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Vanadium-catalyzed enantioselective oxidation of allyl sulfides

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ABSTRACT

The enantioselective oxidation of allyl sulfides with a vanadyl complex of 3,5-diiodosalicylidene *tert*-leucinol as a catalyst and aqueous hydrogen peroxide as an oxidant afforded chiral allyl sulfoxides with high enantioselectivities of up to 97.3% ee and moderate yields.

1. Introduction

Chiral sulfoxides have important and diverse applications in the fields of medicine, catalysis, and organic synthesis.[1] Chiral allyl sulfoxides are an important subclass of chiral sulfoxides. Some chiral allyl sulfoxides show biological activities. For example, alliin [(+)-(*S*)-2-propenyl-L-cysteine sulfoxide], which exists in garlic, is a chiral allyl sulfoxide, and shows strong antioxidant and hydroxyl radical scavenging properties[2] and promotes an obvious increase in the engulfing capacity of phagocyting cells.[3] Some other chiral allyl sulfoxides have been extensively used as chiral intermediates, and chiral auxiliaries for organic synthesis, especially in the total synthesis of natural products.[4]

The methods for the synthesis of chiral allyl sulfoxides mainly include Andersen's method, biotransformations, and enantioselective methods. The Andersen method was first reported in 1962.[5] Until now, chiral allyl sulfoxides were mainly synthesized by Andersen's method. However, this method is environmentally unfriendly, not atom-economical, and the separation of alkyl methylsulfinate diastereomers is complicated.[4g] Biotransformations are promising processes for the preparation of chiral allyl sulfoxides. Ohta carried out the microbial oxidation of allyl sulfides with *Corynebacterium equi* IFO 3730. Allyl phenyl sulfoxide (100% ee) and allyl tolyl sulfoxide (92.4% ee) can be obtained by this method.[6] Gonzalo utilized 4-hydroxyacetophenone monooxygenase from *Pseudomonas fluorescens* ACB as an oxidative biocatalyst to transform allyl phenyl sulfide into its sulfoxide with up to 98% ee.[7] Enantioselective sulfoxidation is a straightforward and atom-economical protocol. Chemists have developed enantioselective sulfide oxidations catalyzed by Ti,[8] V,[9] Fe,[10] and so on,[1] but the enantioselective oxidation of allyl sulfide has been less studied. Recently Bolm reported the iron-catalyzed oxidation of allyl phenyl sulfide to give 63% ee.[10b]

Chiral allyl aryl sulfoxides were reported to racemize readily,[11] but the extremely high ee values obtained in biotransformations[6,7] demonstrate that optically active allyl aryl sulfoxides are relatively stable within a certain time. As part of our continuous studies on enantioselective sulfoxidations,[12] we herein report the vanadium-catalyzed enantioselective oxidation of allyl sulfides.

2. Results and discussion

2.1. The effects of various factors on vanadium-catalyzed oxidation of allyl phenyl sulfide 1a

Chiral catalysts are one of the most important factors for a catalytically enantioselective reaction, and the chiral ligand is the key to high enantioselectivity. Therefore, we mainly investigated the effect of the vanadyl catalyst on the oxidation of allyl phenyl sulfide **1a**. The preformed chiral vanadyl complexes **3** were prepared from vanadyl acetoacetonate and chiral salicylidene amino alcohols derived from salicylaldehydes and chiral amino alcohols according to the literature (Fig. 1).[9] When the vanadyl complexes **3a**–**3d** derived from salicylaldehyde and alaninol, isoleucinol, valinol and *tert*-leucinol, respectively, were used for the sulfoxidation, an obvious increase in enantioselectivity from 33.5% ee to 65.9% ee was observed, which correlates with the size of the R^2 group in the salicylidene amino alcohols from methyl, to isobutyl, to isopropyl, to *tert*-butyl (Table 1, entries 1–4). The more bulky the R^2 group, the higher the ee value of allyl phenyl sulfoxide **2a**.

When a bulky *tert*-butyl group was used as the R^3 group in vanadyl complexes **3e**–**3h** of salicylidene amino alcohols, ee values from 22.0% ee to 55.7% ee corresponding to the size of the R^2 group in complexes **3e**–**3h** were observed, but the enantioselectivities decreased, (Table 1, entries 5–8).

When an iodo group was used as the R^3 group in vanadyl complexes **3i**–**3l**, higher enantioselectivities (44.3–72.0%) were observed when compared to vanadyl complexes **3a**–**3d** with R^3 = H and vanadyl complexes **3e**–**3h** with R^3 = *tert*-butyl, (Table 1, entries

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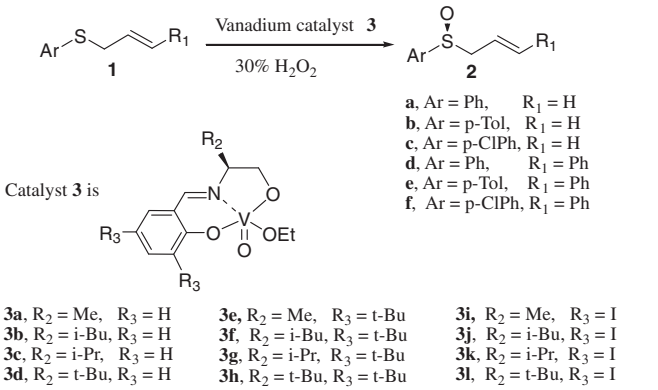

Figure 1. Oxidation of allyl sulfides **1** catalyzed by chiral vanadium complexes **3** derived from salicylidene amino alcohols.

Table 1
Effects of various factors on the sulfide oxidation[a]

Entry	Catalyst	H_2O_2 (equiv)	Yield[b] (%)	ee[c] (%)
1	**3a**	1.2	61.3	33.5
2	**3b**	1.2	70.1	51.2
3	**3c**	1.2	67.3	56.0
4	**3d**	1.2	73.2	65.9
5	**3e**	1.2	49.2	22.0
6	**3f**	1.2	68.2	46.2
7	**3g**	1.2	58.0	51.0
8	**3h**	1.2	64.3	55.7
9	**3i**	1.2	63.2	46.3
10	**3j**	1.2	69.1	55.4
11	**3k**	1.2	71.5	65.9
12	**3l**	1.2	75.4	72.0
13[d]	**3l**	1.2	78.0	84.6
14[d,e]	**3l**	1.2	75.2	73.8
15[d,f]	**3l**	1.2	70.6	84.4
16[d]	**3l**	0.8	57.0	51.1
17[d]	**3l**	1.6	62.1 (13.6)	90.6
18[d]	**3l**	2.0	49.0 (27.3)	88.2
19[d,g]	**3l**	1.6	58.2 (16.2)	92.8
20[d,h]	**3l**	1.6	57.0 (15.5)	97.3

[a] Reaction conditions: vanadium–Schiff base complex **3**, allyl phenyl sulfide **1** (1.0 mmol) and 30% aqueous H_2O_2 in 2 ml CH_2Cl_2 in an ice-water bath (about 0 °C) for 16 h, unless otherwise mentioned.
[b] Isolated yield after column chromatography. Data in parentheses are the yields of allyl phenyl sulfone.
[c] The ee values were determined by HPLC analysis on a Chiralcel OD-H column. The absolute configurations were assigned by comparing specific rotations.[6,7,9b] All of the sulfoxide configurations were (*S*).
[d] Vanadium–Schiff base complexes purified by silica column chromatography were used in the sulfide oxidation.
[e] Reaction temperature was room temperature (about 25 °C).
[f] Reaction was kept in ice-salt bath (about −15 to −20 °C).
[g] 2 mol % vanadium–Schiff base complexes was used.
[h] 3 mol % vanadium–Schiff base complexes was used.

9–12 vs 1–4 and 5–8). Perhaps the bulky *tert*-butyl group influences the effective coordination of the sulfide to vanadium.[12b]

Canadyl complexes **3l** derived from L-*tert*-leucinol and 3,5-diiodosalicylaldehyde gave the highest ee value of 72.0% (Table 1, entry 12), but this was still not high enough for practical purposes.

While trying to improve the enantioselectivity of allyl phenyl sulfoxide, we noticed that the thin-layer chromatography of vanadyl complex **3l** showed more than one spot on the silica gel plate, and means that the vanadyl complex was not pure. Hence, vanadyl complex **3l** was purified on a silica gel chromatography column and the purified complex **3l** was used to evaluate the oxidation of allyl phenyl sulfide again. The ee value was improved to 84.6% with the purified complex **3l**, and the yield was good (Table 1, entry 13).

The reaction temperature was then examined. The reaction at room temperature (about 25 °C) gave a lower ee value of 72.8% (Table 1, entry 14). When the reaction was kept at a lower temperature at about −15 to −20 °C in an ice-salt bath, the ee value was nearly the same as that in the ice-water bath, but the yield decreased (Table 1, entry 15 vs 13).

From the experience of our previous research[12a,d] and Jackson's study,[9b] we knew that the amount of hydrogen peroxide could influence the vanadium-catalyzed sulfide oxidation, and excess oxidant may cause a kinetic resolution during the sulfoxidation. When less than 1 equiv of H_2O_2 was used, both the enantioselectivity and the yield decreased (Table 1, entry 16). When 1.6 equiv of H_2O_2 wasere employed, the ee value increased to 90.6% and an overoxidised product sulfone was seen (13.6% yield) (Table 1, entry 17). When the oxidant was further increased to 2 equiv, the ee value decreased marginally, but the yield noticeably decreased while the sulfone yield increased (up to 29.3%) (Table 1, entry 18).

The effects of the amounts of catalyst were investigated with the aim of improving the ee value of the allyl phenyl sulfoxide. When the amounts of vanadyl complex **3l** increased to 2 and 3 mol %, the enantioselectivities of allyl phenyl sulfoxide increased up to 92.8% and 97.3%, respectively (Table 1, entries 19 and 20 vs 17). Therefore, the conditions of 3% catalyst and 1.6 equiv of 30% aqueous H_2O_2 were used for other allyl sulfides (Table 2).

Table 2
Vanadium-catalyzed oxidation of allyl and cinnamyl aryl sulfides with the catalyst **3l**[a]

Entry	Substrate	Sulfoxide	Yield[b] (%)	ee[c] (%)
1	**1a**	**2a**	57 (15.5)	97.3
2	**1b**	**2b**	50 (20.7)	89.6
3	**1c**	**2c**	56 (17.2)	92.7
4	**1d**	**2d**	51 (28.0)	81.5
5	**1e**	**2e**	43 (32.8)	72.0
6	**1f**	**2f**	47 (27.5)	73.8

[a] Reaction conditions: purified vanadyl complexes **3l** (0.015 mmol), sulfide (0.5 mmol) and aqueous H_2O_2 (30%, 0.8 mmol), at 0 °C, 16 h.
[b] Isolated yield based on sulfide. Data in parentheses are the yields of the sulfones.
[c] Determined by HPLC on a Daicel Chiralcel OD-H column. The absolute configurations were assigned by comparing specific rotations.[6,7,9b] All of the sulfoxides configurations were (*S*).

The absolute configuration of the product allyl phenyl sulfoxide **2a** was assigned as (*S*) by comparison of its specific rotation ($[\alpha]_D^{22} = -160.2$) with the literature data ($[\alpha]_D^{25} = 164.8$ for 98% ee (*S*)-form[7] and +176 for 100% ee (*R*)-form[6]). All of the configurations of allyl phenyl sulfoxide **2a** were (*S*) for the (*S*)-form catalysts **3** (Table 1, entries 1–20). The configurations of product **2** were determined by the configuration of the amino alcohol moieties in vanadyl complexes **3**.

2.2. Vanadium-catalyzed oxidation of allyl and cinnamyl aryl sulfides with the ligand 3l

Once the optimal reaction conditions were determined, various allyl aryl sulfides **1a–1c** and cinnamyl aryl sulfides **1d–1f** were investigated. Under the optimal reaction conditions, allyl *p*-tolyl sulfide and allyl *p*-chlorophenyl sulfide were oxidized into the corresponding sulfoxides with 92% and 93% ee, respectively (Table 2, entries 2 and 3 vs 1). It is clear that the electronic properties of the *para*-substituent, on the phenyl group, of methyl or chloro did not have any significant effect. However, under the same reaction conditions, three kinds of aryl cinnamyl sulfides produced the corresponding sulfoxides with lower enantioselectivities (Table 2,

entries 4–6 vs 1–3). Cinnamyl phenyl sulfoxide was obtained in 81.5% ee. The enantioselectivities of cinnamyl *p*-tolyl sulfoxide and cinnamyl *p*-chlorophenyl sulfoxide were even lower, 72.0% and 73.8% ee, respectively. This is probably because the similar bulky aryl groups on the cinnamyl aryl sulfides decreased the chiral discrimination of chiral vanadyl catalyst **3l**.

3. Conclusions

Chiral allyl sulfoxides are of importance, and are mainly synthesized by Andersen's method. We have developed a vanadium-catalyzed allyl sulfide oxidation protocol. Various vanadyl complexes of salicylidene amino alcohols were investigated; the vanadyl complex of 3,5-diiodosalicylidene *tert*-leucinol, purified by column chromatography was the best catalyst. The effects of the reaction temperature, the amount of hydrogen peroxide and the amount of vanadyl catalysts on the sulfide oxidation were examined and the optimal conditions were obtained. In the presence of 1.6 equiv of 30% aqueous H_2O_2 and 3 mol % of chromatography-purified vanadyl complex of 3,5-diiodosalicylidene *tert*-leucinol, allyl phenyl sulfide was oxidized for 16 h inat ice-water bath to give allyl phenyl sulfoxide with 97.3% ee and 57.0% yield. Under the same conditions, other allyl sulfides and cinnamyl sulfides were oxidized to give the corresponding sulfoxides with good to excellent enantioselectivities and moderate yields.

4. Experimental

4.1. General

Chemicals were purchased from Aldrich, Acros, Aladdin, or Kelong Chemicals Company, and used without further purification. Silica Gel (300–400 mesh) for column chromatography was used. The (*R*)- and (*S*)-2-amino alcohols were synthesized by reduction of the corresponding commercially available amino acids as described.[13] Schiff base ligands and vanadium–Schiff base complexes **3a**–**3l** were prepared according to the literature.[8d,9c,g,12a] Complex **3l** was purified by silica gel chromatography column using a solution (gradiently from 20:1 to 3:1 (v/v)) of petroleum ether and ethyl acetate as an eluent. The optical rotation and IR spectrum of complex **3l** could not be taken due to its dark brown color. The ^{1}H and ^{13}C NMR spectra were consistent with the literature data.[9g]

The purities of all synthesized compounds were checked by thin-layer chromatography (TLC) using various organic solvents. Melting points were recorded on a Thermo electrothermal melting-point apparatus. The rotation data were measured on an American Rudolf Autopol IV automatic polarimeter. The IR spectra were recorded on a Bruker Tensor-27 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 400 MHz NMR spectrometer at 400 and 100 MHz, respectively, using 5 mm cylindrical tubes. Chemical shifts were referenced to $CDCl_3$ residual solvent signal (δ (^{1}H) = 7.26, δ (^{13}C) = 77.0) or internal reference TMS, with positive values in the low-field direction. Molecular weights were recorded on an Agilent LC–MS (LC 1100, MS G1956A) spectrometer equipped with an autosampler. The ee values were determined by chiral HPLC analysis with a UV–vis detector (λ 254 nm) on a Daicel Chiralcel OD-H analytical column (250 mm × 4.6 mm × 5 μm). Elemental analyses were carried out on a Carlo Erba 1106 Elemental analyzer.

4.2. Synthesis of aryl allyl sulfides

A modified Takaya procedure was adopted to synthesize these aryl allyl sulfides.[14] To a 250 ml round-bottomed -flask fitted with a magnetic stirrer bar was added 95% ethanol (30 ml), KOH (3.54 g, 0.15 mol), and aromatic thiophenol (0.13 mol). Allyl chloride (5.80 g, 0.13 mol) was added dropwise to the resulting solution within 20 min. The mixture was stirred at reflux for an additional 40 min. The mixture was condensed under reduced pressure on a rotary evaporator. The resulting residue was distributed in diethyl ether and water. The organic layer was separated, and the aqueous layer extracted with diethyl ether twice. The combined organic layer was washed with 2 M aqueous NaOH solution, water, and then dried over anhydrous K_2CO_3. The organic layer was condensed under reduced pressure on a rotary evaporator. The resulting residue was purified on a silica gel column with petroleum ether as an eluent to give the allyl aryl sulfide.

4.2.1. Allyl phenyl sulfide 1a

Colorless oil 12.3 g (63% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35–7.25 (m, 4H), 7.24–7.16 (m, 1H), 5.93–5.83 (m, 1H), 5.16–5.05 (m, 2H), 3.56–3.53 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.9, 133.5, 129.8, 128.7, 126.2, 117.6, 37.1; ESI-MS (MeOH): m/z = 151 $(M+H)^+$, 173 $(M+Na)^+$.

4.2.2. Allyl 4-tolyl sulfide 1b

Colorless oil 14.5 g (68% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27–7.24 (m, 2H), 7.10–7.08 (d, 1H, J = 8.0 Hz), 5.90–5.83 (m, 1H), 5.11–5.02 (m, 2H), 3.51–3.49 (m, 2H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.4, 133.8, 132.0, 130.6, 129.5, 117.4, 37.9, 21.0; ESI-MS (MeOH): m/z = 165 $(M+H)^+$, 187 $(M+Na)^+$.

4.2.3. Allyl 4-chlorophenyl sulfide 1c

Colorless oil 14.6 g (61% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28–7.22 (m, 4H), 5.89–5.79 (m, 1H), 5.13–5.06 (m, 2H), 3.52–3.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.3, 133.2, 132.3, 131.3, 128.9, 117.9, 37.4; ESI-MS (MeOH): m/z = 185 $(M+H)^+$, 207 $(M+Na)^+$.

4.3. Synthesis of aryl cinnamyl sulfides

The general synthesis of aryl cinnamyl sulfides was according to Guindon's procedure.[15] To a solution of cinnamyl alcohol (2 mmol) in dry dichloroethane (5 ml) was added dried zinc iodide (1.2 mmol). Aromatic thiophenol (2 mmol) was then added, and the mixture was stirred at room temperature for 3 h. The reaction was quenched with water (4 ml), and the reaction products were extracted with CH_2Cl_2 (3 × 10 ml). The combined organic layer was washed with 2 M KOH aqueous solution, and dried over anhydrous $MgSO_4$. The solution was evaporated under reduced pressure on a rotary evaporator. The resulting residue was purified on a column of silica gel (300–400 mesh) with petroleum as the eluent to give aryl cinnamyl sulfide.

4.3.1. Cinnamyl phenyl sulfide 1d

Pale white solid 0.41 g (91% yield). Mp 76–78 °C [lit. mp. 77–78].[16] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39–7.36 (m, 2H), 7.32–7.16 (m, 8H), 6.42 (d, 1H, J = 15.7 Hz), 6.24 (dt, 1H, J = 15.7, 7.2 Hz), 3.70 (dd, 2H, J = 7.1, 1.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.7, 135.8, 132.7, 130.2, 128.8, 128.5, 127.5, 126.4, 126.3, 125.0, 37.1; ESI-MS (MeOH): m/z = 227 $(M+H)^+$, 249 $(M+Na)^+$.

4.3.2. Cinnamyl *p*-tolyl sulfide 1e

Pale white solid 0.43 g (89% yield). Mp 66–68 °C [lit. mp. 67–68 °C].[17] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32–7.18 (m, 7H), 7.08 (d, 2H, J = 8.0 Hz), 6.38 (d, 1H, J = 15.7 Hz), 6.24 (dt, 1H, J = 15.7, 7.1 Hz), 3.65 (d, 2H, J = 7.1 Hz), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.8, 136.6, 132.5, 131.9, 131.1, 129.6, 128.5, 127.5, 126.3, 125.3, 37.8, 21.0; ESI-MS (MeOH): m/z = 241 $(M+H)^+$, 263 $(M+Na)^+$.

4.3.3. Cinnamyl *p*-chlorophenyl sulfide 1f

Pale white solid 0.43 g (83% yield). Mp 79–82 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33–7.26 (m, 6H), 7.25–7.17 (m, 3H), 6.40 (d, 1H, J = 15.7 Hz), 6.21 (dt, 1H, J = 15.8, 7.2 Hz), 3.65 (d, 2H, J = 7.1 Hz), 3.67 (dd, 2H, J = 7.1, 1.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.5, 134.2, 133.0, 132.5, 131.7, 128.9, 128.5, 127.7, 126.3, 124.6, 37.3; ESI-MS (MeOH): m/z = 261 $(M+H)^+$, 283 $(M+Na)^+$.

4.4. Sulfide oxidation procedure

A typical procedure for the enantioselective oxidation of sulfides is as follows. To a 10 ml flask fitted with a magnetic stirrer bar was added a purified preformed vanadyl complex of 3,5-diiodosalicylidene *tert*-leucinol **3l** (0.03 mmol), 2 ml of dichloromethane and allyl (or cinnamyl) aryl sulfide (1.0 mmol). The flask was put into an ice-water bath and the mixture was stirred slowly. After 10 min, 30% aqueous H_2O_2 (1.6 mmol) was added in batches. After slowly stirring for 16 h, the reaction mixture was quenched with saturated aqueous $NaHSO_3$, and extracted with CH_2Cl_2 (3 × 20 ml). The organic layer was washed with saturated brine, and dried over anhydrous $MgSO_4$, and then condensed under reduced pressure on a rotary evaporator. The resulting residue was purified by a silica gel chromatography column with a solution of petroleum ether and ethyl acetate [gradiently from 1:0 to 1:1 (v/v)] as an eluent to afford the sulfoxide. The enantiomeric excess (ee) of the sulfoxide was determined with HPLC on a Daicel Chiralcel OD-H column (250 mm × 4.6 mm × 5 μm).

4.4.1. (*S*)-Allyl phenyl sulfoxide 2a

Pale yellow oil 95 mg (57% yield). Ee 97.3%, $[\alpha]_D^{22} = -160.2$ (c 0.90, EtOH). IR (film): ν 3055–2910, 1635, 1595, 1475, 1445, 1090, 1045 (S=O), 750, 690 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62–7.58 (m, 2H), 7.55–7.48 (m, 2H), 5.70–5.60 (m, 1H), 5.35–5.18 (m, 2H), 3.60–3.49 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.9, 131.1, 129.0, 125.2, 124.3, 123.9, 60.8; ESI-MS (MeOH): m/z = 167 $(M+H)^+$, 189 $(M+Na)^+$. Calcd for $C_9H_{10}OS$ (166.04: C, 65.02; H, 6.06; S, 19.29; found: C, 64.89; H, 6.09; S, 19.26. HPLC (Daicel Chiralcel OD-H 25 cm × 4.6 mm I.D., *n*-hexane/*i*-PrOH = 90:10, flow rate = 0.9 ml/min detected at 254 nm): t_R = 11.8 min for enantiomer (*R*), and t_R = 14.2 min for enantiomer (*S*).

4.4.2. (*S*)-Allyl *p*-tolyl sulfoxide 2b

Pale yellowish oil 90 mg (50% yield). Ee 89.6%, $[\alpha]_D^{22} = -202.1$ (c 0.52, EtOH). IR (film): ν 3068, 2975, 1635, 1595, 1490, 1090, 1045 (S=O), 810 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50–7.48 (d, 2H, J = 8.0 Hz), 7.33–7.31 (d, 2H, J = 7.8 Hz), 5.68–5.59 (m, 1H), 5.34–5.18 (m, 2H), 3.58–3.48 (m, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.5, 139.6, 129.7, 125.4, 124.3, 123.7, 60.9, 21.4; ESI-MS (MeOH): m/z = 181 $(M+H)^+$, 203 $(M+Na)^+$. Calcd for $C_{10}H_{12}OS$ (180.06): C, 66.63; H, 6.71; S, 17.79; found: C, 66.58; H, 6.68; S, 17.69. HPLC (Daicel Chiralcel OD-H 25 cm × 4.6 mm I.D., *n*-hexane/*i*-PrOH = 90:10, flow rate = 0.9 ml/min detected at 254 nm): t_R = 10.6 min for enantiomer (*R*), and t_R = 13.9 min for enantiomer (*S*).

4.4.3. (*S*)-Allyl *p*-chlorophenyl sulfoxide 2c

Yellow oil 112 mg (56% yield). Ee 92.7%, $[\alpha]_D^{22} = -223.1$ (c 0.35, EtOH). IR (film): ν 3073, 2964, 1638, 1600, 1495, 1092, 1047 (S=O), 815 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56–7.49 (m, 4H), 5.69–5.59 (m, 1H), 5.37–5.17 (m, 2H), 3.60–3.47 (m, 2H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.3, 137.3, 129.3, 125.8, 124.7, 124.3, 60.7; ESI-MS (MeOH): m/z = 201 $(M+H)^+$, 223 $(M+Na)^+$. Calcd for C_9H_9ClOS (200.00): C, 53.86, H, 4.52, S, 15.98; found: C, 53.78; H, 4.65; S, 15.77. HPLC (Daicel Chiralcel OD-H 25 cm × 4.6 mm I.D., *n*-hexane/*i*-PrOH = 90:10, flow rate = 0.9 ml/min detected at 254 nm): t_R = 17.3 min for enantiomer (*R*), and t_R = 20.8 min for enantiomer (*S*).

4.4.4. (*S*)-Cinnamyl phenyl sulfoxide 2d

Yellow oil 124 mg (51% yield). Ee 81.5%, $[\alpha]_D^{22} = -146.2$ (c 0.15, EtOH). IR (film): ν 3069, 3027, 2926, 1655, 1599, 1450, 1372, 1150, 1050 (S=O), 964 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62–7.50 (m, 5H), 7.32–7.25 (m, 5H), 6.42 (d, 1H, J = 16 Hz), 6.03–5.95 (m, 1H), 3.75–3.64 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.9, 138.4, 136.1, 131.1, 129.0, 128.6, 128.2, 126.5, 124.4, 116.0, 60.7; ESI-MS (MeOH): m/z = 243 $(M+H)^+$, 265 $(M+Na)^+$. Calcd for $C_{15}H_{14}OS$ (242.07): C, 74.34, H, 5.82, S, 13.23; found: C, 74.25; H, 5.93; S, 13.14. HPLC (Daicel Chiralcel OD-H 25 cm × 4.6 mm I.D., *n*-hexane/*i*-PrOH = 90:10, flow rate = 0.9 ml/min detected at 254 nm): t_R = 13.2 min for enantiomer (*R*), and t_R = 16.3 min for enantiomer (*S*).

4.4.5. (*S*)-Cinnamyl *p*-tolyl sulfoxide 2e

Yellow oil 109 mg (43% yield). Ee 72.0%, $[\alpha]_D^{22} = -173.5$ (c 0.12, EtOH). IR (film): ν 3065, 2967, 1653, 1593, 1370, 1295, 1045 (S=O), 960, 730, 695 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (d, 2H, J = 8 Hz), 7.32–7.23 (m, 8H), 6.45 (d, 1H, J = 16 Hz), 6.02–5.94 (m, 1H), 3.68 (d, 2H, J = 8 Hz), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.6, 139.7, 138.3, 136.1, 129.7, 128.6, 128.1, 126.5, 124.4, 116.2, 60.8, 21.4; ESI-MS (MeOH): m/z = 257 $(M+H)^+$, 279 $(M+Na)^+$. Calcd for $C_{16}H_{16}OS$ (256.09): C, 74.96, H, 6.29, S, 12.51; found: C, 74.82; H, 6.35; S, 12.41. HPLC (Daicel Chiralcel OD-H 25 cm × 4.6 mm I.D., *n*-hexane/*i*-PrOH = 90:10, flow rate = 0.9 ml/min detected at 254 nm): t_R = 12.5 min for enantiomer (*R*), and t_R = 15.4 min for enantiomer (*S*).

4.4.6. (*S*)-Cinnamyl *p*-chlorophenyl sulfoxide 2f

Yellow oil 130 mg (47% yield). Ee 73.8%, $[\alpha]_D^{22} = -189.3$ (c 0.11, EtOH). IR (film): ν 3027, 2973, 1651, 1595, 1494, 1449, 1093, 1041 (S=O), 967, 733, 692 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57–7.48 (m, 4H), 7.34–7.24 (m, 5H), 6.44 (d, 1H, J = 16 Hz), 6.01–5.93 (m, 1H), 3.74–3.63 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.4, 138.8, 137.3, 135.9, 129.3, 128.6, 128.3, 126.5, 125.8, 115.4, 60.7; ESI-MS (MeOH): m/z = 277 $(M+H)^+$, 299 $(M+Na)^+$. Calcd for $C_{15}H_{13}ClOS$ (276.03): C, 65.09, H, 4.73, S, 11.58; found: C, 65.21; H, 4.88; S, 11.49. HPLC (Daicel Chiralcel OD-H 25 cm × 4.6 mm I.D., *n*-hexane/*i*-PrOH = 90:10, flow rate = 0.9 ml/min detected at 254 nm): t_R = 18.5 min for enantiomer (*R*), and t_R = 22.3 min for enantiomer (*S*).

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