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Asymmetric Hydrogenation of β-Keto Sulfonamides and β-Keto Sulfones with a Chiral Cationic Ruthenium Diamine Catalyst

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Abstract: Optically active β-hydroxy sulfonamides and β-hydroxy sulfones are very important building blocks for the preparation of bioactive compounds and pharmaceuticals. In this work, a highly efficient asymmetric hydrogenation of β-keto sulfonamides and β-keto sulfones has been developed using the phosphine-free chiral ruthenium complex Ru(OTf)(TsDPEN)(η^6-*p*-cymene) as the catalyst, to afford the corresponding β-hydroxy sulfonamides and β-hydroxy sulfones in high yields with excellent optical purities. In addition, a cascade asymmetric hydrogenation/dynamic kinetic resolution (DKR) of racemic cyclic β-keto sulfonamides and β-keto sulfones was also realized using the same catalyst, to give the corresponding chiral cyclic β-hydroxy sulfonamides and β-hydroxy sulfones in good yields with excellent enantio- and diastereoselectivities.

Keywords: asymmetric hydrogenation; chiral diamine complexes; β-hydroxy sulfonamides; β-hydroxy sulfones; phosphine-free

Introduction

Compounds bearing a sulfonyl or sulfonamide group are important building blocks in organic synthesis, and are found in a wide range of pharmaceuticals with various biological activities.[1] The sulfonyl and sulfonamide groups are known to improve the water solubility of target compounds by their ability to form hydrogen bonds, and can be used to fine tune the pK_a values of the amino groups due to their strong inductive effect.[2] As a result, the research on pharmaceutical precursors that bear a sulfonyl or a sulfonamide group has been a focal issue in the study of synthetic drugs.[3] For instance, flavocristamide A (**1**) is a naturally occurring sulfonolipid which efficiently inhibits the enzyme DNA polymerase A.[4] Thiazolone-acylsulfonamide (**2**) is an HCV NS5B polymerase allosteric inhibitor, and compound (**3**) has antifungal activity (Figure 1).[5] According to the World Drug Index, there are more than 40 drugs carrying either of these two types of groups.

Specifically, chiral β-hydroxy sulfonamides that contain both sulfonyl and hydroxy groups in their structures are very attractive targets for synthetic studies by virtue of their widespread biological applications as well as their synthetic versatility. β-Hydroxy sulfonamides can be readily converted to corresponding hydroxy- or aminosulfonic acid derivatives,[6] and can also serve as versatile synthetic intermediates for various biologically active compounds, such as β-sultams[6] and acyclic β-aminosulfonyl derivatives (sulfonates, sulfonamides, sulfones).[7] Thus, the devel-

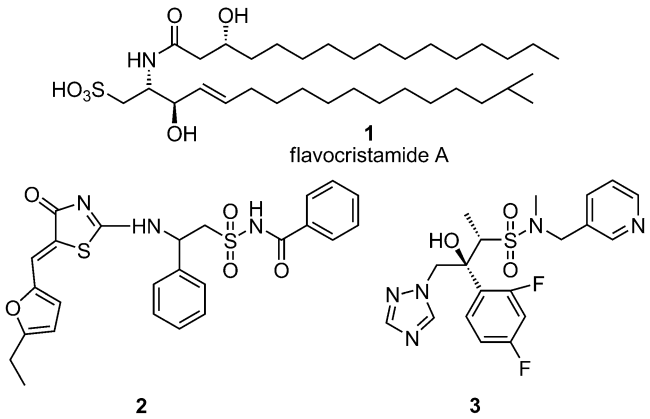
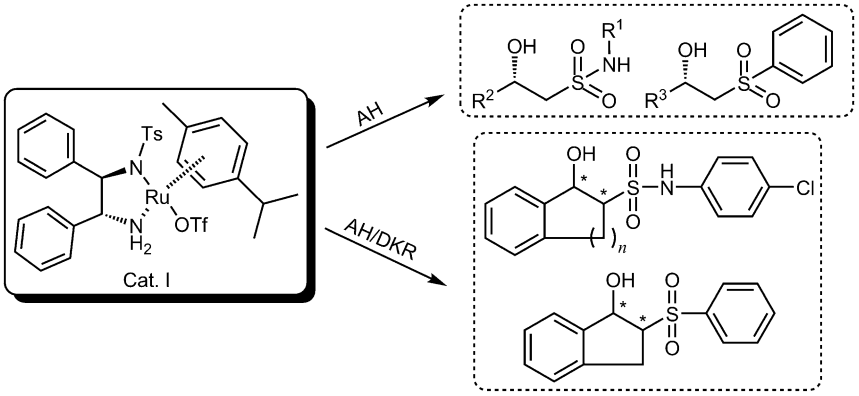


Figure 1. Selected natural products and drugs with sulfonyl groups.



Scheme 1. Asymmetric hydrogenation (AH) and/or DKR of β-keto sulfonamides and β-keto sulfones.

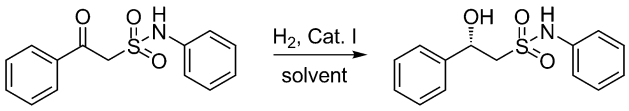
opment of versatile and efficient synthetic protocols for enantioenriched β-hydroxy sulfonamides and β-hydroxy sulfones is of great significance. In this context, however, literature examples on the asymmetric synthesis of chiral β-hydroxy sulfonamides are still rare so far, including the addition of sulfamide to benzaldehyde,[6,8] as well as asymmetric transfer hydrogenation (ATH) of β-keto sulfonamides.[9] Comparing with these methods, asymmetric hydrogenation (AH) of β-keto sulfonamides and β-keto sulfones[10d,e,o,p] represents a more straightforward approach to generate the corresponding optically active compounds, and is more atom-economic and eco-friendly for practical applications.

Currently, most of the reported catalysts for the AH of ketones bear at least one phosphine ligand around the metal center, which are often air sensitive and tedious to prepare.[10] In 2006, it was discovered that cationic ruthenium complexes of chiral monotosylated diamines, well-known catalysts for ATH,[11] can also function as efficient catalysts in the AH of ketones[12] and imines[13] with a slight functional modification. Recently, we also reported that Ru(OTf)(TsDPEN)(η^6-*p*-cymene) (Cat. **I**) [TfO^- = trifluoromethanesulfonate, TsDPEN = *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine] efficiently catalyzed the AH of benzils in methanol, to furnish chiral hydrobenzoins in good yields with excellent enantioselectivities.[12i] The highly polarized catalyst **I** was found to easily ionize in methanol solution, to provide the active Ru cationic species [Ru(TsDPEN)(η^6-*p*-cymene)]$^+$ that has been proven to be of crucial importance for the catalytic activity.[12a,b,14] Herein, we disclose the use of catalyst **I** as an efficient phosphine-free precatalyst for the asymmetric hydrogenation of both β-keto sulfonamides and β-keto sulfones, to provide a range of chiral β-hydroxy sulfonamides and β-hydroxy sulfones in high yields with excellent enantioselectivities. In addition, catalyst **I** was also found to be efficient in the cascade asymmetric hydrogenation/dynamic kinetic resolution (DKR) of racemic cyclic β-keto sulfonamides and β-keto sulfones, to give the corresponding chiral cyclic β-hydroxy sulfonamides and β-hydroxy sulfones in good yields with excellent enantio- and diastereoselectivities (Scheme 1).

Results and Discussion

The AH of 2-oxo-*N*,2-diphenylethanesulfonamide (**4aa**) catalyzed by (*R,R*)-Ru(OTf)(cymene)-(TsDPEN) catalyst **I** was first selected as the model reaction, and the results are summarized in Table 1. Since the Ru-TsDPEN complexes are known to be

Table 1. Optimization of reaction conditions for the AH of β-keto sulfonamide **4aa**.[a]



4aa **5aa**

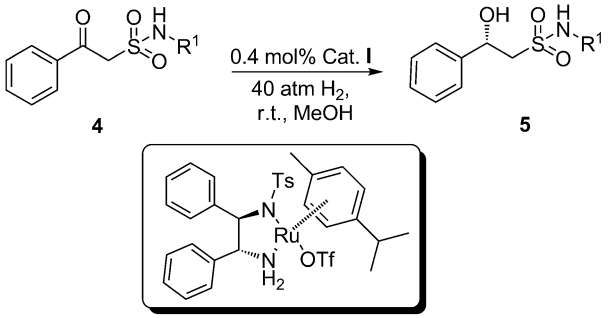
Entry	S/C	Solvent	H_2 [atm]	Yield [%][b]	*ee* [%][c]
1	50	MeOH	0	–	–
2	50	MeOH	40	98	95
3	50	EtOH	40	79	81
4	50	DCM	40	34	-17
5	50	toluene	40	29	17
6	50	dioxane	40	<5	n.d.
7	100	MeOH	40	98	98
8	250	MeOH	40	94	98
9	500	MeOH	40	96	96
10	250	MeOH	30	92	98
11	250	MeOH	50	95	97
12[d]	250	MeOH	40	97	98

[a] *Reaction conditions:* [**4aa**] = 0.2 M, cat. **I** in 1 mL solvent, room temperature, 24 h.
[b] Isolated yield.
[c] Determined by chiral HPLC.
[d] [**4aa**] = 0.1 M.

capable of functioning as a potent catalyst for the asymmetric transfer hydrogenation (ATH) of ketones in protic solvents such as methanol,[13m] a control reaction was first carried out with 2 mol% of catalyst **I** in methanol in the absence of hydrogen gas. In this case, no reduction product was detected after 24 h (entry 1). Under otherwise identical conditions, the reaction proceeded smoothly under 40 atm of H_2 in methanol, affording **5aa** in 98% yield with 95% *ee* (entry 2), thus indicating that the predominant reaction pathway is AH rather than ATH. Encouraged by this promising result, some common solvents, including ethanol, dichloromethane, toluene and dioxane, were screened in the reaction. The alcoholic solvents (MeOH and EtOH) were found to be generally superior to the aprotic ones (entries 2, 3 *vs.* 4–6). Methanol turned out to be the optimal reaction medium in terms of both yield and enantioselectivity, and thus was employed for subsequent AH reaction studies. Furthermore, the influence of catalyst loading was also investigated for the AH of **4aa**, with the substrate/catalyst ratio (S/C) ranging from 100/1 to 500/1 (entries 2 and 7–9). The results showed that the reaction still proceeded smoothly in the presence of a relatively low catalyst loading (0.4 mol%, S/C = 250), to give the AH product **5aa** in 94% yield with 98% *ee* (entry 8). In addition, the reactions under different hydrogen pressures were also studied. With the hydrogen pressure ranging from 30 to 50 atm, the enantioselectivity remained excellent (97–98% *ee*), while the yield of **5aa** fluctuated slightly around 92–96% (entries 9–11). Finally, when the substrate concentration was diluted to 0.1 M, the yield was enhanced slightly to 97% and the enantioselectivity was retained (entry 12 *vs.* 8). Thus, the optimal conditions for AH of **4aa** were finally established as the reaction being performed in methanol under 40 atm of H_2 at ambient temperature, with a substrate concentration of 0.1 M in the presence of 0.4 mol% catalyst **I**.

Having established the optimal reaction conditions, we proceeded to explore the substrate scope of the present protocol. A variety of β-keto sulfonamides bearing *N*-aryl substituents were first investigated for this transformation, and the results are shown in Table 2. Excellent yields and enantioselectivities were obtained under optimized reaction conditions, irrespective of the variations in electronic and steric properties of the substituents attached to the phenyl rings of the sulfonamide motifs. Accordingly, the *N*-aryl substituted sulfamide **4aa**–**4ak** bearing either electron-donating substituents (Me, OMe, *i*-Pr) or electron-withdrawing substituents (F, Cl, Br, CF_3) at *para*-, *ortho*- or *meta*- positions of the phenyl group were all well tolerated, leading to the desired products **5aa**–**5ak** in 92–99% yields with 96–99% *ee*s (entries 1–11).

Table 2. Asymmetric hydrogenation (AH) of the β-keto sulfonamides **4aa–4ak** with *N*-aryl substituents.[a]

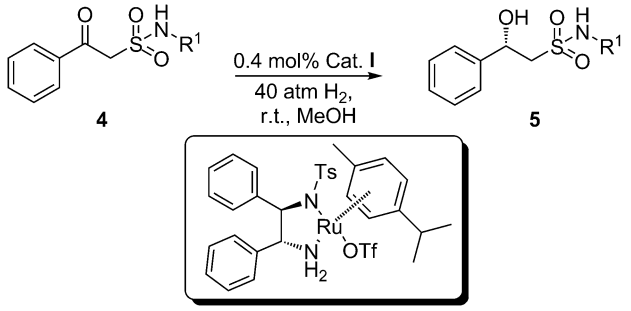


Entry	Substrates	R^1	Product/Yield [%][b]	*ee* [%][c]
1	**4aa**	C_6H_5	**5aa**/97	98
2	**4ab**	4-FC_6H_4	**5ab**/99	97
3	**4ac**	4-ClC_6H_4	**5ac**/98	97
4	**4ad**	4-BrC_6H_4	**5ad**/96	98
5	**4ae**	4-$CH_3C_6H_4$	**5ae**/95	97
6	**4af**	4-$CH_3OC_6H_4$	**5af**/97	99
7	**4ag**	3-ClC_6H_4	**5ag**/95	98
8	**4ah**	2-$CH_3OC_6H_4$	**5ah**/99	97
9	**4ai**	2,4-$Cl_2C_6H_3$	**5ai**/97	97
10	**4aj**	3,5-$(CF_3)_2C_6H_3$	**5aj**/92	96
11	**4ak**	2,6-(*i*-Pr)$_2C_6H_3$	**5ak**/94	96

[a] *Reaction conditions:* [**4**] = 0.1 M, 0.4 mol% cat. **I** in 2 mL solvent, room temperature, 24 h.
[b] Isolated yield.
[c] Determined by chiral HPLC.

Furthermore, several β-keto sulfonamides with *N*-alkyl substituents on sulfonamide motifs were also examined for the AH under optimized reaction conditions (Table 3). Intriguingly, no reaction occurred for 2-oxo-2-phenylethanesulfonamide (**4al**), wherein both substituents on the sulfonamide nitrogen are H atoms (entry 1). For the β-keto sulfonamides substrates **4am–4ap** bearing an ethyl, *n*-butyl, *tert*-butyl, or a benzylsulfonamide group, the corresponding hydrogenated products **5am–5ap** were obtained in consistently excellent enantioselectivities (98–99% *ee*) and high yields (91–97%), respectively (entries 2–5). The hydrogenation of **4ap** was further tested under lowered catalyst loading, which would be of considerable interest from a practical point of view. When the substrate/catalyst ratio was increased gradually from 250 to 1500, the hydrogenation still proceeded smoothly to give the desired product **5ap** in excellent yield (> 95%) and enantioselectivity (> 97%) (entries 5–8). Unfortunately, further reducing catalyst loading to 0.05 mol% (S/C = 2000) led to a substantial decline of the yield to 43% even after a prolonged reaction time (48 h), although the enantioselectivity was maintained (95% *ee*) (entry 9).

Table 3. Asymmetric hydrogenation (AH) of the β-keto sulfonamides **4al–4ap** with *N*-alkyl substituents.[a]

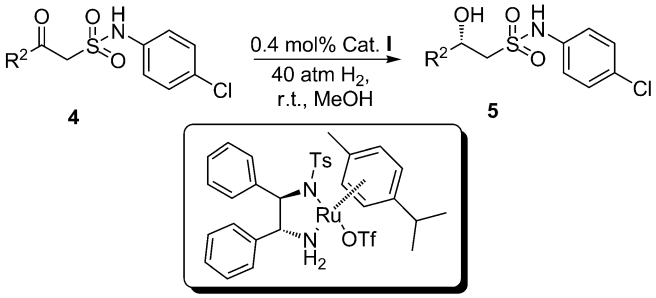


Entry	Substrates	R^1	Product/Yield [%][b]	*ee* [%][c]
1	**4al**	H	–	–
2	**4am**	Et	**5am**/91	99
3	**4an**	*n*-Bu	**5an**/91	99
4	**4ao**	*t*-Bu	**5ao**/92	98
5	**4ap**	Bn	**5ap**/97	99
6[d]	**4ap**	Bn	**5ap**/97	99
7[e]	**4ap**	Bn	**5ap**/96	98
8[f]	**4ap**	Bn	**5ap**/95	97
9[g]	**4ap**	Bn	**5ap**/43	95

[a] *Reaction conditions:* [**4**] = 0.1 M, 0.4 mol% cat. **I** in 2 mL solvent, room temperature, 24 h.
[b] Isolated yield.
[c] Determined by chiral HPLC.
[d] S/C = 500/1.
[e] S/C = 1000/1.
[f] S/C = 1500/1.
[g] S/C = 2000/1, 48 h.

Encouraged by these results, we further examined the AH of β-keto sulfonamides bearing various substituents on ketonic moieties, and the results are shown in Table 4. For substrates **4ac–4gc** carrying either electron-withdrawing groups (F, Cl, Br, NO_2) or electron-donating substituents (Me, OCH_3) at the *para*-position of the phenyl ring, all the reactions proceeded smoothly to afford the products **5ac–5gc** in 92–99% yields with 97 to >99% *ee*s (entries 2–7). For the reactions of substrates **4hc–4lc** bearing mono- or di-substitution on the other positions of phenyl rings (2-Cl, 3-Br, 3-OCH_3, 2,4-Cl_2 and 3,4-Cl_2), good yields and excellent *ee*s (92–98% yields, 95–99% *ee*s) were achieved, regardless of the stereoelectronic features of the substituents (entries 8–12). Furthermore, **4mc** containing a furyl group was also proved to be a suitable substrate for this transformation, affording the corresponding product **5mc** in 93% yield with 97% *ee* (entry 13). In addition, the sulfonamide **4nc** with an aliphatic ketone moiety (Me) was also investigated for this transformation, which furnished the desired product **5nc** in 92% yield with a somewhat declined enantioselectivity (64% *ee*, entry 14). Fortunately, the solid state structure of **5aa** was determined by single

Table 4. Asymmetric hydrogenation (AH) of the β-keto sulfonamides **4ac–4mc**.[a]



Entry	Substrate	R^2	Product/Yield [%][b]	*ee* [%][c]
1	**4ac**	C_6H_5	**5ac**/98	97
2	**4bc**	4-FC_6H_4	**5bc**/99	>99
3	**4cc**	4-ClC_6H_4	**5cc**/98	>99
4	**4dc**	4-BrC_6H_4	**5dc**/97	98
5	**4ec**	4-$NO_2C_6H_4$	**5ec**/98	>99
6	**4fc**	4-$CH_3C_6H_4$	**5fc**/93	99
7	**4gc**	4-$CH_3OC_6H_4$	**5gc**/92	>99
8	**4hc**	2-ClC_6H_4	**5hc**/97	97
9	**4ic**	3-BrC_6H_4	**5ic**/92	98
10	**4jc**	3-$CH_3OC_6H_4$	**5jc**/98	99
11	**4kc**	3,4-$Cl_2C_6H_3$	**5kc**/95	96
12	**4lc**	2,4-$Cl_2C_6H_3$	**5lc**/98	95
13	**4mc**	furyl	**5mc**/93	97
14	**4nc**	CH_3	**5nc**/92	64

[a] *Reaction conditions:* [**4**] = 0.1 M, 0.4 mol% cat. **I** in 2 mL solvent, room temperature, 24 h.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis.

crystal X-ray analysis, which revealed its *S* absolute configuration on the chiral carbon (Figure 2).[15]

Further studies on expansion of the substrate scope revealed that β-keto sulfones were also amenable to the established AH protocol. As shown in Table 5, for

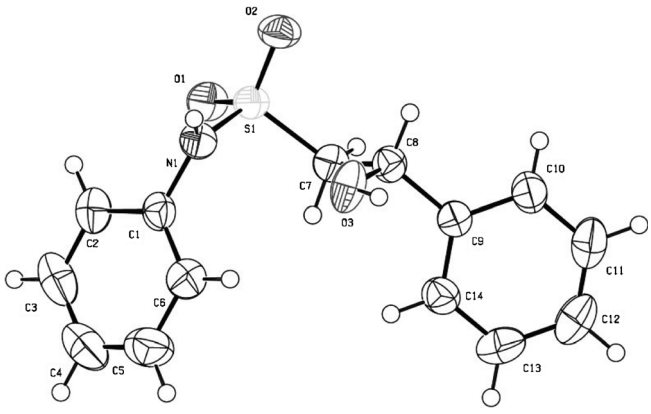
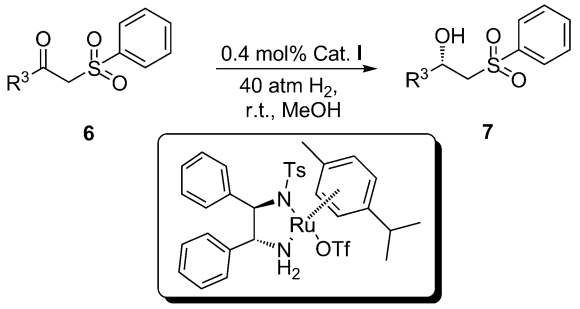


Figure 2. The solid state structure of **5aa**.

Table 5. Asymmetric hydrogenation (AH) of β-keto sulfones **6a–6l**.[a]

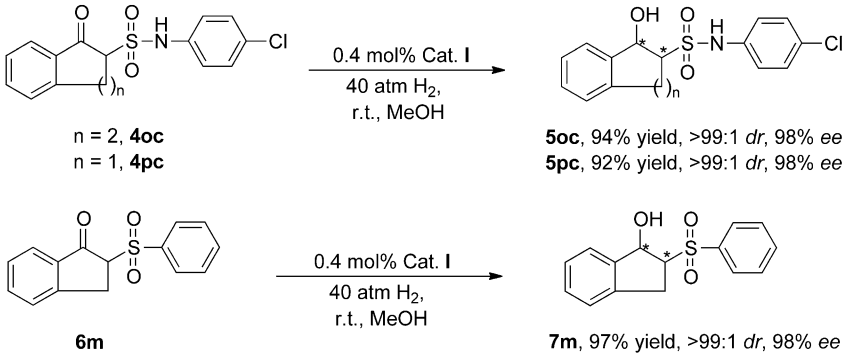


Entry	Substrate	R^3	Product/Yield [%][b]	*ee* [%][c]
1	**6a**	C_6H_5	**7a**/96	98
2	**6b**	4-FC_6H_4	**7b**/93	98
3	**6c**	4-ClC_6H_4	**7c**/94	96
4	**6d**	4-BrC_6H_4	**7d**/97	98
5	**6e**	4-$CH_3C_6H_4$	**7e**/92	98
6	**6f**	2-FC_6H_4	**7f**/95	95
7	**6g**	3-FC_6H_4	**7g**/97	96
8	**6h**	2-naphthyl	**7h**/94	96
9	**6i**	furyl	**7i**/95	98
10	**6j**	thienyl	**7j**/94	98
11	**6k**	CH_3	**7k**/93	82
12	**6l**	CH_3CH_2	**7l**/94	84

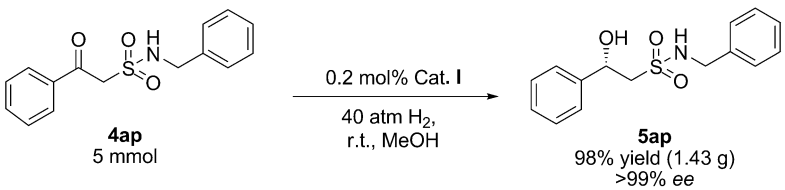
[a] *Reaction conditions:* [**6**] = 0.1 M, 0.4 mol% cat. **I** in 2 mL solvent, room temperature, 24 h.
[b] Isolated yield.
[c] Determined by chiral HPLC.

AH of phenyl β-keto sulfones **6a–6g** bearing either electron-donating or electron-withdrawing groups at *o*-, *m*-, and *p*-positions of the phenyl ring, the corresponding products **7a–7g** were obtained in excellent yields (92–97%) with excellent enantioselectivities (95–98% *ee*) (entries 1–7). In addition, this methodology also proved to be efficient in hydrogenating substrates containing fused aromatic (**6h**) or heteroaromatic rings (**6i** and **6j**), to produce **7h–7j** in 94–95% yields with 96–98% *ee*s, respectively (entries 8–10). Finally, substrates **6k** and **6l** with aliphatic ketone moieties were also tested for this transformation under otherwise identical reaction conditions, which gave the corresponding products **7k** and **7l** in excellent yields (93–94%) with good enantioselectivity (82–84% *ee*), respectively (entries 11 and 12).

The cascade asymmetric hydrogenation/dynamic kinetic resolution (DKR) of racemic cyclic β-keto sulfonamides and β-keto sulfones was also investigated in this work. As shown in Scheme 2, cyclic β-keto sulfamides derived from α-tetralone (**4oc**) or α-indanone (**4pc**), as well as the cyclic β-keto sulfone (**6m**) were hydrogenated smoothly in the presence of 0.4 mol% of catalyst **I**, to give the desired products **5oc**, **5pc** and **7m** in high yields (92–97%) with extremely high *ee* values (98–99%) and excellent diastereoselectivities (>99:1), respectively. Finally, the AH of **4ap** was performed on a gram-scale without any difficulty at a catalyst loading of 0.2 mol%, leading to the targeted product **5ap** (1.43 g) in 98% yield with 99% *ee* (Scheme 3), thus attesting the practical utility of the catalytic protocol.



Scheme 2. Asymmetric hydrogenation/dynamic kinetic resolution of cyclic β-keto sulfamides and β-keto sulfone.



Scheme 3. Gram-scale asymmetric synthesis of **5ap**.

Conclusions

In summary, we have developed an efficient methodology for the synthesis of optically active β-hydroxy sulfonamides and β-hydroxy sulfones *via* asymmetric hydrogenation of β-keto sulfonamides and β-keto sulfones catalyzed by the phosphine-free η^6-*p*-arene/TsDPEN-Ru(II) complex **I**. A wide range of chiral chain β-hydroxy sulfonamides and β-hydroxy sulfones were obtained in high yields and excellent enantioselectivities. The cascade asymmetric hydrogenation/dynamic kinetic resolution (DKR) of cyclic β-keto sulfonamides and β-keto sulfones was also successful using the same catalyst, affording the corresponding chiral β-hydroxy sulfonamides and β-hydroxy sulfones in high yields with excellent enantioselectivities and diastereoselectivities. Further study on the utilization of the protocol for synthesis of biologically important molecules is underway in our laboratory.

Experimental Section

General Remarks

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Methanol was freshly distilled from sodium. Column chromatography purifications were performed using 200–300 mesh silica gel. ^{1}H and ^{13}C NMR spectra were recorded on a Varian-Inova-400 spectrometer. Solvent for NMR is $CDCl_3$ or DMSO, unless the otherwise noted. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on 100 MHz or 75 MHz. Chemical shifts are reported in parts per million relative to the central line of the multiplet at 77.0 ppm for $CDCl_3$, 39.5 ppm for DMSO. Mass spectra were recorded using an Agilent 6120 Quadrupole LC/MS system with ESI resource. High-resolution mass spectra (HR-MS) for all the compounds were determined on a Micromass GCT-TOF mass spertrometer with an ESI source. High-performance liquid chromatography (HPLC) was performed on an Agilent 1200 Series chromatograph using a Chiralpak AD-H/or Chiralcel OD-H/or OJ-H column using 2-propanol/hexane as the eluent. Infrared spectra were obtained on a Varian-1000 FT-IR spectrometer. Optical rotations were measured at 589 nm (Na D line) on a Autopol IV automatic polarimeter.

Synthesis of Substrate and Catalyst

All β-carbonyl sulfonamides and β-keto sulfones were prepared according to the known methods.[16] The catalyst was prepared using the known procedure.[12b]

General Procedure for the Asymmetric Hydrogenation of β-Keto Sulfonamides

β-Keto sulfonamides or β-keto sulfones (0.2 mmol), catalyst **I** (0.8 μmol), and degassed MeOH (2 mL) were added to a glass tube under nitrogen. The tube was then placed into a stainless steel autoclave, which was purged with hydrogen gas for three times before being pressurized with H_2 to 40 atm. Subsequently, the mixture was stirred under this H_2 pressure at room temperature for 24 h. After careful release of the hydrogen, methanol was concentrated to afford the crude product. Purification was performed with a silica gel column eluted with petroleum ether/ethyl acetate (2:1, v/v) to give the pure product. The enantiomeric excess was determined by chiral HPLC analysis.

2-Hydroxy-*N*,2-diphenylethanesulfonamide (5aa): White solid; yield: 97%; 98% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent; flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 22.479 min, t_{major} = 26.241 min; $[\alpha]_D^{27}$: +17.2 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.31 (m, 9H), 7.22 (t, *J* = 6.8 Hz, 1H), 7.05 (s, 1H), 5.35 (d, *J* = 10.4 Hz, 1H), 3.36 (dd, *J* = 14.8, 10.8 Hz, 1H), 3.33 (s, 1H), 3.22 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.93, 136.74, 129.78, 129.14, 128.82, 126.10, 125.86, 122.43, 70.05, 57.47; IR (film): ν_{max} = 3467.6, 3282.7, 2892.1, 1596.8, 1492.0, 1399.9, 1334.9, 1142.1, 1062.1, 992.3, 892.2, 752.5, 699.4 cm^{-1}; ESI-MS: *m*/*z* = 300.0 $[M+Na]^+$; HR-MS: *m*/*z* = 300.0666 $[M+Na]^+$, calcd. for $C_{14}H_{15}NNaO_3S$: 300.0665.

***N*-(4-Fluorophenyl)-2-hydroxy-2-phenylethanesulfonamide (5ab):** White solid; yield: 99%; 97% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 20.880 min, t_{major} = 23.421 min; $[\alpha]_D^{27}$: +14.4 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.26 (m, 7H), 7.18 (s, 1H), 7.04 (t, *J* = 8.4 Hz, 2H), 5.35 (d, *J* = 10.0 Hz, 1H), 3.49 (s, 1H), 3.38 (dd, *J* = 14.4, 10.8 Hz, 1H), 3.16 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.12 (d, $^1J_{C,F}$ = 245 Hz), 140.94, 132.62 (d, $^4J_{C,F}$ = 3 Hz), 129.18, 128.89, 125.84, 125.22 (d, $^3J_{C,F}$ = 6 Hz), 116.52 (d, $^2J_{C,F}$ = 23 Hz), 70.07, 56.99; IR (film): ν_{max} = 3472.7, 3284.9, 2891.4, 1605.0, 1504.3, 1453.9, 1382.9, 1331.7, 1204.7, 1141.4, 1162.3, 993.1, 898.9, 758.0, 705.6 cm^{-1}; ESI-MS: *m*/*z* = 318.0 $[M+Na]^+$; HRMS: *m*/*z* = 318.0568 $[M+Na]^+$, calcd. for $C_{14}H_{14}FNNaO_3S$: 318.0571.

***N*-(4-Chlorophenyl)-2-hydroxy-2-phenylethanesulfonamide (5ac):** White solid; yield: 98%; 97% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 23.052 min, t_{major} = 25.684 min; $[\alpha]_D^{27}$: +17.1 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.24 (m, 9H), 7.22 (s, 1H), 5.33 (d, *J* = 10.4 Hz, 1H), 3.46 (s, 1H), 3.37 (dd, *J* = 14.4, 10.8 Hz, 1H), 3.17 (d, *J* = 14.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.83, 135.38, 131.70, 129.82, 129.19, 128.92, 125.84, 123.85, 70.05, 57.27; IR (film): ν_{max} = 3440.9, 3290.4, 2919.5,1637.7, 1491.6, 1452.3, 1325.6, 1216.8, 1145.2, 1056.6, 997.2, 910.0, 827.7, 742.9, 697.2 cm^{-1}; ESI-MS: *m*/*z* = 334.0 $[M+Na]^+$; HR-MS: *m*/*z* = 334.0288 $[M+Na]^+$, calcd. for $C_{14}H_{14}ClNNaO_3S$: 334.0275.

***N*-(4-Bromophenyl)-2-hydroxy-2-phenylethanesulfonamide (5ad):** White solid; yield: 96%; 98% *ee*. The enantiomer-

ic excess was determined by HPLC [Daicel Chiralcel OD-H with hexane/*i*-PrOH (92:8) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 24.451 min, t_{major} = 32.189 min; $[\alpha]_D^{27}$: +14.5 (*c* 0.40 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.4 Hz, 2H), 7.37–7.29 (m, 5H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.07 (s, 1H), 5.34 (d, *J* = 10.4 Hz, 1H), 3.40 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.24 (s, 1H), 3.21–3.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.77, 135.94, 132.78, 129.24, 129.00, 125.84, 124.12, 119.44, 70.19, 57.23; IR (film): ν_{max} = 3463.2, 3268.1, 2925.9, 1489.9, 1391.0, 1323.1, 1145.4, 1052.3, 999.5, 911.1, 824.2, 700.5 cm^{-1}; ESI-MS: *m*/*z* = 376.3, 378.1 $[M+Na]^+$; HR-MS: *m*/*z* = 377.9775, 379.9753 $[M+Na]^+$, calcd. for $C_{14}H_{14}BrNNaO_3S$: 377.9775, 379.9755.

2-Hydroxy-2-phenyl-*N*-*p*-tolylethanesulfonamide (5ae): White solid; yield: 95%; 97% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent; flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 22.066 min, t_{major} = 23.417 min; $[\alpha]_D^{27}$: +16.2 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.30 (m, 5H), 7.20(d, *J*=7.6 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.08 (s, 1H), 5.34 (d, *J* = 10.0 Hz, 1H), 3.51 (s, 1H), 3.40 (dd, *J* = 14.8, 11.6 Hz, 1H), 3.19 (d, *J* = 14.4 Hz, 1H), 2.33(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.06, 136.12, 134.03, 130.31, 129.09, 128.72, 125.89, 122.99, 69.94, 57.25, 21.11; IR (film): ν_{max} = 3457.6, 3304.7, 3034.3, 1662.9, 1511.4, 1451.5, 1390.6, 1322.9, 1215.5, 1144.9, 1058.2, 999.6, 916.3, 809.7, 765.7, 698.8, 646.6 cm^{-1}; ESI-MS: *m*/*z* = 314.1 $[M+Na]^+$; HR-MS: *m*/*z* = 314.0817 $[M+Na]^+$, calcd. for $C_{15}H_{17}NNaO_3S$: 314.0821.

2-Hydroxy-*N*-(4-methoxyphenyl)-2-phenylethanesulfonamide (5af): White solid; yield: 97%; 99% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 31.477 min, t_{major} = 33.698 min; $[\alpha]_D^{27}$: +13.4 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.32 (m, 5H), 7.26(d, *J*=8.4 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.84 (s, 1H), 5.34 (d, *J* = 10.4 Hz, 1H), 3.79 (s, 3H), 3.39 (dd, *J* = 14.8, 11.2 Hz, 1H), 3.35 (s, 1H), 3.15 (d, *J* = 14.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.40, 141.07, 129.14, 128.79, 125.88, 125.73, 114.90, 70.09, 56.91, 55.71; IR (film): ν_{max} = 3486.8, 3284.9, 2835.5, 1611.8, 1511.3, 1455.6, 1395.4, 1327.3, 1252.5, 1156.6, 1056.1, 903.8, 830.7, 772.3, 663.6, 526.8 cm^{-1}; ESI-MS: *m*/*z* = 330.0 $[M+Na]^+$; HR-MS: *m*/*z* = 330.0778 $[M+Na]^+$, calcd. for $C_{15}H_{17}NNaO_4S$: 330.0770.

***N*-(3-Chlorophenyl)-2-hydroxy-2-phenylethanesulfonamide (5ag):** White solid; yield: 95%; 98% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent; flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 17.933 min, t_{major} = 21.305 min; $[\alpha]_D^{27}$: +19.1 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.25 (m, 8H), 7.18(s, 1H), 7.16 (s, 1H), 5.34 (d, *J* = 10.0 Hz, 1H), 3.47–3.40 (m, 2H), 3.25–3.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.77, 138.08, 135.29, 130.74, 129.21, 128.95, 126.06, 125.87, 122.09, 120.15, 70.06, 57.58; IR (film): ν_{max} = 3487.1, 3110.7, 3037.5, 2862.3, 1593.6, 1473.3, 1398.9, 1319.4, 1252.3, 1223.1, 1142.6, 950.9, 866.2, 783.2, 698.4, 567.3 cm^{-1}; ESI-MS: *m*/*z* = 312.1 $[M+H]^+$; HR-MS: *m*/*z* = 329.0720 $[M+NH_4]^+$, calcd. for $C_{14}H_{18}ClN_2O_3S$: 329.0721.

2-Hydroxy-*N*-(2-methoxyphenyl)-2-phenylethanesulfonamide (5ah): colorless oil; yield: 99%; 97% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 23.753 min, t_{major} = 30.875 min; $[\alpha]_D^{27}$: +36.2 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55(d, *J*=9.6 Hz, 1H), 7.32–7.28 (m, 5H), 7.19 (s, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.99–6.92 (m, 2H), 5.30 (d, *J* = 10.0 Hz, 1H), 3.88 (s, 3H), 3.71 (s, 1H), 3.41 (dd, *J* = 14.4, 10.4 Hz, 1H), 3.29 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.88, 141.00, 128.97, 128.49, 126.23, 125.82, 125.71, 121.68, 121.65, 111.15, 69.28, 59.17, 56.09; IR (film): ν_{max} = 3503.0, 3215.7, 2927.1, 1599.1, 1501.5, 1452.7, 1400.0, 1337.1, 1254.7, 1145.6, 1050.2, 923.7, 750.9 cm^{-1}; ESI-MS: *m*/*z* = 330.1 $[M+Na]^+$; HR-MS: *m*/*z* = 330.0778 $[M+Na]^+$, calcd. for $C_{15}H_{17}NNaO_4S$: 330.0770.

***N*-(2,4-Dichlorophenyl)-2-hydroxy-2-phenylethanesulfonamide (5ai):** White solid; yield: 97%; 97% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 16.130 min, t_{major} = 18.256 min; $[\alpha]_D^{27}$: +24.5 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.8 Hz, 1H), 7.43 (s, 1H), 7.35–7.24 (m, 6H), 7.20 (s, 1H), 5.33 (d, *J* = 10.0 Hz, 1H), 3.49 (dd, *J* = 14.4, 10.4 Hz, 1H), 3.33 (s, 1H), 3.28 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.60, 132.46, 131.32, 129.76, 129.16, 128.88, 128.60, 125.87, 123.34, 69.63, 59.90; IR (film): ν_{max} = 3502.8, 3305.5, 2989.6, 1485.6, 1387.9, 1135.0, 1063.2, 1000.6, 939.6, 856.0, 811.3, 753.4, 692.7 cm^{-1}; ESI-MS: *m*/*z* = 368.0 $[M+Na]^+$; HR-MS: *m*/*z* = 363.0332 $[M+NH_4]^+$, calcd. for $C_{14}H_{17}Cl_2N_2O_3S$: 363.0331.

***N*-[3,5-Bis(trifluoromethyl)phenyl]-2-hydroxy-2-phenylethanesulfonamide (5aj):** White solid; yield: 92%; 96% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralcel OD-H with hexane/*i*-PrOH (92:8) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 9.827 min, t_{major} = 12.038 min; $[\alpha]_D^{27}$: +18.1 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 9.2 Hz, 3H), 7.46 (s, 1H), 7.34–7.31 (m, 5H), 5.38 (d, *J* = 10.0 Hz, 1H), 3.41 (dd, *J* = 14.4, 10.4 Hz, 1H), 3.26 (d, *J* = 14.8 Hz, 1H), 3.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.42, 133.13 (q, $^2J_{C,F}$ = 34 Hz), 129.38, 129.28, 125.79, 123.15 (q, $^1J_{C,F}$ = 272 Hz), 121.94 (br-s), 119.34 (m), 70.39, 57.73; IR (film): ν_{max} = 3557.9, 3432.4, 3280.8, 1621.6, 1424.3, 1377.6, 1341.5, 1280.6, 1183.1, 1141.2, 1052.0, 995.5, 979.5, 744.3, 701.6 cm^{-1}; ESI-MS: *m*/*z* = 436.0 $[M+Na]^+$; HR-MS: *m*/*z* = 431.0866 $[M+NH_4]^+$, calcd. for $C_{16}H_{17}F_6N_2O_3S$: 431.0859.

***N*-(2,6-Diisopropylphenyl)-2-hydroxy-2-phenylethanesulfonamide (5ak):** White solid; yield: 94%; 96% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralcel OD-H with hexane/*i*-PrOH (92:8) as the eluent; flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 9.877 min, t_{major} = 15.044 min; $[\alpha]_D^{27}$: +19.7 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 4.0 Hz, 4H), 7.37–7.30 (m, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.15(s, 1H), 5.44 (d, *J* = 10.0 Hz, 1H), 3.60 (dd, *J* = 14.0, 10.4 Hz, 1H), 3.57–3.48 (m, 2H), 3.46 (s, 1H), 3.41 (d, *J* = 6.0 Hz, 1H), 1.24 (q, *J* = 2.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.38, 141.05, 129.25, 129.17, 128.78, 125.88, 124.34, 70.05, 61.59, 28.91, 24.24; IR (film): ν_{max} = 3495.3, 3287.2, 2972.8, 1626.4, 1457.6, 1385.7, 1318.9, 1152.8, 1052.9, 986.6, 780.6, 761.4, 698.5 cm^{-1}; ESI-MS: *m*/*z* = 384.1 $[M+Na]^+$; HR-MS: *m*/*z* = 362.1789 $[M+H]^+$, calcd. for $C_{20}H_{28}NO_3S$: 362.1784.

***N*-Ethyl-2-hydroxy-2-phenylethanesulfonamide (5am):** Colorless oil; yield: 91%; 99% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralcel OD-H with hexane/*i*-PrOH (92:8) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 18.524 min, t_{major} = 20.664 min; $[\alpha]_D^{27}$: +40.5 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.31 (m, 5H), 5.25 (d, *J* = 9.2 Hz, 1H), 4.83 (s, 1H), 3.59 (s, 1H), 3.39 (dd, *J* = 14.4, 10.4 Hz, 1H), 3.23 (d, *J* = 14.4 Hz 1H), 3.18–3.12 (m, 2H), 2.88 (s, 1H), 1.19 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.37, 129.08, 128.63, 125.88, 69.76, 59.07, 38.68, 37.60, 15.75; IR (film): ν_{max} = 3457.8, 2981.4, 1632.4, 1454.0, 1317.6, 1136.7, 1060.3, 954.2, 785.6, 749.4, 701.9, 558.1 cm^{-1}; ESI-MS: *m*/*z* = 252.1 $[M+Na]^+$; HR-MS: *m*/*z* = 252.0668 $[M+H]^+$, calcd. for $C_{10}H_{15}NNaO_3S$: 252.0665.

***N*-Butyl-2-hydroxy-2-phenylethanesulfonamide (5an):** White solid; yield: 91%; 99% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralcel OJ-H with hexane/*i*-PrOH (92:8) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 16.410 min, t_{major} = 17.347 min; $[\alpha]_D^{27}$: +32.3 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.31 (m, 5H), 5.26 (d, *J* = 9.6 Hz, 1H), 4.92 (s, 1H), 3.64(s, 1H), 3.40 (dd, *J* = 15.2, 10.4 Hz, 1H), 3.22 (d, *J* = 14.4 Hz, 1H), 3.08 (q, *J* = 7.2 Hz, 2H), 1.55–1.48 (m, 2H) 1.38–1.33 (m, 2H), 0.92 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.41, 129.07, 128.61, 125.90, 69.75, 58.97, 43.38, 32.24, 19.96, 13.81; IR (film): ν_{max} = 3457.2, 2959.6, 2058.9, 1638.2, 1424.3, 1306.0, 1127.9, 1079.8, 997.9, 743.0, 699.3, 547.7 cm^{-1}; ESI-MS: *m*/*z* = 280.1 $[M+Na]^+$; HR-MS: *m*/*z* = 280.0980 $[M+Na]^+$, calcd. for $C_{12}H_{19}NNaO_3S$: 280.0978.

***N*-*tert*-Butyl-2-hydroxy-2-phenylethanesulfonamide (5ao):** White solid; yield: 92%; 98% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 13.842 min, t_{major} = 13.767 min; $[\alpha]_D^{27}$: +28.6 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 4.0, 4H), 7.33–7.31 (m, 1H), 5.27 (d, *J* = 9.6 Hz, 1H), 4.70 (d, *J* = 9.2 Hz, 1H), 3.73 (s, 1H), 3.43 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.30 (d, *J* = 14.0 Hz 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.34, 129.04, 128.51, 125.93, 69.82, 63.62, 55.33, 30.51; IR (film): ν_{max} = 3434.8, 3190.7, 2973.8, 1458.1, 1394.5, 1310.4, 1229.6, 1130.7, 1011.2, 878.5, 762.5, 701.7, 563.0 cm^{-1}; ESI-MS: *m*/*z* = 280.1 $[M+Na]^+$; HR-MS: *m*/*z* = 280.0979 $[M+Na]^+$, calcd. for $C_{12}H_{19}NNaO_3S$: 280.0978.

***N*-Benzyl-2-hydroxy-2-phenylethanesulfonamide (5ap):** White solid; yield: 97%; 99% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent; flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 20.033 min, t_{major} = 22.279 min; $[\alpha]_D^{27}$: +40.7 (*c* 1.00 in CH_3COCH_3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.22 (m, 10H), 5.18 (d, *J* = 9.6 Hz, 1H), 5.15–5.08 (m, 1H), 4.32 (d, *J* = 5.6 Hz, 2H), 3.33 (dd, *J* = 14.8, 9.6 Hz, 2H), 3.16 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.12, 136.78, 129.11, 129.05, 128.66, 128.40, 128.32, 125.84, 69.82, 59.73, 47.62; IR (film): ν_{max} = 3401.5, 3247.0, 1605.3, 1494.4, 1447.4, 1423.4, 1310.5, 1138.9, 1060.8, 993.6, 875.3, 752.4, 605.2, 559.8 cm^{-1}; ESI-MS: *m*/*z* = 314.0 $[M+Na]^+$; HR-MS: *m*/*z* = 314.0812 $[M+Na]^+$, calcd- for $C_{15}H_{17}NNaO_3S$: 314.0821.

***N*-(4-Chlorophenyl)-2-(4-fluorophenyl)-2-hydroxyethanesulfonamide (5bc):** White solid; yield: 99%; >99% *ee*. The enantiomeric excess was determined [HPLC on Daicel Chiralcel OD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 16.834 min, t_{major} = 18.811 min; $[\alpha]_D^{27}$: +20.4 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.8 Hz, 2H), 7.24–7.20 (m, 4H), 7.00 (t, *J* = 8.4 Hz, 2H), 6.96 (s, 1H), 5.30 (d, *J* = 10.0 Hz, 1H), 3.36 (dd, *J* = 14.8, 10.8 Hz, 1H), 3.17 (s, 1H), 3.12 (d, *J* = 14.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.73 (d, $^1J_{C,F}$ = 246 Hz), 136.69, 135.20, 131.65, 129.82, 127.65 (d, $^3J_{C,F}$ = 8 Hz), 123.67, 115.97 (d, $^2J_{C,F}$ = 22 Hz), 69.13, 57.39; IR (film): ν_{max} = 3491.6, 3296.1, 1605.5, 1489.6, 1311.8, 1223.2, 1128.5, 1053.1, 998.1, 835.9, 759.3 cm^{-1}; ESI-MS: *m*/*z* = 352.0 $[M+Na]^+$; HR-MS: *m*/*z* = 352.0196 $[M+Na]^+$, calcd. for $C_{14}H_{13}ClFNNaO_3S$: 352.0189.

***N*,2-Bis(4-chlorophenyl)-2-hydroxyethanesulfonamide (5cc):** White solid; yield: 99%; >99% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (92:8) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 32.376 min, t_{major} = 30.101 min; $[\alpha]_D^{27}$: +27.2 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.27 (m, 5H), 7.21 (t, *J* = 8.0 Hz, 4H), 5.31 (d, *J* = 10.4 Hz, 1H), 3.61 (s, 1H), 3.36 (dd, *J* = 14.4, 11.2 Hz, 1H), 3.16 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.28, 135.17, 134.68, 131.87, 129.90, 129.33, 127.21, 123.77, 69.34, 57.26; IR (film): ν_{max} = 3443.6, 3281.4, 1489.3, 1330.3, 1142.2, 1064.3, 831.3, 778.4, 540.6 cm^{-1}; ESI-MS: *m*/*z* = 368.0 $[M+Na]^+$; HR-MS: *m*/*z* = 367.9880 $[M+Na]^+$, calcd. for $C_{14}H_{13}Cl_2NNaO_3S$ 367.9885.

2-(4-Bromophenyl)-*N*-(4-chlorophenyl)-2-hydroxyethanesulfonamide (5dc): White solid; yield: 97%; 98% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 26.399 min, t_{major} = 23.762 min; $[\alpha]_D^{27}$: +26.8 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 5.29 (d, *J* = 10.0 Hz, 1H), 3.49 (s, 1H), 3.35 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.17 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.76, 135.13, 132.30, 131.91, 129.92, 127.52, 123.79, 122.83, 69.43, 57.18; IR (film): ν_{max} = 3448.8, 3297.2, 1490.0, 1388.1, 1326.7, 1142.1, 1064.9, 1002.0, 915.7, 834.4, 587.6 cm^{-1}; ESI-MS: *m*/*z* = 411.9 $[M+Na]^+$; HR-MS: *m*/*z* = 411.9371 $[M+Na]^+$, calcd- for $C_{14}H_{13}BrClNNaO_3S$: 411.9380.

***N*-(4-Chlorophenyl)-2-hydroxy-2-(4-nitrophenyl)-ethanesulfonamide (5ec)**: White solid; yield: 98%; >99% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{major} = 44.095 min; $[\alpha]_D^{27}$: +29.8 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.13 (s, 1H), 5.37 (d, *J* = 10.0 Hz, 1H), 3.67 (s, 1H), 3.28 (dd, *J* = 14.4 10.4 Hz, 1H), 3.15 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 155.99, 153.10, 152.25, 142.50, 134.49, 132.91, 128.78, 126.78, 73.04, 63.48; IR (film): ν_{max} = 3453.3, 3287.5, 1603.0, 1515.6, 1350.0, 1144.7, 1002.3, 920.9, 852.0,696.2,532.8 cm^{-1}; ESI-MS: *m*/*z* = 379.0 $[M+Na]^+$; HR-MS: *m*/*z* = 379.0123 $[M+Na]^+$, calcd. for $C_{14}H_{13}ClN_2NaO_5S$: 379.0126.

***N*-(4-Chlorophenyl)-2-hydroxy-2-*p*-tolylethanesulfonamide (5fc):** White solid; yield: 93%; 99% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-

H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 20.680 min, t_{major} = 23.234 min; $[\alpha]_D^{27}$: +21.5 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.8 Hz, 3H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.14 (dd, *J* = 13.2 8.0 Hz, 4H), 5.29 (d, *J* = 10.0 Hz, 1H), 3.42 (s, 1H), 3.40–3.36 (m, 1H), 3.17 (d, *J* = 13.6 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.81, 137.90, 135.44, 131.63, 129.82, 129.79, 125.81, 123.85, 69.88, 57.26, 21.35; IR (film): ν_{max} = 3447.4, 3295.1, 1493.2, 1316.8, 1134.1, 1090.3, 1004.4, 823.9, 594.7 cm^{-1}; ESI-MS: *m*/*z* = 348.0 $[M+Na]^+$; HR-MS: *m*/*z* = 348.0421 $[M+Na]^+$, calcd. for $C_{15}H_{16}ClNNaO_3S$: 348.0432.

***N*-(4-Chlorophenyl)-2-hydroxy-2-(4-methoxyphenyl)-ethanesulfonamide (5gc):** White solid; yield: 92%; >99% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 35.086 min, t_{major} = 31.594 min; $[\alpha]_D^{27}$: +21.4 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 7.2 Hz, 2H), 7.17–7.11 (m, 5H), 6.77 (d, *J* = 7.6 Hz, 2H), 5.21 (d, *J* = 10.4 Hz, 1H), 3.67 (s, 3H), 3.31 (dd, *J* = 14.0 10.8 Hz, 1H), 3.19 (s, 1H), 3.07 (d, *J* = 14.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.02, 135.48, 132.92, 131.64, 129.79, 127.21, 123.86, 114.52, 69.74, 57.19, 55.54; IR (film): ν_{max} = 3444.0, 3114.1, 1611.4, 1493.2, 1397.0, 1333.8, 1222.0, 1128.1, 1045.9, 944.1, 837.1, 538.7 cm^{-1}; ESI-MS: *m*/*z* = 364.0 $[M+Na]^+$; HR-MS: *m*/*z* = 364.0380 $[M+Na]^+$, calcd. for $C_{15}H_{16}ClNNaO_4S$: 364.0381.

2-(2-Chlorophenyl)-*N*-(4-chlorophenyl)-2-hydroxyethanesulfonamide (5hc): White solid; yield: 97%; 97% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 21.667 min, t_{major} = 26.282 min; $[\alpha]_D^{27}$: +35.6 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 7.2 Hz, 1H), 7.45 (s, 1H), 7.28–7.24 (m, 7H), 5.71 (d, *J* = 10.0 Hz, 1H), 3.84 (s, 1H), 3.42 (d, *J* = 14.8 Hz, 1H), 3.27 (dd, *J* = 14.8 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.14, 135.31, 131.47, 131.36, 129.86, 129.80, 127.74, 127.24, 123.30, 66.73, 55.76; IR (film): ν_{max} = 3537.8, 3276.5, 1632.9, 1492.3, 1394.7, 1324.2, 1291.6, 1105.2, 1044.3, 919.2, 827.5, 765.3, 702.7,559.4 cm^{-1}; ESI-MS: *m*/*z* = 368.0 $[M+Na]^+$; HR-MS: *m*/*z* = 367.9891 $[M+Na]^+$, calcd- for $C_{14}H_{13}Cl_2NNaO_3S$: 367.9885.

2-(3-Bromophenyl)-*N*-(4-chlorophenyl)-2-hydroxyethanesulfonamide (5ic): White solid; yield: 92%; 98% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 22.329 min, t_{major} = 26.168 min; $[\alpha]_D^{27}$: +26.1 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.44 (m, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.24 (dd, *J* = 11.6 3.6 Hz, 4H), 5.33 (d, *J* = 10.0 Hz, 1H), 3.37 (dd, *J* = 14.4 10.4 Hz, 1H), 3.25 (s, 1H), 3.18 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.02, 135.04, 131.88, 130.71, 129.87, 128.87, 124.42, 123.77, 123.17, 69.25, 57.2; IR (film): ν_{max} = 3503.3, 3270.2, 1490.8, 1318.6, 1287.4, 1135.1, 1088.0, 833.3, 789.8, 593.9 cm^{-1}; ESI-MS: *m*/*z* = 411.9 $[M+Na]^+$; HR-MS: *m*/*z* = 411.9385 $[M+Na]^+$, calcd. for $C_{14}H_{13}BrClNNaO_3S$: 411.9380.

***N*-(4-Chlorophenyl)-2-hydroxy-2-(3-methoxyphenyl)-ethanesulfonamide (5jc):** Colorless oil; yield: 98%; 99% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 31.424 min, t_{major} = 34.240 min; $[\alpha]_D^{27}$: +12.0 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (s, 1H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 3H), 6.84–6.81 (m, 3H), 5.30 (d, *J* = 10.0 Hz, 1H), 3.75 (s, 3H), 3.67 (s, 1H), 3.40 (dd, *J* = 14.4 10.8 Hz, 1H), 3.21 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.12, 142.55, 135.39, 131.61, 130.28, 129.80, 123.77, 117.99, 114.06, 111.59, 69.85, 57.29, 55.48; IR (film): ν_{max} = 3474.7, 3275.1, 1600.4, 1491.8, 1326.9, 1263.6, 1149.7, 1046.0, 924.3, 728.7, 697.5 cm^{-1}; ESI-MS: *m*/*z* = 364.1 $[M+Na]^+$; HR-MS: *m*/*z* = 364.0385 $[M+Na]^+$, calcd. for $C_{15}H_{16}ClNNaO_4S$: 364.0381.

***N*-(4-Chlorophenyl)-2-(3,4-dichlorophenyl)-2-hydroxyethanesulfonamide (5kc):** White solid; yield: 95%; 96% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralcel OD-H with hexane/*i*-PrOH (92:8) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 24.197 min, t_{major} = 26.996 min; $[\alpha]_D^{27}$: −25.4 (*c* 0.80 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.18 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 5.31 (d, *J* = 10.0 Hz, 1H), 3.58 (s, 1H), 3.35 (dd, *J* = 14.4, 10.8 Hz, 1H), 3.18 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.91, 134.94, 133.38, 132.94, 132.07, 131.15, 129.99, 127.87, 125.11, 123.79, 68.89, 57.24; IR (film): ν_{max} = 3436.6, 32843, 1491.7, 1386.5, 1329.7, 1147.3, 1074.9, 1007.6, 909.5, 773.0, 624.7 cm^{-1}; ESI-MS: *m*/*z* = 402.0 $[M+Na]^+$; HR-MS: *m*/*z* = 401.9505 $[M+Na]^+$, calcd. for $C_{14}H_{12}Cl_3NNaO_3S$: 401.9496.

***N*-(4-Chlorophenyl)-2-(2,4-dichlorophenyl)-2-hydroxyethanesulfonamide (5lc):** White solid; yield: 98%; 95% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 28.958 min, t_{major} = 34.207 min; $[\alpha]_D^{27}$: +37.3 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.6 Hz 1H), 7.27–7.22 (m, 7H), 5.62 (d, *J* = 9.2 Hz, 1H), 3.66 (s, 1H), 3.37 (d, *J* = 14.4 Hz, 1H), 3.23–3.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.67, 135.06, 131.95, 131.72, 129.89, 129.64, 128.27, 128.10, 123.27, 66.42, 55.76; IR (film): ν_{max} = 3522.8, 3256.2, 1590.2, 1491.9, 1388.9, 1321.5, 1143.2, 1072.2, 924.1, 826.6, 737.3, 570.3 cm^{-1}; ESI-MS: *m*/*z* = 402.0 $[M+Na]^+$; HR-MS: *m*/*z* = 401.9510 $[M+Na]^+$, calcd. for $C_{14}H_{12}Cl_3NNaO_3S$: 401.9496.

***N*-(4-Chlorophenyl)-2-(furan-2-yl)-2-hydroxyethanesulfonamide (5mc):** White solid; yield: 93%; 97% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 26.901 min, t_{major} = 29.079 min; $[\alpha]_D^{27}$: +78.0 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (s, 1H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.12 (s, 1H), 7.30–6.27 (m, 2H), 5.34 (d, *J* = 10.0 Hz, 1H), 3.58 (dd, *J* = 14.8, 6.4 Hz, 1H), 3.32 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.65, 143.16, 135.24, 131.72, 129.82, 123.79, 110.78, 107.75, 63.80, 54.22; IR (film): ν_{max} = 3432.6, 3284.0, 1493.1, 1391.7, 1320.0, 1138.4, 1089.6, 1018.6, 818.6, 747.3, 529.4 cm^{-1}; ESI-MS: *m*/*z* = 324.0 $[M+Na]^+$; HR-MS: *m*/*z* = 324.0062 $[M+Na]^+$, calcd. for $C_{12}H_{12}ClNNaO_4S$: 324.0068.

***N*-(4-Chlorophenyl)-2-hydroxypropane-1-sulfonamide (5nc):** White solid; yield: 92%; 64% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (70:30) as the eluent, flow:

1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 5.516 min, t_{major} = 5.031 min; $[\alpha]_D^{27}$: −15.2 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 4.47–4.41 (m, 1H), 3.24 (s, 1H), 3.18 (dd, *J* = 14.4, 10 Hz, 1H), 3.09 (dd, *J* = 14.4, 2.0 Hz, 1H), 1.26 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.30, 131.41, 129.77, 123.25, 69.75, 63.74, 57.54, 23.04; IR (film): ν_{max} = 3474.4, 3431.6, 1444.9, 1304.4.1, 1284.3, 1137.8, 1063.5, 1024.1, 754.8, 691.1, 654.3, 628.5 cm^{-1}; ESI-MS: *m*/*z* = 372.0 $[M+Na]^+$; HR-MS: *m*/*z* = 272.0119 $[M+Na]^+$, calcd. for $C_9H_{12}ClNNaO_3S$: 272.0119.

***N*-(4-Chlorophenyl)-1-hydroxy-1,2,3,4-tetrahydronaphthalene-2-sulfonamide (5oc):** White solid; yield: 94%; 98% *ee*, >99:1 *dr*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 25.708 min, t_{major} = 31.198 min; $[\alpha]_D^{27}$: +21.8 (*c* 0.80 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 7.2 Hz, 1H), 7.38–7.20 (m, 6H), 7.11 (d, *J* = 6.8 Hz, 1H), 6.91 (s, 1H), 5.28 (s, 1H), 3.45–3.42 (m, 1H), 2.99–2.94 (m, 1H), 2.55 (s, 1H), 2.25–2.16 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 137.78, 137.68, 134.97, 130.02, 129.08, 128.47, 127.80, 127.53, 125.92, 121.29, 65.25, 61.92, 27.85, 17.84; IR (film): ν_{max} = 3453.5, 3376.9, 3294.4, 1491.9, 1391.8, 1324.6, 1271.4, 1131.8, 967.6, 834.5, 778.8, 737.7, 602.1 cm^{-1}; ESI-MS: *m*/*z* = 360.8 $[M+Na]^+$; HR-MS: *m*/*z* = 360.8105 $[M+Na]^+$, calcd. for $C_{16}H_{16}ClNNaO_3S$: 360.8109.

***N*-(4-Chlorophenyl)-1-oxo-2,3-dihydro-1*H*-indene-2-sulfonamide (5pc):** White solid; yield: 92%; 98% *ee*; >99:1 *dr*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 30.437 min, t_{major} = 25.587 min; $[\alpha]_D^{27}$: −9.5 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.40 (m, 1H), 7.29 (t, *J* = 3.6 Hz, 2H), 7.24 (s, 2H), 7.16–7.14 (m, 3H), 6.95 (s, 1H), 5.44 (t, *J* = 7.2 Hz, 1H), 4.05 (dd, *J* = 15.2, 6.8 Hz, 1H), 3.54 (dd, *J* = 17.2, 6.8 Hz, 1H), 3.23 (dd, *J* = 16.8, 8.8 Hz, 1H), 2.91 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 143.29, 139.81, 137.60, 129.08, 128.40, 127.63, 126.97, 124.65, 124.51, 121.33, 73.60, 63.59, 31.93; IR (film): ν_{max} = 3397.8, 3231.6, 1492.8, 1395.1, 1326.4, 1135.7, 1017.3, 957.1, 828.9, 751.8, 567.2 cm^{-1}; ESI-MS: *m*/*z* = 346.0 $[M+Na]^+$; HR-MS: *m*/*z* = 346.0278 $[M+Na]^+$, calcd. for $C_{15}H_{14}ClNNaO_3S$: 346.0281.

Phenyl-2-(phenylsulfonyl)ethanol (7a): White solid; yield: 96%; 98% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (90:10) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 28.651 min, t_{major} = 32.484 min; $[\alpha]_D^{27}$: +32.0 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.6 Hz, 2H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.31–7.29 (m, 5H), 5.27 (d, *J* = 10.0 Hz, 1H), 3.72 (s, 1H), 3.51 (dd, *J* = 14.4 10.4 Hz, 1H), 3.33 (dd, *J* = 14.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.76, 139.25, 134.19, 129.54, 128.84, 128.42, 128.06, 125.74, 68.53, 64.00; IR (film): ν_{max} = 3481.1, 1447.3, 1281.9, 1135.3, 1135.7, 1084.3, 1062.2, 966.2, 829.6, 785.4, 762.1, 744.8, 704.9, 681.4 cm^{-1}; ESI-MS: *m*/*z* = 285.1 $[M+Na]^+$; HR-MS: *m*/*z* = 285.0553 $[M+Na]^+$, calcd. for $C_{14}H_{14}NaO_3S$: 285.0556.

1-(4-Fluorophenyl)-2-(phenylsulfonyl)ethanol (7b): White solid; yield: 93%; 98% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (70:30) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 9.996 min, t_{major} = 11.015 min; $[\alpha]_D^{27}$: +37.6 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95–7.93 (m, 2H), 7.71–7.67 (m, 1H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.29–7.25 (m, 2H), 7.01–6.97 (m, 2H), 5.27 (d, *J* = 9.6, 1H), 3.80 (s, 1H), 3.48 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.31 (dd, *J* = 14.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.58 (d, $^1J_{C,F}$ = 246 Hz), 139.17, 136.60, 134.29, 129.60, 128.05, 127.56 (d, $^3J_{C,F}$ = 9 Hz), 115.74 (d, $^2J_{C,F}$ = 21 Hz), 67.92, 63.97; IR (film): ν_{max} = 3478.3, 1604.2, 1509.8, 1446.2, 1281.7, 1224.9, 1168.1, 1135.9, 1065.4, 843.2, 768.7, 743.6, 682.1 cm^{-1}; ESI-MS: *m*/*z* = 303.0 $[M+Na]^+$; HR-MS: *m*/*z* = 303.0471 $[M+Na]^+$, calcd. for $C_{14}H_{13}FNaO_3S$: 303.0462.

1-(4-Chlorophenyl)-2-(phenylsulfonyl)ethanol (7c): White solid; yield: 93%; 98% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (70:30) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 11.071 min, t_{major} = 11.650 min; $[\alpha]_D^{27}$: +42.2 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.26 (d, *J* = 10.0, 1H), 3.80 (s, 1H), 3.46 (dd, *J* = 14.4 10.0 Hz, 1H), 3.31 (dd, *J* = 14.4 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.28, 139.13, 134.33, 134.18, 129.63, 129.01, 128.06, 127.19, 67.92, 63.88; IR (film): ν_{max} = 3475.8, 1489.9, 1284.1, 1133.8, 1083.4, 1073.3, 995.7, 835.7, 782.2, 751.8, 684.4 cm^{-1}; ESI-MS: *m*/*z* = 346.0 $[M+Na]^+$; HR-MS: *m*/*z* = 319.0166 $[M+Na]^+$, calcd. for $C_{14}H_{13}ClNaO_3S$: 319.0166.

1-(4-Bromophenyl)-2-(phenylsulfonyl)ethanol (7d): White solid; yield: 97%; 98% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak OJ-H with hexane/*i*-PrOH (60:40) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 13.091 min, t_{major} = 16.323 min; $[\alpha]_D^{27}$: +32.1 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 7.5 Hz, 2H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 5.23 (d, *J* = 9.6, 1H), 3.83 (s, 1H), 3.46 (dd, *J* = 14.1, 9.9 Hz, 1H), 3.29 (dd, *J* = 14.4, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.81, 139.11, 134.29, 131.91, 129.59, 128.03, 127.50, 122.26, 67.94, 63.78; IR (film): ν_{max} = 3474.8, 1469.9, 1282.5, 1133.8, 1087.4, 1079.3, 995.7, 835.7, 772.2, 753.8, 674.4 cm^{-1}; ESI-MS: *m*/*z* = 363.0 $[M+Na]^+$; HR-MS: *m*/*z* = 362.9648 $[M+Na]^+$, calcd. for $C_{14}H_{13}BrNaO_3S$: 362.9661.

2-(Phenylsulfonyl)-1-*p*-tolylethanol (7e): White solid; yield: 92%; 98% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (70:30) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 10.429 min, t_{major} = 11.103 min; $[\alpha]_D^{27}$: +37.4 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.6 Hz, 2H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.23 (d, *J* = 10.0, 1H), 3.63 (d, *J* = 1.6, 1H), 3.50 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.32 (dd, *J* = 14.4, 1.2 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.28, 138.27, 137.80, 134.17, 129.54, 129.51, 128.08, 125.69, 68.41, 64.00, 21.22; IR (film) ν_{max}: 3485.2, 1447.8, 1286.6 1132.8, 1067.2, 997.8, 820.6, 788.4, 764.2, 741.4,720.8, 682.3 cm^{-1}; ESI-MS: *m*/*z* = 299.1 $[M+Na]^+$; HR-MS: *m*/*z* = 299.0701 $[M+Na]^+$, calcd. for $C_{15}H_{16}NaO_3S$: 299.0712.

1-(2-Fluorophenyl)-2-(phenylsulfonyl)ethanol (7f): White solid; yield: 95%; 95% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (70:30) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]:

t_{minor} = 9.022 min, t_{major} = 11.641 min; $[\alpha]_D^{27}$: +27.0 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 7.6 Hz, 2H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.64–7.56 (m, 3H), 7.31–7.26 (m, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.98(d, *J*=9.6 Hz, 1H), 5.50 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 1H), 3.54–3.52(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.10 (d, $^1J_{C,F}$ = 245 Hz), 138.97, 134.24, 129.87 (d, $^3J_{C,F}$ = 8 Hz), 129.55, 128.08, 127.71 (d, $^3J_{C,F}$ = 12 Hz), 127.40 (d, $^4J_{C,F}$ = 4 Hz), 124.70 (d, $^4J_{C,F}$ = 3 Hz), 115.38 (d, $^2J_{C,F}$ = 21 Hz), 63.15, 62.31; IR (film): ν_{max} = 3491.0, 1583.8, 1492.9, 1449.9, 1285.8, 1225.6, 1165.5, 1135.4, 1065.4, 949.5, 812.6, 767.2, 748.1, 730.3, 681.5 cm^{-1}; ESI-MS: *m*/*z* = 303.0 $[M+Na]^+$; HR-MS: *m*/*z* = 303.0462, $[M+Na]^+$, calcd. for $C_{14}H_{13}FNaO_3S$: 303.0462.

1-(3-Fluorophenyl)-2-(phenylsulfonyl)ethanol (7g): White solid; yield: 97%; 96% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (70:30) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 8.046 min, t_{major} = 9.221 min; $[\alpha]_D^{27}$: +33.6 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97–7.95 (m, 2H), 7.72–7.68 (m, 1H), 7.60 (t, *J* = 7.2 Hz, 2H), 7.06–7.03 (m, 2H), 6.98–6.94 (m, 1H), 5.29 (d, *J* = 10.0 Hz, 1H), 3.81 (d, *J* = 2.0 Hz, 1H), 3.47 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.31 (dd, *J* = 14.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.06 (d, $^1J_{C,F}$ = 246 Hz), 143.30 (d, $^3J_{C,F}$ = 7 Hz), 139.11, 134.37, 130.48 (d, $^3J_{C,F}$ = 8 Hz), 129.66, 128.08, 121.31, 115.32 (d, $^2J_{C,F}$ = 21 Hz), 112.89 (d, $^1J_{C,F}$ = 22 Hz), 67.94, 63.91; IR (film): ν_{max} = 3468.9, 1614.4, 1591.5, 1448.3, 1287.9, 1240.4, 1138.5, 1071.6, 919.5, 873.9, 785.4, 744.2, 687.6, 695.1 cm^{-1}; ESI-MS: *m*/*z* = 303.0 $[M+Na]^+$; HR-MS: *m*/*z* = 303.0466 $[M+Na]^+$, calcd. for $C_{14}H_{13}FNaO_3S$: 303.0462.

1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethanol (7h): White solid; yield: 94%; 96% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (70:30) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 12.380 min, t_{major} = 13.349 min; $[\alpha]_D^{27}$: +44.6 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97–7.95 (m, 2H), 7.80–7.77 (m, 4H), 7.68–7.64 (m, 2H), 7.56 (t, *J* = 8.0 Hz, 2H), 7.49–7.45 (m, 2H), 7.36–7.34 (m, 1H), 5.45 (d, *J* = 10.0 Hz, 1H), 3.84 (d, *J* = 1.6 Hz, 1H), 3.59 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.43 (dd, *J* = 14.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.25, 138.02, 134.20, 133.23, 129.54, 128.80, 128.09, 127.78, 126.55, 126.41, 124.88, 123.35, 68.70, 63.95; IR (film): ν_{max} = 3502.7, 1445.9, 1389.6, 1282.8, 1239.7, 1163.7, 1135.9, 1082.9, 1058.3, 878.0, 841.9, 827.5, 800.4, 763.2, 681.6, 625.6 cm^{-1}; ESI-MS: *m*/*z* = 335.1 $[M+Na]^+$; HR-MS: *m*/*z* = 335.0706 $[M+Na]^+$, calcd. for $C_{18}H_{16}NaO_3S$: 335.0712.

1-(Furan-2-yl)-2-(phenylsulfonyl)ethanol (7i): White solid; yield: 95%; 98% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (70:30) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 9.484 min, t_{major} = 10.180 min; $[\alpha]_D^{27}$: +17.2 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 2H), 7.28–7.26 (m, 1H), 6.28–6.26 (m, 2H), 5.28–5.24 (m, 1H), 3.67 (dd, *J* = 14.4, 4.8 Hz, 1H), 3.59 (d, *J* = 3.6 Hz, 1H), 3.53 (dd, *J* = 14.4, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.58, 142.72, 139.13, 134.18, 129.52, 128.10, 110.55, 107.49, 62.79, 60.66; IR (film): ν_{max} = 3482.2, 1448.3, 1397.3, 1285.3, 1136.1, 1083.4, 1055.2, 997.7, 923.6, 798.5, 755.3, 734.0,683.7 cm^{-1}; ESI-MS: *m*/*z* = 275.0 $[M+Na]^+$; HR-MS: *m*/*z* = 275.0348 $[M+Na]^+$, calcd. for $C_{12}H_{12}NaO_4S$: 275.0349.

2-(Phenylsulfonyl)-1-(thiophen-2-yl)ethanol (7j): White solid; yield: 94%; 98% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (70:30) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 10.870 min, t_{major} = 13.183 min; $[\alpha]_D^{27}$: +16.8 (*c* 1.00 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.6 Hz, 2H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 2H), 7.24–7.22 (m, 1H), 6.92–6.90 (m, 2H), 5.55–5.53 (m, 1H), 3.83 (d, *J* = 2.4 Hz, 1H), 3.62 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.46 (dd, *J* = 14.4, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.25, 139.13, 134.27, 129.55, 128.09, 126.89, 125.65, 124.32, 64.99, 63.82; IR (film): ν_{max} = 3479.9, 1447.3, 1390.5, 1284.3, 1135.6, 1083.9, 1061.0, 793.6, 762.2, 722.4, 683.6 cm^{-1}; ESI-MS: *m*/*z* = 291.0 $[M+Na]^+$; HR-MS: *m*/*z* = 291.0111 $[M+Na]^+$, calcd. for $C_{12}H_{12}NaO_3S_2$: 291.0120.

1-(Phenylsulfonyl)propan-2-ol (7k): Colorless oil; yield: 93%; 82% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (70:30) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 14.051 min, t_{major} = 8.809 min; $[\alpha]_D^{27}$: +8.4 (*c* 0.25 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 7.6 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 2H), 4.33–4.29 (m, 1H), 3.44 (s, 1H), 3.23 (dd, *J* = 14.4, 9.2 Hz, 1H), 3.16 (dd, *J* = 14.4, 2.0 Hz, 1H), 1.23 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.24, 134.19, 129.58, 128.00, 63.44, 62.45, 22.68; IR (film): ν_{max} = 3499.5, 1447.3, 1289.4, 1140.6, 1082.4, 1043.5, 938.2, 744.5, 687.2, 637.3 cm^{-1}; ESI-MS: *m*/*z* = 223.0 $[M+Na]^+$; HR-MS: *m*/*z* = 201.0586 $[M+H]^+$, calcd. for $C_9H_{13}O_3S$: 201.0580.

1-(Phenylsulfonyl)butan-2-ol (7l): Colorless oil; yield: 94%; 84% *ee*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (70:30) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 12.019 min, t_{major} = 9.024 min; $[\alpha]_D^{27}$: +8.5 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.6 Hz, 2H), 7.68–7.64 (m, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 4.08–4.06 (m, 1H), 3.36 (s, 1H), 3.25–3.15 (m, 2H), 1.58–1.45 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.35, 134.11, 129.53, 127.97, 67.20, 62.01, 29.55, 9.40; IR (film): ν_{max} = 3506.3, 1447.2, 1290.6, 1140.1, 977.9, 790.3, 745.4, 687.4 cm^{-1}; ESI-MS: *m*/*z* = 215.1 $[M+H]^+$; HR-MS: *m*/*z* = 215.0734 $[M+Na]^+$, calcd. for $C_{10}H_{15}O_3S$: 215.0736.

2-(Phenylsulfonyl)-2,3-dihydro-1*H*-inden-1-ol (7m): White solid; yield: 97%; 98% *ee*, >99:1 *dr*. The enantiomeric excess was determined by HPLC [Daicel Chiralpak AD-H with hexane/*i*-PrOH (70:30) as the eluent, flow: 1.0 mL min^{-1}; λ = 210 nm]: t_{minor} = 11.421 min, t_{major} = 9.323 min; $[\alpha]_D^{27}$: +7.2 (*c* 0.50 in CH_3COCH_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.0 Hz, 2H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 6.8 Hz, 1H), 7.33–7.26 (m, 3H), 5.34 (t, *J* = 6.0 Hz, 1H), 4.01–3.96 (m, 1H), 3.71 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.37 (d, *J* = 6.8 Hz, 1H), 3.19 (dd, *J* = 16.0, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.84, 139.76, 139.31, 133.96, 129.55, 129.28, 128.61, 127.86, 125.08, 124.93, 74.67, 67.01, 31.46; IR (film): ν_{max} = 3474.4, 1444.9, 1304.4, 1284.3, 1137.8, 1084.8, 1063.5, 754.8, 724.2, 691.2, 654.3 cm^{-1}; ESI-MS: *m*/*z* = 297.1 $[M+H]^+$; HR-MS: *m*/*z* = 297.0550 $[M+Na]^+$, calcd. for $C_{15}H_{14}NaO_3S$: 297.0556.

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[15] Crystal structure of **5aa**: $C_{14}H_{15}NO_3$ S, M = 277.33; a block crystal (0.60 × 0.60 × 0.40 mm mm), T = 293(2), λ (Mo-Ka) = 0.71070 Å, monoclinic, space group: P 21, a = 7.3822(17) Å, b = 13.429(3) Å, c = 13.736(3) Å, V = 1361.8(6) Å3, 11502 total reflections, 2475 unique, R_{int} = 0.0426, $R1$ = 0.0225 (I > 2 σ), $wR2$ = 0.0869, Absolute structure parameter: 0.02(9). CCDC 876361 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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