.35), 97 (100); Elemental analysis calcd for $C_{12}H_{15}BrO_2S$: C, 47.53; H, 4.99; Found: C, 47.22; H, 4.94.

More polar isomer: 94.1% ee determined by HPLC analysis (Chiralcel OJ–H, n-hexane–*i*-PrOH = 90 : 10, 0.5 mL min^{-1}, λ = 254 nm, t_R = 13.593 min (major), 16.710 min (minor)), $[\alpha]_D^{20}$ = –190.2 (c = 1.337, $CHCl_3$); oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.53 (m, 2 H), 7.42-7.29 (m, 2 H), 5.98 (d, J = 9.3 Hz, 1 H), 5.37-5.21 (m, 1 H), 3.97 (s, 1 H), 2.43-2.22 (m, 1 H), 1.86-1.66 (m, 1 H), 1.36 (d, J = 6.3 Hz, 3 H), 0.92 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9 141.0, 140.6, 132.3, 125.8, 125.0, 62.8, 22.9, 17.6, 12.0; IR (neat, cm^{-1}) 3390, 3080, 2970, 2928, 2871, 1651, 1570, 1469, 1384, 1289, 1152, 1112, 1078, 1066, 1042, 1006; MS (70 eV, EI) m/z (%) 287 (M^+–OH (^{81}Br), 85.43), 285 (M^+–OH (^{79}Br), 82.61), 97 (100); Elemental analysis calcd for $C_{12}H_{15}BrO_2S$: C, 47.53; H, 4.99; Found: C, 47.45; H, 5.09.

22. Synthesis of 2-deuterium-3-ethyl-1-phenyl-1-(phenylsulfinyl)pent-1(*Z*)-en-3-ol (*Z*-3h-D). The reaction of **1h**

(90.3 mg, 0.30 mmol) in DOAc (3.0 mL) and D_2O (6 μL) at room temperature under the protection of N_2 for 24 h afforded *Z*-**3h**-D (petroleum–ethyl acetate = 3 : 1) (85.3 mg, 78%): solid; m.p. 132–134 °C (n-hexane–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.52 (m, 2 H), 7.43-7.30 (m, 3 H), 7.30-7.19 (m, 3 H), 7.15-7.05 (m, 2 H), 6.10 (s, 0.03 H), 5.04 (s, 1 H), 1.90-1.66 (m, 4 H), 1.12-0.96 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7 (t, J = 22.8 Hz, 1 C), 144.8, 142.2, 135.0, 130.8, 129.4, 128.7, 128.5, 128.1, 125.9, 76.8, 34.7, 34.1, 8.49, 8.46; IR (KBr, cm^{-1}) 3288, 3056, 2962, 2932, 2874, 2845, 1639, 1582, 1490, 1475, 1459, 1443, 1282, 1186, 1078, 1016; MS (70 eV, EI) *m*/*z* (%): 315 (M^+, 0.05), 87 (100); Elemental analysis calcd for $C_{19}H_{21}DO_2S$: C, 72.43; H, 7.35; Found: C, 72.40; H, 7.31.

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9 Crystal data for compound (S_s,3*R*)-(*Z*)-**3e**: $C_{2.33}H_{3.33}O_{0.33}S_{0.17}$, MW = 42.06, Triclinic, space group *P*1, final *R* indices [$I > 2\sigma(I)$], R_1 = 0.0464, wR_2 = 0.0959, *R* indices (all data) R_1 = 0.1844, wR_2 = 0.1170, a = 5.4734(6) Å, b = 9.0484(10) Å, c = 14.9986(18) Å, α = 83.446(5)°, β = 89.906(5)°, γ = 89.581(4)°, V = 737.94(15) Å^3, T = 296(2) K, Z = 12, reflections collected/unique 10241/4695 (R_{int} = 0.1050), number of observations [$I > 2\sigma(I)$] 2287, parameters: 307. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center. CCDC 772770†.