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Stereochemically Controlled Asymmetric 1,2-Reduction of Enones Mediated by a Chiral Sulfoxide Moiety and a Lanthanum(III) Ion

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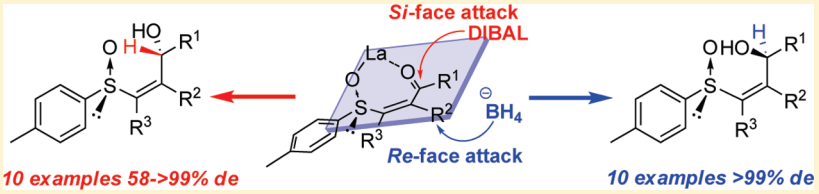
Supporting Information

ABSTRACT:



Enantiomerically pure (*Z*)-β-sulfinyl allylic alcohols of either handedness can be readily prepared from (*Z*)-β-sulfinyl enones using $NaBH_4$ or DIBAL reductants in the presence of $LaCl_3$ as a chelating agent. A chiral sulfoxide auxiliary induces the remote 1,2-asymmetric reduction (1,4-induction) to afford various chiral allylic alcohols in high yields with excellent stereoselectivities (up to 100% de).

INTRODUCTION

Asymmetric synthesis of chiral allylic alcohols plays an important role in organic and bioorganic chemistry because these chiral moieties provide valuable bioactivities.[1] Given that chiral allylic alcohols in their enantiomerically pure form are useful building blocks in organic synthesis,[2] many efficient methodologies for accessing such species have been developed in the past decades, including selective 1,2-reduction of α,β-unsaturated carbonyl compounds,[3] kinetic resolution of the corresponding racemic compounds,[4] and addition of vinyl groups to aldehydes.[5] Moreover, various diastereoselective reductions of the carbonyl group in chiral α-unsubstituted-β-ketosulfoxides using DIBAL with or without a Lewis acid have been reported.[6] The asymmetric inductions, achieved in the presence of a Lewis acid, might originate from a conformationally rigid structure that involves a six-membered ring formed via chelation of the Lewis acid, such as $ZnCl_2$ or $Yb(OTf)_3$, with the sulfinyl oxygen atom and the carbonyl group. The reversal in diastereoselectivity upon the use of DIBAL alone can be rationalized by the dipole model.[7] However, treatment of α-monosubstituted-β-ketosulfoxides with DIBAL in the presence or absence of a Lewis acid gives somewhat decreased stereoselectivities and/or poor yields of the corresponding chiral alcohols.[8] For instance, α-unsaturated β-substituted ketosulfoxides (α-sulfinyl enones) do not undergo reduction with DIBAL. Therefore, the quest for an efficient general method for stereoselective asymmetric reduction of α-sulfinyl enones constitutes an important challenge. Recently, we have described a highly stereoselective reduction of α-sulfinyl enones using $NaBH_4$ with $YbCl_3$ in the methanol (a Luche reduction[9]) and an asymmetric sigmatropic rearrangement of α-sulfinyl enones under mild conditions (Figure 1).[10]

In the course of the above studies, we have demonstrated that the asymmetric Luche reduction can be induced at a remote position with respect to the chiral sulfoxide moiety. Notably, only a few examples of the remote controlled asymmetric reduction of ketosulfoxides are currently known. These include DIBAL reductions of ε-ketosulfoxide (1,6-asymmetric induction),[11] 3-(4-tolylsulfinyl)-2-thienyl ketone (1,4-asymmetric induction),[12] and 4-(4-tolylsulfinyl)-2-butanone and its derivatives (1,4-asymmetric induction).[13] More recently, García Ruano[14] described the 1,5-asymmetric induction of a sulfinyl ketone[14a] and a sulfinyl enone.[14b] However, in most cases, these substrates feature a cyclic moiety at the sulfoxide's α-position, so a rigid conformation of the ring formed upon binding of the ketone and the sulfoxide to the Lewis acid can be readily achieved. Herein, we report the first results concerning the stereoselective reduction of chain structural (*Z*)-β-sulfinyl enones (α,β-unsaturated-γ-ketosulfoxides) using a modified Luche reduction strategy to obtain enantiomerically pure (*Z*)-β-sulfinyl allylic alcohols and derivatives thereof.

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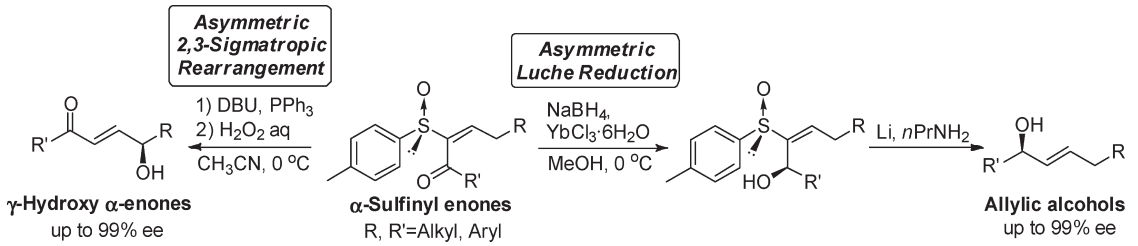
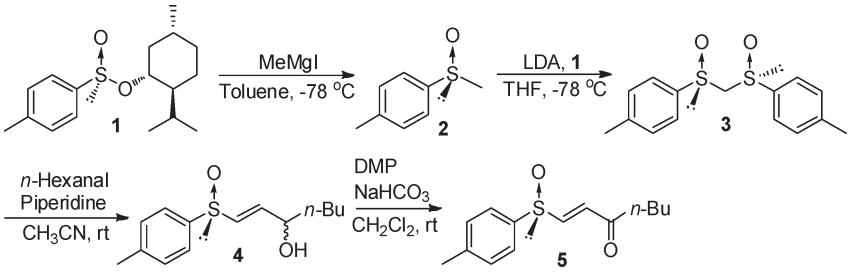
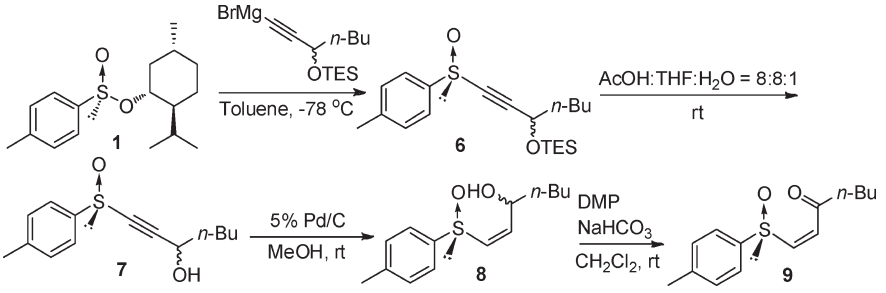


Figure 1. Asymmetric Luche reduction and asymmetric sigmatropic rearrangement of α-sulfinyl enones.

Scheme 1. Synthesis of Chiral (*E*)-*β*-Sulfinyl Enone from *l*-Menthyl Sulfinate



Scheme 2. Synthesis of Chiral (*Z*)-*β*-Sulfinyl Enone from *l*-Menthyl Sulfinate

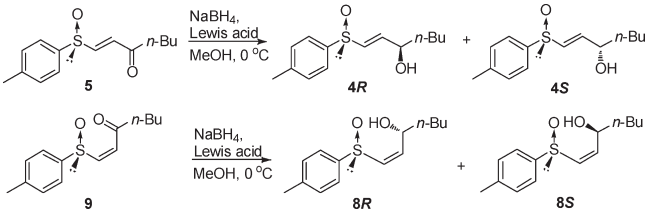


RESULTS AND DISCUSSION

Initially, we considered the influence of the geometrical structure, i.e., (*E*) vs (*Z*) form, of *β*-sulfinyl enone on the outcome of the asymmetric reduction. The synthesis of optically pure (*E*)-*β*-sulfinyl enone **5** to be used in trial asymmetric reduction reactions was accomplished by subjecting (*Rs*)-methyl-4-tolyl sulfoxide **2** to a conventional four-step transformation as summarized in Scheme 1.[15] On the other hand, optically pure (*Z*)-*β*-sulfinyl enone **9** was prepared according to Scheme 2. Treating 3-silyloxy-1-heptynylmagnesium bromide with *l*-menthyl (*Ss*)-4-tolylsulfinate at −78 °C afforded (*Ss*)-3-silyloxy-1-heptynyl sulfoxide **6** in a 90% yield.[16] Removal of the silyl group under acidic conditions gave an 87% yield of alkynyl **7**,[17] Pd/C reduction of which afforded (*Z*)sulfinyl allylic alcohol **8** in a 42% yield. Oxidation of alcohol **8** under mild conditions was accomplished by employing Dess−Martin periodinane (DMP) to give (*Z*)-*β*-sulfinyl enone **9** in a 90% yield.[18]

Table 1 summarizes the results of the reductions of **5** and **9** with $NaBH_4$ in the presence of Lewis acids $YbCl_3 \cdot 6H_2O$ (our previously reported method[10a]) or $LaCl_3 \cdot 7H_2O$. The reductions of (*E*)-*β*-sulfinyl enone **5** did not have good stereochemical outcomes, as 47:53 or 40:60 mixtures of epimers **4*R*** and **4*S*** were

Table 1. Influence of Asymmetric Reduction for Geometrical Isomer 5 and 9 Using $NaBH_4$ with Lewis acid



entry	substrate	Lewis acid	4*R*:4*S*	8*R*:8*S*	yield (%)
1	**5**	$YbCl_3$	47:53	–	99
2	**5**	$LaCl_3$	40:60	–	99
3	**9**	$YbCl_3$	–	0:100	96
4	**9**	$LaCl_3$	–	0:100	99

obtained by using $YbCl_3 \cdot 6H_2O$ (entry 1) or $LaCl_3 \cdot 7H_2O$ (entry 2), respectively, although both reactions afforded excellent product yields. In sharp contrast, the reductions of (*Z*)-*β*-sulfinyl enone **9** in the presence of either lanthanoid chloride hydrate proceeded with high stereoselectivities (entries 4 and 5: dr 100:0) and

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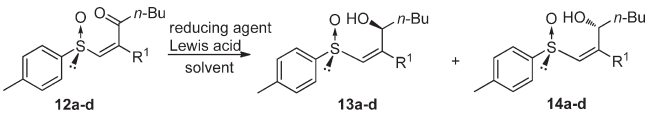
afforded the allylic alcohol product in excellent yields. The latter result may be rationalized by the fact that the (*Z*) form of *β*-sulfinyl enone features closer mutual proximity of the carbonyl and sulfoxide moieties compared to its (*E*) form, which facilitates chelation of the lanthanoid chloride via the oxygen atoms of the carbonyl and sulfoxide groups to form a conformationally rigid seven-membered metallacycle.[12]

Next, we explored the stereochemical outcome of the reduction of (*Z*)-*β*-sulfinyl enone **12a** and its analogues under various conditions (Table 2). Enones **12a**−**d** were easily prepared from **6a** in good yields by treating the latter with the appropriate organocuprate[19] followed by removal of the silyl ether and DMP oxidation steps (Scheme 3). The use of $LiBH_4$, $NaBH_4$, and KBH_4 to reduce (*Z*)-*β*-sulfinyl enone **12a** provided high yields of the allylic alcohol products, albeit with mediocre stereoselectivities (dr 24:76−21:79, entries 1−3).

Employing DIBAL as the reducing agent instead of the borohydrides resulted in inversion of the stereoselectivity (entry 5). Addition of $ZnCl_2$ or $CeCl_3$ to the above DIBAL reduction reaction did not improve the extent of its stereoselectivity outcome (entries 6 and 7). When the DIBAL/$YbCl_3$ reduction system was used, a higher but opposite stereoselectivity was observed in the formation of the allylic alcohols (entry 5 vs entry 8). Fortunately, when the reduction process was conducted in the presence of $Yb(OTf)_3$, a 3:97 diastereomeric ratio of epimers was obtained, which allowed isolating the diastereomerically pure **14a** by means of flash column chromatography in a 97% yield (entry 9).[14a] However, the reductions of bulkier enones **12b** and **12c** using the DIBAL/$Yb(OTf)_3$ system proceeded with a slightly decreased stereoselectivity (14:86) and afforded the corresponding allylic alcohols in only 31% and 41% yields, respectively (entries 10, 11). Interestingly, the best stereochemical results in the DIBAL reductions of (*Z*)-*β*-sulfinyl enones **12** were obtained by employing anhydrous $LaCl_3$ as a chelating additive. Indeed, these reduction reactions were almost completely stereoselective and provided high yields of the corresponding alcohols (entries 12−15). We also considered the previously discovered asymmetric reduction system $NaBH_4/LaCl_3$ in the conversion of *β*-sulfinyl enones **12a**−**c** to the corresponding allylic alcohols. The stereoselectivities of these reactions were essentially perfect (dr 100:0) and opposite to those of the related processes involving the DIBAL reductant. Notably, the allylic alcohols **13** were produced in nearly quantitative (99%) yields using the $NaBH_4/LaCl_3$ reduction system (entries 16−19).

Table 2. Reduction of (*Z*)-α-Methyl-*β*-Sulfinyl Enone 12



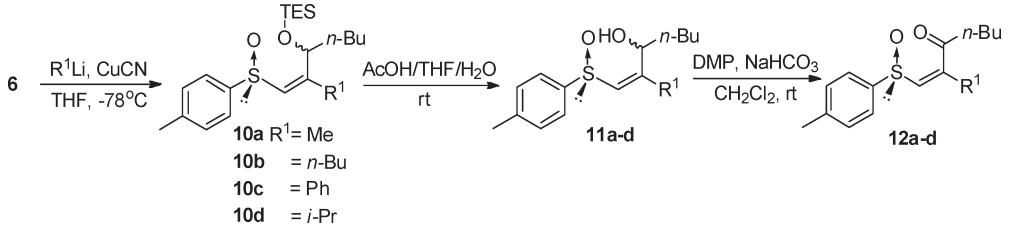
entry	substrate	solvent	reducing reagent	Lewis acid	**13:14**	yield (%)[c]
1	**12a**	MeOH	$LiBH_4$		24:76	75
2	**12a**	MeOH	$NaBH_4$		22:78	99
3	**12a**	MeOH	KBH_4		21:79	96
4	**12a**	MeOH	$NaBH(OMe)_3$		19:81	99
5	**12a**	THF	DIBAL		87:13	99
6	**12a**	THF	DIBAL	$ZnCl_2$	19:81	99
7[a]	**12a**	THF	DIBAL	$CeCl_3$	17:83	96
8[a]	**12a**	THF	DIBAL	$YbCl_3$	6:94	99
9	**12a**	THF	DIBAL	$Yb(OTf)_3$	3:97	99
10	**12b**	THF	DIBAL	$Yb(OTf)_3$	16:84	31
11	**12c**	THF	DIBAL	$Yb(OTf)_3$	16:84	41
12[b]	**12a**	THF	DIBAL	$LaCl_3$	0:100	88
13[b]	**12b**	THF	DIBAL	$LaCl_3$	6:94	95
14[b]	**12c**	THF	DIBAL	$LaCl_3$	3:97	89
15[b]	**12d**	THF	DIBAL	$LaCl_3$	0:100	99
16[a]	**12a**	MeOH	$NaBH_4$	$LaCl_3$	100:0	99
17[a]	**12b**	MeOH	$NaBH_4$	$LaCl_3$	100:0	99
18[a]	**12c**	MeOH	$NaBH_4$	$LaCl_3$	100:0	99
19[a]	**12d**	MeOH	$NaBH_4$	$LaCl_3$	100:0	99

[a] $LaCl_3 \cdot 7H_2O$ was used. [b] Anhydrous $LaCl_3$ was used. [c] Diastereomeric mixture yield.

The assignment of the absolute configuration for **13a** was facilitated by converting it into allylic alcohol **16a**, and the %ee value was determined for the 2-nitrobenzoate derivative **17a** using HPLC equipped with a chiral stationary phase column (Scheme 4). Specifically, oxidation of the chiral sulfoxide moiety in **13a** using magnesium monoperphthalate (MMPP) followed by removal of the sulfone from **15a** by treatment with sodium amalgam afforded optically pure allylic alcohol **16a** in an excellent yield. The allylic alcohol **16a** was then transformed into its 2-nitrobenzoate derivative **17a** to calculate the enantiomeric excess. Preparation of the required racemic allylic alcohol **16a** was easily accomplished by treating methacrolein with *n*-butyl magnesium iodide to give racemic **16a** in quantitative yield.

In order to assess the applicability of our findings to stereoselective reduction of variously substituted *β*-sulfinyl enones, we synthesized several *β*-sulfinyl enones starting from the optically active sulfinate **1**. The substitution reactions of *l*-menthyl sulfinate **1** with 1-alkynyl Grignard reagents gave 3-silyloxy-alkynyl sulfoxides **18a** (R^2 = Me), **18b** (R^2 = *i*-Pr), and **18c** (R^2 = Ph) as diastereoisomeric mixtures in good to moderate yields (**18a,** 74%; **18b**, 81%; **18c**, 38%). The silyloxy-alkynyl sulfoxides **18a**−**c** were treated with MeCuCNLi, and deprotection of **19a**−**c** under acidic conditions followed by oxidation of the resulting alcohols using DMP afforded enones **21a**−**c** in 72% (**21a**), 76% (**21b**), and 41% (**21c**) overall (three steps) yields as single enantiomers.

Scheme 3. Synthesis of α-Substituted (*Z*)-*β*-Sulfinyl Enone 12



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Scheme 4. Desulfurization and Determination of Absolute Configuration

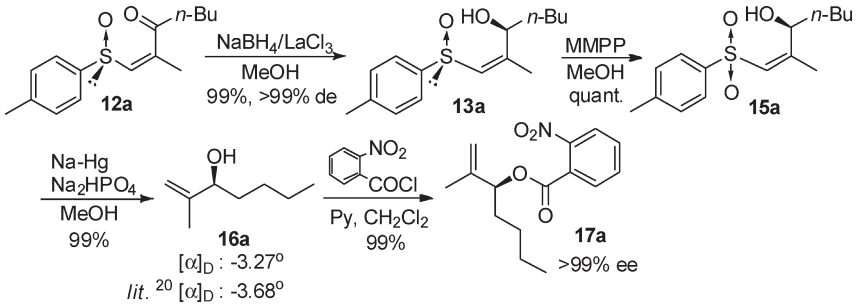
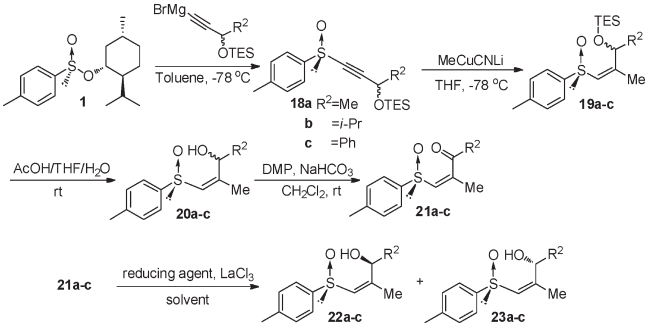


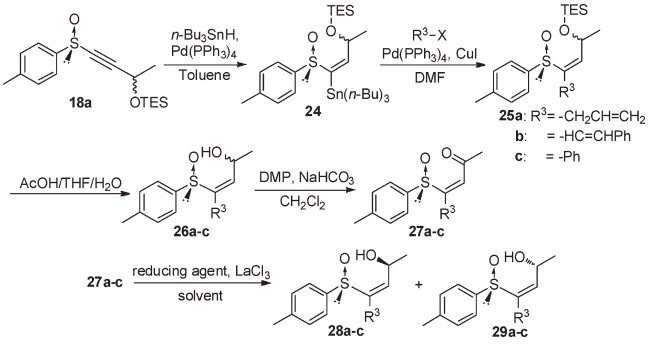
Table 3. Synthesis of (*Z*)-β-Sulfinyl Enones 21 and Asymmetric Reduction of 21



entry	substrate	reducing agent	solvent	**22:23**	yield (%)
1[a]	**21a**	$NaBH_4$	MeOH	100:0	99
2[a]	**21b**	$NaBH_4$	MeOH	100:0	99
3[a]	**21c**	$NaBH_4$	MeOH	100:0	99
4[b]	**21a**	DIBAL	THF	0:100	89
5[b]	**21b**	DIBAL	THF	2:98	95[c]
6[b]	**21c**	DIBAL	THF	14:86	91[c]

[a] $LaCl_3 \cdot 7H_2O$ was used. [b] Anhydrous $LaCl_3$ was used. [c] Diastereomeric mixture yield.

Table 4. Synthesis of (*Z*)-β-Sulfinyl Enones 27 and Asymmetric Reduction of 27



entry	substrate	reducing agent	solvent	**28:29**	yield (%)
1[a]	**27a**	$NaBH_4$	MeOH	100:0	95
2[a]	**27b**	$NaBH_4$	MeOH	100:0	69
3[a]	**27c**	$NaBH_4$	MeOH	99.5:0.5	97
4[b]	**27a**	DIBAL	THF	2:98	67[c]
5[b]	**27b**	DIBAL	THF	21:79	63[c]
6[b]	**27c**	DIBAL	THF	11:89	54[c]

[a] $LaCl_3 \cdot 7H_2O$ was used. [b] Anhydrous $LaCl_3$ was used. [c] Diastereomeric mixture yield.

The results of stereocontrolled reductions of **21a**−**c** are summarized in Table. 3. In all but one case, nearly exclusive formation of the desired chiral sulfinyl allylic alcohols was observed. However, reduction of compound **21c** with DIBAL proved to have somewhat decreased stereoselectivity (entry 6). This may be attributed to the influence of the phenyl substituent, which affects rigidity of the seven-membered metallacycle formed during the course of the reaction.

Finally, we synthesized (*Z*)-β-substituted-β-sulfinyl enones **27** and investigated the influence of the β-substituent on the stereocontrol of the reduction. The (*Z*)-β-substituted-β-sulfinyl enones **27** were easily synthesized by treating alkynyl sulfoxide **18a** with *n*-Bu_3SnH in the presence of a catalytic amount of $Pd(PPh_3)_4$ followed by the Stille coupling of the intermediate **24** to install the β-substituent.[21] The silyl ether was then removed as described above, and the resulting alcohols were oxidized using DMP to afford (*Z*)-β-substituted-β-sulfinyl enones **27** in good yields.

The results collected in Tables 3 and 4 indicate that the chiral sulfoxide moiety is effective in controlling the stereoselectivity of the reduction of β-sulfinyl enones under appropriate conditions. Prior to the reduction event, the La^{3+} ion likely undergoes chelation by β-sulfinyl enone molecules that coordinate via their sulfinyl and carbonyl oxygen atoms to form seven-membered metallacycles within the complex (Figure 2).[22] The metal ion coordination sphere should involve coordinated solvent molecules (methanol or THF) as well. It is well established that complexation of MeOH to a Ln^{3+} ion increases acidity of the coordinated alcohol's hydrogen atom, which in turn activates BH_4^- toward reduction by forming methoxyborohydride.[9c] Thus, the $NaBH_4$ reduction of the ketone moiety should occur from the direction opposite to the sulfoxide's lone pair (Figure 2, top). On the other hand, in THF medium the reduction attack should preferentially take place from the least sterically congested direction, especially if a relatively bulky reducing agent, such as DIBAL, is employed (Figure 2, bottom). Thus, the stereochemical outcomes of the reduction in MeOH and THF media would be mutually opposite as is indeed observed. The data in Table 3 (entry 6) and Table 4 (entries 5 and 6) are consistent with the phenyl substituent of the enone blocking significantly DIBAL's access to the carbonyl group.

In conclusion, we presented the first evidence of the efficiency of the sulfinyl group as a remote chiral inductor and $LaCl_3$ as a

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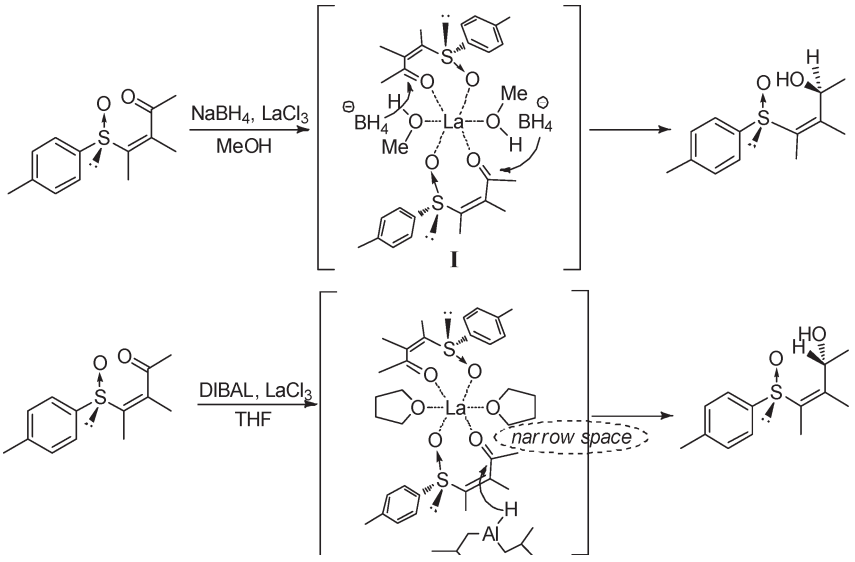

Figure 2. Proposed mechanism of stereocontrolled reduction of (Z)-β-sulfinyl enones.

chelating agent in the stereocontrolled reduction of the enones' carbonyl group. The choice of $NaBH_4$ or DIBAL as reducing agents in the presence of $LaCl_3$ dictates the stereochemical configuration of the allylic alcohol product. In this article, we proposed two mechanistic possibilities to rationalize the stereoselectivity outcomes of the reported reductions of enones: one is essentially a Luche-type reduction model while the other invokes formation of a sterically hindered complex. Removal of the sulfoxide moiety via its oxidation with MMPP followed by desulfurization of the resulting sulfone using Na−Hg constitutes a convenient route to optically pure allylic alcohols.

EXPERIMENTAL SECTION

Typical Procedure A for (*S*)-Stereoselective Reduction (*Z*)-β-Sulfinyl Enones with $NaBH_4$ Mediated by $LaCl_3 \cdot 7H_2O$. $LaCl_3 \cdot 7H_2O$ (2 equiv) was added to a solution of (*Z*)-β-sulfinyl enone (1 equiv) in methanol (9 mL/mmol) at room temperature, and the mixture was stirred for 10 min. $NaBH_4$ (2 equiv) was transferred to the above solution at 0 °C and the reaction mixture was stirred for 10 min. The mixture was then quenched with saturated aqueous NH_4Cl solution and extracted with EtOAc. The organic extract was washed sequentially with saturated aqueous NH_4Cl solution and brine. After being dried over anhydrous Na_2SO_4, the solution was concentrated under reduced pressure to give crude (*Z*)-(3*S*,*Rs*)-β-sulfinyl allylic alcohol. The diastereomeric ratio of the crude product was calculated from HPLC analysis. The crude product was purified by flash column chromatography on silica gel, (eluent: hexane/EtOAc) to give pure (*Z*)-(3*S*,*Rs*)-β-sulfinyl allylic alcohol in a good yield.

Typical Procedure B for (*R*)-Stereoselective Reduction of (*Z*)-β-Sulfinyl Enones with DIBAL Mediated by Anhydrous $LaCl_3$[23]. A mixture of (*Z*)-β-sulfinyl enone (1 equiv) and anhydrous $LaCl_3$ (2 equiv) in THF (14 mL/mmol of (*Z*)-β-sulfinyl enone) was stirred at room temperature for 1 h. Diisobutylalminum hydride (2 equiv) was then added dropwise to the above solution at −78 °C, and the resulting mixture was stirred for 2 h. The reaction mixture was quenched with MeOH and extracted with ether. The organic extract was washed sequentially with saturated aqueous Na_2CO_3 and brine. After being dried over anhydrous Na_2SO_4, the solution was concentrated under reduced pressure to give crude (*Z*)-(3*R*,*Rs*)-β-sulfinyl allylic alcohol. The diastereomeric ratio of the crude product was calculated from HPLC analysis. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc) to give pure (*Z*)-(3*R*,*Rs*)-β-sulfinyl allylic alcohol in a good yield.

*(E)-(3RS,Rs)-1-(4-Tolylsulfinyl)-1-hepten-3-ol (**4**).* An excess amount of piperidine (1.0 mL, 5.1 mmol) and *n*-hexanal (0.66 mL, 10.3 mmol) were added to a solution of (*Ss*,*Ss*)-bis-4-tolylsulfinyl methane **3** (0.5 g, 1.7 mmol) in acetonitrile (7 mL) at room temperature. After being stirred for 21 h, the reaction mixture was quenched with saturated aqueous NH_4Cl solution and the product was extracted with CH_2Cl_2. The extract was washed with brine and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure. The resulting residue was subjected to flush chromatography on silica gel (eluent: hexane/EtOAc = 1:1) to afford diastereomeric mixture of (*E*)-(3*RS*,*Rs*)-1-(4-tolylsulfinyl)-1-hepten-3-ol **4** (0.426 g, 1.69 mmol) in a 99% yield as a viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.49 (d, 4H, J = 7.9 Hz), 7.30 (d, 4H, J = 7.9 Hz), 6.60 (dd, 2H, J = 14.9, 4.4 Hz), 6.44 (dd, 2H, J = 14.9, 1.7 Hz), 4.33 (s, 2H), 2.40 (s, 6H), 2.21−2.16 (m, 2H), 1.63−1.54 (m, 3H), 1.42−1.29 (m, 8H), 0.89 (t, 6H, J = 7.2 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 141.7, 141.6, 141.1, 141.0, 140.4, 134.1, 134.0, 130.1, 124.8, 124.7, 71.0, 36.5, 27.3, 22.5, 21.4, 13.9. IR (neat): 3387, 2954, 2923, 2863, 1457, 1081, 1030, 808 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{14}H_{21}O_2S$ [M + H]$^+$: 253.12622; found: 253.12629. LRMS (FAB$^+$): 253(100), 166(18)

*(E)-(Rs)-1-(4-Tolylsulfinyl)-1-hepten-3-one (**5**).* Dess−Martin periodinane (1.1 g, 2.6 mmol) and $NaHCO_3$ (0.68 g, 8.1 mmol) were added to a solution of (*E*)-sulfinyl allylic alcohol **4** (0.41 g, 1.62 mmol) in CH_2Cl_2 at room temperature. After being stirred for 0.5 h, the reaction mixture was quenched with H_2O and the product was extracted with CH_2Cl_2. The extract was washed with brine and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure. The residue was subjected to flash chromatography on silica gel (eluent: hexane/EtOAc = 3:1) afford (*E*)-(*Rs*)-1-(4-tolylsulfinyl)-1-hepten-3-one **5** (0.39 g, 1.57 mmol) as a viscous oil. $[\alpha]_D$ = +453° (c = 0.81, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.59 (d, 2H, J = 7.9 Hz), 7.34 (d, 2H, J = 7.9 Hz), 7.33 (d, 1H, J = 14.8 Hz), 7.00 (d, 1H, J = 14.8 Hz), 0.91 (t, 3H, J = 7.5 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 197.5, 148.6, 142.6, 138.2, 130.5, 129.4, 125.0, 42.5, 25.7, 22.2, 21.4, 13.8 ppm. IR (neat): 2863, 1689, 1592, 1455, 1051, 973, 804 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{14}H_{19}O_2S$ [M + H]$^+$: 251.11057; found: 251.11050. LRMS (FAB$^+$): 251(100), 235(5)

*(3RS,Ss)-1-(4-Tolylsulfinyl)-3-(triethylsilyloxy)-1-heptyne (**6**).* An excess amount of 3-(triethylsilyloxy)-1-heptyne (5.35 g, 23.6 mmol) was

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added dropwise to a 3.8 M solution of EtMgBr in Et_2O solution (15.8 mmol, 4.16 mL) at room temperature under argon. After being stirred for 1 h, the mixture was cooled to −78 °C. Then, *l*-menthyl (−)-(*S*)-4-toluenesulfinate (2.32 g, 7.91 mmol) dissolved in 41 mL of toluene was added to the reaction mixture dropwise, and the resulting solution was stirred −78 °C for a period of 1 h. The reaction mixture was then warmed to 0 °C and stirred for an additional 15 min before being quenched with saturated aqueous NH_4Cl solution. The quenched reaction mixture was extracted with EtOAc, and the organic extracts were combined, washed with brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc/CH_2Cl_2, 20:1:1) to afford a diastereomeric mixture of (3*RS*,*Ss*)-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-heptyne **6** (2.59 g, 7.12 mmol) in a 90% yield as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.67 (d, 4H, J = 8.2 Hz), 7.33 (d, 4H, J = 8.2 Hz), 4.48 (t, 2H, J = 6.6 Hz), 2.42 (s, 6H), 1.72−1.66 (m, 4H), 1.39−1.27 (m, 8H), 0.95−0.85 (m, 24H), 0.56 (quin, 12H, J = 7.3 Hz) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$), δ: 142.3, 140.8, 130.1, 125.1, 104.7, 104.5, 82.0, 63.0, 62.9, 37.5, 27.1, 22.3, 22.2, 21.4, 13.9, 6.6, 4.6 ppm. IR (neat): 2954, 2875, 2175, 1462, 1414, 1340, 1240, 1090, 1063, 1012, 810, 746 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{20}H_{33}O_2SiS$ [M + H]$^+$: 365.19705; found: 365.19701. LRMS (FAB$^+$): 365, 335, 291, 233, 201, 115.

*(3RS,Ss)-1-(4-Tolylsulfinyl)-1-heptyn-3-ol (**7**).* (*Z*)-(3*RS*,*Rs*)-1-(4-Tolylsulfinyl)-3-(triethylsilyloxy)-1-heptyne **6** (0.47 g, q.29 mmol) was transferred to a reaction flask containing a 17 mL 8:8:1 mixture of AcOH, THF, and H_2O at room temperature, and the resulting solution was stirred for 10 h. The cooled solution was then diluted with H_2O and quenched with solid $NaHCO_3$. The product was extracted with EtOAc, and the combined organic extracts were washed with brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: hexane/EtOAc = 3:1) to give a diastereomeric mixture of (*Z*)-(3*RS*,*Rs*)-1-(4-tolylsulfinyl)-1-heptyn-3-ol 7 (0.28 g, 1.12 mmol) in 87% yield as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.70 (d, 4H, J = 8.2 Hz), 7.66 (d, 4H, J = 8.2 Hz), 4.53 (t, 2H, J = 6.6 Hz), 2.44 (s, 6H), 2.13 (d, 1H, J = 5.9 Hz), 2.12 (d, 1H, J = 5.9 Hz), 1.80−1.69 (m, 4H), 1.45−1.30 (m, 8H),0.90 (t, 3H, J = 7.2 Hz), 0.88 (t, 3H, J = 7.2 Hz) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$), δ: 142.6, 140.5, 130.2, 125.2, 103.8, 104.5, 82.6, 82.5, 62.6, 36.5, 27.1, 22.2, 21.5, 13.8 ppm.

*(Z)-(3R,Rs)-1-(4-Tolylsulfinyl)-1-hepten-3-ol (**8R**).* A suspension of (*Z*)-(3*RS*,*Rs*)-1-(4-tolylsulfinyl)-1-heptyn-3-ol **7a** (0.05 g, 0.19 mmol) and 5% Pd/C (0.15 g) in MeOH was stirred for 24 h under hydrogen at room temperature. The resulting suspension was filtered through the Celite column, and then the filtrate was condensed under reduced pressure. The residue was purified with flash chromatography (hexane/EtOAc = 3:1) gave a solitary product of **8*R*** (21.2 mg, 0.084 mmol) in 42% yield as a yellow liquid. $[\alpha]_D$ = −185° (*c* = 0.82, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.57 (d, 2H, J = 8.3 Hz), 7.31 (d, 2H, J = 8.3 Hz), 6.20 (d, 1H, J = 10.5 Hz), 6.13 (dd, 1H, J = 10.5, 7.5 Hz), 4.89−4.85 (m, 1H), 2.51 (bs, 1H), 2.41 (s, 3H), 1.72−1.60 (m, 3H), 1.50−1.34 (m, 4H), 0.93 (t, 3H, J = 7.1 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 142.3, 141.5, 140.8, 137.2, 130.1, 124.6, 68.9, 37.2, 27.4, 22.6, 21.4, 14.0 ppm. IR (neat): 3368, 2928, 1652, 1595, 1078, 810, 758 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{14}H_{21}O_2S$ [M + H]$^+$: 253.12622; found: 253.12617. LRMS (FAB$^+$): 253 (100), 235 (50), 187 (35).

*(Z)-(3S,Rs)-1-(4-Tolylsulfinyl)-1-hepten-3-ol (**8S**).* Procedure A. **9** (0.030 g, 0.120 mmol), $LaCl_3 \cdot 7H_2O$ (0.090 g, 0.241 mmol), $NaBH_4$ (0.008 mg, 0.197 mmol), MeOH (1.5 mL). Purification by means of column chromatography on silica gel (eluent: CH_2Cl_2/EtOAc = 1:1) afforded **8a** (30.5 mg, 0.114 mmol) in a 100% isolated yield (dr 100:0) as a colorless oil. $[\alpha]_D$ = −69° (*c* = 0.92, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.56 (d, 2H, J = 8.0 Hz), 7.28 (d, 2H, J = 8.0 Hz), 6.17 (d, 1H, J = 10.2 Hz), 6.12 (dd, 1H, J = 10.2, 7.1 Hz), 4.89 (q, 1H, J = 7.1 Hz), 3.10 (s, 1H), 2.31 (s, 3H), 1.68−1.59 (m, 2H), 1.47−1.34 (m, 4H), 0.91 (t, 3H, J = 7.3 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 142.8, 141.2, 140.6, 136.5, 129.9, 124.4, 68.6, 36.9, 27.2, 22.4, 21.2, 13.9 ppm. IR (KBr): 3346, 3035, 2953, 1651, 1060, 810, 698 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{14}H_{21}O_2S$ [M + H]$^+$: 253.12622; found: 253.12621. LRMS (FAB$^+$): 253 (72), 57 (25).

*(Z)-(Rs)-1-(4-Tolylsulfinyl)-1-hepten-3-one (**9**).* The enantiomerically pure **8b** (0.046 g, 0.18 mmol) was treated with a 15% DMP solution in CH_2Cl_2 (0.28 mmol, ca. 0.82 mL) and $NaHCO_3$ (0.076 g, 0.91 mmol) in 4.5 mL of CH_2Cl_2 at room temperature. The reaction mixture was extracted with CH_2Cl_2. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography (eluent: hexane/EtOAc = 1:1) to afford optically pure (*Z*)-(*Rs*)-1-(4-tolylsulfinyl)-1-hepten-3-one **9** (0.040 g, 0.16 mmol) in a 89% yield as a pale yellow oil. $[\alpha]_D$ = −597.0° (*c* = 1.44, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.78 (d, 2H, J = 7.8 Hz), 7.29 (d, 2H, J = 7.8 Hz), 6.70 (d, 1H, J = 10.0 Hz), 6.58 (d, 1H, J = 10.0 Hz), 2.65 (dt, 1H, J = 17.0, 7.4 Hz), 2.54 (dt, 1H, J = 17.0 Hz), 2.39 (s, 3H), 1.66−1.59 (m, 2H), 1.35 (sext, 2H, J = 7.4 Hz), 0.92 (t, 3H, J = 7.4 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 199.9, 154.3, 141.6, 141.1, 129.9, 129.3, 125.2, 42.7, 25.7, 22.1, 21.4, 13.7 ppm. IR (neat): 3019, 2957, 1688, 1585, 1458, 1074, 811, 723 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{14}H_{19}O_2S$ [M + H]$^+$: 251.11057; found: 251.11084. LRMS (FAB$^+$) 251 (100), 203 (18). $C_{22}H_{29}O_2SiS$ [M + H]$^+$: 385.16575; found: 385.16569. LRMS (FAB$^+$): 385, 355, 271, 253.

*(Z)-(3RS,Rs)-2-Methyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-heptene (**10a**).* A 1.50 M solution of MeLi in Et_2O (0.825 mmol, 0.55 mL) was added dropwise to a suspension of CuCN (0.075 g, 0.840 mmol) in 5 mL of THF (5 mL) at −78 °C under argon atmosphere, and the resulting solution was stirred for 1 h. Then, a solution of alkynyl sulfoxide **6** (0.100 g, 0.274 mmol) in 1.5 mL of THF was added to the above mixture dropwise via syringe to afford a yellow solution that was stirred at −78 °C for 1 h. The reaction was quenched with saturated aqueous NH_4Cl, and the product was extracted with EtOAc. The extracts were washed with saturated brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: hexane/EtOAc = 4:1) to give both diastereomers (**10a**-(3*S*): **10a**-(3*R*) = 1:1) in good yield.

(*Z*)-(3*S*,*Rs*)-2-Methyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-heptene **10a**-(3*S*) (0.051 g, 0.135 mmol), 47% isolated yield. $[\alpha]_D$: −196° (*c* = 0.99, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.49 (d, 2H, J = 8.0 Hz), 7.29 (d, 2H, J = 8.0 Hz), 6.00 (d, 1H, J = 1.4 Hz), 5.08 (dd, 1H, J = 7.9, 5.0 Hz), 2.40 (s, 3H), 1.85 (d, 3H, J = 1.4 Hz), 1.60−1.67 (m, 1H), 1.29−1.40 (m, 4H), 1.15−1.20 (m, 1H), 0.98 (t, 9H, J = 8.0 Hz), 0.89 (t, 3H, J = 7.3 Hz), 0.68 (q, 6H, J = 8.0 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 153.1, 141.6, 141.1, 131.7, 129.9, 124.3, 70.5, 36.2, 30.8, 28.0, 22.5, 21.2, 17.4, 13.9, 6.7, 4.7 ppm. IR (neat): 2951, 1618, 1078, 1045, 801 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{21}H_{37}O_2SiS$ [M + H]$^+$: 381.22835; found: 381.22860. LRMS (FAB$^+$): 381 (62), 249 (94), 115 (53).

(3*R*,*Rs*)-2-Methyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-heptene **10a**-(3*R*) (0.051 g, 0.135 mmol), 49% isolated yield: $[\alpha]_D$ = −81° (*c* = 0.96 acetone). ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.52 (d, 2H, J = 7.7 Hz), 7.31 (d, 2H, J = 7.7 Hz), 6.03 (d, 1H, J = 0.9 Hz), 5.12 (t, 1H, J = 7.1 Hz), 2.41 (s, 3H), 1.86 (d, 3H, J = 1.4 Hz), 1.60−1.72 (m, 2H), 1.37 (q, 2H, J = 7.4 Hz), 1.29−1.48 (m, 2H), 0.95 (t, 9H, J = 7.4 Hz), 0.92 (t, 3H, J = 7.4 Hz), 0.62 (q, 6H, J = 1.4, 8.0 Hz) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$), δ:155.3, 142.0, 141.0, 131.4, 129.8, 124.1, 71.1, 36.4, 27.6, 22.6, 21.3, 17.8, 13.9, 6.7, 4.8 ppm. IR (KBr): 2954, 1616, 1081, 1042, 834 cm^{-1}. HRMS (FAB$^+$) Calcd $C_{21}H_{37}O_2SiS$ [M + H]$^+$: 381.22835; found: 381.22812. LRMS (FAB$^+$): 381 (68), 249 (100), 115 (50).

*(Z)-(3RS,Rs)-2-Butyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-heptene (**10b**).* A 1.55 M solution of *n*-BuLi in hexane (6.15 mmol, 3.97 mL)

was added dropwise via syringe to a suspension of CuCN (0.550 g, 6.14 mmol) in 41 mL of THF at −78 °C under argon atmosphere, and the resulting solution was stirred for 1.5 h. Then, a solution of alkynyl sulfoxide **6** (0.746 g, 2.05 mmol) in 10 mL of THF was added to the above mixture dropwise via syringe to afford a yellow solution that was stirred at −78 °C for 2.5 h. The reaction was quenched with saturated aqueous NH_4Cl, and the product was extracted with EtOAc. The extracts were washed with saturated brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: hexane/EtOAc = 4:1) to give pure (*Z*)-(3*RS*,*Rs*)-2-butyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-heptene **10b** (0.649 g, 1.54 mmol) in a 75% diastereomeric mixture yield (3*R*:3*S* = 1:1) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.51 (d, 2H, J = 8.6 Hz), 7.49 (d, 2H, J = 8.6 Hz), 7.31 (d, 2H, J = 8.6 Hz), 7.29−7.30 (d, 2H, J = 8.9 Hz), 6.01 (s, 1H), 5.98 (s, 1H), 5.12 (t, 1H, J = 6.6 Hz), 5.09 (dd, 1H, J = 5.2, 8.0 Hz), 2.41 (s, 3H), 2.40 (s, 3H), 2.25−2.37 (m, 2H), 2.08−2.19 (m, 2H), 1.61−1.68 (m, 4H), 1.25−1.46 (m, 16H), 0.85−0.99 (m, 30H), 0.64 (q, 12H, J = 8.0 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 159.2, 157,3, 142.4, 141.9, 141.1, 141.0, 130.8, 130.6, 129.98, 129.92, 124.6, 124.4, 71.7, 71.2, 37.0, 36.8, 29.9, 29.8, 29.5, 29.3, 28.3, 27.8, 22.69, 22.63, 22.60, 21.4, 14.01, 13.98, 13.89, 13.87, 6.9, 4.9, 4.8 ppm. IR (neat): 2956, 2875, 1462, 1240, 1082, 1043, 808, 748 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{24}H_{43}O_2SiS$ [M + H]$^+$: 423.27530; found: 423.27508. LRMS (FAB$^+$): 423 (69), 405 (77), 393 (47), 349 (37), 291 (100), 123 (34), 115 (78).

*(Z)-(3RS,Rs)-2-Phenyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-heptene (**10c**).* A 1.15 M solution of PhLi in cyclohexane-Et_2O (2.46 mmol, 2.14 mL) was added dropwise via syringe to a suspension of CuCN (0.220 g, 2.46 mmol) in 16 mL of THF at −78 °C under argon atmosphere, and the resulting solution was stirred for 1 h. Then, a solution of alkynyl sulfoxide **6** (0.300 g, 0.823 mmol) in 4 mL of THF was added dropwise via syringe to afford a yellow solution that was stirred at −78 °C for 1 h. The reaction was quenched with saturated aqueous NH_4Cl, and the product was extracted with EtOAc. The extracts were washed with saturated brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: hexane/EtOAc = 4:1) to give pure (*Z*)-(3*RS*,*Rs*)-2-phenyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-heptene **10c** (0.244 g, 0.552 mmol) in a 67% diastereomeric mixture yield (3*R*:3*S* = 1:1) as a yellow oil.^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.60 (m, 4H), 7.46 (m, 4H), 7.26−7.33 (m, 10H), 6.35 (s, 1H), 6.34 (s, 1H), 5.26−5.29 (m, 1H), 5.26 (t, 1H, J = 6.5 Hz), 2.41 (s, 3H), 2.40 (s, 3H), 1.48−1.61 (m, 4H), 1.18−1.38 (m, 8H), 1.00 (t, 9H, J = 8.0 Hz), 0.97 (t, 9H, J = 8.0 Hz), 0.81−0.85 (m, 6H), 0.67−0.73 (m, 12H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 154.6, 153.5, 142.2. 141.7, 141.4, 141.2, 137.8, 137.4, 135.5, 134.9, 130.1, 129.9, 129.4, 128.79, 128.35, 128.23, 128.15, 128.09, 124.77, 124.67, 115.5, 72.8, 72.0, 37.3, 37.1, 28.1, 27.6, 22.5, 21.4, 13.96, 13.91, 7.0, 6.9, 5.1, 4.9 ppm. IR (neat): 2954, 2875, 1597, 1493, 1460, 1414, 1240, 1083, 1043, 808, 748, 698 cm^{-1}. HRMS (FAB) Calcd for $C_{26}H_{39}O_2SiS$ [M + H]$^+$: 443.24400; found: 443.24404. LRMS (FAB): 443 (63), 425 (65), 369 (28), 311 (100), 123 (22), 115 (70).

*(Z)-(3RS,Rs)-2-(1-Methylethyl)-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-heptene (**10d**).* A 0.7 M solution of *i*-PrLi in pentane (4.10 mmol, 5.85 mL) was added dropwise via syringe to a suspension of CuCN (0.367 g, 4.10 mmol) in 27 mL of THF at −78 °C under argon atmosphere, and the resulting solution was stirred for 1 h. Then a solution of alkynyl sulfoxide **6** (0.500 g, 1.37 mmol) in 8 mL of THF was added dropwise via syringe to afford a yellow solution that was stirred at −78 °C for 2.5 h. The reaction was quenched with saturated aqueous NH_4Cl, and the product was extracted with EtOAc. The extracts were washed with saturated brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: hexane/EtOAc = 4:1) to give pure (*Z*)-(3*RS*,*Rs*)-2-(1-methylethyl)-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-heptene **10d** (0.433 g, 1.06 mmol) in a 78% diastereomeric mixture yield (3*R*:3*S* = 1:1) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.48−7.51 (m, 4H), 7.29−7.32 (m, 4H), 6.06 (s, 1H), 6.05 (s, 1H), 5.10 (t, 1H, J = 6.9 Hz), 5.07 (t, 1H, J = 7.2 Hz), 2.69−2.77 (m, 2H), 2.41 (s, 3H), 2.40 (s, 3H), 1.62−1.72 (m, 4H), 1.25−1.46 (m, 8H), 1.13 (d, 3H, J = 6.87 Hz), 1.08 (d, 3H, J = 6.87 Hz), 1.02 (d, 3H, J = 6.53 Hz), 0.96−1.00 (m, 21H), 0.92 (t, 3H, J = 7.22 Hz), 0.88 (t, 3H, J = 7.22 Hz), 0.62−0.69 (m, 12H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$), δ: 164.8, 163.2, 142.5, 141.9, 141.0, 140.8, 130.59, 130.50, 129.94, 129.89, 124.7, 124.4, 72.3, 71.7, 37.0, 36.9, 28.47, 28.36, 28.1, 27.9, 24.0, 23.9, 23.5, 23.4, 22.72, 22.68, 21.3, 14.00, 13.95, 6.9, 5.0, 4.9 ppm. IR (neat): 2958, 2875, 1462, 1240, 1082, 1043, 808, 742 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{23}H_{41}O_2SiS$ [M + H]$^+$: 409.25965;found: 409.25892. LRMS (FAB$^+$): 409 (50), 391 (50), 379 (35), 335 (24), 277 (100), 115 (38).

*(Z)-(Rs)-2-Methyl-1-(4-tolylsulfinyl)-1-hepten-3-one (**12a**).* (*Z*)-(3*RS*,*Rs*)-2-methyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-heptene **10a** (1.14 g, 3.0 mmol) was transferred to a reaction flask containing a 40 mL 6:1:3 mixture of AcOH, THF, and H_2O at room temperature, and the resulting solution was stirred for 45 min. The cooled solution was then diluted with H_2O and quenched with solid $NaHCO_3$ solid. The product was extracted with EtOAc, and the combined organic extracts were washed with brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: hexane/EtOAc = 1:2) to give a diastereomeric mixture of (*Z*)-(3*RS*,*Rs*)-2-methyl-1-(4-tolylsulfinyl)-1-hepten-3-ol **11a** (0.795 g, 3.0 mmol) in quantitative yield. Compound **11a** (0.795 g, 3.0 mmol) was treated with a 15% DMP solution in CH_2Cl_2 solution (4.78 mmol, ca. 13.7 mL) and $NaHCO_3$ (1.33 g, 15.9 mmol) in 80 mL of CH_2Cl_2 at room temperature. The reaction mixture was then extracted with CH_2Cl_2. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography (eluent: hexane/EtOAc = 1:2) to afford optically pure (*Z*)-(*Rs*)-2-methyl-1-(4-tolylsulfinyl)-1-hepten-3-one **12a** (0.732 g, 2.77 mmol) in a 92% yield as a pale yellow oil. $[\alpha]_D$ = −453° (c = 1.10, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.74 (d, 2H, J = 8.0 Hz), 7.29 (d, 2H, J = 8.0 Hz), 6.30 (dd, 1H, J = 0.9, 1.4 Hz), 2.59−2.72 (m, 2H), 2.39 (s, 3H), 2.08 (d, 3H, J = 1.4 Hz), 1.65 (quin, 2H, J = 7.5 Hz), 1.37 (sext, 2H, J = 7.5 Hz), 0.94 (t, 3H, J = 7.5 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 202.3, 144.7, 141.19, 141.14, 129.8, 124.9, 40.2, 25.3, 22.1, 21.3, 19.4, 13.8 ppm. IR (neat): 2934, 1687, 1593, 1462, 1072, 817 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{15}H_{21}O_2S$ [M + H]$^+$: 265.12622; found: 265.12619. LRMS (FAB$^+$): 265 (100), 221 (9), 191 (7).

*(Z)-(Rs)-2-Butyl-1-(4-tolylsulfinyl)-1-hepten-3-one (**12b**).* (*Z*)-(3*RS*,*Rs*)-2-Butyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-heptene **10b** (0.561 g, 1.33 mmol) was transferred to a reaction flask containing a 20 mL 6:1:3 mixture of AcOH, THF, and H_2O at room temperature, and the resulting solution was stirred at for 1.5 h. The cooled solution was diluted with H_2O and quenched with solid $NaHCO_3$. The product was extracted with EtOAc, and the combined extracts were washed with brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: CH_2Cl_2/EtOAc = 1:1) to give a diastereomeric mixture of (*Z*)-(3*RS*,*Rs*)-2-butyl-1-(4-tolylsulfinyl)-1-hepten-3-ol **11b** (0.410 g, 1.33 mmol) in quantitative yield. The diastereomeric mixture **11b** (0.410 g, 1.33 mmol) was treated with a 15% DMP solution in CH_2Cl_2 (2.13 mmol, ca. 6.2 mL) and $NaHCO_3$ (0.591 g, 7.10 mmol) in 40 mL of CH_2Cl_2 at room temperature. The reaction mixture was extracted with CH_2Cl_2. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography (eluent: hexane/EtOAc = 1:1) to afford optically pure (*Z*)-(*Rs*)-2-butyl-1-(4-tolylsulfinyl)-1-hepten-3-one **12b** (0.408 g, 1.33 mmol) in quantitative yield as a yellow liquid. $[\alpha]_D$ = −313.2° (c = 1.70, acetone). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.74 (d, 2H, J = 8.0 Hz), 7.29 (d, 2H, J = 8.0 Hz), 6.30 (dd, 1H, J = 0.9, 1.4 Hz), 2.59−2.72 (m, 2H), 2.39 (s, 3H), 2.08 (d, 3H, J = 1.4 Hz), 1.65 (quin, 2H, J = 7.5 Hz), 1.37 (sext, 2H, J = 7.5 Hz), 0.94 (t, 3H,J = 7.5 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$),

δ: 203.5, 149.0, 141.0, 140.9, 129.8, 124.7, 40.7, 32.7, 29.5, 25.4, 22.2, 22.1, 21.3, 13.8, 13.6 ppm. IR (neat): 2956, 1689, 1591, 1460, 1077, 811 cm^{-1}. HRMS (FAB^+) Calcd for $C_{18}H_{27}O_2S$ $[M + H]^+$: 307.17316; found: 307.17311. LRMS (FAB^+): 307 (100), 249 (16), 123 (14).

*(Z)-(Rs)-2-Phenyl-1-(4-tolylsulfinyl)-1-hepten-3-one (**12c**).* (Z)-(3*RS*,*Rs*)-2-Phenyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-heptene **10c** (0.291 g, 0.658 mmol) was transferred to a reaction flask containing an 8 mL 6:1:3 mixture of AcOH, THF, and H_2O at room temperature, and the resulting solution was stirred for 2 h. The cooled reaction mixture was diluted with H_2O and quenched with solid $NaHCO_3$. The product was extracted with EtOAc, and the combined extracts were washed with brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: hexane/EtOAc = 1:2) to give a diastereomeric mixture of (Z)-(3*RS*,*Rs*)-2-phenyl-1-(4-tolylsulfinyl)-1-hepten-3-ol **11c** (0.215 g, 0.656 mmol) in a 99% yield. The diastereomeric mixture **11c** (0.215 g, 0.656 mmol) was treated with a 15% DMP solution in CH_2Cl_2 (0.99 mmol, ca. 2.9 mL) and $NaHCO_3$ (0.274 g, 3.29 mmol) in 18 mL of CH_2Cl_2 at room temperature. The reaction mixture was extracted with CH_2Cl_2. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography (eluent: hexane/EtOAc = 1:2) to afford optically pure (Z)-(*Rs*)-2-phenyl-1-(4-tolylsulfinyl)-1-hepten-3-one **12c** (0.184 g, 0.565 mmol) in an 86% yield as a pale yellow solid. Mp: 43.5 °C $[\alpha]_D = -174.3°$ (*c* = 1.10, acetone). ^1H NMR (500 MHz, $CDCl_3$), δ: 7.74 (d, 2H, *J* = 8.3 Hz), 7.37−7.40 (m, 3H), 7.29−7.32 (m, 4H), 6.55 (s, 1H), 2.67 (t, 2H, *J* = 7.5 Hz), 2.39 (s, 3H), 1.64−1.69 (m, 2H), 1.30−1.37 (m, 2H), 0.89 (t, 3H, *J* = 7.44 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 203.7, 148.9, 141.4, 140.4, 139.4, 133.7, 130.0, 129.9, 129.1, 127.4, 124.9, 42.5, 25.7, 22.1, 21.4, 13.8 ppm. IR (neat): 2957, 2870, 1698, 1592, 1492, 1449, 1125, 1043, 810, 756, 697 cm^{-1}. HRMS (FAB^+) Calcd for $C_{20}H_{23}O_2S$ $[M + H]^+$: 327.14186; found: 327.14218. LRMS (FAB^+): 327 (98), 107 (13).

*(Z)-(Rs)-2-(1-Methylethyl)-1-(4-tolylsulfinyl)-1-hepten-3-one (**12d**).* (Z)-(3*RS*,*Rs*)-2-(1-Methylethyl)-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-heptene **10d** (0.232 g, 0.568 mmol) was transferred to a reaction flask containing an 8 mL 6:1:3 mixture of AcOH, THF, and H_2O at room temperature, and the resulting solution was stirred for 1 h. The reaction mixture was then diluted with H_2O and quenched with solid $NaHCO_3$. The product was extracted with EtOAc, and the combined extracts were washed with brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: hexane/EtOAc = 1:2) to give a diastereomeric mixture of (Z)-(3*RS*,*Rs*)- 2-(1-methylethyl)-1-(4-tolylsulfinyl)-1-hepten-3-ol **11d** (0.154 g, 0.524 mmol) in a 92% yield. The diastereomeric mixture **11d** (0.154 g, 0.524 mmol) was treated with a 15% DMP solution in CH_2Cl_2 (0.79 mmol, ca. 2.3 mL) and $NaHCO_3$ (0.220 g, 2.63 mmol)) in 15 mL of CH_2Cl_2 at room temperature. The reaction mixture was extracted with CH_2Cl_2. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography (eluent: hexane/EtOAc = 1:2) to afford optically pure (Z)-(*Rs*)-2-(1-methylethyl)-1-(4-tolylsulfinyl)-1-hepten-3-one **12d** (0.141 g, 0.483 mmol) in a 92% yield as a pale yellow oil. $[\alpha]_D = -275.0°$ (*c* = 1.30, acetone). ^1H NMR (500 MHz, $CDCl_3$), δ: 7.63 (d, 2H, *J* = 8.3 Hz), 7.29 (d, 2H, *J* = 8.1 Hz), 6.14 (d, 1H, *J* = 1.1 Hz), 2.66−2.82 (m, 3H), 2.40 (s, 3H), 1.65−1.71 (m, 2H), 1.41 (sext, 2H, *J* = 7.45 Hz), 1.14 (d, 3H, *J* = 6.59 Hz), 1.02 (d, 3H, *J* = 6.87 Hz), 0.95 (t, 3H, *J* = 7.45 Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ: 204.9, 156.8, 141.1, 140.7, 136.4, 129.9, 124.7, 42.0, 31.3, 25.5, 22.3, 21.45, 21.38, 20.4, 13.9 ppm. IR (neat): 2962, 2872, 1694, 1462, 1081, 1043, 811 cm^{-1}. HRMS (FAB^+) Calcd for $C_{17}H_{25}O_2S$ $[M + H]^+$: 293.15751; found: 293.15749. LRMS (FAB^+) 293 (100), 235 (20), 123 (14).

*(Z)-(Rs,3S)-2-Methyl-1-(4-tolylsulfinyl)-1-hepten-3-ol (**13a**).* Procedure A. **12a** (30 mg, 0.113 mmol), $LaCl_3 \cdot 7H_2O$ (84.3 mg, 0.227 mmol), $NaBH_4$ (7.15 mg, 0.189 mmol), MeOH (1.5 mL). Purification by means of column chromatography on silica gel (eluent: CH_2Cl_2/EtOAc = 1:1) afforded **13a** (30.5 mg, 0.114 mmol) in a 100% isolated yield (dr 100:0) as a white solid. Mp: 47.5 °C. $[\alpha]_D = -221°$ (*c* = 0.5, acetone). ^1H NMR (500 MHz, $CDCl_3$), δ: 7.50 (d, 2H, *J* = 7.8 Hz), 7.31 (d, 2H, *J* = 7.8 Hz), 5.07−5.10 (m, 1H), 2.62 (d, 1H, *J* = 3.7 Hz), 2.41 (s, 3H), 1.88 (d, 3H, *J* = 1.1 Hz), 1.72−1.79 (m, 2H), 1.25−1.51 (m, 5H), 0.92 (t, 3H, *J* = 7.1 Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ: 153.0, 141.4, 141.0, 132.7, 129.9, 124.2, 71.0, 35.1, 27.7, 22.5, 21.3, 18.2, 13.9 ppm. IR (KBr): 3384, 2952, 1617, 1445, 1079, 1041, 853 cm^{-1}. HRMS (FAB^+) Calcd for $C_{15}H_{23}O_2S$ $[M + H]^+$: 267.14186; found: 267.14236. LRMS (FAB^+): 267 (72), 249 (25).

*(Z)-(Rs,3S)-2-Butyl-1-(4-tolylsulfinyl)-1-hepten-3-ol (**13b**).* Procedure A. **12b** (105 mg, 0.343 mmol), $LaCl_3 \cdot 7H_2O$ (243 mg, 0.654 mmol), $NaBH_4$ (25 mg, 0.654 mmol), MeOH (3.6 mL). Purification by means of column chromatography on silica gel (eluent: hexane/EtOAc = 1:1) afforded **13b** (105 mg, 0.341 mmol) in a 99% isolated yield (dr 100:0) as a white solid. Mp: 38.5 °C. $[\alpha]_D = -136°$ (*c* = 1.47, acetone). ^1H NMR (500 MHz, $CDCl_3$), δ: 7.54 (d, 2H, *J* = 8.0 Hz), 7.27 (d, 2H, *J* = 8.0 Hz), 5.98 (s, 1H), 4.94−4.97 (m, 1H), 2.40 (s, 3H), 2.20−2.27 (m, 1H), 2.11−2.17 (m, 1H), 1.66−1.76 (m, 2H), 1.37−1.54 (m, 6H), 1.30 (quin, 2H, *J* = 7.2 Hz), 0.94 (t, 3H, *J* = 7.2 Hz), 0.87 (t, 3H, *J* = 7.3 Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ: 156.8, 141.6, 141.0, 131.8, 129.9, 124.4, 71.9, 35.8, 31.3, 27.9, 22.5, 22.4, 21.3, 13.9, 13.8 ppm. IR (KBr): 3305, 2955, 1596, 1458, 1085, 1048, 853 cm^{-1}. HRMS (FAB^+) Calcd for $C_{18}H_{29}O_2S$ $[M + H]^+$: 309.18881; found: 309.18910. LRMS (FAB^+): 309(100), 291(58).

*(Z)-(Rs,3S)-2-Phenyl-1-(4-tolylsulfinyl)-1-hepten-3-ol (**13c**).* Procedure A. **12c** (100 mg, 0.306 mmol), $LaCl_3 \cdot 7H_2O$ (227 mg, 0.612 mmol), $NaBH_4$ (34.9 mg, 0.918 mmol), MeOH (3.6 mL). Purification by means of column chromatography on silica gel (eluent: CH_2Cl_2/EtOAc = 2:1) afforded **13c** (100 mg, 0.305 mmol) in a 99% isolated yield (dr 100:0) as a white solid. Mp: 82 °C. $[\alpha]_D = -54.2°$ (*c* = 1.02, acetone). ^1H NMR (500 MHz, $CDCl_3$), δ: 7.64 (d, 2H, *J* = 8.0 Hz), 7.28−7.36 (m, 7H), 6.20 (s, 1H), 5.08−5.12 (m, 1H), 3.47 (d, 1H, *J* = 5.7 Hz), 2.40 (s, 3H), 1.59−1.72 (m, 2H), 1.25−1.50 (m, 4H), 0.85 (t, 3H, *J* = 7.16 Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ: 154.7, 141.4, 141.3, 138.3, 135.0, 130.1, 128.7, 128.4, 127.6, 124.8, 72.9, 36.1, 27.9, 22.4, 21.4, 13.9 ppm. IR (KBr): 3306, 2929, 2856, 2364, 1728, 1491, 1444, 1287, 1076, 995, 807, 756, 697 cm^{-1}. HRMS (FAB^+) Calcd for $C_{20}H_{25}O_2S$ $[M + H]^+$: 329.15751; found: 329.15757. LRMS (FAB^+): 329 (92), 311 (47), 149 (63).

*(Z)-(Rs,3S)-2-(1-Methylethyl)-1-(4-tolylsulfinyl)-1-hepten-3-ol (**13d**).* Procedure A. **12d** (79 mg, 0.270 mmol), $LaCl_3 \cdot 7H_2O$ (200 mg, 0.540 mmol), $NaBH_4$ (20.5 mg, 0.540 mmol), MeOH (3.2 mL). Purification by means of column chromatography on silica gel (eluent: CH_2Cl_2/EtOAc = 1:1) afforded **13d** (79 mg, 0.269 mmol) in a 99% isolated yield (dr 100:0) as a white solid. Mp: 79.0 °C. $[\alpha]_D = -130.2°$ (*c* = 1.01, acetone). ^1H NMR (500 MHz, $CDCl_3$), δ: 7.53 (d, 2H, *J* = 8.0 Hz), 7.30 (d, 2H, *J* = 8.3 Hz), 5.97 (s, 1H), 4.79−4.84 (m, 1H), 2.80 (d, 1H, *J* = 5.8 Hz), 2.55 (sep, 1H, *J* = 6.8 Hz), 2.41 (s, 3H), 1.65−1.80 (m, 2H), 1.53−1.58 (m, 1H), 1.35−1.44 (m, 3H), 1.09 (d, 3H, *J* = 6.9 Hz), 1.04 (d, 3H, *J* = 6.9 Hz), 0.94 (t, 3H, *J* = 6.9 Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ: 163.5, 141.7, 141.1, 130.3, 130.0, 124.7, 72.5, 36.2, 30.9, 28.2, 23.1, 22.7, 22.5, 21.4, 14.0 ppm. IR (KBr): 3271, 2962, 2862, 2367, 1594, 1459, 1317, 1083, 1045, 999, 805, 626, 484 cm^{-1}. HRMS (FAB^+) Calcd for $C_{17}H_{27}O_2S$ $[M + H]^+$: 295.17316; found: 295.17311. LRMS (FAB^+): 295 (89), 277 (57), 123 (15).

*(Z)-(Rs,3R)- 2-Methyl-1-(4-tolylsulfinyl)-1-hepten-3-ol (**14a**).* Procedure B. **12a** (70 mg, 0.263 mmol), $LaCl_3$ (129 mg, 0.526 mmol), DIBAL (1.01 M solution in toluene, 0.52 mL, 0.53 mmol), THF (2.8 mL). Purification by means of column chromatography on silica gel (eluent: CH_2Cl_2/EtOAc = 2:1) afforded **14a** (60 mg, 0.225 mmol) in an 88% isolated yield (dr 0:100) as a white solid. Mp: 106.0 °C. $[\alpha]_D = -250°$

(c = 0.98, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.53 (d, 2H, J = 8.1 Hz), 7.31 (d, 2H, J = 8.1 Hz), 6.03 (d, 1H, J = 1.2 Hz), 5.03−5.05 (m, 1H), 2.62 (d, 1H, J = 3.7 Hz), 2.40 (s, 3H), 2.14 (s, 1H), 1.87 (d, 3H, J = 1.1 Hz), 1.64−1.76 (m, 2H), 1.33−1.53 (m, 4H), 0.93 (t, 3H, J = 7.1 Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ: 153.9, 141.2, 140.9, 131.9, 130.0, 124.3, 69.8, 34.5, 28.0, 22.5, 21.3, 17.7, 13.9 ppm. IR (KBr): 3401, 2935, 1623, 1445, 1079, 1041, 817 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{15}H_{23}O_2S$ $[M + H]^+$: 267.14186; found: 267.14188. LRMS (FAB$^+$): 267 (100), 249 (43).

*(Z)-(Rs,3R)-2-Butyl-1-(4-tolylsulfinyl)-1-hepten-3-ol (**14b**).* Procedure B. **12b** (100 mg, 0.327 mmol), $LaCl_3$ (246 mg, 0.654 mmol), DIBAL (1.01 M solution in toluene, 0.66 mL, 0.65 mmol), THF (5.0 mL). Purification by means of column chromatography on silica gel (eluent: hexane/EtOAc = 1:1) afforded **14b** (100 mg, 0.325 mmol) in a 95% isolated yield (dr 6:94) as a white solid. Mp: 49.0 °C. $[\alpha]_D$ = −162° (c = 1.10, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.51 (d, 2H, J = 8.0 Hz), 7.30 (d, 2H, J = 8.0 Hz), 5.99 (s, 1H), 5.01−5.04 (m, 1H), 3.14 (s, 3H), 2.40 (s, 3H), 2.28−2.35 (m, 1H), 2.08−2.15 (m, 1H), 1.73−1.79 (m, 1H), 1.23−1.52 (m, 7H), 0.91 (t, 3H, J = 7.2 Hz), 0.87 (t, 3H, J = 7.2 Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ: 157.5, 141.26, 140.20, 131.4, 130.0, 124.4, 70.9, 35.2, 30.5, 30.4, 29.8, 28.1, 22.5, 21.3, 13.9, 13.8 ppm. IR (KBr): 3408, 2956, 1612, 1459, 1150, 1082, 829 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{18}H_{29}O_2S$ $[M + H]^+$: 309.18881; found: 309.18872. LRMS (FAB$^+$): 309 (100), 291 (67).

*(Z)-(Rs,3R)-2-Phenyl-1-(4-tolylsulfinyl)-1-hepten-3-ol (**14c**).* Procedure B. **12c** (150 mg, 0.460 mmol), $LaCl_3$ (225 mg, 0.920 mmol), DIBAL (1.01 M solution in toluene, 0.90 mL, 0.92 mmol), THF (4.5 mL). Purification by means of column chromatography on silica gel (eluent: CH_2Cl_2/EtOAc = 2:1) afforded a mixture of **14c** and its diastereomer (151 mg, 0.460 mmol) in a 89% yield (dr 3:97) as a white solid. Mp: 138 °C. $[\alpha]_D$ = −24.6° (c = 1.07, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.62 (d, 2H, J = 8.3 Hz), 7.35−7.39 (m, 2H), 7.28−7.34 (m, 5H), 6.25 (s, 1H), 5.11−5.16 (m, 1H), 3.16 (d, 1H, J = 5.4 Hz), 2.41 (s, 3H), 1.75−1.83 (m, 1H), 1.55−1.63 (m, 1H), 1.44−1.52 (m, 1H), 1.25−1.33 (m, 3H), 0.85 (t, 3H, J = 6.9 Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ: 154.5, 141.5, 141.3, 137.8, 135.5, 130.1, 128.8, 128.3, 127.7, 124.7, 72.3, 35.9, 28.0, 22.4, 21.4, 13.9 ppm. IR (KBr): 3306, 3054, 2931, 2858, 2364, 1597, 1492, 1444, 1323, 1077, 1039, 828, 802, 760, 701 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{20}H_{25}O_2S$ $[M + H]^+$: 329.15751; found: 329.15721. LRMS (FAB$^+$): 329 (97), 311 (60), 263 (9), 123 (17).

*(Z)-(Rs,3R)-2-(1-Methylethyl)-1-(4-tolylsulfinyl)-1-hepten-3-ol (**14d**).* Procedure B. **12d** (75 mg, 0.257 mmol), $LaCl_3$ (125 mg, 0.510 mmol), DIBAL (1.01 M solution in toluene, 0.51 mL, 0.51 mmol), THF (3 mL). Purification by means of column chromatography on silica gel (eluent: CH_2Cl_2/EtOAc = 2:1) afforded **14d** (76 mg, 0.259 mmol) in a 99% isolated yield (dr 0:100) as a white solid. Mp: 72.5 °C. $[\alpha]_D$ = −154.8° (c = 1.01, acetone). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.53 (d, 2H, J = 8.3 Hz), 7.30 (d, 2H, J = 8.0 Hz), 6.02 (s, 1H), 4.86−4.90 (m, 1H), 2.64 (d, 1H, J = 4.8 Hz), 2.60 (quin, 1H, J = 6.6 Hz), 2.41 (s, 3H), 1.76−1.84 (m, 2H), 1.51−1.57 (m, 1H), 1.30−1.40 (m, 3H), 1.13 (d, 3H, J = 6.9 Hz), 1.02 (d, 3H, J = 6.9 Hz), 0.92 (t, 3H, J = 7.2 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 163.4, 141.4, 141.1, 130.8, 130.0, 124.6, 71.9, 35.8, 29.9, 28.4, 23.24, 23.20, 22.5, 21.4, 14.0 ppm. IR (KBr): 3255, 2962, 2933, 2868, 1633, 1460, 1369, 1078, 1038, 993, 810 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{17}H_{27}O_2S$ $[M + H]^+$: 295.17316; found: 295.17295. LRMS (FAB$^+$): 295 (100), 277 (82), 221 (11), 123 (22).

*(Z)-(3S)-2-Methyl-1-tosylhept-1-en-3-ol (**15a**).* To a cold (0 °C) solution of (Z)-(Rs, 3S)-2-methyl-1-(4-tolylsulfinyl)-1-hepten-3-ol **13a** (730 mg, 2.75 mmol) in 28 mL of MeOH was added MMPP·$6H_2O$ (2.56 g, 5.18 mmol). The mixture was warmed to room temperature, while stirring. The reaction progress was monitored by TLC. Upon completion of the reaction, the mixture was quenched with saturated aqueous $NaHCO_3$. After removal of most MeOH under reduced pressure, the mixture was diluted with EtOAc. The organic and aqueous phases were separated, and the aqueous phase was extracted with EtOAc. The combined organic fractions were washed with brine and dried over anhydrous Na_2SO_4. The drying agent was filtered off, and the filtrate was concentrated under reduced pressure. The resulting residue was subjected to flash chromatography on silica gel (eluent: hexane/EtOAc = 1:1) to afford (Z)-(3S)-2-methyl-1-(4-tolylsulfonyl)-1-hepten-3-ol **15a** (767 mg, 2.73 mmol) in a 99% yield as a colorless oil. $[\alpha]_D$ = −74.3° (c = 0.98, acetone). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.79 (d, 2H, J = 8.3 Hz), 7.33 (d, 2H, J = 7.9 Hz), 6.15 (d, 1H, J = 1.1 Hz), 5.24−5.27 (m, 1H), 2.44 (s, 3H), 2.31 (d, 1H, J = 5.2 Hz), 1.89 (d, 3H, J = 1.4 Hz), 1.60−1.66 (m, 1H), 1.37−1.47 (m, 2H), 1.22−1.34 (m, 3H), 0.89 (t, 3H, J = 7.2 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 158.2, 144.3, 139.0, 129.9, 127.2, 127.1, 68.6, 34.6, 27.8, 22.5, 21.6, 19.1, 14.0 ppm. IR (KBr): 3482, 2956, 2867, 1618, 1441, 1291, 1143, 1085, 1052, 1014, 854, 813, 668, 569, 533 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{15}H_{23}O_3S$ $[M + H]^+$: 283.13678; found: 283.13687. LRMS (FAB$^+$): 283 (49), 265 (100), 109 (95).

*(3S)-2-Methylhept-1-en-3-ol (**16a**).* A solution of (Z)-(3S)-2-methyl-1-tosylhept-1-en-3-ol **15a** (250 mg, 0.886 mmol) in 9.0 mL of methanol was transferred into a flask containing a suspension of anhydrous Na_2HPO_4 (500 mg, 3.52 mmol) and ca. 5% sodium amalgam (5.59 g, 13.2 mmol) in dry methanol at room temperature. The reaction mixture was stirred at room temperature for 30 min. Then, the contents of the reaction flask were extracted with CH_2Cl_2. The organic extract was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography (eluent: neat CH_2Cl_2) to give pure (3S)-2-methylhept-1-en-3-ol **16a** (112 mg, 0.875 mmol) in a 99% yield at colorless oil. $[\alpha]_D$ = −3.27° (c = 1.10, EtOH). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 4.93−4.94 (m, 1H), 4.82−4.83 (m, 1H), 4.04−4.08 (m, 1H), 1.72 (s, 3H), 1.51−1.57 (m, 3H), 1.31−1.38 (m, 3H), 1.23−1.29 (m, 1H), 0.91 (t, 3H, J = 7.22 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 147.7, 110.9, 76.0, 34.7, 27.8, 22.6, 17.5, 14.1 ppm. IR (KBr): 3354, 3074, 2933, 2862, 1651, 1452, 1020, 897 cm^{-1}.

*(S)-2-Methylhept-1-en-3-yl 2-Nitrobenzoate (**17a**).* (S)-2-Methyl-1-hept-1en-3-ol **16a** (60 mg, 0.469 mmol) and 2-nitrobenzoyl chloride (262 mg, 1.41 mmol) were dissolved in 7.5 mL of CH_2Cl_2. A few drops of pyridine were added to this reaction mixture at room temperature. The mixture was stirred while the reaction progress was monitored by TLC. Upon completion of the reaction, the mixture was quenched with saturated aqueous NH_4Cl. The product was extracted with CH_2Cl_2, and the combined extracts were washed with brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: hexane/EtOAc/CH_2Cl_2 = 5:1:1) to quantitatively afford (S)-2-methylhept-1-en-3-yl 2-nitrobenzoate **17a** (130 mg, 0.469 mmol) as a colorless oil. $[\alpha]_D$ = +25.4° (c = 1.24, EtOH). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.87 (dd, 1H, J = 1.4 Hz, 8.3 Hz), 7.76 (dd, 1H, J = 1.7 Hz, 7.5 Hz), 7.65−7.68 (m, 1H), 7.61−7.64 (m, 1H), 5.42 (t, 1H, J = 6.8 Hz), 5.04 (s, 1H), 4.97−4.98 (m, 1H), 1.76−1.82 (m, 1H), 1.75 (s, 3H), 1.65−1.71 (m, 1H), 1.26−1.40 (m, 4H), 0.92 (t, 3H, J = 7.21 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 164.5, 148.4, 142.3, 132.6, 131.7, 130.0, 127.8, 123.8, 114.1, 80.3, 31.8, 27.3, 22.4, 17.8, 14.0 ppm. IR (KBr): 3082, 2956, 2870, 1730, 1537, 1448, 1354, 1286, 1128, 1072, 908, 787, 735, 698 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{15}H_{19}NO_4$ $[M + H]^+$: 277.13139; found: 277.13177. LRMS (FAB$^+$): 277 (25), 150 (17).

*(3RS,Ss)-1-(4-Tolylsulfinyl)-3-(triethylsilyloxy)-1-butyne (**18a**).* An excess amount of 3-(triethylsilyloxy)-1-butyne (4.3 g, 23.3 mmol) was added dropwise to a 3.8 M solution of EtMgBr in Et_2O (15.3 mmol, 4.0 mL) at room temperature under argon. After being stirred for 1 h, the mixture was cooled to −78 °C. Then, l-menthyl (−)-(S)-4-toluenesulfinate (2.24 g, 7.63 mmol) dissolved in 28 mL of toluene was added to the reaction mixture dropwise, and the resulting solution was stirred at −20 °C for a period of 1 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl solution, and extracted with EtOAc. The organic extracts were combined, washed with brine, and dried over

anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc, 20:1 to *n*-hexane/CH_2Cl_2, 20:1) to give a diastereomeric mixture of (3*RS*,*Ss*)-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-butyne **18a** (1.86 g, 5.63 mmol, dr 1:1) in a 74% yield as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.67 (d, 4H, J = 8.0 Hz), 7.33 (d, 4H, J = 8.0 Hz), 4.69−4.63 (m, 2H), 2.43 (s, 6H), 1.45 (d, 3H, J = 6.59 Hz), 1.43 (d, 3H, J = 6.59 Hz), 0.93−0.89 (m, 18H), 0.60−0.55 (m, 12H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 142.5, 142.4, 140.5, 130.1, 125.2, 125.1, 105.1, 104.9, 80.9, 80.9, 58.9, 58.9, 24.4, 21.5, 6.6, 4.6 ppm. IR (neat): 2954, 2877, 2171, 1458, 1413, 1336, 1240, 1095, 1062, 1012, 980, 810, 746 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{17}H_{27}O_2SiS$ [M + H]$^+$: 323.15010; found: 323.15021. LRMS (FAB$^+$) 323, 293, 191, 143, 115.

*(3RS,Ss)-4-Methyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-pentyne (**18b**).* An excess amount of 4-methyl-3-(triethylsilyloxy)-1-pentyne (5.41 g, 25.5 mmol) was added dropwise to a 3.8 M solution of EtMgBr in Et_2O (16.7 mmol, 4.39 mL) at room temperature under argon. After being stirred for 1 h, the mixture was cooled to −78 °C. Then, *l*-menthyl (−)-(*S*)-4-toluenesulfinate (2.50 g, 8.52 mmol) dissolved in 30 mL of toluene was added to the reaction mixture dropwise, and the resulting solution was stirred at −78 °C for 1 h. The reaction mixture was then warmed to 0 °C and stirred for an additional 45 min before being quenched with saturated aqueous NH_4Cl solution. The quenched reaction mixture was extracted with EtOAc, and the organic extracts were combined, washed with brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc, 20:1 to *n*-hexane/CH_2Cl_2, 20:1) to give a diastereomeric mixture of (3*RS*,*Ss*)-4-methyl-1-(4-tolylsulfinyl)-3- (triethylsilyloxy)-1-pentyne **18b** (6.86 mmol, 2.40 g, dr 1:1) in an 81% yield as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.68 (d, 4H, J = 8.0 Hz), 7.34 (d, 4H, J = 8.0 Hz), 4.28 (d, 1H, J = 6.3 Hz), 4.26 (d, 1H, J = 5.7 Hz), 2.43 (s, 6H), 1.92−1.81 (m, 2H), 0.98−0.88 (m, 30H), 0.62−0.55 (m, 12H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$), δ: 142.4, 142.4, 140.8, 140.7, 130.1, 125.1, 103.9, 103.8, 82.4, 82.2, 68.4, 68.3, 35.2, 35.1, 21.5, 18.1, 17.9, 17.7, 17.6, 6.9, 4.7 ppm. IR (neat): 2958, 2877, 2175, 1462, 1240, 1089, 1016, 808, 742 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{19}H_{31}O_2SiS$ [M + H]$^+$: 351.18140; found: 351.18106. LRMS (FAB$^+$): 351, 321, 291, 219, 187, 170, 115.

*(3RS,Ss)-3-Phenyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-propyne (**18c**).* An excess amount of 3-phenyl-3-(triethylsilyloxy)-1-propyne (5.07 g, 20.6 mmol) was added dropwise to a 3.8 M solution of EtMgBr in Et_2O (13.7 mmol, 3.61 mL) at 0 °C under argon. After being stirred for 45 min at room temperature, the mixture was cooled to −78 °C. Then, *l*-menthyl (−)-(*S*)-4-toluenesulfinate (2.42 g, 8.25 mmol) dissolved in 36 mL of toluene was added to the reaction mixture dropwise, and the resulting solution was stirred at −78 °C for 1 h. The reaction mixture was then warmed to −20 °C and stirred for an additional 4 h before being quenched with saturated aqueous NH_4Cl solution. The quenched mixture was extracted with EtOAc, and the organic extracts were combined, washed with brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc, 20:1 to *n*-hexane/CH_2Cl_2, 20:1) to afford a diastereomeric mixture of (3*RS*,*Ss*)-3-phenyl-1-(4-tolylsulfinyl)-3- (triethylsilyloxy)-1-propyne **18c** (1.19 g, 3.08 mmol, dr 1:1) in a 38% yield as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.67 (d, 2H, J = 8.3 Hz), 7.65 (d, 2H, J = 8.3 Hz), 7.44−7.39 (m, 4H), 7.36−7.29 (m, 10H), 5.62 (s, 1H), 5.61 (s, 1H), 2.42 (s, 3H), 2.41 (s, 3H), 0.94−0.88 (m, 18H), 0.65−0.58 (m, 12H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 142.6, 142.5, 140.6, 140.5, 139.6, 130.3, 130.2, 128.7, 128.6, 128.5, 128.4, 126.2, 125.3, 125.2, 103.3, 103.2, 83.1, 83.0, 64.9, 21.6, 6.8, 6.7, 4.8 ppm. IR (neat): 2954, 2877, 2177, 1493, 1454, 1414, 1240, 1089, 1062, 1009, 811, 746, 698 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{22}H_{29}O_2SiS$ [M+H]$^+$: 385.16575; found 385.16569. LRMS (FAB$^+$) 385, 355, 271, 253.

*(Z)-(3RS,Rs)-2-Methyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-butene (**19a**).* A 1.04 M solution of MeLi in Et_2O (3.28 mmol, 3.15 mL) was added dropwise via syringe to a suspension of CuCN (0.292 g, 3.26 mmol) in 22 mL of THF at −78 °C under argon atmosphere, and the resulting solution was stirred for 1 h. Then, a solution of alkynyl sulfoxide **18a** (0.352 g, 1.09 mmol) in 6 mL of THF was added to the above mixture dropwise via syringe to afford a yellow solution that was stirred at −78 °C for 2 h. The reaction was quenched with saturated aqueous NH_4Cl, and the product was extracted with EtOAc. The extracts were washed with brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: hexane/EtOAc = 4:1) to give a diastereomeric mixture of (*Z*)-(3*RS*,*Rs*)-2-methyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-butene **19a** (346 mg, 1.02 mmol, dr 1:1) in a 94% yield as a yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.51 (d, 2H, J = 8.0 Hz), 7.47 (d, 2H, J = 8.3 Hz), 7.29−7.33 (m, 4H), 5.98 (s, 1H), 5.93 (s, 1H), 5.33 (q, 1H, J = 6.3 Hz), 5.29 (q, 1H, J = 6.3 Hz), 2.41 (s, 3H), 2.40 (s, 3H), 1.88 (d, 3H, J = 1.4 Hz), 1.87 (d, 3H, J = 1.4 Hz), 1.40 (d, 3H, J = 6.3 Hz), 1.26 (d, 3H, J = 6.3 Hz), 0.95−1.00 (m, 18H), 0.60−0.69 (m, 12H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$), δ: 156.3, 153.9, 142.0, 141.7, 141.1, 141.0, 130.9, 130.5, 130.0, 129.9, 124.2, 67.1, 66.6, 23.6, 23.3, 21.4, 17.8, 17.2, 6.8, 4.8, 4.7 ppm.; IR (neat): 2956, 1493, 1458, 1375, 1240, 1088, 1043, 808, 746 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{18}H_{31}O_2SiS$ [M + H]$^+$: 339.18140; found: 339.18139. LRMS (FAB$^+$): 339 (100), 321 (73), 309 (47), 207 (78), 159 (98), 123 (26), 115 (49).

*(Z)-(3RS,Rs)-2,4-Dimethyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-pentene (**19b**).* A 1.04 M solution of MeLi in Et_2O (9.72 mmol, 9.35 mL) was added dropwise via syringe to a suspension of CuCN (0.870 g, 9.71 mmol) in 65 mL of THF at −78 °C under argon atmosphere, and the resulting solution was stirred for 1 h. Then a solution of alkynyl sulfoxide **18b** (1.14 g, 3.24 mmol) in 16 mL of THF was added to the above mixture dropwise via syringe to afford a yellow solution that was stirred at −78 °C for 2 h. The reaction was quenched with saturated aqueous NH_4Cl, and the product was extracted with EtOAc. The extracts were washed with brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: hexane/EtOAc = 4:1) to give a diastereomeric mixture of (*Z*)-(3*RS*,*Rs*)-2,4-dimethyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-pentene **19b** (0.968 g, 2.64 mmol, dr 1:1) in a 81% yield as a pale yellow liquid.

(*Z*)-(3*S*,*Rs*)-2,4-dimethyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-pentene **19b-(*S*)** (0.441 g, 1.21 mmol): 37% yield. $[\alpha]_D$ = −153.6° (c = 1.18, acetone). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.53 (d, 2H, J = 7.2 Hz), 7.26 (d, 2H, J = 7.9 Hz), 6.11 (s, 1H), 4.68 (d, 1H, J = 8.6 Hz), 2.40 (s, 3H), 1.86 (s, 3H), 1.75−1.81 (m, 1H), 1.05 (d, 3H, J = 6.53 Hz), 0.99 (t, 9H, J = 7.9 Hz), 0.69−0.73 (m, 9H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$), δ: 152.6, 141.6, 141.2, 133.3, 130.0, 124.7, 76.2, 33.2, 21.4, 19.43, 19.35, 17.8, 6.9, 4.9 ppm. IR (neat): 2956, 2877, 1462, 1240, 1078, 1043, 794, 744 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{20}H_{35}O_2SiS$ [M + H]$^+$: 367.21269; found: 367.21258. LRMS (FAB$^+$): 367 (65), 337 (48), 307 (36), 235 (71), 219 (10), 187 (35), 115 (52).

(*Z*)-(3*R*,*Rs*)-2,4-Dimethyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-pentene **19b-(*R*)** (0.525 g, 1.43 mmol): 44% yield. $[\alpha]_D$ = −54.6° (c = 1.24, acetone). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.53 (d, 2H, J = 8.2 Hz), 7.32 (d, 2H, J = 7.9 Hz), 6.12 (d, 1H, J = 1.1 Hz), 4.72 (d, 1H, J = 8.3 Hz), 2.42 (s, 3H), 1.86 (d, 3H, J = 1.4 Hz), 1.80−1.85 (m, 1H), 1.07 (d, 3H, J = 6.53 Hz), 0.94−0.97 (m, 12H), 0.58−0.66 (m, 6H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$), δ: 154.8, 142.1, 141.2, 132.6, 130.0, 124.4, 76.7, 33.2, 21.4, 19.4, 19.1, 18.2, 6.9, 5.0 ppm. IR (neat): 2956, 2877, 1464, 1240, 1080, 1043, 835, 785, 742 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{20}H_{35}O_2SiS$ [M + H]$^+$: 367.21269; found: 367.21271. LRMS (FAB$^+$): 367 (90), 337 (54), 307 (69), 235 (100), 219 (13), 187 (46), 115 (87).

*(Z)-(3RS,Rs)-2-Methyl-3-phenyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-propene (**19c**).* A 1.04 M solution of MeLi in Et_2O (5.27 mmol, 5.16 mL) was added dropwise via syringe to a suspension of CuCN (0.480 g, 5.36 mmol) in 36 mL of THF at −78 °C under argon atmosphere, and the resulting solution was stirred for 1 h. Then, a solution of alkynyl sulfoxide **18c** (0.687 g, 1.79 mmol) in 9 mL of THF was added to the above mixture dropwise via syringe to afford a yellow solution that was stirred at −78 °C for 1 h. The reaction was quenched with saturated aqueous NH_4Cl and the product was extracted with EtOAc. The extracts were washed with brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: hexane/EtOAc = 4:1) to give a diastereomeric mixture of (*Z*)-(3*RS, Rs*)-2-methyl-3-phenyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-propene **19c** (356 mg, 0.889 mmol, dr 1:1) in a 50% yield as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.57−7.60 (m, 4H), 7.48 (d, 2H, J = 8.0 Hz), 7.25−7.37 (m, 12H), 6.37 (s, 1H), 6.27 (s, 1H), 6.11 (d, 1H, J = 1.0 Hz), 6.10 (d, 1H, J = 0.9 Hz), 2.43 (s, 3H), 2.40 (s, 3H), 1.80 (d, 3H, J = 1.14 Hz), 1.70 (d, 3H, J = 1.44 Hz), 0.94−0.99 (m, 18H), 0.64−0.73 (m, 12H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 154.7, 152.7, 141.9, 141.8, 141.4, 141.28, 141.24, 141.0, 132.2, 131.7, 130.04, 130.02, 128.32, 128.27, 128.19, 127.5, 127.4, 125.9, 124.6, 124.4, 72.07, 72.03, 21.41, 21.38, 17.6, 17.5, 6.8, 4.9, 4.8 ppm. IR (neat): 2956, 2877, 1599, 1492, 1452, 1240, 1092, 1066, 1041, 849, 794, 742, 700 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{23}H_{33}O_2SiS$ [M + H]$^+$: 401.19705; found: 401.19677. LRMS (FAB$^+$): 401 (27), 383 (50), 371 (26), 269 (100), 261 (21), 221 (40), 129 (85), 115 (53).

*(Z)-(Rs)-2-Methyl-1-(4-tolylsulfinyl)-1-buten-3-one (**21a**).* (*Z*)-(3*RS, Rs*)-2-Methyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-butene **19a** (1.15 g, 3.40 mmol) was transferred to a reaction flask containing a 40 mL 6:1:3 mixture of AcOH, THF, and H_2O at room temperature, and the resulting solution was stirred for 1 h 15 min. The cooled reaction mixture was then diluted with H_2O and quenched with solid $NaHCO_3$. The product was extracted with EtOAc, and the organic extracts were combined and washed with brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: CH_2Cl_2/EtOAc = 1:1) to give a diastereomeric mixture of (*Z*)-(3*RS,Rs*)-2-methyl-1-(4-tolylsulfinyl)-1-buten-3-ol **20a** (0.687 g, 3.07 mmol) in a 90% yield. Compound **20a** (0.418 g, 1.86 mmol) was treated with a 15% DMP solution in CH_2Cl_2 (2.8 mmol, ca. 8.0 mL) and $NaHCO_3$ (0.785 g, 9.35 mmol) in 46 mL of CH_2Cl_2 at room temperature. The mixture was then extracted with CH_2Cl_2, and the combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4.The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography (eluent: hexane/EtOAc = 1:3) to afford optically pure (*Z*)-(*Rs*)-2-methyl-1-(4-tolylsulfinyl)-1-buten-3-one **21a** (0.350 g, 1.57 mmol)) in a 85% yield as a yellow oil. $[\alpha]_D$ = −427.1° (*c* = 1.55, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.74 (d, 2H, J = 8.3 Hz), 7.29 (d, 2H, J = 8.0 Hz), 6.35 (d, 1H, J = 1.4 Hz), 2.40 (s, 3H), 2.38 (s, 3H), 2.10 (d, 3H, J = 1.4 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 199.6, 146.0, 141.5, 141.34, 141.29, 130.0, 125.1, 28.3, 21.4, 19.7 ppm. IR (neat) 2920, 1688, 1588, 1490, 1443, 1360, 1304, 1181, 1036, 809 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{12}H_{15}O_2S$ [M + H]$^+$: 223.07927; found: 223.07931. LRMS (FAB$^+$): 223 (100), 123 (14).

*(Z)-(Rs)-2,4-Dimethyl-1-(4-tolylsulfinyl)-1-penten-3-one (**21b**).* (*Z*)-(3*RS,Rs*)-2,4-Dimethyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-pentene **19b** (0.655 g, 1.79 mmol) was transferred to a reaction flask containing a 25 mL 6:1:3 mixture of AcOH, THF, and H_2O at room temperature, and the resulting solution was stirred for 1 h. Then, the reaction mixture was diluted with H_2O and quenched with solid $NaHCO_3$. The product was extracted with EtOAc, and the combined extracts were washed with brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: hexane/EtOAc = 1:3) to give a diastereomeric mixture of (*Z*)-(3*RS,Rs*)-2,4-dimethyl-1-(4-tolylsulfinyl)-1-penten-3-ol **20b** (0.428 g, 1.70 mmol) in a 95% yield. Compound **20b** (0.428 g, 1.70 mmol) was treated with a 15% DMP solution in CH_2Cl_2 (2.55 mmol, ca. 7.44 mL) and $NaHCO_3$ (0.708 g, 8.50 mmol) in 46 mL of CH_2Cl_2 at room temperature. The mixture was extracted with CH_2Cl_2. The combined extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography (eluent: hexane/EtOAc = 1:3) to afford optically pure (*Z*)-(*Rs*)-2,4-dimethyl-1-(4-tolylsulfinyl)-1-penten-3-one **21b** (0.424 g, 1.69 mmol) in a 99% yield as a pale yellow oil. $[\alpha]_D$ = −382.8° (*c* = 1.12, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.73 (d, 2H, J = 8.3 Hz), 7.30 (d, 2H, J = 8.6 Hz), 6.33 (d, 1H, J = 1.4 Hz), 3.03 (m, 1H), 2.39 (s, 3H), 2.10 (d, 3H, J = 1.5 Hz), 1.21 (d, 3H, J = 6.9 Hz), 1.17 (d, 3H, J = 6.5 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 206.5, 143.4, 141.2, 140.8, 130.0, 124.8, 37.8, 21.3, 19.6, 17.9, 17.4 ppm. IR (neat): 2973, 1690, 1592, 1491, 1448, 1382, 1079, 1039, 810 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{14}H_{19}O_2S$ [M + H]$^+$: 251.11057; found: 251.11072. LRMS (FAB$^+$): 251 (100), 207 (20), 191 (12), 123 (10).

*(Z)-(Rs)-2-Methyl-3-phenyl-1-(4-tolylsulfinyl)-1-propen-3-one (**21c**).* (*Z*)-(3*RS,Rs*)-2-Methyl-3-phenyl-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-propene **19c** (0.227 g, 0.567 mmol) was transferred to a reaction flask containing a 7 mL 6:1:3 mixture of AcOH, THF, and H_2O at room temperature and the resulting solution was stirred for 2 h. The reaction mixture was then diluted with H_2O and quenched with solid $NaHCO_3$. The product was extracted with EtOAc, and the combined extracts were washed with brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: hexane/EtOAc = 1:2) to give a diastereomeric mixture of (*Z*)-(3*RS,Rs*)-2-methyl-3-phenyl-1-(4-tolylsulfinyl)-1-propen-3-ol **20c** (0.151 g, 0.528 mmol) in a 93% yield. Then, the diastereomeric mixture **20c** (0.151 g, 0.528 mmol) was treated with a 15% DMP solution in CH_2Cl_2 (0.792 mmol, ca. 2.31 mL) and $NaHCO_3$ (0.220 g, 2.64 mmol) in 15 mL of CH_2Cl_2 at room temperature. The reaction mixture was extracted with CH_2Cl_2. The combined washings were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography (eluent: hexane/EtOAc = 1:2) to afford optically pure (*Z*)-(*Rs*)-2-methyl-3-phenyl-1-(4-tolylsulfinyl)-1-propen-3-one **21c** (0.133 g, 0.468 mmol) in an 89% yield as a pale yellow solid. Mp: 84.0 °C. $[\alpha]_D$ = −257.1° (*c* = 0.20, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.99 (d, 2H, J = 8.3 Hz), 7.65−7.68 (m, 1H), 7.54−7.57 (m, 4H), 7.31 (d, 2H, J = 8.0 Hz), 6.42 (d, 1H, J = 1.5 Hz), 2.41 (s, 3H), 2.14 (d, 3H, J = 1.4 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 196.4, 146.5, 141.4, 140.2, 136.8, 134.6, 134.4, 130.0, 129.5, 129.1, 124.4, 21.4, 21.3 ppm. IR (KBr): 3052, 2917, 1667, 1588, 1490, 1448, 1318, 1297, 1216, 1175, 1077, 1038, 1014, 954, 812, 708, 501 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{17}H_{17}O_2S$ [M + H]$^+$: 285.09492; found: 285.09479. LRMS (FAB$^+$): 285 (93), 105 (63).

*(Z)-(Rs,3S)-2-Methyl-1-(4-tolylsulfinyl)-1-buten-3-ol (**22a**).* Procedure A. **21a** (75 mg, 0.338 mmol), $LaCl_3 \cdot 7H_2O$ (243 mg, 0.656 mmol), $NaBH_4$ (24.8 mg, 0.656 mmol), MeOH (3 mL). Purification by means of column chromatography on silica gel (eluent: CH_2Cl_2/EtOAc = 1:3) afforded **22a** (76 mg, 0.339 mmol, in a 100% isolated yield (de = >99%) as a colorless oil. $[\alpha]_D$ = −176.9° (*c* = 1.05, acetone), ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.53 (d, 2H, J = 8.3 Hz), 7.30 (d, 2H, J = 8.0 Hz), 6.00 (s, 1H), 5.22−5.27 (m, 1H), 2.55 (m, 1H), 2.40 (s, 3H), 1.89 (d, 3H, J = 1.4 Hz), 1.45 (d, 3H, J = 6.3 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), δ: 153.7, 141.4, 141.2, 132.1, 130.0, 124.3, 67.1, 22.2, 21.4, 18.2 ppm. IR (neat): 3380, 2978, 2904, 1615, 1432, 1291, 1159, 1109, 1077, 1003, 813, 790, 622, 493 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{12}H_{17}O_2S$ [M + H]$^+$: 225.09492; found: 225.09493. LRMS (FAB$^+$): 225 (92), 207 (28), 123 (14).

*(Z)-(Rs,3S)-2,4-Dimethyl-1-(4-tolylsulfinyl)-1-penten-3-ol (**22b**).* Procedure A. **21b** (100 mg, 0.40 mmol), $LaCl_3 \cdot 7H_2O$ (297 mg, 0.80 mmol), $NaBH_4$ (45.6 mg, 1.20 mmol), MeOH (3.6 mL). Purification by means of

column chromatography on silica gel (CH_2Cl_2/EtOAc = 2:1) afforded **22b** (102 mg, 0.40 mmol) in a 100% isolated yield (dr 100:0) as a white solid. Mp: 91.5 °C. $[\alpha]_D = -173.5°$ (c = 1.10, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.52 (d, 2H, J = 8.0 Hz), 7.28 (d, 2H, J = 8.0 Hz), 6.07 (s, 1H), 4.64 (dd, 1H, J = 3.7 Hz, 4.9 Hz), 2.60(m, 1H), 2.40 (s, 3H), 1.81−1.92 (m, 4H), 1.10 (d, 3H, J = 6.6 Hz), 0.97 (d, 3H, J = 6.9 Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ: 151.9, 141.6, 141.1, 134.3, 130.0, 124.3, 32.1, 21.3, 19.1, 18.8, 18.3 ppm. IR (KBr): 3363, 2960, 2366, 1623, 1440, 1308, 1083, 999, 797 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{14}H_{21}O_2S$ [M + H]$^+$: 253.12622; found: 253.12615. LRMS (FAB$^+$): 253 (100), 235 (25), 191 (13), 123 (13).

*(Z)-(Rs,3R)-3-Phenyl-1-(4-tolylsulfinyl)-1-propen-3-ol (**22c**).* Procedure A. **21c** (55 mg, 0.192 mmol), $LaCl_3 \cdot 7H_2O$ (143 mg, 0.384 mmol), $NaBH_4$ (14.5 mg, 0.384 mmol), MeOH (2.0 mL). Purification by means of column chromatography on silica gel (eluent: CH_2Cl_2/EtOAc = 3:1) afforded **22c** (55 mg, 0.192 mmol) in a 100% isolated yield (dr 100:0) as a white solid. Mp: 160.5 °C. $[\alpha]_D = -0.102°$ (c = 1.02, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.57 (d, 2H, J = 8.0 Hz), 7.48 (d, 2H, J = 7.7 Hz), 7.35 (t, 3H, J = 7.1 Hz), 7.28 (d, 2H, J = 8.3 Hz), 6.24 (d, 1H, J = 4.0 Hz), 6.10 (d, 1H, J = 1.1 Hz), 3.43 (d, 1H, J = 4.0 Hz), 2.40 (s, 3H), 1.69 (d, 3H, J = 1.43 Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ: 151.3, 141.5, 141.3, 140.4, 134.0, 130.1, 128.6, 127.9, 125.8, 124.4, 72.5, 21.4, 18.3 ppm. IR (KBr): 3314, 2920, 2361, 1598, 1492, 1446, 1290, 1086, 1057, 1005, 846, 819, 744, 636, 481 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{17}H_{19}O_2S$ [M + H]$^+$: 287.11057; found: 287.11053. LRMS (FAB$^+$): 287 (100), 269 (46), 253 (18), 129 (45).

*(Z)-(Rs,3R)-2-Methyl-1-(4-tolylsulfinyl)-1-buten-3-ol (**23a**).* Procedure B. **21a** (75 mg, 0.328 mmol), $LaCl_3$ (161 mg, 0.656 mmol), DIBAL (1.01 M solution in toluene, 0.65 mL, 0.66 mmol), THF (3.3 mL). Purification by means of column chromatography on silica gel (eluent: CH_2Cl_2/EtOAc = 1:3) afforded **23a** (65 mg, 0.290 mmol) in an 89% isolated yield (dr 0:100) as a white emulsion . $[\alpha]_D = -241.7°$ (c = 1.05, acetone). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.48 (d, 2H, J = 7.9 Hz), 7.31 (d, 2H, J = 8.5 Hz), 5.96 (s, 1H), 5.28−5.32 (m, 1H), 3.54 (m, 1H), 2.41 (s, 3H), 1.90 (d, 3H, J = 1.4 Hz), 1.34 (d, 3H, 6.53 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ:154.2, 141.3, 141.0, 131.6, 130.1, 124.2, 66.2, 21.4, 17.6 ppm. IR (KBr): 3377, 2976, 2922, 1618, 1493, 1441, 1294, 1157, 1078, 1026, 908, 808, 740, 625 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{12}H_{17}O_2S$ [M + H]$^+$: 225.09492; found: 225.09485. LRMS (FAB$^+$): 225 (35), 207 (10), 165 (5).

*(Z)-(Rs,3R)-2,4-Dimethyl-1-(4-tolylsulfinyl)-1-penten-3-ol (**23b**).* Procedure B. **21b** (100 mg, 0.40 mmol), $LaCl_3$ (196 mg, 0.799 mmol), DIBAL (1.01 M solution in toluene, 0.80 mL, 0.80 mmol), THF (4 mL). Purification by means of column chromatography on silica gel (eluent: CH_2Cl_2/EtOAc = 2:1) afforded **23b** (96 mg, 0.381 mmol) in a 95% isolated yield (dr 2:98) as a white solid. Mp: 187 °C. $[\alpha]_D = -251.0°$ (c = 1.07, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.53 (d, 2H, J = 8.0 Hz), 7.31 (d, 2H, J = 8.1 Hz), 6.11 (d, 1H, J = 1.4 Hz), 4.69 (dd, 1H, J = 4.0 Hz, 5.1 Hz), 3.40 (d, 1H, J = 4.0 Hz), 2.40 (s, 3H), 1.84−1.90 (m, 4H), 1.13 (d, 3H, J = 6.3 Hz), 0.79 (d, 3H, J = 6.9 Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ: 152.8, 141.3, 141.1, 133.8, 130.1, 124.5, 75.8, 31.7, 21.4, 19.4, 19.1, 18.0 ppm. IR (KBr): 3389, 2954, 2919, 2871, 2366, 1620, 1442, 1375, 1323, 1085, 1035, 813, 782, 626 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{14}H_{21}O_2S$ [M + H]$^+$: 253.12622; found: 253.12623. LRMS (FAB$^+$): 253 (100), 235 (33), 191 (12), 123 (13).

*(Z)-(Rs,3S)-3-Phenyl-1-(4-tolylsulfinyl)-1-propen-3-ol (**23c**).* Procedure B. **21c** (100 mg, 0.352 mmol), $LaCl_3$ (172 mg, 0.702 mmol), DIBAL (1.01 M solution in toluene, 0.70 mL, 0.70 mmol), THF (3.5 mL). Purification by means of column chromatography on silica gel (eluent: CH_2Cl_2/EtOAc = 2:1) afforded **23c** (91 mg, 0.319 mmol) in a 91% isolated yield (dr 14:86) as a white solid. Mp: 123.5 °C. $[\alpha]_D = -93.6°$ (c = 1.03, acetone). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.51 (d, 2H, J = 8.3 Hz), 7.27−7.39 (m, 7H), 6.30 (d, 1H, J = 3.7 Hz), 6.16 (d, 1H, J = 1.1 Hz), 4.57 (d, 1H, J = 4.0 Hz), 2.41 (s, 3H), 1.81 (d, 3H, J = 1.14 Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ: 152.8, 141.5, 140.8, 140.7, 132.7, 130.1, 128.4, 127.6, 126.1, 124.5, 71.6, 21.4, 18.1 ppm. IR (KBr): 3330, 3029, 2950, 2917, 1601, 1492, 1444, 1374, 1266, 1082, 1030, 833, 802, 730, 622 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{17}H_{19}O_2S$ [M + H]$^+$: 287.11057; found: 287.11048. LRMS (FAB$^+$): 287 (100), 269 (70), 253 (13), 129 (69), 123 (32).

*(E)-(3RS,Ss)-1-(Tributylstannyl)-3-(triethylsilyloxy)-1-(4-tolylsulfinyl)-butene (**24**).* Under argon atmosphere, a 25 mL two-necked round-bottom flask equipped with a magnetic stir bar was charged sequentially with (3*RS*,*Ss*)-1-(4-tolylsulfinyl)-3-(triethylsilyloxy)-1-butyne **18a** (0.748 g, 2.32 mmol), toluene (15 mL), $Pd(PPh_3)_4$, (0.054 g, 0.046 mmol), and Bu_3SnH (ca. 0.71 mL, 2.32 mmol). The mixture was stirred at −20 °C for 1 h. After removal of the solvent under reduced pressure, the residue was diluted with light petroleum ether and filtered to remove the palladium catalyst. The resulting solution was concentrated under reduced pressure, and the residue was subjected to flash column chromatography on silica gel (eluent: hexane/EtOAc = 5:1) to give diastereomeric mixture of (*E*)-(3*RS*,*Ss*)-1-(tributylstannyl)-3-(triethylsilyloxy)-1-(4-tolylsulfinyl) butene **24** (1.07 g, 1.75 mmol, dr 1:1) in a 75% yield as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.54 (d, 2H, J = 8.2 Hz), 7.39 (d, 2H, J = 8.3 Hz), 7.25−7.27 (m, 4H), 6.21 (d, 1H, J = 8.2 Hz), 6.17 (d, 1H, J = 6.5 Hz), 4.92−4.99 (m, 2H), 2.39 (s, 3H), 2.39 (s, 3H), 1.18−1.44 (m, 36H), 0.98 (t, 9H, J = 8.25 Hz), 0.94 (t, 9H, J = 7.90 Hz), 0.80−0.92 (m, 24H), 0.66 (q, 6H, J = 7.90 Hz), 0.59 (q, 6H, J = 7.21 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 153.8, 152.1, 151.7, 142.4, 142.3, 140.4, 140.2, 129.7, 129.5, 125.1, 124.9, 68.1, 66.7, 28.78, 28.77, 28.71, 27.29, 27.24, 24.6, 24.1, 21.3, 13.64, 13.63, 11.60, 11.56, 6.8, 5.0, 4.8 ppm. IR (neat): 2954, 1460, 1415, 1375, 1240, 1136, 1082, 1039, 1012, 806, 744, 673 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{29}H_{55}O_2SiSSn$ [M + H]$^+$: 615.27139; found: 615.27096. LRMS (FAB$^+$): 615 (8), 557 (100), 483 (10), 291 (7), 159 (41), 115 (100).

*(Z)-(6RS,Ss)-6-(Triethylsilyloxy)-4-(4-tolylsulfinyl)hepta-1,4-diene (**25a**).* (*E*)-(3*RS*,*Ss*)-1-(Tributylstannyl)-3-(triethylsilyloxy)-1-(4-tolylsulfinyl)-1-butene **24** (0.300 g, 0.489 mmol) and 3-bromo-1-propene (48.0 μL, 0.565 mmol) were dissolved in 5.2 mL of DMF at room temperature under argon atmosphere. To this solution were then added $Pd(PPh_3)_4$ (0.030 g, 0.026 mmol) and CuI (0.073 g, 0.386 mmol). The mixture was stirred at room temperature, and the reaction progress was monitored by TLC for the disappearance of the starting organostannane. Upon completion of the reaction, the mixture was diluted with EtOAc and washed with brine. The organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel (eluent: hexane/EtOAc = 5:1) to give diastereomeric mixture of (*Z*)-(6*RS*,*Rs*)-6-(triethylsilyloxy)-4-(4-tolylsulfinyl)hept-1,4-diene **25a** (0.165 g, 0.453 mmol, dr 1:1) in a 93% yield as a colorless oil.

(*Z*)-(6*S*,*Ss*)-6-(Triethylsilyloxy)-4-(4-tolylsulfinyl)hepta-1,4-diene: **25a-(*S*)** $[\alpha]_D = -181.8°$ (c = 0.80, acetone). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.40 (d, 2H, J = 8.3 Hz), 7.29 (d, 2H, J = 7.9 Hz), 5.94−5.96 (m, 1H), 5.53−5.60 (m, 1H), 5.27−5.31 (m, 1H), 5.05 (d, 1H, J = 9.9 Hz), 4.96−5.00 (m, 1H), 3.13−3.17 (m, 1H), 2.52 (dd, 1H, J = 7.4 Hz, 9.6 Hz), 2.41 (s, 3H), 1.33 (d, 3H, J = 6.18 Hz), 0.99 (t, 9H, J = 8.25 Hz), 0.66 (q, 6H, J = 7.91 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 142.1, 141.7, 140.9, 139.1, 134.1, 129.9, 124.3, 118.3, 64.1, 28.5, 24.8, 21.4, 6.8, 4.8 ppm. IR (neat): 2956, 2877, 1639, 1490, 1458, 1371, 1238, 1084, 1051, 1001, 918, 808, 775, 744 cm^{-1}. HRMS (FAB$^+$) Calcd for $C_{20}H_{33}O_2SiS$ [M + H]$^+$: 365.19705; found: 365.19705. LRMS (FAB$^+$): 365 (32), 347 (41), 335 (38), 233 (100), 123 (29), 115 (37).

(*Z*)-(6*R*,*Ss*)-6-(Triethylsilyloxy)-4-(4-tolylsulfinyl)hept-1,4-diene: **25a-(*R*)** $[\alpha]_D = -183.4°$ (c = 0.73, acetone). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.48 (d, 2H, J = 8.2 Hz), 7.30 (d, 2H, J = 8.0 Hz), 5.96−5.97 (m, 1H), 5.51−5.58 (m, 1H), 5.27−5.30 (m, 1H), 5.02−5.04 (m, 1H), 4.94−4.97 (m, 1H), 3.03 (dd, 1H, J = 6.5 Hz, 10.3 Hz), 2.46 (dd, 1H, J = 7.1 Hz, 9.7 Hz), 2.41 (s, 3H), 1.41 (d, 3H, J = 6.53 Hz), 0.98 (t, 9H, J =

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7.91 Hz), 0.62−0.66 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 142.4, 142.1, 140.8, 138.9, 134.1, 129.7, 124.5, 118.2, 65.2, 29.3, 25.1, 21.3, 6.9, 5.2 ppm. IR (neat): 2956, 2877, 1458, 1238, 1082, 1049, 1005, 918, 810 cm^{-1}. HRMS (FAB^+) Calcd for $C_{20}H_{33}O_2SiS$ $[M + H]^+$: 365.19705; found: 365.19744. LRMS (FAB^+): 365 (29), 347 (36), 335 (21), 233 (100), 123 (20), 115 (40).

(Z)-(Ss)-4-(4-Tolylsulfinyl)hepta-1,4-dien-6-one (**27a**). (*Z*)-(6*RS*,*Ss*)-6-(Triethylsilyloxy)-4-(4-tolylsulfinyl)hept-1,4-diene **25a** (0.145 g, 0.398 mmol) was transferred to a reaction flask containing a 10 mL 8:8:1 mixture of AcOH, THF, and H_2O at room temperature, and the resulting solution was stirred for 4 h. The cooled reaction mixture was diluted with H_2O and quenched with solid $NaHCO_3$. The product was extracted with EtOAc, and the combined extracts were washed with brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: CH_2Cl_2/EtOAc = 1:1) to give a diastereomeric mixture of (*Z*)-(6*RS*,*Ss*)-4-(4-tolylsulfinyl)hept-1,4-dien-6-ol **26a** (0.078 g, 0.312 mmol) in a 79% yield. The diastereomeric mixture **26a** (0.067 g, 0.268 mmol) was treated with a 15% DMP solution in CH_2Cl_2 (0.40 mmol, ca. 1.2 mL) and $NaHCO_3$ (0.112 g, 1.34 mmol) in 6.7 mL of CH_2Cl_2 at room temperature. The mixture was then extracted with CH_2Cl_2. The combined washings were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography (eluent: hexane/EtOAc = 1:1) to afford optically pure (*Z*)-(*Rs*)-4-(4-tolylsulfinyl)hepta-1,4-dien-6-one **27a** (0.066 g, 0.267 mmol) in a 99% yield as a yellow solid. Mp: 73.5 °C. $[\alpha]_D = -540.9°$ (*c* = 0.864, acetone). ^1H NMR (600 MHz, $CDCl_3$), δ: 7.72 (d, 2H, *J* = 8.25 Hz), 7.27 (d, 2H, *J* = 8.59 Hz), 6.55 (s, 1H), 5.56−5.63 (m, 1H), 5.16 (d, 1H, *J* = 9.97 Hz), 5.10 (d, 1H, *J* = 17.2 Hz), 3.43 (dd, 1H, *J* = 6.87, 11.0 Hz), 2.94 (dd, 1H, *J* = 6.53, 11.4 Hz), 2.39 (s, 3H), 2.35 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ 196.3, 164.2, 141.0, 140.3, 133.3, 129.8, 129.5, 124.9, 119.5, 30.4, 28.6, 21.3 ppm. IR (KBr): 1683, 1605, 1418, 1357, 1188, 1076, 1039, 930, 820 cm^{-1}. HRMS (FAB^+) Calcd for $C_{14}H_{17}O_2S$ $[M + H]^+$: 249.09492; found: 249.09494. LRMS (FAB^+): 249 (96), 143 (22), 123 (19).

(1E,3Z)-(Ss)-1-Phenyl-3-(4-tolylsulfinyl)hexa-1,3-dien-5-one (**27b**). (*E*)-(3*RS*,*Ss*)-1-(Tributylstannyl)-3-(triethylsilyloxy)-1-(4-tolylsulfinyl)-1-butene **24** (0.450 g, 0.734 mmol) and (*E*/*Z*)-2-bromostyrene (119 μL, 0.924 mmol) were dissolved in 7.7 mL of DMF under argon atmosphere at room temperature. The compounds $Pd(PPh_3)_4$ (44 mg, 0.0385 mmol) and CuI (109 mg, 0.577 mmol) were then added to the above solution. The resulting mixture was stirred at room temperature, and the reaction progress was monitored by TLC for the disappearance of the starting organostannane. Upon reaction completion, the mixture was diluted with EtOAc and washed with brine. The resulting solution was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel (eluent: hexane/EtOAc = 5:1) to give crude (1*E*/*Z*,3*Z*)-(5*RS*,*Ss*)-1-phenyl-3-(4-tolylsulfinyl)-5-(triethylsilyloxy)hexa-1,3-diene (an *E*:*Z* = 9:1 mixture by ^1H NMR) as a yellow oil. The above intermediate product was added to a 8 mL 6:1:3 mixture of AcOH, THF, and H_2O, and the resulting solution was stirred at room temperature for 1 h. The mixture was then diluted with H_2O and quenched with solid $NaHCO_3$. The product was extracted with EtOAc, and the organic extract was washed with brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: CH_2Cl_2/EtOAc = 1:1) to give a diastereomeric mixture of (1*E*,3*Z*)-(5*RS*,*Ss*)-1-phenyl-3-(4-tolylsulfinyl)hexa-1,3-dien-5-ol **26b** (0.160 g, 0.511 mmol, dr 1:1) in a 70% yield. The diastereomeric mixture **26b** (0.150 g, 0.48 mmol) was treated with a 15% DMP solution in CH_2Cl_2 (0.72 mmol, ca. 2.1 mL) and $NaHCO_3$ (0.200 g, 2.40 mmol) in 13 mL of CH_2Cl_2 at room temperature. Then, the mixture was extracted with CH_2Cl_2. The extract was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography (eluent: hexane/EtOAc = 1:1) to afford optically pure (1*E*/*Z*,3*Z*)-(*Ss*)-1- phenyl-3-(4-tolylsulfinyl)hexa-1,3-dien-5-one **27b** (0.147 g, 0.471 mmol) in a 98% yield (the *E*:*Z* ratio was 85:15 by HPLC analysis). The product was treated with petroleum ether, and the slurry was heated at 70 °C for a few minutes. Then, the slurry was filtered to collect the (*Z*)-isomer, and the resulting solid was dried under reduce pressure to obtain (1*E*,3*Z*)-(*Ss*)-1-phenyl-3-(4-tolylsulfinyl)hexa-1,3-dien-5-one **27b** (0.070 g, 0.224 mmol) in a 44% yield as a yellow solid. Mp: 119.0 °C. $[\alpha]_D = -260.2°$ (*c* = 0.790, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$), δ: 7.77 (d, 2H, *J* = 7.90 Hz), 7.52 (d, 2H, *J* = 7.20 Hz), 7.43 (d, 1H, *J* = 16.1 Hz), 7.32−7.37 (m, 3H), 7.24 (d, 2H, *J* = 8.6 Hz), 7.21 (d, 1H, *J* = 16.9 Hz), 6.92 (s, 1H), 2.39 (s, 3H), 2.36 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 196.0, 161.2, 141.6, 141.2, 136.9, 135.7, 129.7, 129.6, 128.9, 127.7, 125.5, 122.8, 116.3, 30.6, 21.4 ppm. IR (KBr): 3039, 2915, 1670, 1547, 1356, 1333, 1190, 1037, 957, 814, 758, 692, 631, 509 cm^{-1}. HRMS (FAB^+) Calcd for $C_{19}H_{19}O_2S$ $[M + H]^+$: 311.11057; found: 311.11058. LRMS (FAB^+): 311 (62), 171 (58).

(Z)-(Ss)-1-Phenyl-1-(4-tolylsulfinyl)-1-buten-3-one (**27c**). (*E*)-(3*RS*,*Ss*)-1-(Tributylstannyl)-3-(triethylsilyloxy)-1-(4-tolylsulfinyl)-1-butene **24** (0.320 g, 0.521 mmol) and iodobenzene (67 μL, 0.603 mmol) were dissolved in 5.5 mL of DMF under argon atmosphere at room temperature. The compounds $Pd(PPh_3)_4$ (0.031 g, 0.027 mmol) and CuI (0.078 g, 0.411 mmol) were then added to the above solution. The resulting mixture was stirred at room temperature, and the reaction progress was monitored by TLC for the disappearance of the starting organostannane. Upon reaction completion, the mixture was diluted with EtOAc and washed with brine. The organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel (eluent: hexane/EtOAc = 5:1) to afford the crude intermediate product, which was treated with a 5 mL 6:1:3 mixture of AcOH, THF, and H_2O at room temperature. The resulting mixture was stirred at 45 °C for 1 h. Then, the cooled solution was diluted with H_2O and quenched with solid $NaHCO_3$. The product was extracted with EtOAc, and the combined washings were washed with brine. Removal of the solvent under reduced pressure was followed by chromatography of the residue on silica gel (eluent: hexane/EtOAc = 1:1) to give a diastereomeric mixture of (*Z*)-(3*RS*,*Ss*)-1-phenyl-1-(4-tolylsulfinyl)-1-buten-3-ol **26c** (0.106 g, 0.371 mmol, dr 1:1) in a 71% yield. The diastereomeric mixture **26c** (0.106 g, 0.371 mmol) was treated with a 15% DMP solution in CH_2Cl_2 (0.56 mmol, ca. 1.6 mL) and $NaHCO_3$ (0.155 g, 1.85 mmol) in 10 mL of CH_2Cl_2 at room temperature. The resulting mixture was extracted with CH_2Cl_2. The extract was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography (eluent: hexane/EtOAc = 1:1) to quantitatively afford optically pure (*Z*)-(3*R*,*Ss*)-1-phenyl-1-(4-tolylsulfinyl)-1-buten-3-one **27c** (0.105 g, 0.371 mmol) as a yellow solid. Mp: 88.9 °C. $[\alpha]_D = -225.1°$ (*c* = 1.05, acetone). ^1H NMR (600 MHz, $CDCl_3$), δ: 7.51 (d, 2H, *J* = 8.3 Hz), 7.36−7.39 (m, 1H), 7.27−7.30 (m, 2H), 7.18 (d, 2H, *J* = 8.0 Hz), 7.10 (d, 2H, *J* = 6.9 Hz), 6.66 (s, 1H), 2.44 (s, 3H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 197.0, 160.8, 141.1, 140.1, 131.4, 130.9, 129.6, 129.5, 127.8, 125.3, 30.7, 21.4 ppm. IR (KBr): 3044, 2916, 1689, 1604, 1486, 1349, 1308, 1168, 1076, 1042, 808, 696 cm^{-1}. HRMS (FAB^+) Calcd for $C_{17}H_{17}O_2S$ $[M + H]^+$: 285.09492; found: 285.09498. LRMS (FAB^+): 285 (52), 145 (17), 123 (17), 77 (44).

(Z)-(Ss,6S)-4-(4-Tolylsulfinyl)hepta-1,4-dien-6-ol (**28a**). Procedure A. **27a** (66 mg, 0.267 mmol), $LaCl_3 \cdot 7H_2O$ (198 mg, 0.534 mmol), $NaBH_4$ (20.2 mg, 0.534 mmol), MeOH (2.5 mL). Purification by means of column chromatography on silica gel (eluent: hexane/EtOAc = 1:1) afforded **28a** (63.5 mg, 0.254 mmol) in a 95% isolated yield (dr 100:0) as a colorless oil. $[\alpha]_D = -221.3°$ (*c* = 0.90, acetone). ^1H NMR (600 MHz, $CDCl_3$), δ: 7.55 (d, 2H, *J* = 6.5 Hz), 7.29 (d, 2H, *J* = 7.5 Hz), 5.91 (d, 1H,

J = 8.6 Hz), 5.52−5.57 (m, 1H), 5.24−5.28 (m, 1H), 5.05 (d, 1H, J = 10.0 Hz), 4.98 (d, 1H, J = 16.8 Hz), 3.07 (dd, 1H, J = 6.8 Hz, 10.3 Hz), 2.53 (dd, 1H, J = 7.2 Hz, 9.6 Hz), 2.40 (s, 3H), 2.15 (d, 1H, J = 4.1 Hz), 1.43 (d, 3H, J = 6.2 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 145.4, 140.9, 139.8, 138.7, 133.9, 129.8, 124.6, 118.4, 63.9, 29.1, 24.4, 21.4 ppm. IR (KBr): 3379, 2974, 2922, 1640, 1492, 1428, 1032, 921, 813, 755, 624, 549 cm^{-1}. HRMS (FAB^+) Calcd for $C_{14}H_{19}O_2S$ $[M + H]^+$: 251.11057; found: 251.11052. LRMS (FAB^+): 251 (66), 233 (55).

(1E,3Z)-(Ss,5S)-1-Phenyl-3-(4-tolylsulfinyl)hexa-1,3-dien-5-ol (***28b***). Procedure A. **27b** (70 mg, 0.224 mmol), $LaCl_3 \cdot 7H_2O$ (166 mg, 0.448 mmol), $NaBH_4$ (12.7 mg, 0.336 mmol), MeOH (5 mL). Purification by means of column chromatography on silica gel (eluent: hexane/EtOAc = 1:1) afforded **28b** (48.5 mg, 0.155 mmol) in a 69% isolated yield (dr 100:0) as a white solid. Mp: 131.8 °C. $[\alpha]_D = -2.88°$ (c = 0.666, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$), δ 7.59 (d, 2H, J = 8.0 Hz), 7.22−7.34 (m, 7H), 6.95 (d, 1H, J = 16.3 Hz), 6.66 (dd, 1H, J = 0.9 Hz, 16.3 Hz), 6.29 (d, 1H, J = 8.3 Hz), 5.19−5.23 (m, 1H), 2.79 (d, 1H, J = 4.6 Hz), 2.37 (s, 3H), 1.42 (d, 3H, J = 6.3 Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$), δ: 144.3, 141.1, 139.4, 139.3, 136.2, 133.6, 129.9, 128.6, 128.4, 126.8, 124.5, 120.6, 63.4, 23.8, 21.3 ppm. IR (KBr): 3323, 3035, 2966, 2924, 1628, 1493, 1452, 1076, 1054, 1022, 960, 875, 815, 752, 692, 638 cm^{-1}. HRMS (FAB^+) Calcd for $C_{19}H_{21}O_2S$ $[M + H]^+$: 313.12622; found: 313.12628. LRMS (FAB^+): 313 (14), 295 (35), 173 (26), 129 (23).

(Z)-(Ss,3S)-1-Phenyl-1-(4-tolylsulfinyl)-1-buten-3-ol (***28c***). Procedure A. **27b** (74 mg, 0.260 mmol), $LaCl_3 \cdot 7H_2O$ (193 mg, 0.520 mmol), $NaBH_4$ (19.7 mg, 0.520 mmol), MeOH (2.5 mL). Purification by means of column chromatography on silica gel (eluent: hexane/EtOAc = 1:1) afforded **28c** (72 mg, 0.251 mmol) in a 97% isolated yield (dr 99.5:0.5) as a white solid. Mp: 136 °C. $[\alpha]_D = -21.0°$ (c = 0.99, acetone). ^1H NMR (600 MHz, $CDCl_3$), δ: 7.34 (d, 2H, J = 8.3 Hz), 7.23−7.30 (m, 3H), 7.16 (d, 2H, J = 8.3 Hz), 7.13 (d, 2H, J = 8.3 Hz), 6.18 (d, 1H, 8.3 Hz), 5.33−5.36 (m, 1H), 2.98 (d, 1H, J = 5.2 Hz), 2.34 (s, 3H), 1.46 (d, 3H, J = 6.5 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 146.3, 142.4, 141.1, 138.8, 133.9, 129.7, 128.9, 128.7, 128.1, 124.9, 63.4, 23.9, 21.4 ppm. IR (KBr) 3339, 3035, 2973, 2369, 1493, 1442, 1145, 1060, 1023, 813, 768, 695, 636, 519 cm^{-1}. HRMS (FAB^+) Calcd for $C_{17}H_{19}O_2S$ $[M + H]^+$: 287.11057; found: 287.11055. LRMS (FAB^+): 287 (23), 269 (26), 165 (12).

(Z)-(Ss,6R)-4-(4-Tolylsulfinyl)hepta-1,4-dien-6-ol (***29a***). Procedure B. **27a** (43 mg, 0.173 mmol), $LaCl_3$ (85 mg, 0.346 mmol), DIBAL (1.01 M solution in toluene, ca. 0.35 mL, 0.35 mmol), THF (2.5 mL). Purification by means of column chromatography on silica gel (eluent: hexane/EtOAc = 2:1) afforded **29a** (29 mg, 0.116 mmol) in a 67% isolated yield (dr 2:98) as a white solid. Mp: 49.0 °C. $[\alpha]_D = -216.9°$ (c = 1.07, acetone). ^1H NMR (600 MHz, $CDCl_3$), δ: 7.42 (d, 2H, J = 8.0 Hz), 7.30 (d, 2H, J = 7.9 Hz), 5.97−5.99 (m, 1H), 5.51−5.58 (m, 1H), 5.32−5.35 (m, 1H), 5.05 (d, 1H, J = 9.9 Hz), 4.96−4.99 (m, 1H), 3.05−3.09 (m, 2H), 2.52 (dd, 1H, J = 7.2 Hz, 10.7 Hz), 2.41 (s, 3H), 1.38 (d, 3H, J = 6.5 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 143.3, 141.5, 141.2, 138.5, 133.9, 130.0, 124.6, 118.4, 63.3, 29.2, 23.1, 21.4 ppm. IR (KBr): 3431, 2979, 1639, 1406, 1043, 931, 808, 548, 476 cm^{-1}. HRMS (FAB^+) Calcd for $C_{14}H_{19}O_2S$ $[M + H]^+$: 251.11057; found: 251.11060. LRMS (FAB^+): 251 (58), 233 (47).

(1E,3Z)-(Ss,5R)-1-Phenyl-3-(4-tolylsulfinyl)hexa-1,3-dien-5-ol (***29b***). Procedure B. **27b** (100 mg, 0.321 mmol), $LaCl_3$ (153 mg, 0.625 mmol), DIBAL (1.01 M solution in toluene, 0.63 mL, 0.63 mmol), THF (5 mL). Purification by means of column chromatography on silica gel (eluent: hexane/EtOAc = 1:1) afforded **29b** (63.3 mg, 0.202 mmol) in a 63% diastereomeric mixture yield (dr 21:79) as a colorless emulsion. $[\alpha]_D = -3.05°$ (c = 1.06, acetone). ^1H NMR (600 MHz, $CDCl_3$), δ: 7.46 (d, 2H, J = 8.3 Hz), 7.24−7.30 (m, 7H), 6.78 (d, 1H, J = 16.2 Hz), 6.62 (d, 1H, J = 16.4 Hz), 6.31 (d, 1H, J = 8.6 Hz), 5.31−5.34 (m, 1H), 3.66 (s, 1H), 2.36 (s, 3H), 1.38 (d, 3H, J = 6.5 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 141.8, 141.3, 140.0, 139.1, 136.2, 133.3, 130.1, 128.6, 128.3, 126.8, 124.7, 118.8, 63.3, 22.9, 21.4 ppm. IR (KBr): 3404, 2970, 1624, 1493, 1446, 1032, 881, 808, 750, 692, 623, 567, 498 cm^{-1}. HRMS (FAB^+) Calcd for $C_{19}H_{21}O_2S$ $[M + H]^+$: 313.12622; found: 313.12635. LRMS (FAB^+): 313 (37), 295 (71), 173 (58).

(Z)-(Ss,3R)-1-Phenyl-1-(4-tolylsulfinyl)-1-buten-3-ol (***29c***). Procedure B. **27c** (0.100 g, 0.355 mmol), $LaCl_3$ (0.174 g, 0.710 mmol), DIBAL (1.01 M solution in toluene, 0.72 mL, 0.71 mmol), THF (5.5 mL). Purification by means of column chromatography on silica gel (eluent: hexane/EtOAc = 1:1) afforded a mixture of **29c** and its diastereomer (0.058 g, 0.203 mmol) in a 54% yield (dr 11:89) as an emulsion. $[\alpha]_D = -16.6°$ (c = 0.39, acetone, R: S = 85:15 diastereomeric ratio by ^1H NMR). ^1H NMR (600 MHz, $CDCl_3$), δ: 7.16−7.27 (m, 5H), 7.14 (d, 2H, J = 7.9 Hz), 7.07 (d, 2H, J = 7.6 Hz), 6.21 (d, 1H, J = 7.6 Hz), 5.37−5.41 (m, 1H), 3.70 (m, 1H), 2.31 (s, 3H), 1.45 (d, 3H, J = 6.5 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$), δ: 144.5, 144.0, 141.5, 138.5, 133.6, 129.7, 129.1, 128.5, 127.9, 125.3, 62.9, 23.4, 21.4 ppm. IR (KBr): 3398, 2970, 2924, 1597, 1491, 1444, 1286, 1144, 1082, 1039, 808, 764, 700, 634, 515 cm^{-1}. HRMS (FAB^+) Calcd for $C_{17}H_{19}O_2S$ $[M + H]^+$: 287.11057; found: 287.11062. LRMS (FAB^+): 287 (24), 269 (25), 123 (14).

■ ASSOCIATED CONTENT

Supporting Information. Copies of ^1H NMR spectra for compounds **4**−**29**. This material is available free of charge via the Internet at http://pubs.acs.org

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