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Enantioselective ring-opening reaction of *meso*-epoxides with ArSH catalyzed by a C_2-symmetric chiral bipyridyldiol-titanium complex

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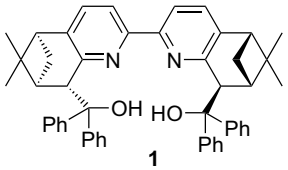
Abstract—This study describes a C_2-symmetric ligand comprising a central bipyridine-pinene-derived core and two functionalized diphenylmethanol subunits. [8′-(Hydroxy-diphenyl-methyl)-10,10,10′,10′-tetramethyl-[5,5′]bi[6-aza-tricyclo[7.1.1.0^{2,7}]undecyl]-2(7),3,5,2′(7′),3′,5′-hexaen-8-yl]-diphenyl-methanol **1** is an effective catalyst in the asymmetric ring opening (ARO) of *meso*-epoxides with PhSH and inductions of up to 69% ee. Importantly, there was a correlation between Hammett substituent constants and enantiomeric excesses; the electron-donating substituents at the *meta*- and *para*-positions of the substituted stilbene oxides had good enantioselectivity during the epoxide ring opening using PhSH.

1. Introduction

The asymmetric ring opening (ARO) of *meso*-epoxides with diverse nucleophiles is an important transformation in organic synthesis because it is a potent strategy for the formation of 1,2-bifunctionalized systems, while at the same time, it establishes two contiguous stereogenic centers.[1] Manifold nucleophiles have been successfully utilized in the asymmetric ring opening reactions, with most being heteroatom-based. These methodologies have provided practical access to enantioenriched β-azido alcohols,[2,3] β-halohydrins,[4,5] β-cyanohydrins,[3a,6] β-hydroxy sulfides,[7] β-benzoyloxy alcohols,[8] β-aryloxy alcohols,[9] and β-amino alcohols.[10] Of these, sulfur nucleophiles are useful and lead to the construction of synthetically valuable β-hydroxy mercaptans or β-hydroxy sulfides. Few studies have investigated the desymmetrization reaction of *meso*-epoxides by using a thiol as a nucleophile.[7] This ring-opening reaction is generally performed in the presence of a catalyst, such as Zn(II) D-tartrates,[7a] Ga/Li bis(binaphthoxide) complex[7b] or metal salen complexes.[7c,d] The products, β-hydroxysulfides, can be obtained with high regio- and stereoselectivity. Shibasaki and Jacobsen et al. reported a catalytic asymmetric ring opening of epoxides with *t*-BuSH using gallium–lithium-bis(binaphthoxide) (GaLB) complex and (salen)Cr(III) complex as a catalyst in prominent enantiomeric excess.[7b,c] However, the nucleophile was limited to *t*-BuSH. Conversely, Hou et al. reported the catalytic asymmetric ring opening of epoxides with ArSH using a (salen)Ti(IV) complex as a catalyst. Although the enantioselectivity was unsatisfactory, Hou's approach was a facile and convenient method for synthesizing chiral β-hydroxy sulfide compounds.[7d] We have reported that the catalytic addition of diethylzinc[11a] and trimethylsilyl cyanide[11b] to various substituted benzaldehydes obtains alcohols with enantiomeric excess, typically ranging from 2% to 99% using catalytic amounts of titanium tetraisopropoxide and chiral bipyridyl-diol **1** derived from (1*R*)-(+)-α-pinene (Scheme 1). In this study, a Ti-ligand **1** complex was utilized as the enantioselective catalyst of asymmetric ring opening of *meso*-epoxides with PhSH.



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Scheme 1.

2. Results and discussion

All substituted stilbene oxides were prepared from substituted benzaldehydes and substituted benzylbromide via a

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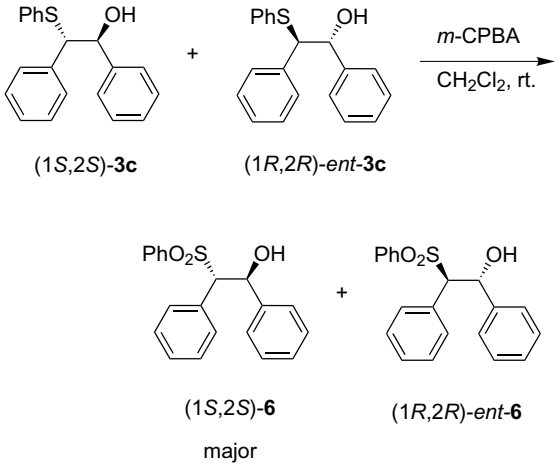
Wittig reaction,[12] followed by epoxidation using *m*CPBA.[13] The preparation of 2,3-bis-(4-methoxy-phenyl)-oxirane was unsuccessful. 2,3-Di-*o*-tolyl-oxirane, 2,3-bis-(2-chloro-phenyl)-oxirane, 2,3-bis-(2-cyano-phenyl)-oxirane, 2,3-bis-(2-nitro-phenyl)-oxirane, and 2,3-bis-(4-nitro-phenyl)-oxirane cannot perform the corresponding ring-opening reaction of epoxides with PhSH, in the presence of catalyst or without catalyst at room temperature or refluxing in acetonitrile.

Asymmetric ring-opening of a *meso*-epoxide with thiophenol was performed in the presence of catalyst Ti(IV)-**1** complex as described below. The Ti(O-*i*-Pr)$_4$ was added to a stirred solution of ligand **1** in acetonitrile under nitrogen. The resulting mixture was stirred at room temperature for 1 h, then epoxide and PhSH were added. The reaction mixture was stirred at room temperature for 30 h, then filtered through a plug of silica gel, and washed with dichloromethane. Following purification by flash column chromatography, the enantiomeric excesses of 2-phenylsulfanyl-cyclohexanol were determined by HPLC analysis using a chiral column (Chiralcel OD-H column).

Sharpless reported that a stoichiometric amount of Ti(O-*i*-Pr)$_4$ was necessary for the reaction to proceed.[14] The ring opening reaction of *cis*-stilbene oxide with PhSH 5 mol % of chiral ligand **1** and Ti(O-*i*-Pr)$_4$ was performed under various reaction conditions. Table 1 displays the enantiomeric excesses of 1,2-diphenyl-2-phenylsulfanyl-ethanol. The optimal amount of Ti(O-*i*-Pr)$_4$ was 1.5 equiv in acetonitrile with 51% ee. The desymmetrization of stilbene oxides was performed by using PhSH, in the presence of various amounts of ligand **1** and 1.5 equiv Ti(O-*i*-Pr)$_4$. The enantiomeric excesses of 1,2-diphenyl-2-phenylsulfanyl-ethanol are shown in Table 1 which clearly shows that using 20 mol % of ligand gave best ee (69%). The configuration of **3c** was determined by comparing the literature's[15] specific rotation, retention time of HPLC and NMR spectrum of sulfone **6** (Scheme 2).

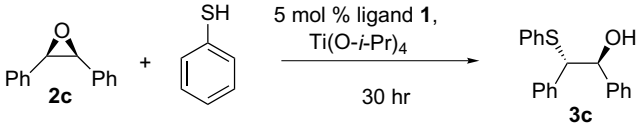


Scheme 2. Absolute configurations of the major isomers of **3c** and **6**.

The enantiomeric excesses of the ARO of *meso*-epoxides in the presence of Ti(IV)-**1** complex were *cis*-stilbene oxide (66% ee), cyclohexene oxide (17% ee) and cyclopentene oxide (0% ee). Notably, *cis*-stilbene oxide for the ARO reaction gave a better result than the other epoxides. The desymmetrization of stilbene oxides using PhSH, in the presence of various amounts of ligand **1** and 1.5 equiv Ti(O-*i*-Pr)$_4$, the enantiomeric excesses of 1,2-diphenyl-2-phenylsulfanyl-ethanol were acquired (Table 1, entries 8–11). The optimal amount of catalyst was 20 mol % of ligand **1** (69% ee).

The electronic effects in asymmetric hydroborations,[16] epoxidations,[17] and alkylations[11] have been reported. In our previous study,[11] the Hammett substituent constants were strongly correlated with enantiomeric excesses of the alkylation of *meta*-substituted benzaldehydes using diethylzinc in the presence of Ti(IV)-bipyridyldiol **1**. Additionally, Ti(IV)-bipyridyldiol **1** acted as an interesting chiral catalyst for the enantioselective addition of TMSCN to various

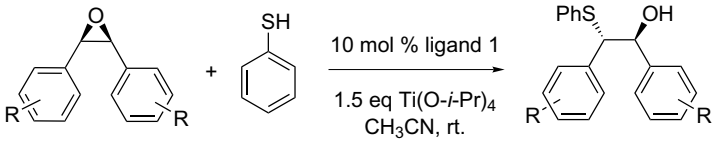
Table 1. Enantiomeric excess (%) of ARO of *cis*-stilbene oxide in the presence of Ti(IV)-**1** complex in various reaction conditions



Entry	Solvents	Ti(O-*i*-Pr)$_4$ (mol %)/ligand (mol %)	Yield (%)	ee (%)	Config.[b]
1	Hexane	5/5	12	4	(1*S*,2*S*)
2	Toluene	5/5	4	2	(1*S*,2*S*)
3	Acetonitrile	5/5	43	29	(1*S*,2*S*)
4	Tetrahydrofuran	5/5	23	0	(1*S*,2*S*)
5	*p*-Xylene	5/5	24	11	(1*S*,2*S*)
6[c]	Acetonitrile	5/5	28	10	(1*S*,2*S*)
7[c]	Acetonitrile	5/5	8	11	(1*S*,2*S*)
8	Acetonitrile	150/5	41	51	(1*S*,2*S*)
9	Acetonitrile	150/10	73	66	(1*S*,2*S*)
10[a]	Acetonitrile	150/10	51	66	(1*S*,2*S*)
11	Acetonitrile	150/20	76	69	(1*S*,2*S*)

[a] PhSH was added dropwise over 6 h.
[b] Compared with Ref. 15.
[c] Reaction temperature: entry 6 (0 °C), entry 7 (−20 °C) and others (25 °C).

Table 2. Enantiomeric excess (%) of ARO of substituted stilbene oxides in the presence of Ti(IV)-**1** complex



4a-h **5a-h**

Entry	R[a]	Product	Yield[b] (%)	ee[c] (%)	Substituent constants[18]
1	*m*-OMe	**5a**	77	45	+0.12
2	*m*-Me	**5b**	18	60	−0.07
3	*p*-Me	**5c**	76	45	−0.17
4	*m*-Cl	**5d**	96	64	+0.37
5	*p*-Cl	**5e**	87	36	+0.23
6	*m*-CN	**5f**	50	48	+0.56
7	*p*-CN	**5g**	40	23	+0.66
8	*m*-NO_2	**5h**	53	20	+0.71

[a] All the substituted stilbene oxides were prepared from substituted benzaldehydes and substituted benzylbromide via a Wittig reaction[12] followed by epoxidation by *m*CPBA.[13]
[b] Isolated yield.
[c] The ee values were determined by HPLC on a chiral Chiralcel OD-H column.

substituted benzaldehydes, yielding cyanohydrins with (*S*)-configurations with enantiomeric excesses, generally ranging from 2% to 98% ee. Notably, electron-releasing substituents at the *meta*- and *para*-positions of the substituted benzaldehydes were highly enantioselective during cyanation using TMSCN.

This study examined the reactions of substituted stilbene oxides with thiophenol at 25 °C in the presence of ligand **1** (10 mmol %) and Ti(O-*i*-Pr)$_4$ (1.5 equiv) in acetonitrile (Table 2). Hammett substituent constants were highly correlated with the enantiomeric excesses produced by the asymmetric ring opening of *para*- and *meta*-substituted stilbene oxides using PhSH. Electron-donating substituents on the *meta*-position exhibited high enantiomeric excesses, whereas electron-withdrawing substituents on the *meta*-position gave low enantiomeric excesses (Fig. 1). On the other hand, electron-donating substituents at the *para*-position exhibited high enantiomeric excesses, whereas relatively strong electron-withdrawing substituents at the *para*-position displayed low enantiomeric excesses (Fig. 2). The electron-donating substituents of substituted stilbene oxides can enhance the π–π interaction between

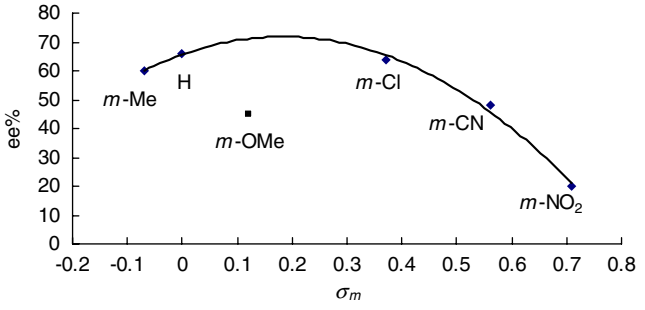


Figure 1. The correlation of substituent constants (σ_m) and the enantiomeric excesses of the ARO of *meta*-substituted stilbene oxides in the presence of Ti(IV)-**1** complex.

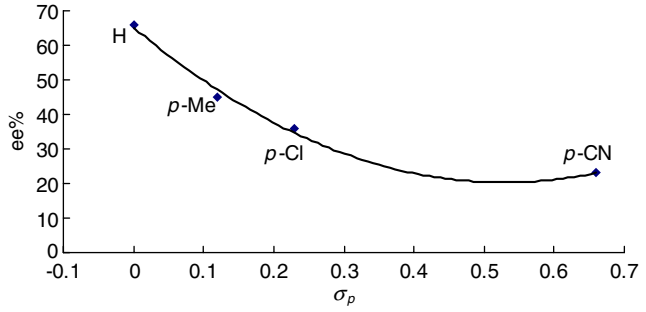


Figure 2. The correlation of substituent constants (σ_p) and the enantiomeric excesses of the ARO of *para*-substituted stilbene oxides in the presence of Ti(IV)-**1** complex.

the phenyl group of ligand **1** and the aromatic ring of substituted stilbene oxides. Therefore, the aromatic ring of substituted stilbene oxides can be fixed tightly and induced a highly enantioselective ring opening reaction. The reaction of stilbene oxide with thiophenol at 25 °C in the presence of ligand **1** (10 mmol %) and Ti(O-*i*-Pr)$_4$ (1.5 equiv) in acetonitrile gave a highly enantioselective product (66% ee). Substituted stilbene oxides with a small substituent induced a high enantioselectivity.

3. Conclusion

In this study, a chiral bipyridinyldiol **1** was prepared from highly enantiopure (1*R*)-(+)-α-pinene (>97% ee).[11a] The Ti(IV)-bipyridinyldiol complex acted as a chiral catalyst for the enantioselective addition of PhSH to various substituted stilbene oxides, and attained synthetically versatile β-hydroxy sulfides in optically active forms, generally ranging from 20% to 69% ee. Notably, electron-releasing substituents at the *meta*- and *para*-positions of the substituted stilbene oxides gave good enantioselectivity during epoxide ring opening using PhSH.

4. Experimental

4.1. General

All reactions were carried out in anhydrous solvents. THF and diethyl ether were distilled from sodium-benzophenone under argon. Toluene, CH_3CN, CH_2Cl_2, xylene, and hexane were distilled from CaH_2. ^1H NMR spectra were obtained at 300 or 400 MHz (as indicated), and ^{13}C NMR spectra were obtained at 75.5 or 100.6 MHz using a Bruker NMR spectrometer. Chemical shifts (δ) are reported in ppm relative to $CDCl_3$ (7.26 and 77.0 ppm). Mass spectra (MS) and high resolution mass spectra (HRMS) were determined on a Finnigan/Thermo Quest MAT 95XL mass spectrometer. Infrared spectra were recorded using a JASCO FT/IR 410 spectrometer. All asymmetric reactions were conducted in dry glassware under nitrogen using a standard glovebox. Enantiomeric excesses were determined using Lab Alliance Series III high performance liquid chromatography (HPLC) with a Chiracel OD-H chiral column (Daicel Chemical Industries, LTD). Optical rotations were measured using a JASCO P-1010 polarimeter at the indicated temperature using a sodium lamp (D line, 589 nm). Flash column chromatography was performed using MN silica gel 60 (70–230 mesh) purchased from Macherey-Nagel.

4.2. Synthesis of substituted stilbenes

The typical procedure for preparing substituted stilbenes is as follows. Aromatic aldehydes (5 mmol) and 18-crown-6 (0.5 mmol) were added to a solution of phosphonium salt (5 mmol) in dichloromethane (25 mL). The mixture was cooled to −78 °C, and freshly powdered potassium hydroxide (10 mmol) was added under magnetic stirring. After stirring at −78 °C for 6 h, the mixture was diluted with dichloromethane, filtered off, and washed with water. The organic phase was dried over anhydrous magnesium sulfate. After filtration and concentration of the organic phase, the residue was purified by flash column chromatography using silica gel as the stationary phase and ethyl acetate–hexane (1:49) as mobile phase. Thus, substituted stilbenes were produced.

4.2.1. *cis*-3,3′-Dimethoxystilbene. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.18 (t, $J = 7.8$ Hz, 2H), 6.86–6.73 (m, 6H), 6.58 (s, 2H), 3.66 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 159.4, 138.6, 130.4, 129.2, 121.5, 113.9, 113.3, 55.1. IR (KBr): 3066, 2946, 2834, 1930, 1845, 1598, 1045, 781, 686 cm^{-1}. MS m/z: 240 (M^+, 100), 209 (21), 165 (45), 153 (23), 91 (2). HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{16}O_2$, 240.1150; found, 240.1142.

4.2.2. *trans*-3,3′-Dimethoxystilbene. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.31–7.05 (m, 8H), 6.8 (d, $J = 7.4$ Hz, 2H), 3.85 (s, 6H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 159.9, 138.7, 129.6, 128.9, 119.3, 113.4, 111.8, 55.2. IR (KBr): 2960, 2933, 1954, 781, 692 cm^{-1}.

4.2.3. *cis*-3,3′-Dimethylstilbene. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.19–7.02 (m, 8H), 6.54 (s, 2H), 2.27 (s, 6H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 137.6, 137.2, 130.2, 129.6, 128.0, 127.8, 125.9, 21.3. IR (KBr): 3010, 2919, 1918, 1598, 771, 734 cm^{-1}. MS m/z: 208 (M^+, 100), 193 (50), 178 (50), 165 (11), 115 (15), 91 (9). HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{16}$, 208.1252; found, 208.1247.

4.2.4. *trans*-3,3′-Dimethylstilbene. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.42–7.24 (m, 6H), 7.11–7.08 (m, 4H), 2.40 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 138.2, 137.4, 128.6, 128.4, 127.2, 123.7, 21.4. IR (KBr): 3025, 2915, 1600, 1488, 968, 788, 696 cm^{-1}.

4.2.5. *cis*-4,4′-Dimethylstilbene. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.17 (d, $J = 8.0$ Hz, 4H), 7.04 (d, $J = 7.9$ Hz, 4H), 6.51 (s, 2H), 2.31 (s, 6H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 136.7, 134.5, 129.5, 128.9, 128.7, 21.2. IR (KBr): 3010, 2915, 1909, 1508, 823, 777 cm^{-1}. MS m/z: 208 (M^+, 100), 193 (63), 178 (33), 165 (11), 115 (28), 91 (10). HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{16}$, 208.1252; found, 208.1253.

4.2.6. *trans*-4,4′-Dimethylstilbene. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.41 (d, $J = 8.0$ Hz, 4H), 7.17 (d, $J = 8.0$ Hz, 4H), 7.03 (s, 2H), 2.35 (s, 6H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 137.2, 134.7, 129.3, 127.6, 126.3, 21.2. IR (KBr): 3018, 2910, 1909, 1513, 970, 819 cm^{-1}.

4.2.7. *cis*-3,3′-Dichlorostilbene. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.21–7.06 (m, 8H), 6.57 (s, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 138.5, 134.2, 130.0, 129.5, 128.8, 127.5, 126.9. IR (KBr): 3066, 3016, 1940, 1870, 1702, 1589, 1473, 1425, 798, 678 cm^{-1}. MS m/z: 252 (M^++4, 6), 250 (M^++2, 41), 248 (M^+, 64), 212 (23), 178 (100), 106 (11), 88 (25). HRMS-EI (m/z): $[M]^+$ calcd for $C_{14}H_{10}Cl_2$, 248.0160; found, 248.0151.

4.2.8. *trans*-3,3′-Dichlorostilbene. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.50 (s, 2H), 7.38–7.23 (m, 6H), 7.03 (s, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 138.7, 134.7, 129.9, 128.6, 127.9, 126.4, 124.8. IR (KBr): 3434, 3056, 1592, 1565, 966, 887, 771, 684 cm^{-1}.

4.2.9. *cis*-4,4′-Dichlorostilbene. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.21 (d, $J = 6.5$ Hz, 4H), 7.15 (d, $J = 6.5$ Hz, 4H), 6.63 (s, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 135.2, 133.0, 130.1, 129.6, 128.5. IR (KBr): 3415, 3021, 2923, 1895, 1486, 1083, 1012, 877, 821, 736 cm^{-1}. MS m/z: 252 (M^++4, 8), 250 (M^++2, 53), 248 (M^+, 83), 212 (20), 178 (100), 151 (10), 88 (19). HRMS-EI (m/z): $[M]^+$ calcd for $C_{14}H_{10}Cl_2$, 248.0160; found, 248.0152.

4.2.10. *cis*-3,3′-Dicyanostilbene. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.54–7.32 (m, 8H), 6.75 (s, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 137.4, 132.9, 132.2, 131.2, 130.2, 129.3, 118.3, 112.9. IR (KBr): 3430, 3056, 2227, 1722, 1596, 1477, 813, 678 cm^{-1}. MS m/z: 230 (M^+, 100), 215 (16), 203 (16), 190 (14), 115 (6), 88 (8). HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{10}N_2$, 230.0844; found, 230.0848.

4.2.11. *cis*-4,4′-Dicyanostilbene. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.55 (d, $J = 6.6$ Hz, 4H), 7.29 (d, $J = 6.7$ Hz, 4H), 6.74 (s, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 140.9, 132.3, 131.2, 129.4, 118.5, 111.4. IR (KBr): 3052,

2223, 1602, 1504, 1411, 1180, 892, 831, 576, 545 cm^{-1}. MS *m/z*: 230 (M^+, 100), 215 (17), 202 (11), 190 (18), 127 (7), 88 (7). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{10}N_2$, 230.0844; found, 230.0842.

4.2.12. *cis*-3,3′-Dinitrostilbene. ^1H NMR (300 MHz, $CDCl_3$, δ): 8.10–8.06 (m, 4H), 7.54–7.25 (m, 4H), 6.80 (s, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 148.5, 137.7, 134.6, 130.4, 129.5, 123.7, 122.6. IR (KBr): 3070, 2863, 1702, 1515, 1348, 1083, 809, 765, 719, 669 cm^{-1}. MS *m/z*: 270 (M^+, 100), 176 (62), 165 (63), 151 (25), 76 (12). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{14}H_{10}N_2O_4$, 270.0641; found, 270.0637.

4.3. Synthesis of substituted stilbene oxides

The typical procedure for preparing substituted stilbene oxides is as follows. To a solution of substituted stilbene (2 mmol) in dichloromethane (20 mL) was added *m*CPBA (5 mmol) at 0 °C. After stirring at room temperature for 15 h, the mixture was diluted with diethyl ether, and washed with 5% $NaHCO_3$. The organic phase was dried over anhydrous magnesium sulfate. Following filtration and concentration, the residue was purified by column chromatography using silica gel as the stationary phase and ethyl acetate/hexane (1:19) as mobile phase to yield the stilbene oxides.

4.3.1. 2,3-Bis-(3-methoxy-phenyl)-oxirane 4a. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.13–7.07 (t, $J = 7.3$ Hz, 2H), 6.82 (d, $J = 7.5$ Hz, 2H), 6.71–6.68 (m, 4H), 4.32 (s, 2H), 3.67 (s, 6H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 159.1, 135.9, 128.8, 119.3, 113.6, 112.0, 59.7, 55.1. IR (KBr): 2957, 2834, 1585, 1491, 1044, 795, 694 cm^{-1}. MS *m/z*: 256 (M^+, 100), 238 (86), 227 (75), 149 (42), 135 (54), 121 (48), 91 (58), 77 (63). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{16}O_3$, 256.1099; found, 256.1106.

4.3.2. 2,3-Di-*m*-tolyl-oxirane 4b. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.09–6.94 (m, 8H), 4.30 (s, 2H), 2.19 (s, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 137.3, 134.5, 129.0, 128.4, 123.9, 59.9, 21.4. IR (KBr): 3031, 2921, 1094, 1770, 1608, 1418, 1216, 800, 754, 698 cm^{-1}. MS *m/z*: 224 (M^+, 49), 209 (38), 195 (100), 180 (28), 165 (37), 119 (77), 103 (34), 91 (52), 77 (26). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{16}O$, 224.1201; found, 224.1203.

4.3.3. 2,3-Di-*p*-tolyl-oxirane 4c. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.07 (d, $J = 6.3$ Hz, 4H), 7.00 (d, $J = 8.0$ Hz, 4H), 4.29 (s, 2H), 2.24 (s, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 137.1, 131.5, 128.5, 126.8, 59.8, 21.1. IR (KBr): 2921, 1911, 1725, 1515, 1172, 900, 804, 765 cm^{-1}. MS *m/z*: 224 (M^+, 38), 209 (31), 195 (100), 180 (16), 165 (18), 119 (28), 103 (33), 91 (18), 77 (13). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{16}O$, 224.1201; found, 224.1202.

4.3.4. 2,3-Bis-(3-chloro-phenyl)-oxirane 4d. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.19–7.02 (m, 8H), 4.32 (s, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 135.9, 134.0, 129.2, 128.0, 126.9, 124.8, 59.0. IR (KBr): 3424, 2962, 2927, 2764, 1596, 1569, 1479, 1429, 788, 678, 593 cm^{-1}. MS *m/z*: 268 (M^++4, 3), 266 (M^++4, 17), 264 (M^+, 26), 246 (21), 229 (36), 201 (12), 194 (33), 165 (48), 139 (31), 89 (100), 75 (13). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{10}Cl_2O$, 264.0109; found, 264.0110.

4.3.5. 2,3-Bis-(4-chloro-phenyl)-oxirane 4e. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.18 (d, $J = 8.4$ Hz, 4H), 7.09 (d, $J = 9.0$ Hz, 4H), 4.31 (s, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 133.6, 132.5, 128.3, 59.1. IR (KBr): 3430, 1917, 1598, 1492, 1419, 1087, 1012, 875, 798, 763, 501 cm^{-1}. MS *m/z*: 268 (M^++4, 1), 266 (M^++4, 7), 264 (M^+, 13), 250 (26), 237 (40), 235 (73), 229 (26), 165 (49), 141 (100), 139 (70), 89 (56), 77 (46). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{10}Cl_2O$, 264.0109; found, 264.0114.

4.3.6. 2,3-Bis-(3-cyano-phenyl)-oxirane 4f. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.57–7.30 (m, 8H), 4.42 (s, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 135.2, 131.7, 130.8, 130.2, 129.0, 118.1, 112.5, 58.6. IR (KBr): 3066, 2227, 1481, 917, 806, 690 cm^{-1}. MS *m/z*: 246 (M^+, 95), 228 (59), 217 (100), 190 (44), 130 (24), 115 (86), 102 (18), 88 (36), 63 (12). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{10}N_2O$, 246.0793; found, 246.0802.

4.3.7. 2,3-Bis-(4-cyano-phenyl)-oxirane 4g. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.51 (d, $J = 5.6$ Hz, 4H), 7.29 (d, $J = 8.1$ Hz, 4H), 4.45 (s, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 138.8, 132.2, 131.9, 129.4, 127.3, 59.1. IR (KBr): 3438, 3056, 2225, 1608, 1506, 1417, 1182, 894, 833, 813, 584 cm^{-1}. MS *m/z*: 246 (M^+, 100), 230 (85), 217 (74), 190 (54), 130 (29), 115 (98), 102 (24), 88 (42), 63 (15). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{10}N_2O$, 246.0793; found, 246.0787.

4.3.8. 2,3-Bis-(3-nitro-phenyl)-oxirane 4h. ^1H NMR (300 MHz, $CDCl_3$, δ): 8.23–8.01 (m, 4H), 7.55 (d, $J = 7.7$ Hz, 2H), 7.42–7.37 (t, $J = 7.9$ Hz, 2H), 4.53 (s, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 135.6, 132.5, 129.2, 123.1, 121.7, 58.8. IR (KBr): 3079, 1697, 1531, 1349, 1309, 1089, 935, 744 cm^{-1}. MS *m/z*: 286 (M^+, 3), 269 (5), 257 (2), 239 (7), 193 (4), 165 (22), 135 (100), 105 (75), 89 (65), 77 (12), 63 (28). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{14}H_{10}N_2O_5$, 286.0590; found, 286.0593.

4.4. Representative procedure for the asymmetric ring opening of epoxides by Ti-ligand 1 complex

To a stirred solution of ligand **1** (7.0 mg, 0.01 mmol) in CH_3CN (1.0 mL) under nitrogen, Ti(O-*i*-Pr)$_4$ (43 μL, 0.15 mmol) was added. The resulting mixture was stirred at room temperature for 1 h, then epoxide (0.1 mmol) and PhSH (0.1 mmol) were added. The reaction mixture was stirred at room temperature for 30 h, filtered through a plug of silica gel, and washed with 5 mL CH_2Cl_2. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography to furnish the corresponding asymmetric ring opening product. Enantiomeric excess was determined by HPLC analysis using a chiral column (Chiralcel OD-H column, flow rate 0.25 mL/min).

4.4.1. 1,2-Diphenyl-2-phenylsulfanyl-ethanol 3c.[15] Yield: 66%. $[\alpha]_D^{21} = +54.8$ (*c* 1.1, CH_3Cl). HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 90:10, flow rate 0.25 mL/min) t_R

21.2 and 25.1 min. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.30–7.13 (m, 13H), 7.01 (m, 2H), 4.95 (d, $J = 8.5$ Hz, 1H), 4.36 (d, $J = 8.6$ Hz, 1H), 3.29 (br, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 140.4, 139.2, 132.4, 128.8, 128.5, 128.1, 127.9, 127.7, 127.4, 127.2, 126.9, 77.3, 63.9.

4.4.2. 1,2-Bis-(3-methoxy-phenyl)-2-phenylsulfanyl-ethanol 5a. Yield: 77%. $[\alpha]_D^{21} = +45.6$ (c 1.1, CH_3Cl). HPLC (Daicel Chiralcel OD-H, hexane/i-PrOH = 90:10, flow rate 0.25 mL/min) t_R 32.8 and 44.0 min. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.30–7.19 (m, 5H), 7.09–7.06 (m, 2H), 6.72–6.58 (m, 6H), 4.92 (d, $J = 8.3$ Hz, 1H), 4.32 (d, $J = 8.3$ Hz, 1H), 3.68 (s, 3H), 3.66 (s, 3H), 3.22 (br, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 159.3, 142.0, 140.7, 134.2, 132.3, 129.1, 128.9, 128.8, 127.4, 121.0, 119.2, 114.0, 113.6, 113.0, 112.2, 63.7, 55.1. IR (KBr): 3457, 3057, 2835, 1599, 1488, 1436, 1043, 692 cm^{-1}. MS m/z: 366 (M^+, 0.01), 348 (0.7), 241 (0.8), 230 (100), 197 (12), 135 (18), 121 (30), 109 (14), 91 (10), 77 (15). HRMS-EI (m/z): $[M]^+$ calcd for $C_{22}H_{22}O_3S$, 366.1290; found, 366.1290.

4.4.3. 2-Phenylsulfanyl-1,2-di-*m*-tolyl-ethanol 5b. Yield: 18%. $[\alpha]_D^{21} = +57.7$ (c 0.3, CH_3Cl). HPLC (Daicel Chiralcel OD-H, hexane/i-PrOH = 90:10, flow rate 0.25 mL/min) t_R 14.6 and 18.3 min. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.36–7.19 (m, 6H), 7.08–6.83 (m, 7H), 4.91 (d, $J = 8.2$ Hz, 1H), 4.34 (d, $J = 8.2$ Hz, 1H), 3.23 (br, 1H), 2.24 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 140.3, 139.1, 137.6, 134.4, 132.2, 129.2, 128.8, 128.4, 138.3, 128.0, 127.7, 127.4, 127.3, 125.6, 124.0, 63.6, 21.3. IR (KBr): 3438, 3052, 3023, 2918, 1605, 1479, 742, 693 cm^{-1}. MS m/z: 334 (M^+, 0.01), 316 (0.8), 225 (0.7), 214 (100), 179 (6), 165 (12), 135 (5), 119 (23), 105 (44), 91 (31), 77 (13). HRMS-EI (m/z): $[M]^+$ calcd for $C_{22}H_{22}OS$, 334.1391; found, 334.1397.

4.4.4. 2-Phenylsulfanyl-1,2-di-*p*-tolyl-ethanol 5c. Yield: 76%. $[\alpha]_D^{21} = +35.9$ (c 1.1, CH_3Cl). HPLC (Daicel Chiralcel OD-H, hexane/i-PrOH = 90:10, flow rate 0.25 mL/min) t_R 15.6 and 22.3 min. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.30–7.20 (m, 6H), 7.06 (d, $J = 8.1$ Hz, 2H), 7.00 (d, $J = 8.3$ Hz, 2H), 6.8 (s, 3H), 4.92 (d, $J = 8.5$ Hz, 1H), 4.36 (d, $J = 8.5$ Hz, 1H), 3.21 (br, 1H), 2.26 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 137.5, 137.3, 136.8, 136.2, 134.4, 132.2, 128.8, 128.6, 128.5, 128.4, 128.3, 127.2, 126.8, 63.4, 21.1. IR (KBr): 3502, 3052, 3023, 2918, 1511, 1438, 1173, 813, 689 cm^{-1}. MS m/z: 334 (M^+, 0.05), 316 (0.9), 233 (1), 213 (100), 195 (8), 165 (14), 135 (6), 128 (23), 105 (58), 91 (42), 77 (22). HRMS-EI (m/z): $[M]^+$ calcd for $C_{22}H_{22}OS$, 334.1391; found, 334.1385.

4.4.5. 1,2-Bis-(3-chloro-phenyl)-2-phenylsulfanyl-ethanol 5d. Yield: 96%. $[\alpha]_D^{21} = +43.6$ (c 1.5, CH_3Cl). HPLC (Daicel Chiralcel OD-H, hexane/i-PrOH = 90:10, flow rate 0.25 mL/min) t_R 20.1 and 26.3 min. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.24–7.05 (m, 11H), 6.95 (d, $J = 7.3$ Hz, 1H), 6.88 (d, $J = 7.3$ Hz, 1H), 4.88 (d, $J = 8.2$ Hz, 1H), 4.24 (d, $J = 8.3$ Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 142.1, 140.9, 134.1, 133.1, 132.8, 129.4, 129.2, 129.0, 128.6, 128.1, 128.0, 127.7, 126.8, 126.7, 125.1, 75.9, 63.3. IR (KBr): 3422, 3058, 2919, 1594, 1476, 741, 692 cm^{-1}. MS m/z: 374 (M^+, 0.02), 356 (0.1), 265 (0.1), 233 (100), 197 (24), 165 (21), 139 (15), 125 (23), 105 (17), 91 (2), 77 (22). HRMS-EI (m/z): $[M]^+$ calcd for $C_{20}H_{16}Cl_2OS$, 374.0299; found, 374.0307.

4.4.6. 1,2-Bis-(4-chloro-phenyl)-2-phenylsulfanyl-ethanol 5e. Yield: 87%. $[\alpha]_D^{21} = +6.9$ (c 1.5, CH_3Cl). HPLC (Daicel Chiralcel OD-H, hexane/i-PrOH = 90:10, flow rate 0.25 mL/min) t_R 19.2 and 33.6 min. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.26–7.11 (m, 9H), 7.06 (d, $J = 6.5$ Hz, 2H), 6.93 (d, $J = 6.6$ Hz, 2H), 4.87 (d, $J = 7.9$ Hz, 1H), 4.25 (d, $J = 7.8$ Hz, 1H), 3.12 (br, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 138.6, 137.4, 133.7, 133.2, 132.8, 129.8, 129.0, 128.4, 128.2, 127.9, 75.9, 63.2. IR (KBr): 3356, 3096, 1489, 1089, 741, 690 cm^{-1}. MS m/z: 374 (M^+, 0.1), 356 (0.1), 265 (0.2), 233 (100), 197 (25), 165 (22), 139 (16), 125 (19), 111 (11), 91 (2), 77 (23). HRMS-EI (m/z): $[M]^+$ calcd for $C_{20}H_{16}Cl_2OS$, 374.0299; found, 374.0300.

4.4.7. 1,2-Bis-(3-cyano-phenyl)-2-phenylsulfanyl-ethanol 5f. Yield: 50%. $[\alpha]_D^{21} = +13.8$ (c 0.7, CH_3Cl). HPLC (Daicel Chiralcel OD-H, hexane/i-PrOH = 90:10, flow rate 1.00 mL/min) t_R 39.0 and 52.0 min. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.51–7.46 (m, 3H), 7.31–7.22 (m, 8H), 4.98 (d, $J = 7.9$ Hz, 1H), 4.24 (d, $J = 7.9$ Hz, 1H), 3.35 (br, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 141.4, 140.2, 133.0, 132.2, 132.0, 131.8, 131.2, 130.4, 129.3, 129.1, 128.5, 118.3, 112.5, 75.4, 62.9. IR (KBr): 3447, 3056, 2918, 2229, 1581, 1480, 744, 690 cm^{-1}. MS m/z: 356 (M^+, 0.1), 271 (0.8), 247 (0.6), 224 (62), 190 (40), 146 (22), 132 (40), 104 (57), 91 (5), 77 (100). HRMS-EI (m/z): $[M]^+$ calcd for $C_{22}H_{16}N_2OS$, 356.0983; found, 356.0989.

4.4.8. 1,2-Bis-(4-cyano-phenyl)-2-phenylsulfanyl-ethanol 5g. Yield: 40%. $[\alpha]_D^{21} = +5.0$ (c 0.6, CH_3Cl). HPLC (Daicel Chiralcel OD-H, hexane/i-PrOH = 90:10, flow rate 0.75 mL/min) t_R 43.8 and 72.0 min. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.63–6.69 (m, 13H), 5.00 (d, $J = 8.1$ Hz, 1H), 4.29 (d, $J = 8.1$ Hz, 1H), 3.38 (br, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 145.1, 144.0, 133.1, 132.8, 132.2, 132.1, 132.0, 131.9, 129.9, 129.4, 129.3, 128.5, 128.4, 128.3, 127.5, 127.0, 118.3, 112.1, 111.6, 74.5, 63.4. IR (KBr): 3447, 3061, 2922, 2227, 1606, 1064, 472, 690 cm^{-1}. MS m/z: 356 (M^+, 0.03), 338 (0.6), 246 (0.6), 224 (100), 190 (13), 146 (6), 130 (21), 116 (23), 89 (6), 77 (18). HRMS-EI (m/z): $[M]^+$ calcd for $C_{22}H_{16}N_2OS$, 356.0983; found, 356.0984.

4.4.9. 1,2-Bis-(3-nitro-phenyl)-2-phenylsulfanyl-ethanol 5h. Yield: 53%. $[\alpha]_D^{21} = -6.8$ (c 0.7, CH_3Cl). HPLC (Daicel Chiralcel OD-H, hexane/i-PrOH = 90:10, flow rate 1.00 mL/min) t_R 36.0 and 46.0 min. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.20–8.03 (m, 3H), 7.9 (s, 1H), 7.42–7.25 (m, 9H), 5.12 (d, $J = 7.8$ Hz, 1H), 4.43 (d, $J = 7.8$ Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 148.1, 142.0, 140.6, 134.5, 133.2, 131.9, 129.3, 129.1, 128.6, 123.4, 123.2, 122.7, 121.8, 75.3, 62.7. IR (KBr): 3465, 3070, 1526, 1348, 737, 688 cm^{-1}. MS m/z: 396 (M^+, 0.1), 378 (0.2), 287 (0.3), 244 (100), 228 (62), 198 (42), 165 (20), 121 (12),

110 (8), 89 (5), 77 (12). HRMS-EI (m/z): $[M]^+$ calcd for $C_{20}H_{16}N_2O_5S$, 396.0780; found, 396.0781.

4.5. 2-Benzenesulfonyl-1,2-diphenyl-ethanol 6[15]

To a solution of **3c** (62 mg, 0.20 mmol) in 5 mL CH_2Cl_2 was added *m*CPBA (~70%, 120 mg, 0.49 mmol) at 0 °C. After stirring at room temperature for 15 h, the mixture was diluted with CH_2Cl_2 and washed with water. The organic phase was dried over anhydrous magnesium sulfate. Following filtration and concentration, the residue was purified by column chromatography using silica gel as the stationary phase and ethyl acetate/hexane (2:8) as a mobile phase to give product **6** (60 mg, 90%). $[\alpha]_D^{22} = +35.8$ (c 0.8, CH_3Cl). HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 70:30, flow rate 1.20 mL/min) t_R 10.8 and 25.5 min. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.98–6.89 (m, 15H), 5.77 (d, $J = 9.6$ Hz, 1H), 4.48 (d, $J = 9.6$ Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 139.5, 137.6, 133.8, 130.8, 130.3, 128.9, 128.7, 128.5, 128.1, 127.3, 77.6, 73.9.

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