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Highly efficient synthesis of chiral β-hydroxy sulfides with high enantiomeric purity via CBS-oxazaborolidine-catalyzed borane reduction

Byung Tae Cho,* Ok Kyoung Choi and Dong Jun Kim

Department of Chemistry, Hallym University, Chunchon 200-702, South Korea

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Abstract—A simple and efficient synthesis of chiral β-hydroxy *p*-tolylsulfides with high enantiomeric purity by CBS-oxazaborolidine-catalyzed asymmetric borane reduction of β-keto *p*-tolylsulfides using *N*-ethyl-*N*-isopropylaniline–borane complex as the borane carrier is reported.

1. Introduction

Enantiopure β-hydroxy sulfides are widely used as intermediates in the synthesis of chiral oxiranes,[1] aziridines,[2] thiiranes,[3] tetrahydrofurans[4] and β-hydroxy esters.[5] Moreover, they are easily oxidized to β-hydroxy sulfoxides[6a,b] or sulfones[7] which serve as extremely useful chiral building blocks for the synthesis of a variety of chiral organic compounds, such as chiral oxiranes,[6c,d] allylic alcohols,[6e,f,7a] lactones,[6g,7b–e] macrolides,[6h–l] pheromones,[6m–o] and tetrahydrofurans[7f] because the α-carbon atom of sulfenyl or sulfonyl groups of the compounds can be further functionalized by the formation of sulfur-stabilized carbanions.[8] For the synthesis of β-hydroxy sulfides, only biological methods,[9] such as asymmetric reduction of β-keto sulfides using bakers' yeast,[1c,5,10] and lipase-mediated kinetic resolution of racemic β-hydroxy sulfides,[11] have been presented. However, despite providing high enantioselectivity, such biological methods suffer from the disadvantage of affording the products in low chemical yields. In recent years, a number of stoichiometric and catalytic asymmetric reducing agents which give high enantioselectivities for ketone reduction have been reported.[12] Although asymmetric reduction of β-keto sulfides using these chiral reducing agents is expected to be one of the most convenient methods for the preparation of optically active β-hydroxy sulfides, to our knowledge, there have been no reports of such reductions. Therefore, as part of our ongoing programs on the asymmetric reduction of various α-functionalized ketones using chiral reducing agents,[13] we undertook a study into CBS–oxazaborolidine-catalyzed asymmetric borane reduction of β-keto sulfides. We report herein a highly efficient synthesis of optically active β-hydroxy sulfides with high enantiomeric purity using this methodology.

2. Results and discussion

We selected commercially available CBS–oxazaborolidine reagent **1**[14] and *N*-ethyl-*N*-isopropylaniline–borane complex **2** as a representative catalyst and borane carrier, respectively, because **1** consistently provided the best enantioselectivity[12c] and **2** proved to be more useful than borane–THF and borane–dimethylsulfide as borane carriers for oxazaborolidine-catalyzed asymmetric borane reduction of various α-functionalized ketones.[13b–f] The reduction was carried out by slow addition of β-keto sulfides **3** over 1.5 h to a solution of 1.0 equiv. of the reagent **2** in the presence of 10 mol% of **1** in THF at 25°C (Scheme 1). As shown in Table 1, all of the reductions examined afforded the corresponding β-hydroxy sulfides **4** within 10 min in near quantitative yields. Their enantiomeric purities were determined by HPLC analysis using Whelk-O1, Chiralcel OD or OD-H chiral column. We first examined the influence of different substituents on sulfur (R′ = *n*-Bu, *t*-Bu, Ph and *p*-tolyl) on the enantioselectivity for the reduction of α-sulfanylacetophenone derivatives **3a–d**. Among them, the reduction of **3d** bearing a *p*-tolylsulfanyl

* Corresponding author. E-mail: btcho@hallym.ac.kr

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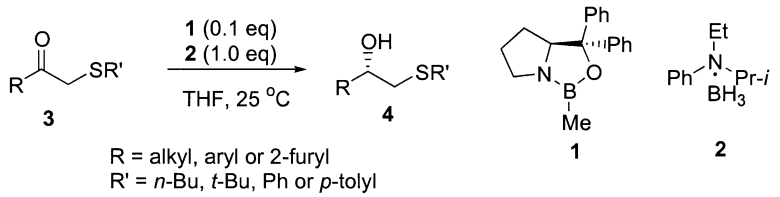

Scheme 1.

Table 1. Asymmetric reduction of β-keto sulfides **3** in the presence of 0.1 equiv. of **1** with 1.0 equiv. of **2** in THF at 25°C[a]

Entry	Optically active β-hydroxy sulfides **4**						
	Cpd	R	R′	Yield[b] (%)	$[\alpha]_D^{22}$ in $CHCl_3$	% e.e.[c]	Config.[f]
1	**4a**	Ph	*n*-Bu	94	+62.6 (*c* 1.33)	92	*S*
2	**4b**	Ph	*t*-Bu	91	+53.8 (*c* 1.08)	78	*S*
3	**4c**	Ph	Ph	98	−11.5 (*c* 1.00)	97	*S*[g]
4	**4d**	Ph	*p*-Tolyl	98	−17.1 (*c* 1.16)	99	*S*[h]
5	**4e**	*p*-Tolyl	*p*-Tolyl	97	−30.6 (*c* 1.20)	99	*S*
6	**4f**	*p*-$MeOC_6H_4$	*p*-Tolyl	98	−40.1 (*c* 1.00)	99	*S*
7	**4g**	*m*-ClC_6H_4	*p*-Tolyl	97	−30.3 (*c* 1.13)	>99	*S*
8	**4h**	*p*-ClC_6H_4	*p*-Tolyl	98	−45.1 (*c* 1.03)	>99	*S*
9	**4i**	*p*-FC_6H_4	*p*-Tolyl	98	−13.1 (*c* 1.15)	>99	*S*
10	**4j**	*p*-$NO_2C_6H_4$	*p*-Tolyl	97	−80.9 (*c* 1.12)	>99	*S*
11	**4k**	2-Naphthyl	*p*-Tolyl	98	−69.3 (*c* 1.37)	99	*S*
12	**4l**	2-Furyl	*p*-Tolyl	99	−30.4 (*c* 2.27)	97	*S*
13	**4m**	Et	Ph	96	+45.8 (*c* 1.60)	73[d]	*S*[i]
14	**4n**	Et	*p*-Tolyl	96	+44.0 (*c* 1.51)	74[d]	*S*
15	**4o**	*n*-Pentyl	*p*-Tolyl	98	+34.8 (*c* 1.02)	74	*S*
16	**4p**	*i*-Pr	*p*-Tolyl	97	+80.0 (*c* 1.35)	88[e]	*S*
17	**4q**	*i*-Bu	*p*-Tolyl	97	+34.1 (*c* 1.17)	81[d]	*S*
18	**4r**	*t*-Bu	*p*-Tolyl	98	+117.8 (*c* 1.34)	99[d]	*S*
19	**4s**	*c*-Hex	*p*-Tolyl	97	+54.9 (*c* 1.05)	99	*S*

[a] [**3**] = 0.5 M. The reduction was complete within 10 min to give the β-hydroxy sulfides **4**.
[b] Isolated and purified yields.
[c] Determined by HPLC analysis using a 25 cm Whelk-O1 chiral column, unless otherwise indicated.
[d] Determined by HPLC analysis using a 25 cm Chiralcel OD-H chiral column.
[e] Determined by HPLC analysis of its sulfone obtained by oxidation using a 25 cm Chiralcel OD chiral column.
[f] Absolute configuration except for **4c**,**d** and **4m** is unknown, but probably *S* based on comparison of the elution order of HPLC analysis and/or the sign of the specific rotation value with those of the *p*-tolyl- or phenylsulfanyl analogues **4c**, **4d** and **4m** reported: Refs. 2, 16 and 17.
[g] Based on $[\alpha]_D^{20}$ −12.5 (*c* 13.9, $CHCl_3$), *S*, 100% e.e.: Ref. 16.
[h] Based on $[\alpha]_D^{19}$ +20 (*c* 0.276, $CHCl_3$), *R*: Ref. 2.
[i] Based on $[\alpha]_D$ +64.3 (*c* 1.0, $CHCl_3$), *S*, >98% e.e.: Ref. 17.

group afforded the best result to give **4d** in 99% e.e. Compounds with aliphatic sulfanyl groups were reduced with somewhat lower enantioselectivity. The reduction of other aromatic β-keto sulfides **3e**–**k** bearing *m*- and *p*-substituted phenyl (*m*-XC_6H_4; X = Cl and *p*-XC_6H_4; X = Me, MeO, F, Cl and NO_2) and 2-naphthyl groups furnished the corresponding β-hydroxy sulfides **4e**–**k** with very high enantioselectivity approaching 100% e.e. Inductive effects from the substituent groups of the phenyl ring on the enantioselectivity were not observed (entries 4–11). Also, the same reduction of a heterocyclic analogue having a 2-furyl group provided high enantioselectivity (entry 12). For aliphatic analogues, the reduction of more hindered β-keto *p*-tolylsulfides bearing branched alkyl groups such as *tert*-butyl and cyclohexyl groups gave very high enantioselectivity (99% e.e.), whereas in the case of unhindered β-keto sulfides containing unbranched alkyl groups such as ethyl and *n*-pentyl groups provided 74% e.e. (entries 18 and 19 versus 14 and 15). The reduction of aliphatic analogues having isopropyl and isobutyl groups afforded e.e.s of 88 and 81%, respectively (entries 16 and 17). It is a general phenomenon in the oxazaborolidine-catalyzed borane reduction that a large difference in the steric bulk between the two substituents adjacent to the carbonyl leads to high enantioselectivity. All of the product β-hydroxy sulfides **4** obtained are consistently enriched in the (*S*)-enantiomer. The stereochemical course can be explained by the generally accepted mechanism for oxazaborolidine-catalyzed borane reduction,[12f] where the β-keto sulfides **3** are attacked by hydride on their *Re* faces to provide (*S*)-**4** (Fig. 1).[15] On the basis of the proposed mechanism, it is an interesting observation that the ethyl group acts unusually as the more bulky group than the phenylthiomethyl or *p*-tolylthiomethyl groups in the reduction of **3m** and **3n** to give products **4m** and **4n** with (*S*)-configuration (entries 14 and 15). Such

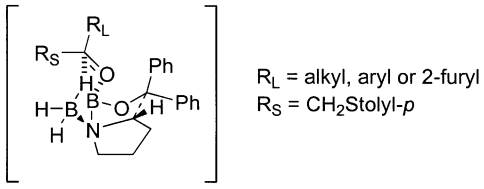

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Figure 1.

unusual phenomena have also been observed in other CBS–oxazaborolidine-catalyzed borane reductions of α-functionalized ketones such as β-keto *p*-tolylsulfones,[13a] α-sulfonyloxy ketones,[13c] α-siloxy ketones,[13f] α-(2-tetrahydropyranyloxy)ketones[13d] and α-keto acetals,[13e] although the reason is so far unclear.

3. Conclusion

We have established a simple and efficient synthetic method for optically active β-hydroxy *p*-tolylsulfides with high enantiomeric purity which can be widely used as starting materials, chiral building blocks, ligands and intermediates for preparation of numerous optically active substances by employing CBS–oxazaborolidine-catalyzed asymmetric borane reduction of the corresponding β-keto sulfides using *N*-ethyl-*N*-isopropylaniline–borane complex as the borane carrier. The reduction provided almost enantiopure β-hydroxy *p*-tolylsulfides in both aromatic and more hindered aliphatic analogues. This is the first example of the synthesis of such compounds by chemical methods. Further work to extend the scope of this methodology is in progress and will be reported in due course.

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 200 or 400 MHz for ^{1}H and 50 or 100 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 are uncorrected. Enantiomeric excesses (e.e.s) of the product β-hydroxy sulfides were determined with a HPLC apparatus fitted with a 25 cm Whelk-O1 (Regis), Chiralcel OD, or Chiralcel OD-H (Daicel) chiral column.

4.2. Materials

Most of the organic compounds utilized in this study were commercial products of the highest purity. They were further purified by distillation where necessary. THF was distilled over sodium benzophenone ketyl and stored in ampoules under nitrogen atmosphere. The CBS reagent **1** and *N*-ethyl-*N*-isopropylaniline–borane complex **2** were purchased from the Aldrich Chemical Company. β-Keto *p*-tolylsulfides **3** were prepared by reaction of 2-halo-1-arylethanones with the corresponding sodium alkyl or arylthiolates according to the known procedure.[10a]

4.3. General procedure for CBS–oxazaborolidine-catalyzed borane reduction of β-keto sulfides 3

To a solution of **1** (0.2 mmol; 0.2 M, 1.0 mL) in THF was added a solution of *N*-ethyl-*N*-isopropylaniline–borane complex **2** (2.0 mmol; 2.0 M, 1.0 mL) in THF. To this mixture was added slowly a THF solution of **3** (1 M, 2 mL, 2 mmol) over a period of 1.5 h using a syringe pump at 25°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 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) (eluent A), ethyl acetate/hexane (1/2) (eluent B) or ether/petroleum ether (1/9) (eluent C) as the eluent. The enantiomeric excesses of **4** were determined by HPLC analysis using Whelk-O1, Chiralcel OD, or Chiralcel OD-H chiral column. Absolute configurations were assigned by comparison of the values reported in the literature or analogy based on the elution order of HPLC analysis and/or the sign of the specific rotation values compared to those of the *p*-tolyl- or phenylsulfanyl analogues published.

4.3.1. (*S*)-(+)-2-(*n*-Butylsulfanyl)-1-phenylethanol 4a. R_f 0.46 (eluent A); oil; 94% yield; IR (neat, cm^{-1}): 3420, 2928, 1452, 1053, 697; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, 3H, $J=7.3$ Hz), 1.42 (m, 2H), 1.59 (m, 2H), 2.54 (t, 2H, $J=7.3$ Hz), 2.71 (dd, 1H, $J=13.8$, 9.5 Hz), 2.92 (dd, 1H, $J=13.8$, 3.6 Hz), 3.03 (d, 1H, $J=2.5$ Hz), 4.73 (ddd, 1H, $J=9.4$, 3.6, 2.4 Hz), 7.28 (m, 1H), 7.33–7.38 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.62, 21.90, 31.71, 31.79, 42.10, 71.54, 125.75, 127.78, 128.47, 142.53. Anal. calcd for $C_{12}H_{18}OS$: C, 68.52; H, 8.63; S, 15.25. Found: C, 68.46; H, 8.67; S, 15.21%; $[\alpha]_D^{22}$ +62.6 (*c* 1.33, $CHCl_3$), *S*; HPLC analysis using a Whelk-O1 chiral column [*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm] showed it to be 92% e.e. [$t_R(S)$ 4.45 min and $t_R(R)$ 5.15 min].

4.3.2. (*S*)-(+)-2-(*tert*-Butylsulfanyl)-1-phenylethanol 4b. R_f 0.44 (eluent A); oil; 91% yield; IR (neat, cm^{-1}): 3413, 2929, 1455, 1364, 1162, 1056, 696; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (s, 9H), 2.78 (dd, 1H, $J=13.0$, 9.5 Hz), 2.92 (br s, 1H), 2.97 (dd, 1H, $J=13.0$ and 3.7 Hz), 4.74 (dd, 1H, $J=9.5$, 3.6 Hz), 7.29 (m, 1H), 7.34–7.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.10, 38.72, 42.73, 72.44, 125.70, 127.80, 128.48, 142.81. Anal. calcd for $C_{12}H_{18}OS$: C, 68.52; H, 8.63; S, 15.25. Found: C, 68.59; H, 8.74; S, 15.35%; $[\alpha]_D^{22}$ +53.8 (*c* 1.08, $CHCl_3$), *S*; HPLC analysis using a Whelk-O1 chiral column [*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector:

254 nm] showed it to be 78% e.e. [$t_R(S)$ 4.38 min and $t_R(R)$ 4.86 min].

4.3.3. (*S*)-(−)-2-(Phenylsulfanyl)-1-phenylethanol 4c. R_f 0.56 (eluent B); oil; 98% yield; IR (neat, cm^{-1}): 3415, 3061, 1583, 1492, 1053, 738, 694; ^1H NMR (200 MHz, $CDCl_3$) δ 2.87 (d, 1H, $J=2.4$ Hz), 3.08 (dd, 1H, $J=13.9$, 9.6 Hz), 3.34 (dd, 2H, $J=13.9$, 3.4 Hz), 4.72 (m, 1H), 7.26–7.46 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 44.70, 72.26, 126.54, 127.52, 128.71, 129.27, 129.86, 130.93, 135.48, 142.79. Anal. calcd for $C_{14}H_{14}OS$: C, 73.01; H, 6.13; S, 13.92. Found: C, 72.95; H, 6.09; S, 13.87%; $[\alpha]_D^{22}$ −11.5 (*c* 1.0, $CHCl_3$), *S*; {lit.[16] $[\alpha]_D^{20}$ −12.5 (*c* 13.9, $CHCl_3$), *S*, 100% e.e.}; HPLC analysis using a Whelk-O1 chiral column [*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm] showed it to be 97% e.e. [$t_R(S)$ 5.29 min and $t_R(R)$ 6.49 min].

4.3.4. (*S*)-(−)-2-(*p*-Tolylsulfanyl)-1-phenylethanol 4d. R_f 0.55 (eluent B); oil; 98% yield; IR (neat, cm^{-1}): 3420, 1510, 1452, 1054, 803, 697; ^1H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.61 (d, 1H, $J=2.4$ Hz), 3.03 (dd, 1H, $J=13.9$, 9.6 Hz), 3.27 (dd, 2H, $J=13.9$, 3.1 Hz), 4.67 (ddd, 1H, $J=9.6$, 3.1, 2.6 Hz), 7.12 (d, 2H, $J=8.0$ Hz), 7.24–7.30 (m, 1H), 7.32–7.34 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.02, 44.82, 71.47, 125.83, 125.84, 127.88, 128.49, 129.92, 130.93, 131.05, 137.10, 142.16. Anal. calcd for $C_{15}H_{16}OS$: C, 73.73; H, 6.60; S, 13.12. Found: C, 73.91; H, 6.69; S, 13.23%; $[\alpha]_D^{22}$ −17.13 (*c* 1.16, $CHCl_3$), *S*; {lit.[2] $[\alpha]_D^{19}$ +20 (*c* 0.276, $CHCl_3$), *R*}; HPLC analysis using a Whelk-O1 chiral column [*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm] showed it to be 99% e.e. [$t_R(S)$ 6.13 min and $t_R(R)$ 7.92 min].

4.3.5. (*S*)-(−)-2-(*p*-Tolylsulfanyl)-1-*p*-tolylethanol 4e. R_f 0.24 (eluent C); oil; 97% yield; IR (neat, cm^{-1}): 3415, 2866, 1513, 1055, 804; ^1H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 6H), 2.83 (d, 1H, $J=2.3$ Hz), 3.03 (dd, 1H, $J=13.4$, 9.5 Hz), 3.25 (dd, 1H, $J=13.6$, 3.5 Hz), 4.65 (ddd, 1H, $J=9.5$, 3.5, 1.8 Hz), 7.12–7.16 (m, 4H), 7.23 (d, 2H, $J=8.1$ Hz), 7.32–7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.06, 21.15, 44.75, 71.34, 125.80, 129.21, 129.93, 131.01, 137.07, 137.66, 139.20. Anal. calcd for $C_{16}H_{18}OS$: C, 74.38; H, 7.02; S, 12.41. Found: C, 74.27; H, 7.17; S, 12.52%; $[\alpha]_D^{22}$ −30.6 (*c* 1.2, $CHCl_3$), *S*; HPLC analysis using a Whelk-O1 chiral column [*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm] showed it to be 99% e.e. [$t_R(S)$ 5.61 min and $t_R(R)$ 7.26 min].

4.3.6. (*S*)-(−)-2-(*p*-Tolylsulfanyl)-1-(*p*-methoxyphenyl)-ethanol 4f. R_f 0.49 (eluent B); oil; 98% yield; IR (neat, cm^{-1}): 3422, 1612, 1513, 1248; ^1H NMR (200 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.85 (d, 1H, $J=2.1$ Hz), 3.03 (dd, 1H, $J=13.7$, 9.5 Hz), 3.24 (dd, 1H, $J=13.7$, 3.7 Hz), 3.80 (s, 3H), 4.63 (m, 1H), 6.87 (d, 2H, $J=8.5$ Hz), 7.13 (d, 2H, $J=7.9$ Hz), 7.24–7.28 (m, 2H), 7.34 (d, 2H, $J=7.9$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.71, 45.35, 55.95, 71.77, 114.59, 127.83, 130.63, 131.71, 134.98, 137.77, 160.02. Anal. calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61; S, 11.69. Found: C, 70.17; H, 6.69; S, 11.73%; $[\alpha]_D^{22}$ −40.1 (*c* 1.0, $CHCl_3$), *S*; HPLC analysis using a Whelk-O1 chiral column [*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm] showed it to be 99% e.e. [$t_R(S)$ 8.47 min and $t_R(R)$ 14.29 min].

4.3.7. (*S*)-(−)-2-(*p*-Tolylsulfanyl)-1-(*m*-chlorophenyl)-ethanol 4g. R_f 0.21 (eluent C); oil; 97% yield; IR (neat, cm^{-1}): 3424, 2922, 1598, 1492, 1094, 803; ^1H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.97 (dd, 1H, $J=14.0$, 9.6 Hz), 2.98 (d, 1H, J = 2.2 Hz), 3.25 (dd, 1H, $J=13.9$, 3.3 Hz), 4.62 (ddd, 1H, $J=9.6$, 3.3, 2.0 Hz), 7.14 (d, 2H, $J=7.8$ Hz), 7.18–7.20 (m, 1H), 7.22–7.28 (m, 2H), 7.33–7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.08, 44.96, 70.76, 124.00, 126.07, 127.99, 129.78, 130.04, 130.39, 131.38, 134.43, 137.48, 144.17. Anal. calcd for $C_{15}H_{15}ClOS$: C, 64.62; H, 5.42; S, 11.50. Found: C, 64.58; H, 5.63; S, 11.57%; $[\alpha]_D^{22}$ −30.3 (*c* 1.13, $CHCl_3$), *S*; HPLC analysis using a Whelk-O1 chiral column [*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm] showed it to be >99% e.e. [$t_R(S)$ 5.22 min and $t_R(R)$ 5.63 min].

4.3.8. (*S*)-(−)-2-(*p*-Tolylsulfanyl)-1-(*p*-chlorophenyl)-ethanol 4h. R_f 0.22 (eluent C); mp 50–51°C; 98% yield; IR (neat, cm^{-1}): 3416, 2922, 1597, 1492, 1089, 803; ^1H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.95 (d, 1H, $J=2.4$ Hz), 2.97 (dd, 1H, $J=14.0$, 9.5 Hz), 3.23 (dd, 1H, $J=14.0$, 3.5 Hz), 4.63 (ddd, 1H, $J=9.5$, 3.5, 2.1 Hz), 7.13 (d, 2H, $J=8.0$ Hz), 7.25–7.29 (m, 4H), 7.30–7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.07, 44.94, 70.76, 127.24, 128.65, 130.02, 130.50, 131.31, 133.56, 137.42, 140.60. Anal. calcd for $C_{15}H_{15}ClOS$: C, 64.62; H, 5.42; S, 11.50. Found: C, 64.63; H, 5.72; S, 11.63%; $[\alpha]_D^{22}$ −45.1 (*c* 1.03, $CHCl_3$), *S*; HPLC analysis using a Whelk-O1 chiral column [*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm] showed it to be >99% e.e. [$t_R(S)$ 5.19 min and $t_R(R)$ 6.18 min].

4.3.9. (*S*)-(−)-2-(*p*-Tolylsulfanyl)-1-(*p*-fluorophenyl)-ethanol 4i. R_f 0.18 (eluent C); 32–34°C; 98% yield; IR (neat, cm^{-1}): 3413, 2974, 1605, 1511, 1224, 1059, 837, 805; ^1H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.93 (d, 1H, $J=2.2$ Hz), 2.99 (dd, 1H, $J=13.7$, 9.5 Hz), 3.23 (dd, 1H, $J=13.7$, 3.5 Hz), 4.65 (ddd, 1H, $J=9.5$, 3.5, 2.0 Hz), 6.99–7.04 (m, 2H), 7.13 (d, 2H, $J=8.1$ Hz), 7.28–7.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.07, 44.99, 70.82, 115.26, 115.48, 127.51, 127.56, 130.00, 130.62, 131.25, 137.35, 137.86, 137.88, 161.15, 163.60. Anal. calcd for $C_{15}H_{15}FOS$: C, 68.67; H, 5.76; S, 12.22. Found: C, 68.64; H, 5.59; S, 12.09%; $[\alpha]_D^{22}$ −13.1 (*c* 1.15, $CHCl_3$), *S*; HPLC analysis using a Whelk-O1 chiral column [*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm] showed it to be >99% e.e. [$t_R(S)$ 5.06 min and $t_R(R)$ 5.86 min].

4.3.10. (*S*)-(−)-2-(*p*-Tolylsulfanyl)-1-(*p*-nitrophenyl)-ethanol 4j. R_f 0.09 (eluent C); 56–58°C; 97% yield; IR (neat, cm^{-1}): 3498, 1599, 1515, 1342; ^1H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.96 (dd, 1H, $J=14.0$, 9.5 Hz), 3.15 (d, 1H, $J=2.1$ Hz), 3.27 (dd, 1H, $J=14.0$, 3.5 Hz), 4.74 (ddd, 1H, $J=9.5$, 3.5, 2.0 Hz), 7.15 (d, 2H, $J=8.0$ Hz), 7.33–7.37 (m, 2H), 7.49–7.52 (m, 2H), 8.16–8.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.10, 45.10, 70.45, 123.73, 126.68, 129.88, 130.15,

131.67, 137.89, 147.46, 149.35; Calcd. for $C_{15}H_{15}NO_3S$: C, 62.26; H, 5.23; N, 4.84; S, 11.08. Found: C, 62.25; H, 5.37; N, 4.79; S, 10.90%; $[\alpha]_D^{22}$ −80.9 (*c* 1.12, $CHCl_3$), *S*; HPLC analysis using a Whelk-O1 chiral column [*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm showed it to be >99% e.e. [$t_R(S)$ 7.73 min and $t_R(R)$ 8.36 min].

4.3.11. (*S*)-(−)-2-(*p*-Tolylsulfanyl)-1-(2′-naphthyl)ethanol 4k. R_f 0.15 (eluent C); 63–64°C; 98% yield; IR (neat, cm^{-1}): 3235, 1511, 1000, 825; ^1H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.03 (d, 1H, $J=2.0$ Hz), 3.10 (dd, 1H, $J=13.9$, 9.5 Hz), 3.34 (dd, 1H, $J=13.9$, 3.5 Hz), 4.83 (ddd, 1H, $J=9.5$, 3.5, 1.5 Hz), 7.12 (d, 2H, $J=7.9$ Hz), 7.35 (d, 2H, $J=8.1$ Hz), 7.41–7.48 (m, 3H), 7.78–7.81 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.06, 40.79, 71.56, 123.77, 124.76, 125.96, 126.19, 127.68, 127.95, 128.32, 129.96, 130.81, 131.19, 133.09, 132.24, 137.21, 139.50. Anal. calcd for $C_{19}H_{18}NOS$: C, 77.51; H, 6.16; S, 10.89. Found: C, 77.46; H, 6.46; S, 10.86%; $[\alpha]_D^{22}$ −69.3 (*c* 1.37, $CHCl_3$), *S*; HPLC analysis using a Whelk-O1 chiral column [*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm] showed it to be 99% e.e. [$t_R(R)$ 7.67 min and $t_R(S)$ 10.63 min].

4.3.12. (*S*)-(−)-2-(*p*-Tolylsulfanyl)-1-(2′-furyl)ethanol 4l. R_f 0.47 (eluent B); oil; 99% yield; IR (neat, cm^{-1}): 3406, 3026, 1493, 805,738; ^1H NMR (200 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.79 (d, 1H, $J=4.0$ Hz), 3.23 (dd, 1H, $J=13.8$, 8.5 Hz), 3.37 (dd, 1H, $J=13.8$, 4.5 Hz), 4.73 (m, 1H), 6.28–6.34 (m, 2H), 7.12 (d, 2H, $J=8.2$ Hz), 7.26–7.37 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.69, 41.80, 66.23, 107.67, 110.95, 130.63, 131.32, 131.93, 137.94, 142.99, 154.96. Anal calcd for $C_{13}H_{14}O_2S$: C, 66.64; H, 6.02; S, 13.68. Found: C, 66.56; H, 6.06; S, 13.56%; $[\alpha]_D^{22}$ −30.4 (*c* 2.27, $CHCl_3$), *S*; HPLC analysis using a Whelk-O1 chiral column [*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm] showed it to be 97% e.e. [$t_R(S)$ 5.55 min and $t_R(R)$ 6.13 min].

4.3.13. (*S*)-(+)-1-(Benzenesulfanyl)-2-butanol 4m. R_f 0.38 (eluent A); oil; 96% yield; IR (neat, cm^{-1}): 3406, 3042, 1581, 735; ^1H NMR (200 MHz, $CDCl_3$) δ 0.97 (t, 3H, $J=7.6$ Hz), 1.57 (m, 2H), 2.43 (d, 1H, $J=3.4$ Hz), 2.84 (dd, 1H, $J=8.9$, 13.4 Hz), 3.17 (dd, 1H, $J=3.4$, 13.4 Hz), 3.60 (m, 1H), 7.17–7.42 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 10.59, 29.62, 42.49, 71.27, 127.28, 129.76, 130.73, 136.01. Anal calcd for $C_{10}H_{14}OS$: C, 65.89; H, 7.74; S, 17.59. Found: C, 65.92; H, 7.80; S, 17.52%; $[\alpha]_D^{22}$ +45.78 (*c* 1.60, $CHCl_3$), *S*; {lit.[17] $[\alpha]_D$ +64.3 (*c* 1.0, $CHCl_3$), *S*, >98% e.e.}; HPLC analysis using a Chiralcel OD-H column [*iso*-PrOH/hexane: 1/99; flow rate: 1.0 mL/min; detector: 254 nm] showed it to be 73% e.e. [$t_R(R)$ 28.20 min and $t_R(S)$ 33.31 min].

4.3.14. (*S*)-(+)-1-(*p*-Tolylsulfanyl)-2-butanol 4n. R_f 0.23 (eluent C); oil; 96% yield; IR (neat, cm^{-1}): 3416, 2968, 1511, 803; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, 3H, $J=7.5$ Hz), 1.54 (m, 2H), 2.32 (s, 3H), 2.48 (br s, 1H), 2.79 (dd, 1H, $J=8.9$, 13.7 Hz), 3.10 (dd, 1H, $J=3.4$, 13.6 Hz), 3.56 (m, 1H), 7.11 (d, 2H, $J=7.9$ Hz), 7.30 (d, 2H, $J=8.1$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.00, 21.03, 28.91, 42.61, 70.47, 129.86, 130.90, 131.38, 136.91. Anal calcd for $C_{10}H_{14}OS$: C, 65.89; H, 7.74; S, 17.59. Found: C, 65.92; H, 7.80; S, 17.52%; $[\alpha]_D^{22}$ +44.0 (*c* 1.51, $CHCl_3$), *S*; HPLC analysis using a Chiralcel OD-H column [*iso*-PrOH/hexane: 1/99; flow rate: 0.3 mL/min; detector: 254 nm] showed it to be 74% e.e. [$t_R(S)$ 54.14 min and $t_R(R)$ 57.82 min].

4.3.15. (*S*)-(+)-1-(*p*-Tolylsulfanyl)-2-heptanol 4o. R_f 0.4 (eluent A); oil; 98% yield; IR (neat, cm^{-1}): 3404, 2911, 1490, 799; ^1H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, 3H, $J=6.4$ Hz), 1.27–1.49 (m, 8H), 2.32 (s, 3H), 2.45 (d, 1H, $J=3.1$ Hz), 2.78 (dd, 1H, $J=9.0$, 13.6 Hz), 3.11 (dd, 1H, $J=3.2$, 13.6 Hz), 3.63 (m, 1H), 7.11 (d, 2H, $J=7.9$ Hz), 7.31 (d, 2H, $J=8.2$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.67, 21.73, 23.22, 26.02, 32.46, 36.68, 43.68, 69.88, 130.57, 131.61, 132.05, 137.61. Anal calcd for $C_{14}H_{22}OS$: C, 70.54; H, 9.30; S, 13.45. Found: C, 70.46; H, 9.36; S, 13.51%; $[\alpha]_D^{22}$ +34.8 (*c* 1.02, $CHCl_3$), *S*; HPLC analysis using a Whelk-O1 chiral column [*iso*-PrOH/hexane: 1/9; flow rate: 0.3 mL/min; detector: 254 nm] showed it to be 74% e.e. [$t_R(S)$ 26.83 min and $t_R(R)$ 28.72 min].

4.3.16. (*S*)-(+)-1-(*p*-Tolylsulfanyl)-3-methyl-2-butanol 4p. R_f 0.42 (eluent A); oil; 97% yield; IR (neat, cm^{-1}): 3444, 2964, 1512, 803; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, 3H, $J=6.7$ Hz), 0.95 (d, 1H, $J=6.7$ Hz), 1.76 (m, 1H), 2.32 (s, 3H), 2.46 (d, 1H, $J=3.0$ Hz), 2.78 (dd, 1H, $J=9.6$, 13.6 Hz), 3.15 (dd, 1H, $J=2.9$, 13.6 Hz), 3.38 (m, 1H), 7.11 (d, 2H, $J=8.1$ Hz), 7.30 (d, 2H, $J=8.1$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.67, 18.65, 21.04, 32.80, 40.62, 73.64, 129.86, 130.87, 131.31, 136.89. Anal calcd for $C_{12}H_{18}OS$: C, 68.52; H, 8.22; S, 16.33. Found: C, 68.43; H, 8.23; S, 16.52%; $[\alpha]_D^{22}$ +80.0 (*c* 1.35, $CHCl_3$), *S*; To determine its optical purity, **4p** was oxidized to the corresponding sulfone by *m*-chloroperbenzoic acid. HPLC analysis of the sulfone compound using a Chiralcel OD column [*iso*-PrOH/hexane: 1/9; flow rate: 0.6 mL/min; detector: 254 nm] showed it to be 88% e.e. [$t_R(R)$ 20.40 min and $t_R(S)$ 24.53 min].

4.3.17. (*S*)-(+)-1-(*p*-Tolylsulfanyl)-4-methyl-2-pentanol 4q. R_f 0.42 (eluent A); oil; 97% yield; IR (neat, cm^{-1}): 3423, 2911, 1508, 800; ^1H NMR (200 MHz, $CDCl_3$) δ 0.87 (d, 3H, $J=4.8$ Hz), 0.90 (d, 3H, $J=4.9$ Hz), 1.27 (m, 1H), 1.48 (m, 1H), 1.79 (m, 1H), 2.32 (s, 3H), 2.42 (d, 1H, $J=3.4$ Hz), 2.77 (dd, 1H, $J=8.9$, 13.7 Hz), 3.09 (dd, 1H, $J=3.4$, 13.7 Hz), 3.71 (m, 1H), 7.11 (d, 2H, $J=7.9$ Hz), 7.31 (d, 2H, $J=8.2$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.67, 22.74, 23.97, 25.48, 44.10, 45.82, 68.03, 130.56, 131.50, 132.11, 137.57. Anal calcd for $C_{13}H_{20}OS$: C, 69.59; H, 8.98; S, 14.29. Found: C, 69.65; H, 9.03; S, 14.34%; $[\alpha]_D^{22}$ +34.10 (*c*1.17, $CHCl_3$), *S*; HPLC analysis using a Chiralcel OD-H column [*iso*-PrOH/hexane: 1/99; flow rate: 0.6 mL/min; detector: 254 nm] showed it to be 81% e.e. [$t_R(S)$ 21.28 min and $t_R(R)$ 22.58 min].

4.3.18. (*S*)-(+)-1-(*p*-Tolylsulfanyl)-3,3-dimethyl-2-butanol 4r. R_f 0.49 (eluent A); oil; 98% yield; IR (neat, cm^{-1}): 3488, 2869, 1512, 1364, 1008, 823; ^1H NMR (400

MHz, $CDCl_3$) δ 0.92 (s, 9H), 2.32 (s, 3H), 2.58 (d, 1H, $J=2.4$ Hz), 2.69 (dd, 1H, $J=11.0$, 13.8 Hz), 3.22 (m, 1H), 3.25 (m, 1H), 7.11 (d, 2H, $J=8.1$ Hz), 7.28–7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.04, 25.76, 34.58, 38.85, 76.08, 129.86, 130.81, 131.14, 136.88. Anal calcd for $C_{13}H_{20}OS$: C, 69.59; H, 8.98; S, 14.29. Found: C, 69.22; H, 9.23; S, 14.52%; $[\alpha]_D^{22}$ +117.8 (*c* 1.34, $CHCl_3$), *S*; HPLC analysis using a Chiralcel OD-H column [*iso*-PrOH/hexane: 1/99; flow rate: 0.75 mL/min; detector: 254 nm] showed it to be 99% e.e. [$t_R(R)$ 9.89 min and $t_R(S)$ 11.40 min].

4.3.19. (*S*)-(+)-2-(*p*-Tolylsulfanyl)-1-cyclohexylethanol 4s. R_f 0.44 (eluent A); oil; 97% yield; IR (neat, cm^{-1}): 3438, 2928, 1492, 1448, 1091, 1035, 803; ^1H NMR (200 MHz, $CDCl_3$) δ 0.94–1.87 (m, 11H), 2.32 (s, 3H), 2.48 (d, 1H, $J=3.1$ Hz), 2.80 (dd, 1H, $J=9.4$, 13.7 Hz), 3.18 (dd, 1H, $J=2.8$, 13.4 Hz), 3.37 (m, 1H), 7.11 (d, 2H, $J=7.9$ Hz), 7.30 (d, 2H, $J=7.9$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.69, 26.70, 26.81, 27.06, 28.85, 29.67, 41.34, 43.37, 73.69, 130.55, 131.46, 132.04, 137.58. Anal. calcd for $C_{15}H_{22}OS$: C, 71.95; H, 8.86; S, 12.81. Found: C, 72.02; H, 8.91; S, 12.72%; $[\alpha]_D^{22}$ +54.9 (*c* 1.05, $CHCl_3$), *S*; HPLC analysis using a Whelk-O1 column [*iso*-PrOH/hexane: 1/99; flow rate: 0.6 mL/min; detector: 254 nm] showed it to be 99% e.e. [$t_R(S)$ 12.87 min and $t_R(R)$ 14.26 min].

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