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Highly enantioselective synthesis of multifunctionalized allylic building blocks via oxazaborolidine-catalyzed borane reduction

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Abstract—A simple and convenient synthesis of optically active alkenyl β-hydroxy sulfides with high enantiomeric excess by CBS-oxazaborolidine-catalyzed borane reduction of the corresponding β-keto sulfides and its application to synthesis of chiral alkenic diols have been established.

1. Introduction

Optically active allylic alcohols represent an important structural motif and have attracted synthetic chemists for their wide range of applications.[1,2] Most syntheses of chiral allylic alcohols are based on kinetic resolution of racemic allylic alcohols by chemical[3] or biological process,[2c–e,4] asymmetric hydrogenation,[5] or enantioselective reduction[6] of vinylic ketones and reductive elimination of 2,3-epoxy[7] or *O*-isopropylidene halides[8] and *O*-isopropylidene acetal tosylhydrazones.[9] On the other hand, non-racemic β-hydroxy sulfides are widely used as starting materials for the synthesis of a variety of chiral intermediates in the synthesis of chiral oxiranes,[10a–c] aziridines,[10d] thiiranes,[10e] terahydrofurans[10f,g] and β-hydroxy esters.[10h,i] Moreover, they are easily oxidized to β-hydroxy sulfoxides or sulfones, which serve as extremely useful chiral building blocks for the synthesis of a variety of chiral organic compounds,[11a,b] such as chiral oxiranes,[11c,d] allylic alcohols,[11e,f,12a] lactones,[11g,p,12b–e] macrolides,[11h–l] pheromones,[11m–o] diols[11q] and tetrahydrofurans[12f] because the α-carbon atom of sulfinyl or sulfonyl groups of the compounds can be further functionalized by the formation of sulfur-stabilized carbanions.[10b,13] Very recently we reported highly efficient synthesis of β-hydroxy sulfides with high enantiomeric purity by CBS-oxazaborolidine-catalyzed borane reduction.[14] Using the same methodology, we therefore undertook to study the synthesis of optically active allylic alcohols bearing an adjacent sulfamyl group, which could be used as versatile chiral intermediates for synthesis of biologically active substances.

2. Results and discussion

The overall synthetic route is outlined in Scheme 1. The starting alkenyl β-keto sufides **3** were obtained from condensation of α-alkenyl esters **1** with methyl *p*-tolyl sulfoxide in the presence of base, followed by deoxygenation of product alkenyl β-keto sulfoxides **2**. Thus, methyl *p*-tolyl sulfoxide was reacted with LDA in THF at −78 °C for 1 h and the resulting mixture was added to the alkenic esters **1** in THF at −78 °C using the literature procedure.[15] The reactions were maintained at −78 °C for 24 h with stirring to provide alkenyl β-keto sulfoxides **2** in 55–65% yield. When **2** was treated with sodium iodide in the presence of trifluoroacetic anhydride in acetone at 0 °C according to the known procedure,[16] alkenyl β-keto sulfides **3** were obtained in 88–95% yield. Finally, (*S*)-CBS-oxazaborolidine (**5**)-catalyzed asymmetric borane reduction of **3** using *N*-ethyl-*N*-isopropylaniline–borane complex **6** as borane carrier was carried out.[14] To minimize the hydroboration of alkenyl group by borane, these reductions were performed by use of 0.5 equiv of **6** at 0 °C. As shown Table 1, all the reduction examined afforded the corresponding β-hydroxy sulfides **4** within 10 min in high yields. Their optical purities were determined by HPLC analysis using a Chiralcel OD-H or Whelk-O1 chiral column. The reduction of keto sulfides **3** bearing acyclic (**3a** and **3b**), exocylic (**3c**) and endocyclic (**3d**) alkenyl groups furnished the corresponding alkenyl β-hydroxy sulfides **4a–d** with 90–95% ee (runs 1–4). For aryl-substituted analogues (**3e–h**), the reduction provided very high enantioselection (runs

Keywords: Asymmetric reduction; Oxazaborolidine-catalyzed reduction; Chiral alkenyl β-hydroxy sulfides; Dianion alkylation; Chiral α,β-unsaturated diol.
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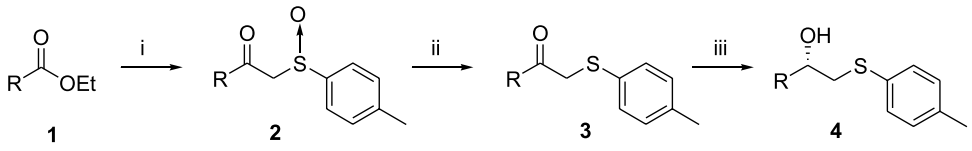
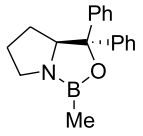


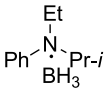
a: R = Me_2C=CH **b**: R = (*E*)-*n*-PrCH=CH **c**: R = Cycloheptylidenyl

d: R = 1-Cyclohexenyl **e**: R = (*E*)-PhCH=CH **f**: R = (*E*)-4-MeC_6H_4CH=CH

g: R = (*E*)-4-ClC_6H_4CH=CH **h**: R = (*E*)-1-NaphthylCH=CH **i**: R = (*E*)-2-FurylCH=CH



(*S*)-**5**



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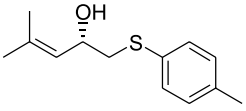
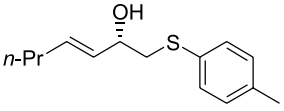
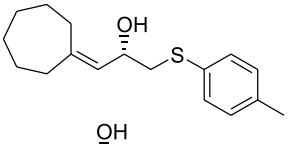
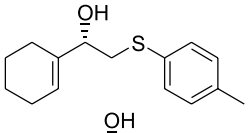
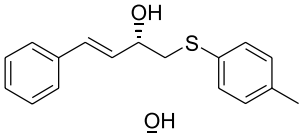
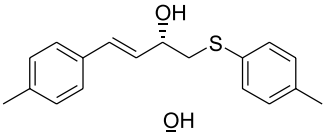
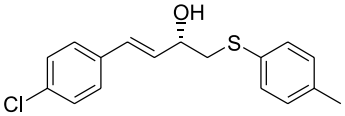
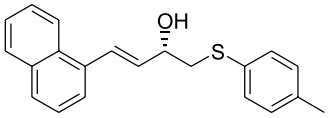
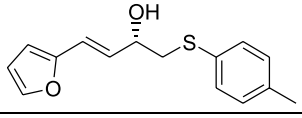
Scheme 1. (i) LDA (2.1 equiv), MeSOtolyl-*p* (2.0 equiv), −78 °C, THF, 24 h, 55–65% yield. (ii) NaI (2.0 equiv), $(CF_3CO)_2O$ (3.0 equiv), 0 °C, acetone, 88–95% yield. (iii) (*S*)-**5** (0.1 equiv), **6** (0.5 equiv), 0 °C, 93–99% yield.

Table 1. Preparation of optically active allylic β-hydroxy sulfides[a]

Run no.	Product **4**		Yield (%)[b]	$[\alpha]_D^{20}$ in $CHCl_3$	ee (%)	Abs. Config
1		**4a**	93	−10.05 (*c* 1.51)	90[c]	S[d]
2		**4b**	95	−1.71 (*c* 1.04)	97[c]	*S*[d]
3		**4c**	97	−0.61 (*c* 0.8)	90[c]	*S*[d]
4		**4d**	95	+6.92 (*c* 2.01)	95[c]	*S*[e]
5		**4e**	97	−92.33 (*c* 0.50)	98[f]	*S*[e]
6		**4f**	98	−114.12 (*c* 0.72)	98[c]	*S*[d]
7		**4g**	99	−110.51 (*c* 1.11)	98[e]	*S*[d]
8		**4h**	99	−64.93 (*c* 5.51)	96[c]	*S*[d]
9		**4i**	95	−97.32 (*c* 1.13)	97[c]	*S*[d]

[a] By reduction of **3** with 0.5 equiv of **6** in the presence of 0.1 equiv of **5** in THF at 0 °C.
[b] Isolated yield.
[c] Determined by HPLC analysis using a 25 cm Chiralcel OD-H chiral column.
[d] Determined by HPLC analysis using a 25 cm Whelk O1 chiral column.
[e] Absolute configuration is unknown, but probably *S* based on comparison of the elution order of HPLC analysis of **4d** and **4e**.
[f] By comparison of their known configuration after conversion of **4d** and **4e** into **7** and **8**, respectively.

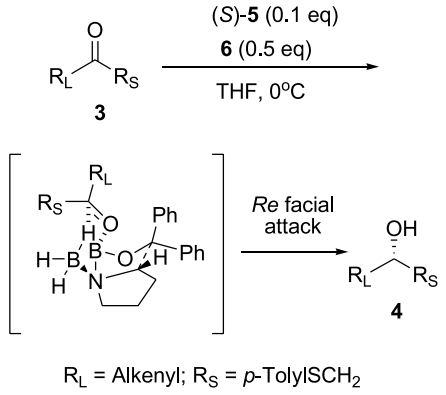


Figure 1.

5–8). Also, the reduction of a heterocyclic analogue **3i** having 2-furyl group gave 95% ee (run 9). In this reaction, we found that β-keto sulfides bearing alkenyl group provided much higher enantioselectivity than the corresponding unhindered aliphatic analogues. For example, the reduction of **4b** containing 1-pentenyl group provided 95% ee, whereas the case of β-keto sulfide having *n*-pentyl group afforded 74% ee.[14] These phenomena are attributable that the alkenyl group behaves as effectively larger than alkyl group in the oxazaborolidine-catalyzed borane reduction,[6] although the reason is unclear so far. All the product β-hydroxy sulfides **4** obtained are consistently enriched in the *S*-enantiomers. The stereochemical course can be explained by the generally accepted mechanism for **5**-catalyzed borane reduction,[12f] where the β-keto sulfides **3** are attacked by hydride on their *Re* faces to provide (*S*)-**4** (Fig. 1).[17] On the other hand, non-racemic alkenic diols, such as **9**[18] and **10**,[19] are frequently used as important starting materials for synthesis of biologically active substances. Since β-hydroxy sulfides are easily converted into diols by Pummerer reaction,[11q] we examined preparation of optically active alkenic diols **9** and **10** from **4d** and **4e**, respectively. When β-hydroxy sulfides **4d** and **4e** were treated with 1.1 equiv of *m*-chloroperbenzoic acid in dichloromethane at 0 °C, the corresponding sulfoxides **7** were obtained in 96–99% yields. It was subsequently reacted with 2.5 equiv of sodium acetate in acetic anhydride at reflux condition to give 1,2-diacetoxy sulfides **8**. Without further purification, these were directly treated with 1.0 equiv of sodium borohydride in 6 N NaOH at room temperature to give chiral 1,2-diols **9** with >95% ee and **10** with 98% ee in 65 and 60% yields from **4d** and **4e**, respectively (Scheme 2).

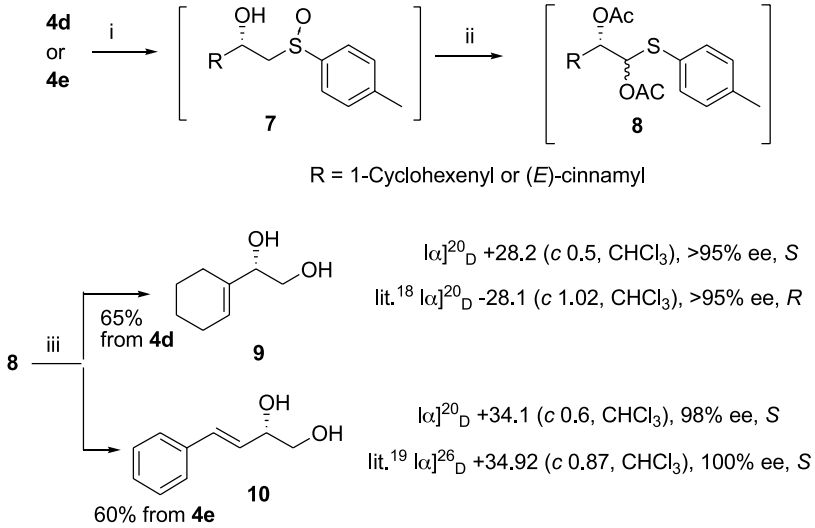
3. Conclusion

We have established a simple and convenient synthesis of optically active alkenic β-hydroxy sulfides, which can be used as versatile chiral intermediates for synthesis of a wide range of non-racemic compounds including biologically active substances by employing **5**-oxazaborolidine-catalyzed borane reduction of the corresponding β-keto sulfides. The reduction provided high enantioselectivity in all the case of acyclic, endocyclic and exocyclic analogues. β-Hydroxy sulfides **4d** and **4e** obtained were successfully converted into chiral alkenic diols **9** and **10** without racemization under Pummerer reaction conditions, respectively.

4. Experimental

4.1. General

All operations with air-sensitive materials were carried out under a nitrogen atmosphere with oven-dried glassware. Liquid materials were transferred with a double-ended needle. The reactions were monitored by TLC using silica gel plates and the products were purified by flash column chromatography on silica gel (Merck; 230–400 mesh). NMR spectra were recorded at 300 MHz for ^{1}H and 75 MHz for ^{13}C using Me_4Si as the internal standard in $CDCl_3$. Optical rotations were measured with a high resolution digital polarimeter. Melting points were uncorrected. Enantiomeric excesses (ees) of the product β-hydroxy sulfides and diols were determined with a HPLC apparatus



Scheme 2. (i) *m*-CPBA (1.1 equiv), CH_2Cl_2, 0 °C. (ii) NaOAc (2.5 equiv), Ac_2O, reflux. (iii) $NaBH_4$ (2.5 equiv), 6 N–NaOH–EtOH, rt.

fitted with a 25 cm Chiralcel OD-H (Daicel) or Whelk-O1 (Regis) chiral column.

4.2. Materials

Most of organic compounds utilized in this study were commercial products of the highest purity. They were further purified by distillation when necessary. THF was distilled over sodium benzophenone ketyl and stored in ampules under nitrogen atmosphere. (*S*)-CBS reagent **5** and *N*-ethyl-*N*-isopropylaniline–borane complex **6** were purchased from the Aldrich Chemical Company.

4.3. Preparation of alkenyl β-keto sulfoxides 2

4.3.1. General procedure.[15] To a solution of LDA (5.5 mmol) in THF (15 mL) was added a solution of methyl *p*-tolyl sulfoxide (5 mmol) in THF (7.5 mL) dropwise at −78 °C. After the mixture was stirred at −78 °C for 1 h and this was slowly added to a solution of α-alkenic ester **1** (5 mmol) in THF (25 mL) at the same temperature via a syringe with stirring. After 24 h at −78 °C, the reaction mixture was decomposed with a saturated ammonium chloride solution (50 mL) and ether (50 mL). Organic layer was separated and the aqueous solution was extracted with ether (3×15 mL). The combined extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered and evaporated. The crude alkenyl β-hydroxy sulfoxides **2** obtained were further purified by a flash column chromatography on silica gel (230–400 mesh) using ethyl acetate/hexane (1/1) as the eluent.

4.3.2. 1-[(*RS*)-*p*-Tolylsulfinyl]-4-methyl-3-penten-2-one 2a. R_f 0.48; oil; 65% yield; IR (neat, cm^{-1}): 3479, 3461, 2976, 2912, 1674, 1615, 1445, 1381, 1227, 1044, 915, 811; ^1H NMR (300 MHz, $CDCl_3$) δ 1.82 (d, 3H, $J=1.1$ Hz), 2.05 (d, 3H, $J=1.1$ Hz), 2.33 (s, 3H), 3.64 (d, 1H, $J=13.20$ Hz), 3.83 (d, 1H, $J=13.20$ Hz), 6.00 (s, 1H), 7.22 (d, 2H, $J=8.22$ Hz), 7.45 (d, 2H, $J=8.25$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.67, 21.79, 28.26, 70.34, 123.64, 124.36, 130.14, 140.37, 142.09, 160.14, 190.30; Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82; S, 13.57. Found: C, 66.12; H, 6.79; S, 13.54.

4.3.3. (3*E*)-1-[(*RS*)-*p*-Tolylsulfinyl]-3-hepten-2-one 2b. R_f 0.45; oil; 62% yield; IR (neat, cm^{-1}): 3475, 2960, 2931, 2872, 1685, 1617, 1457, 1288, 1085, 1046, 1015, 978, 810; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 3H, $J=7.43$ Hz), 1.46 (sextuplet, 2H, $J=7.43$ Hz), 2.18 (qd, 2H, $J=7.01$, 1.51 Hz), 2.40 (s, 3H), 3.87 (d, 1H, $J=13.20$ Hz), 4.08 (d, 1H, $J=13.20$ Hz), 6.09 (m, 1H), 6.81 (m, 1H), 7.23 (d, 2H, $J=7.98$ Hz), 7.51–7.55 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.01, 21.51, 21.80, 35.01, 66.82, 124.41, 130.19, 130.62, 140.14, 142.27, 151.78, 190.83; Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.16; H, 7.25; S, 12.81. Found: C, 67.23; H, 7.28; S, 12.83.

4.3.4. 1-[(*RS*)-*p*-Tolylsulfinyl]-3-cycloheptylidenyl-2-propanone 2c. R_f 0.63; oil; 57% yield; IR (neat, cm^{-1}): 3481,2923, 2853, 1673, 1597, 1444, 1396, 1202, 1088, 1041, 1016, 810; ^1H NMR (300 MHz, $CDCl_3$) δ 1.50–1.62 (m, 8H), 2.32–2.35 (m, 2H), 2.40 (s, 3H), 2.78–2.82 (m, 2H), 3.72 (d, 1H $J=13.20$ Hz), 3.92 (d, 1H, $J=12.93$ Hz), 6.03 (s, 1H), 7.29 (d, 2H, $J=7.98$ Hz), 7.51–7.54 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.80, 26.52, 28.29, 29.53, 30.13, 33.95, 39.71, 70.40, 123.01, 124.43, 130.11, 130.26, 142.05, 171.13, 189.95; Anal. Calcd for $C_{17}H_{22}O_2S$: C, 70.31; H, 7.64; S, 11.04. Found: C, 70.34; H, 7.67; S, 11.24.

4.3.5. 1-[(*RS*)-*p*-Tolylsulfinyl]-2-(cyclohexen-1-yl)-2-ethanone 2d. R_f 0.59; oil; 60% yield; IR (neat, cm^{-1}): 3471, 2938, 2859, 1668, 1597, 1454, 1434, 1245, 1086, 1041, 1023, 809; ^1H NMR (300 MHz, $CDCl_3$) δ 1.61–1.65 (m, 8H), 2.40 (s, 3H), 4.06 (d, 1H, $J=13.20$ Hz), 4.25 (d, 1H, $J=13.20$ Hz), 6.62 (m, 1H), 7.33–7.58 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.64, 21.72, 22.12, 24.17, 26.58, 70.35, 130.22, 131.29, 132.54, 137.35, 140.20, 145.76, 190.82; Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92; S, 12.22. Found: C, 68.56; H, 6.95; S, 12.25.

4.3.6. (3*E*)-1-[(*RS*)-*p*-Tolylsulfinyl]-4-phenyl-3-buten-2-one 2e. R_f 0.34; mp 86–88 °C; 60% yield; IR (KBr, cm^{-1}): 3448, 3044, 3025, 2921, 1652, 1627, 1595, 1449, 1268, 1036, 984, 810, 688; ^1H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H), 4.00 (d, 1H, $J=13.20$ Hz), 4.16 (d, 1H, $J=13.20$ Hz), 6.69 (d, 1H, $J=16.23$ Hz), 7.24–7.41 (m, 5H), 7.46–7.5 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.80, 67.38, 124.44, 125.98, 128.87, 129.19, 130.25, 131.36, 134.08, 142.39, 145.89, 190.57; Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67; S, 11.28. Found: C, 71.89; H, 5.77; S, 11.42.

4.3.7. (3*E*)-1-[(*RS*)-*p*-Tolylsulfinyl]-4-*p*-tolyl-3-buten-2-one 2f. R_f 0.44; mp 82–84 °C; 55% yield; IR (KBr, cm^{-1}): 3264, 3036, 3021, 2917, 1636, 1629, 1597, 1492, 1316, 1159, 1037, 992, 806, 700; ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 6H), 3.98 (d, 1H, $J=13.20$ Hz), 4.16 (d, 1H, $J=13.20$ Hz), 6.65 (d, 1H, $J=15.95$ Hz), 7.16–7.57 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.80, 21.94, 67.41, 124.45, 125.02, 128.41, 128.92, 129.95, 130.22, 131.35, 142.08, 142.33, 146.01, 190.58; Anal. Calcd for $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08; S, 10.75. Found: C, 2.50; H, 6.16; S, 10.85.

4.3.8. (3*E*)-1-[(*RS*)-*p*-Tolylsulfinyl]-4-(*p*-chlorophenyl)-3-buten-2-one 2g. R_f 0.30; mp 116–118 °C; 57% yield; IR (KBr, cm^{-1}): 3421, 3044, 3026, 2921, 1652, 1627, 1595, 1450, 1310, 1296, 1268, 1074, 1037, 984, 810; ^1H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.98 (d, 1H, $J=13.20$ Hz), 4.11 (d, 1H, $J=13.20$ Hz), 6.67 (d, 1H, $J=15.95$ Hz), 7.28–7.55 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.79, 67.35, 124.39, 126.36, 128.60, 129.50, 129.97, 130.26, 132.62, 137.35, 142.41, 144.23, 190.36; Anal. Calcd for $C_{17}H_{15}ClO_2S$: C, 64.04; H, 4.74; S, 10.06. Found: C, 64.17; H, 4.86; S, 10.01.

4.3.9. (3*E*)-1-[(*RS*)-*p*-Tolylsulfinyl]-4-(1′-naphthyl)-3-butene-2-one 2h. R_f 0.35; mp 75–77 °C; 65% yield; IR (KBr, cm^{-1}): 3421, 3335, 3052, 2913, 1644, 1629, 1594, 1493, 1277, 1084, 1041, 978, 813, 732; ^1H NMR (300 MHz, $CDCl_3$) δ 2.27 (s, 3H), 4.01 (d, 1H, $J=13.20$ Hz), 4.13 (d, 1H, $J=13.20$ Hz), 6.69 (d, 1H, $J=15.95$ Hz), 7.20–8.31 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.82, 67.35, 123.39, 124.39, 124.47, 125.60, 125.69, 126.60, 127.42, 128.35, 129.03, 130.29, 131.35, 131.70, 131.81, 133.86, 142.43, 142.95, 190.50; Anal. Calcd for $C_{21}H_{18}O_2S$: C, 75.42; H, 5.42; S, 9.59. Found: C, 75.53; H, 5.54; S, 9.55.

4.3.10. (3*E*)-1-[(*RS*)-*p*-Tolylsulfinyl]-4-(2′-furyl)-3-buten-2-one 2i. R_f 0.30; mp 107–109 °C; 58% yield; IR (KBr, cm^{-1}): 3115, 2923, 1614, 1642, 1595, 1445, 1370, 1265, 1012, 974, 841, 700; ^1H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.93 (d, 1H, $J=13.20$ Hz), 4.10 (d, 1H, $J=13.20$ Hz), 6.48 (m, 1H), 6.60 (d, 1H, $J=15.67$ Hz), 6.70 (d, 1H, $J=3.58$ Hz), 7.25–7.31 (m, 3H), 7.49–7.56 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.78, 67.74, 113.08, 117.63, 123.11, 124.40, 130.21, 131.42, 141.10, 142.29, 145.90, 150.83, 190.07; Anal. Calcd for $C_{15}H_{14}O_2S$: C, 65.67; H, 5.14; S, 11.69. Found: C, 65.76; H, 5.32; S, 11.74.

4.4. Preparation of β-keto sulfides 3 from sulfoxides 2

4.4.1. General procedure.[16] To a suspension of the sulfoxides **2** (2 mmol) and sodium iodide (4 mmol) in acetone (20 mL) at 0 °C was added dropwise trifluoroacetic anhydride (4.8 mmol) at the same temperature with stirring. After 15 min, the solvent was evaporated under reduced pressure. To this, a 1:1 saturated solution of sodium sulfite and sodium bicarbonate was added, extracted with ether (3×15 mL). The combined organic layer was dried over anhydrous magnesium sulfate, filtered and evaporated in vacuo to dryness. The crude alkenyl β-hydroxy sulfides **3** obtained were further purified by a flash column chromatography on silica gel (230–400 mesh) using ethyl acetate/hexane (1/4) as the eluent.

4.4.2. 1-(*p*-Tolylsulfamyl)-4-methyl-3-penten-2-one 3a. R_f 0.56; oil; 93% yield; IR (neat, cm^{-1}): 3425, 2975, 2919, 1679, 1666, 1494, 1445, 1391, 1091, 1041, 804; ^1H NMR (300 MHz, $CDCl_3$) δ 1.90 (d, 3H, $J=1.37$ Hz), 2.11 (d, 3H, $J=1.10$ Hz), 2.30 (s, 3H), 3.59 (s, 2H), 6.26 (m, 1H), 7.06 (d, 2H, $J=8.53$ Hz), 7.22–7.25 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.29, 21.40, 28.20, 45.99, 122.06, 129.94, 130.64, 131.42, 137.06, 158.05, 194.72; Anal. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32; S, 14.55. Found: C, 70.85; H, 7.41; S, 14.57.

4.4.3. (3*E*)-1-(*p*-Tolylsulfamyl)-3-hepten-2-one 3b. R_f 0.47; oil; 91% yield; IR (neat, cm^{-1}): 3390, 3367, 2959, 2930, 2871, 1689, 1626, 1490, 1456, 1089, 1041, 806; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 3H, $J=7.43$ Hz), 1.47 (m, 2H), 2.18 (m, 2H), 2.30 (s, 3H), 3.70 (s, 2H), 6.28 (m, 1H), 6.84 (m, 1H), 7.07 (d, 2H, $J=7.70$ Hz), 7.24–7.27 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.04, 21.41, 21.62, 34.85, 43.54, 128.15, 130.01, 131.19, 137.45, 149.22, 194.27; Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74; S, 13.68. Found: C, 71.79; H, 7.81; S, 13.71.

4.4.4. 1-(*p*-Tolylsulfamyl)-3-cycloheptylidenyl-2-propanone 3c. R_f 0.70; oil; 95% yield; IR (neat, cm^{-1}): 3019, 2923, 2852, 1672, 1604, 1493, 443, 804; ^1H NMR (300 MHz, $CDCl_3$) δ 1.45–1.50 (m, 4H), 1.58–1.63 (m, 4H), 2.30 (s, 3H), 2.34–2.38 (m, 2H), 2.78–2.72 (m, 2H), 3.60 (s, 2H), 6.24 (s, 1H), 7.06 (d, 2H, $J=8.53$ Hz), 7.22–7.25 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.40, 26.67, 28.46, 29.55, 30.16, 33.44, 39.64, 46.07, 121.57, 129.91, 130.04, 130.72, 130.83, 137.03, 168.77, 194.61; Anal. Calcd for $C_{17}H_{22}OS$: C, 74.40; H, 8.08; S, 11.68. Found: C, 74.53; H, 8.29; S, 11.70.

4.4.5. 1-(*p*-Tolylsulfamyl)-2-(cyclohexen-1-yl)-2-ethanone 3d. R_f 0.69; oil; 92% yield; IR (neat, cm^{-1}): 3019, 2933, 2859, 1666, 1634, 1493, 1434, 1277, 1180, 806; ^1H NMR (300 MHz, $CDCl_3$) δ 1.56–1.64 (m, 4H), 2.20–2.24 (m, 4H), 2.31 (s, 3H), 3.91 (s, 2H) 6.80 (m, 1H), 7.01–7.08 (m, 2H), 7.24–7.27 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.42, 21.78, 22.22, 23.67, 26.53, 40.97, 129.92, 131.49, 131.85, 137.35, 138.30, 141.71, 195.46; Anal. Calcd for $C_{15}H_{18}OS$: C, 73.13; H, 7.36; S, 13.02. Found: C, 73.26; H, 7.54; S, 13.06.

4.4.6. (3*E*)-1-(*p*-Tolylsulfamyl)-4-phenyl-3-buten-2-one 3e. R_f 0.67; mp 39–41 °C; 92% yield; IR (KBr, cm^{-1}): 3391, 3058, 3025, 2919, 1683, 1608, 1575, 1494, 1331, 1204, 1073, 979, 808; ^1H NMR (300 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.79 (s, 2H), 6.95 (d, 1H, $J=15.95$ Hz), 7.07 (d, 2H, $J=7.98$ Hz), 7.27–7.58 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.44, 44.29, 123.89, 128.65, 129.10, 130.10, 130.83, 131.40, 134.55, 137.66, 144.05, 194.02; Anal. Calcd for $C_{17}H_{16}OS$: C, 76.08; H, 6.01; S, 11.95. Found: C, 76.25; H, 6.11; S, 11.90.

4.4.7. (3*E*)-1-(*p*-Tolylsulfamyl)-4-*p*-tolyl-3-buten-2-one 3f. R_f 0.56; mp 72–74 °C; 88% yield; IR (KBr, cm^{-1}): 3420, 3021, 2914, 2861, 1678, 1616, 1601, 1566, 1493, 1393, 1183, 1161, 1081, 983, 800; ^1H NMR (300 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.37 (s, 3H), 3.78 (s, 2H), 6.90 (d, 1H, $J=15.95$ Hz), 7.05–7.55 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.42, 21.88, 44.24, 122.95, 128.67, 129.84, 130.07, 131.35, 131.82, 133.95, 137.58, 141.38, 144.14, 194.13; Anal. Calcd for $C_{18}H_{18}OS$: C, 76.56; H, 6.42; S, 11.35. Found: C, 76.54; H, 6.46; S, 11.38.

4.4.8. (3*E*)-1-(*p*-Tolylsulfamyl)-4-(*p*-chlorophenyl)-3-buten-2-one 3g. R_f 0.47; mp 86–88 °C; 93% yield; IR (KBr, cm^{-1}): 3453, 2914, 2874, 1678, 1612, 1587, 1489, 1406, 1343, 1077, 1013, 981, 809; ^1H NMR (300 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.77 (s, 2H), 6.91 (d, 1H, $J=15.96$ Hz), 7.06–7.09 (m, 2H), 7.26–7.52 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.43, 44.33, 124.23, 129.39, 129.75, 130.12, 131.40, 133.06, 136.74, 137.74, 142.49, 193.72; Anal. Calcd for $C_{17}H_{15}ClOS$: C, 67.43; H, 4.99; S, 10.59. Found: C, 67.55; H, 5.05; S, 10.63.

4.4.9. (3*E*)-1-(*p*-Tolylsulfamyl)-4-(1′-naphthyl)-3-buten-2-one 3h. R_f 0.52; mp 62–64 °C; 92% yield; IR (KBr, cm^{-1}): 3025, 2919, 1683, 1656, 1652, 1576, 1494, 1131, 1073, 807, 689; ^1H NMR (300 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.85 (s, 2H), 7.05–7.11 (m, 2H), 7.30–7.52 (m, 6H), 7.75–7.90 (m, 3H), 8.11–8.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.46, 44.40, 123.52, 125.40, 125.61, 126.29, 126.46, 127.15, 128.96, 129.09, 129.92, 130.15, 131.12, 131.43, 131.85, 133.89, 133.97, 140.84, 193.98; Anal. Calcd for $C_{21}H_{18}OS$: C, 79.21; H, 5.70; S, 10.07. Found: C, 79.32; H, 5.89; S, 10.13.

4.4.10. (3*E*)-1-(*p*-Tolylsulfamyl)-4-(2′-furyl)-3-buten-2-one 3i. R_f 0.56; oil; 90% yield; IR (neat, cm^{-1}): 3483, 3124, 3021, 2920, 1674, 1606, 1553, 1493, 1389, 1281, 1264, 1082, 1071, 807; ^1H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.74 (s, 2H), 6.45 (m, 1H), 6.63 (d, 1H, $J=3.58$ Hz), 6.86 (d, 1H, $J=15.40$ Hz), 7.06 (d, 2H, $J=8.53$ Hz), 7.25–7.47 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.43, 44.40, 112.84, 116.45, 121.24, 130.02, 130.06, 130.91, 131.14, 133.86, 137.48, 145.28, 151.25, 193.67; Anal. Calcd for

$C_{15}H_{14}O_2S$: C, 69.74; H, 5.46; S, 12.41. Found: C, 69.77; H, 5.54; S, 12.48.

4.5. Preparation of optically active alkenyl β-hydroxy sulfides 4

4.5.1. General procedure. To a solution of **5** (0.2 mmol; 0.2 M, 1.0 mL) in THF was added a solution of *N*-ethyl-*N*-isopropylaniline–borane complex **6** (1.0 mmol; 2.0 M, 0.5 mL) in THF. To this was added slowly 2.5 mL of THF solution of **3** (2 mmol) over a period of 1.5 h using a syringe pump at 0 °C. After the addition, the reaction mixture was stirred for 10 min, quenched cautiously with methanol (0.5 mL), and stirred for additional 30 min. The solvent was evaporated under reduced pressure. The crude alkenyl β-hydroxy sulfides **4** obtained were further purified by a flash column chromatography on silica gel (230–400 mesh) using ethyl acetate/hexane (1/4) as the eluent. The enantiomeric excesses of **4** were determined by HPLC analysis using a 25 cm Chiralcel OD-H or Whelk-O1 chiral column. Absolute configurations were assigned by comparison of the literature values reported or analogy based on the elution order of HPLC analysis and/or the sign of the optical rotation values compared to those of the *p*-tolyl- or phenylsulfamyl analogues published.[14]

4.5.2. (2*S*)-1-(*p*-Tolylsulfamyl)-4-methyl-3-penten-2-ol 4a. R_f 0.33; oil; 93% yield; IR (neat, cm^{-1}): 3395, 3373, 2969, 2919, 2869, 1493, 1376, 1091, 1017, 982, 804; ^1H NMR (300 MHz, $CDCl_3$) δ 1.53 (d, 3H, $J=1.1$ Hz), 1.64 (d, 3H, $J=1.1$ Hz), 2.24 (s, 3H), 2.27 (d, 1H, $J=2.48$ Hz), 2.80 (dd, 1H, $J=13.62$, 8.66 Hz), 2.97 (dd, 1H, $J=13.48$, 4.13 Hz), 4.30 (m, 1H), 5.10 (m, 1H), 7.00–7.23 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.71, 21.39, 26.12, 42.91, 66.77, 125.68, 129.97, 130.81, 131.61, 136.89; Anal. Calcd for $C_{13}H_{18}OS$: C, 70.22; H, 8.16; S, 14.42. Found: C, 70.25; H, 8.27; S, 14.38; $[\alpha]_D^{20}$ −10.05 (*c* 1.51, $CHCl_3$), *S*; HPLC analysis using a 25 cm Chiralcel OD-H chiral column (*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm) showed it to be 90% ee (t_R(*S*) 5.62 min and t_R(*R*) 6.47 min).

4.5.3. (2*S*, 3*E*)-1-(*p*-Tolylsulfamyl)-3-hepten-2-ol 4b. R_f 0.35; oil; 95% yield; IR (neat, cm^{-1}): 3363, 3356, 2957, 2925, 2870, 1493, 1399, 1090, 1025, 1015, 969, 806; ^1H NMR (300 MHz, $CDCl_3$) δ) δ 0.89 (t, 3H, $J=7.43$ Hz), 1.38 (m, 2H), 1.99 (m, 2H), 2.31 (s, 3H), 2.43 (d, 1H, $J=3.03$ Hz), 2.88 (dd, 1H, $J=13.48$, 8.53 Hz), 3.08 (dd, 1H, $J=13.62$, 3.99 Hz), 4.10 (m, 1H), 5.44 (m, 1H), 5.68 (m, 1H), 7.08–7.10 (m, 2H), 7.23–7.30 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.01, 21.37, 22.49, 34.62, 43.31, 70.53, 129.99, 130.57, 131.14, 131.53, 133.51, 137.04; Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53; S, 13.57. Found: C, 71.17; H, 8.55; S, 13.60; $[\alpha]_D^{20}$ −1.71 (*c* 1.04, $CHCl_3$), *S*; HPLC analysis using a 25 cm Chiralcel OD-H chiral column (*iso*-PrOH/hexane: 1/9; flow rate: 0.3 mL/min; detector: 254 nm) showed it to be 90% ee (t_R(*S*) 17.69 min and t_R(*R*) 18.74 min).

4.5.4. (2*S*)-1-(*p*-Tolylsulfamyl)-3-cycloheptylidenyl-2-propanol 4c. R_f 0.49; oil; 97% yield; IR (neat, cm^{-1}): 3394, 3355. 2921, 2851, 1493, 1435, 1091, 1042, 1017, 986, 803; ^1H NMR (300 MHz, $CDCl_3$) δ 1.47–1.56 (m, 8H), 2.17–2.22 (m, 4H), 2.32 (s, 3H), 2.88 (dd, 1H, $J=13.62$, 8.67 Hz), 3.05 (dd, 1H, $J=13.48$, 4.13 Hz), 4.38 (m, 1H), 5.17 (m, 1H), 7.08 (d, 2H, $J=7.01$ Hz), 7.24–7.23 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.38, 27.59, 29.09, 29.2, 29.95, 30.61, 38.11, 42.94, 66.37, 125.76, 129.95, 130.70, 131.73, 136.83, 146.35; Anal. Calcd for $C_{17}H_{24}OS$: C, 73.86; H, 8.75; S, 11.60. Found: C, 73.90; H, 8.89; S, 11.59; $[\alpha]_D^{20}$ −0.61 (*c* 0.8, $CHCl_3$), *S*; HPLC analysis using a 25 cm Chiralcel OD-H chiral column (*iso*-PrOH/hexane: 1/9; flow rate: 0.3 mL/min; detector: 254 nm) showed it to be 90% ee (t_R(*S*) 18.86 min and t_R(*R*) 20.17 min).

4.5.5. (2*S*)-1-(*p*-Tolylsulfamyl)-2-(cyclohexen-1-yl)-2-ethanol 4d. R_f 0.33; oil; 95% yield; IR (neat, cm^{-1}): 3373, 3364, 2921, 2850, 1493, 1445, 1360, 1240, 1091, 1042, 1017, 974, 802; ^1H NMR (300 MHz, $CDCl_3$) δ 1.07–1.28 (m, 4H), 1.71–1.91 (m, 4H), 2.31 (s, 3H), 2.98 (dd, 1H, $J=13.34$, 7.56 Hz), 3.05 (dd, 1H, $J=13.48$, 3.85 Hz), 3.83 (m, 1H), 4.63 (s, 1H), 7.07 (d, 2H, $J=7.71$ Hz), 7.24–7.23 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.39, 22.80, 22.87, 24.27, 25.31, 41.64, 73.72, 124.42, 129.96, 131.02, 131.61, 136.94, 137.88; Anal. Calcd for $C_{15}H_{20}OS$: C, 72.53; H, 8.12; S, 12.91. Found: C, 72.66; H, 8.34; S, 11.45; $[\alpha]_D^{20}$ −6.92 (*c* 2.01, $CHCl_3$), *S*; HPLC analysis using a 25 cm Chiralcel OD-H chiral column (*iso*-PrOH/hexane: 1/9; flow rate: 0.3 mL/min; detector: 254 nm) showed it to be 95% ee (t_R(*S*) 21.68 min and t_R(*R*) 23.14 min).

4.5.6. (2*S*,3*E*)-1-(*p*-Tolylsulfamyl)-4-phenyl-3-buten-2-ol 4e. R_f 0.35; oil; 97% yield; IR (neat, cm^{-1}): 3395, 3373, 3057, 3024, 2960, 2919, 1493, 1448, 1399, 1091, 1017, 966, 805, 750, 692; ^1H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.64 (d, 1H, $J=3.03$ Hz), 2.97 (dd, 1H, $J=13.62$, 8.40 Hz), 3.18 (dd, 1H, $J=13.62$, 3.99 Hz), 4.33 (m, 1H), 6.16 (dd, 1H, $J=15.68$, 6.33 Hz), 6.60 (d, 1H, $J=15.95$ Hz), 7.09–7.34 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.43, 43.31, 70.50, 126.72, 127.99, 128.73, 129.84, 130.12, 131.17, 131.42, 131.53, 136.59, 137.34; Anal. Calcd for $C_{17}H_{18}OS$: C, 75.51; H, 6.71; S, 11.86. Found: C, 75.57; H, 6.97; S, 11.90; $[\alpha]_D^{20}$ −92.33 (*c* 0.50, $CHCl_3$), *S*; HPLC analysis using a 25 cm Whelk-O1 chiral column (*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm) showed it to be 98% ee (t_R(*S*) 7.21 min and t_R(*R*) 8.78 min).

4.5.7. (2*S*,3*E*)-1-(*p*-Tolylsulfamyl)-4-*p*-tolyl-3-buten-2-ol 4f. R_f 0.37; oil; 98% yield; IR (neat, cm^{-1}): 3405, 3381, 3020, 2919, 1493, 1446, 1410, 1091, 1017, 968, 802; ^1H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 6H), 2.59 (d, 1H, $J=3.03$ Hz), 2.97 (dd, 1H, $J=13.75$, 8.53 Hz), 3.18 (dd, 1H, $J=13.75$, 4.13 Hz), 4.31 (m, 1H), 6.10 (dd, 1H, $J=15.95$, 6.33 Hz), 6.56 (d, 1H, $J=15.68$ Hz), 7.07–7.34 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.40, 21.56, 43.33, 70.63, 126.62, 128.81, 129.42, 130.08, 131.29, 131.36, 131.50, 133.82, 137.26, 137.84; Anal. Calcd for $C_{18}H_{20}OS$: C, 76.01; H, 7.09; S, 11.27. Found: C, 76.23; H, 7.26; S, 11.35; $[\alpha]_D^{20}$ −114.12 (*c* 0.72, $CHCl_3$), *S*; HPLC analysis using a 25 cm Chiralcel OD-H chiral column (*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm) showed it to be 98% ee (t_R(*S*) 10.10 min and t_R(*R*) 14.80 min).

4.5.8. (2*S*,3*E*)-1-(*p*-Tolylsulfamyl)-4-(*p*-chlorophenyl)-3-buten-2-ol 4g. R_f 0.34; oil; 98% yield; IR (neat, cm^{-1}): 3452, 3425, 2921, 1495, 1410, 1301, 1148, 1089, 1037,

1015, 959, 811, 760; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.64 (d, 1H, J=3.03 Hz), 2.97 (dd, 1H, J=13.62, 8.40 Hz), 3.17 (dd, 1H, J=13.75, 4.13 Hz), 4.31 (m, 1H), 6.12 (dd, 1H, J=15.68, 6.05 Hz), 6.55 (dd, 1H, J=15.95, 1.38 Hz), 7.08–7.33 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.40, 43.28, 70.36, 127.90, 128.88, 130.12, 130.20, 130.57, 131.46, 133.60, 135.14, 137.41; Anal. Calcd for $C_{17}H_{17}ClOS$: C, 66.98; H, 5.62; S, 11.63. Found: C, 67.15; H, 5.65; S, 11.73; $[\alpha]_D^{20}$ −110.51 (*c* 1.11, $CHCl_3$), *S*; HPLC analysis using a 25 cm Whelk-O1 chiral column (*iso*-PrOH/hexane: 1/9; flow rate: 0.5 mL/min; detector: 254 nm) showed it to be 98% ee (t_R(*S*) 11.91 min and t_R(*R*) 13.57 min).

4.5.9. (2*S*,3*E*)-1-(*p*-Tolylsulfamyl)-4-(1-naphthyl)-3-buten-2-ol 4h. R_f 0.36; oil; 99% yield; IR (neat, cm^{-1}): 3394, 3374, 3055, 3043, 2918, 1493, 1396, 1091, 1016, 969, 797, 775; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.73 (d, 1H, J=3.30 Hz), 3.06 (dd, 1H, J=13.48, 8.25 Hz), 3.25 (dd, 1H, J=13.62, 4.26 Hz), 4.45 (m, 1H), 6.19 (dd, 1H, J=15.68, 6.05 Hz), 7.11 (d, 2H, J=7.70 Hz), 7.34–8.07 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.43, 43.37, 70.70, 123.97, 124.14, 125.72, 125.97, 126.24, 128.30, 128.69, 130.15, 131.26, 131.32, 131.47, 133.14, 133.75, 134.41, 137.36; Anal. Calcd for $C_{21}H_{20}OS$: C, 78.71; H, 6.29; S, 10.01. Found: C, 78.78; H, 6.44; S, 9.90; $[\alpha]_D^{20}$ −64.93 (*c* 5.51, $CHCl_3$), *S*; HPLC analysis using a 25 cm Chiralcel OD-H chiral column (*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm) showed it to be 96% ee (t_R(*S*) 19.01 min and t_R(*R*) 29.81 min).

4.5.10. (2*S*,3*E*)-1-(*p*-Tolylsulfamyl)-4-(2′-furyl)-3-buten-2-ol 4i. R_f 0.31; oil; 95% yield; IR (neat, cm^{-1}): 3394, 3373, 2920, 1493, 1398, 1091, 1014, 962, 805, 737; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.59 (d, 1H, J=3.30 Hz), 2.93 (dd, 1H, J=13.75, 8.53 Hz), 3.16 (dd, 1H, J=13.62, 3.99 Hz), 4.28 (m, 1H), 6.10 (dd, 1H, J=15.82, 6.05 Hz), 6.21 (d, 1H, J=3.30 Hz), 6.44 (dd, 1H, J=15.48, 1.38 Hz), 6.33 (dd, 1H, J=3.30, 1.65 Hz), 7.07–7.32 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.40, 43.30, 69.99, 108.61, 111.50, 119.65, 128.36, 130.08, 131.16, 131.38, 137.31, 142.26, 152.33; Anal. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19; S, 12.32. Found: C, 69.34; H, 6.32; S, 12.08; $[\alpha]_D^{20}$ −97.35 (*c* 1.13, $CHCl_3$), *S*; HPLC analysis using a 25 cm Chiralceli OD-H chiral column (*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm) showed it to be 97% ee (t_R(*S*) 10.01 min and t_R(*R*) 11.37 min).

4.6. Preparation of alkenyl diols 9 and 10

4.6.1. General procedure. To a solution of **4d** or **4e** (2 mmol) in dichloromethane (10 mL) was added dropwise a solution of *m*-chloroperbenzoic acid (2.2 mmol) in dichloromethane (15 mL) for 10 min at 0 °C. After the mixture was stirred for 30 min at room temperature, organic layer was separated, washed with 2 N NaOH (2×10 mL) and brine (2×10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated to give **7**, which could be used for the following reaction without further purification. A stirred mixture of **7** and NaOAc (5 mmol) in acetic anhydride (6 mL) was heated to reflux for 3 h. After excess of acetic anhydride and acetic acid were removed under reduced pressure, the residue was dissolved in ether (10 mL) and passed through silica gel. Crude 1,2-diacetoxy sulfides **8** obtained from the evaporation of the solvent followed by drying under vacuum were dissolved in ethanol (10 mL). To this was added $NaBH_4$ (3 mmol) in 6 N NaOH (1 mL) and stirred for 4 h at room temperature. After the reaction mixture was extracted with ether (3×10 mL), the combined extracts are concentrated to give **9** or **10**, which was further purified by a flash column chromatography on silica gel (230–400 mesh) using ethyl acetate/hexane (1/1) as the eluent.

4.6.2. (*S*)-1-(Cyclohexen-1-yl)-1,2-ethanediol 9 from 4d. R_f 0.17; mp 68–70 °C (lit.[18] 72–73 °C; 65% yield; IR (KBr, cm^{-1}): 3277, 3252, 2950, 2915, 2873, 1447, 1078, 1054; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55–1.68 (m, 4H), 1.87–2.17 (m, 4H), 3.52–3.63 (m, 2H), 4.08 (m, 1H), 5.75 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.82, 22.90, 25.20, 25.27, 65.67, 76.48, 124.21, 136.77; Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92; S, 11.86. Found: C, 67.53; H, 9.95; $[\alpha]_D^{20}$ +28.2 (*c* 0.50, $CHCl_3$), >95% ee with (*S*)-configuration based on $[\alpha]_D^{20}$ −28.1 (*c* 1.02, $CHCl_3$), >95% ee for (*R*)-**9**.[17]

4.6.3. (2*S*,3*E*)-4-Phenyl-1,2-butenediol 8 from 4e. R_f 0.14; mp 49–51 °C; 60% yield; IR (KBr, cm^{-1}): 3424, 3387, 2948, 2910, 2876, 1447, 1079, 1042; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.57–3.77 (m, 2H), 4.44 (m, 1H), 6.19 (dd, 1H, J=15.95, 6.23 Hz), 6.68 (dd, 1H, J=15.95, 0.83 Hz), 7.24–7.39 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 66.77, 73.51, 126.72, 127.83, 128.15, 128.82, 133.5, 136.43; Anal. Calcd for $C_{10}H_{12}OS$: C, 73.15; H, 7.37. Found: C, 73.09; H, 7.49; $[\alpha]_D^{20}$ +34.1 (*c* 0.50, $CHCl_3$), *S* {lit.[19] $[\alpha]_D^{26}$ +34.92 (*c* 0.87, $CHCl_3$) for (*S*)-**10**}; HPLC analysis using a 25 cm Chiralcel OD-H chiral column (*iso*-PrOH/hexane: 1/9; flow rate: 0.5 mL/min; detector: 254 nm) showed it to be 98% ee (t_R(*S*) 16.63 min and t_R(*R*) 19.07 min).

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