

# Asymmetric Synthesis of Epoxides from Aromatic Aldehydes and Benzyl Halides Catalyzed by $C_2$ Symmetric Optically Active Sulfides Having a Binaphthyl Skeleton

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**ABSTRACT:** Reactions of aromatic aldehydes with benzyl bromide or iodide in the presence of a catalytic amount (10 mol%) of a  $C_2$  symmetric sulfide having a binaphthyl skeleton afford the corresponding *trans*-stilbene oxides in moderate to good yields with moderate enantioselectivities (up to 55% enantiomeric excess). The addition of tetra-*n*-butylammonium iodide to the catalytic reaction system much improves the yield of the epoxides. © 2002 Wiley Periodicals, Inc. *Heteroatom Chem* 13:270–275, 2002; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10028

## INTRODUCTION

Optically active epoxides are versatile intermediates in the synthesis of pharmaceuticals and natural products. Direct asymmetric oxidation of alkenes has been studied as a synthetic method for the preparation of the corresponding *cis*-epoxides with high enantioselectivities [1]. In sharp contrast, the methods for the preparation of *trans*-epoxides with high enantioselectivities reported so far have been limited to only a few cases [2]. Reactions of sulfur ylides with aldehydes are known to give the corresponding

*trans*-epoxides as major products. If chiral sulfur ylides were used, optically active epoxides might be obtained. The first attempt by Trost and co-workers in 1973 [3] to prepare optically active epoxides via chiral sulfur ylides resulted in failure, and since then many asymmetric reactions have been investigated. Recently, reactions of a stoichiometric amount of chiral sulfonium salts [4] with aldehydes have been investigated to afford the corresponding optically active *trans*-epoxides with high enantioselectivities.

In the stoichiometric reaction of sulfur ylides with aldehydes, sulfides are recovered together with the formation of epoxides. If sulfur ylides can be regenerated from the recovered sulfides in situ, the epoxide formation should be achieved in the presence of a catalytic amount of sulfides. In fact, successful examples of such catalytic reaction have been reported [5–8], but turnover frequencies (TOF) are quite low except for the case reported by Aggarwal [6]. These results prompted us to develop a more effective catalytic system for the synthesis of optically active *trans*-epoxides. Herein, we describe the catalytic formation of optically active *trans*-stilbene oxides from sulfur ylides and aldehydes by using a  $C_2$  symmetric optically active sulfide having a binaphthyl skeleton **1** [9] (Fig. 1).

## RESULTS AND DISCUSSION

First, the treatment of benzaldehyde with benzyl bromide in the presence of a stoichiometric amount of

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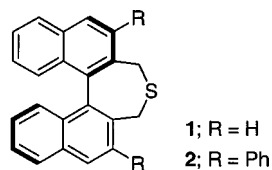
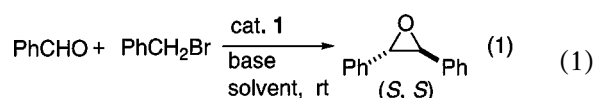


FIGURE 1  $C_2$  symmetric optically active sulfide.

sulfide **1** [10] (to the aldehyde) and KOH in  $\text{CH}_2\text{Cl}_2$  at room temperature for 24 h afforded *trans*-stilbene oxide in 66% yield with 54% enantiomeric excess (ee). No *cis*-stilbene oxide was detected by GLC and  $^1\text{H}$  NMR spectroscopy. Since the stoichiometric reaction proceeded smoothly, we next attempted the catalytic reaction by using 0.1 equiv (to the aldehyde) of **1** under similar reaction conditions (Eq. 1).



Typical results are shown in Table 1. *trans*-Stilbene oxide was produced in 15% yield with 47% ee (S, S) in 48 h (Table 1, entry 1). Interestingly, the addition of tetra-*n*-butylammonium iodide (*n*-Bu<sub>4</sub>NI) to the reaction system much improved the yield of *trans*-stilbene oxide to 44% with 50% ee (S, S) in 24 h (Table 1, entry 2) [11]. Other bases such as KO-*t*-Bu, K<sub>2</sub>CO<sub>3</sub>, and Et<sub>3</sub>N were revealed to be ineffective (Table 1, entries 2–5) and the addition of AgOTf or

TABLE 1 Asymmetric Synthesis of *trans*-Stilbene Oxide using Several Bases and Additives<sup>a</sup>

Entry	Solvent	Base	Additive (equiv)	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1 <sup>d</sup>	CH <sub>2</sub> Cl <sub>2</sub>	KOH	–	15	47
2	CH <sub>2</sub> Cl <sub>2</sub>	KOH	<i>n</i> -Bu <sub>4</sub> NI (1.2)	44	50
3 <sup>d</sup>	CH <sub>2</sub> Cl <sub>2</sub>	KO- <i>t</i> -Bu	<i>n</i> -Bu <sub>4</sub> NI (1.2)	Trace	–
4	CH <sub>2</sub> Cl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	<i>n</i> -Bu <sub>4</sub> NI (1.2)	4	41
5	CH <sub>2</sub> Cl <sub>2</sub>	Et <sub>3</sub> N	<i>n</i> -Bu <sub>4</sub> NI (1.2)	0	–
6	CH <sub>2</sub> Cl <sub>2</sub>	KOH	AgOTf (1.2)	Trace	–
7	CH <sub>2</sub> Cl <sub>2</sub>	KOH	NaI (1.2)	7	18
8	C <sub>6</sub> H <sub>5</sub> Cl	KOH	<i>n</i> -Bu <sub>4</sub> NI (1.2)	Trace	62
9	CCl <sub>4</sub>	KOH	<i>n</i> -Bu <sub>4</sub> NI (1.2)	11	61
10	DMSO	KOH	<i>n</i> -Bu <sub>4</sub> NI (1.2)	69	0
11	CH <sub>3</sub> CN	KOH	<i>n</i> -Bu <sub>4</sub> NI (1.2)	0	–
12 <sup>e</sup>	CH <sub>2</sub> Cl <sub>2</sub>	KOH	<i>n</i> -Bu <sub>4</sub> NI (1.2)	96	32
13 <sup>e</sup>	CH <sub>3</sub> CN	KOH	<i>n</i> -Bu <sub>4</sub> NI (1.2)	57	4
14 <sup>f</sup>	CH <sub>2</sub> Cl <sub>2</sub>	KOH	<i>n</i> -Bu <sub>4</sub> NI (1.2)	8	53

<sup>a</sup>Reaction conditions: benzaldehyde (0.5 mmol), benzyl bromide (0.6 mmol), **1** (0.05 mmol), base (0.6 mmol), solvent (0.4 ml), room temperature, and 24 h under N<sub>2</sub>.

<sup>b</sup>GLC yield after column chromatography.

<sup>c</sup>Determined by HPLC.

<sup>d</sup>Reaction time was 48 h.

<sup>e</sup>H<sub>2</sub>O (40  $\mu$ l) was added.

<sup>f</sup>At 0°C.

NaI prevented the formation of the epoxide (Table 1, entries 6 and 7). Reactions in chlorobenzene and CCl<sub>4</sub> gave the epoxide with 62% ee and 61% ee, respectively, but the yields of the epoxide were quite low (Table 1, entries 8 and 9). Reaction in DMSO produced the epoxide in good yield, but with no enantioselectivity (Table 1, entry 10). As KOH is not soluble in CH<sub>2</sub>Cl<sub>2</sub>, the reactions were carried out in the presence of a small amount of water to dissolve KOH. As a result, the product yields increased, but the enantioselectivity was lowered, unfortunately (entry 12). In various other solvents, no fruitful results were obtained in either product yield or enantioselectivity. The reaction at 0°C proceeded slowly to give the epoxide in low yield with 53% ee (Table 1, entry 14).

The molecular structure of the sulfide **1** was unambiguously clarified by an X-ray structural determination, and an Oak Ridge thermal ellipsoid plot (ORTEP) drawing of one of the three independent molecules of compound **1** in each unit cell is shown in Fig. 2. This ORTEP drawing clearly shows that the space around the sulfur atom may be sterically only slightly hindered. As the introduction of phenyl groups to the 2,6-positions of compound **1** makes the space around the sulfur atom sterically more hindered and higher asymmetric induction may be

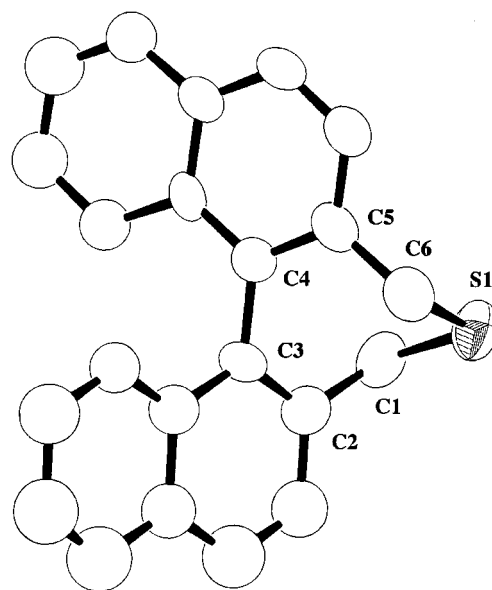
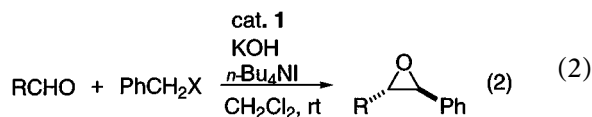


FIGURE 2 The ORTEP drawing of optically active sulfide **1**. Selected bond lengths, angles, torsion angle ( $\text{\AA}$ , deg): S1–C1 = 1.85(1); C1–C2 = 1.52(2); C2–C3 = 1.38(2); C3–C4 = 1.48(1); C4–C5 = 1.39(2); C5–C6 = 1.51(2); C6–S1 = 1.85(1); C1–S1–C6 = 100.4(6); S1–C1–C2 = 109.6(10); S1–C6–C5 = 110.0(9); C2–C3–C4–C5 =  $-58(1)$ .

expected [12], we prepared the optically active sulfide **2** (Fig. 1). Unfortunately, however, the reaction of benzaldehyde with benzyl bromide in the presence of compound **2** (10 mol%) gave only a trace amount of stilbene oxide.

Reactions using other aldehydes and benzyl halides were next investigated in the presence of a catalytic amount of the sulfide **1** (Eq. 2).



Typical results are shown in Table 2. A higher yield of *trans*-stilbene oxide was obtained when benzyl iodide was used in place of benzyl bromide (Table 2, entries 1 vs. 2). It is noteworthy that the addition of *n*-Bu<sub>4</sub>NI improved the yield of *trans*-stilbene oxide even when benzyl iodide was used (Table 2, entries 2 and 3). The reaction of benzyl iodide with other aromatic aldehydes was then examined in the presence of *n*-Bu<sub>4</sub>NI (Eq. 2). The substituent at the para-position of these aldehydes had a major effect on the yield of the corresponding epoxides. The reaction of *p*-methylbenzaldehyde proceeded slowly to give the corresponding epoxide in low yield (Table 2, entry 4), while *p*-chlorobenzaldehyde gave a similar result as with benzaldehyde (Table 2, entry 5). On the contrary, *p*-nitrobenzaldehyde was almost completely consumed, but the expected epoxide was produced and isolated in only low yield because of the formation of various unidentified products. The best enantioselectivity (55% ee) was obtained when 2-naphthaldehyde was used as the aldehyde (Table 2, entry 8).

**TABLE 2** Asymmetric Synthesis of *trans*-Stilbene Oxide Derivatives using Other Aromatic Aldehydes<sup>a</sup>

Entry	R	X	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>	Con g.
1	Ph	Br	44	50	(S, S)
2	Ph	I	79	43	(S, S)
3	Ph <sup>d</sup>	I	26	29	(S, S)
4	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	I	13	52	(S, S)
5	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	I	51	50	(S, S)
6	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> <sup>e</sup>	I	6 <sup>f</sup>	51	(-)
7	1-Naphthyl	I	15	28	(-)
8	2-Naphthyl	I	30 <sup>f</sup>	55	(-)

<sup>a</sup>Reaction conditions: benzaldehyde (0.5 mmol), benzyl halide (0.6 mmol), **1** (0.05 mmol), KOH (0.6 mmol), *n*-Bu<sub>4</sub>NI (0.6 mmol), CH<sub>2</sub>Cl<sub>2</sub> (0.4 ml), room temperature, and 24 h under N<sub>2</sub>.

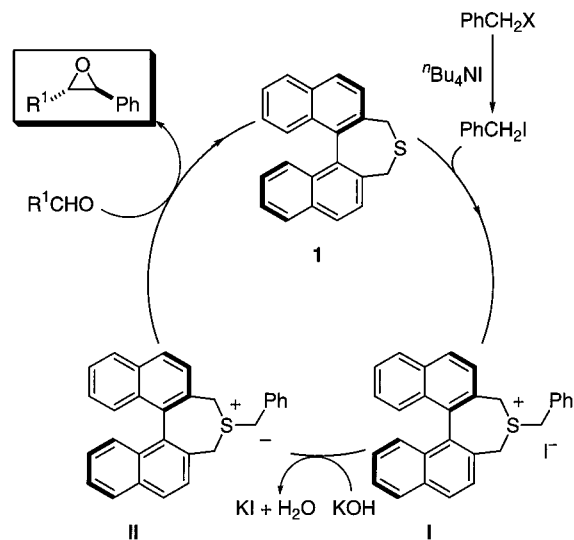
<sup>b</sup>GLC yield after column chromatography.

<sup>c</sup>Determined by HPLC.

<sup>d</sup>In the absence of *n*-Bu<sub>4</sub>NI.

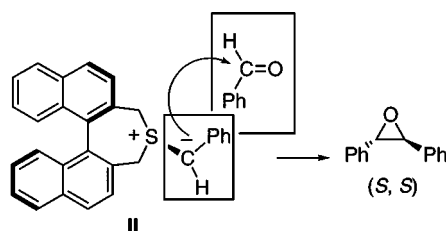
<sup>e</sup>Reaction time was 6 h.

<sup>f</sup>Isolated yield.

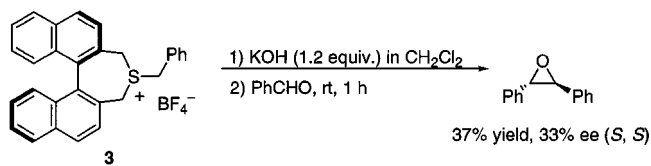


**SCHEME 1** Plausible reaction pathway.

A plausible reaction pathway is shown in Scheme 1. The reaction of the sulfide **1** with benzyl halide affords a sulfonium salt (**I**) which gives the corresponding sulfur ylide (**II**) by deprotonation with KOH. The nucleophilic addition of **II** to the aldehyde results in the formation of the *trans*-epoxide, together with the starting sulfide **1**. In our catalytic system, asymmetric induction can be rationalized by assuming the model shown in Scheme 2. Thus, the sulfur ylide **II** may exist in the form depicted in the scheme that emphasizes the interaction between the phenyl group and the binaphthyl skeleton. The nucleophilic attack of the carbon of compound **II** to the *re* face of the aldehyde would be favored leading to the formation of *trans*-(*S,S*)-stilbene oxide consistent with the experimental result. The reaction of benzyl bromide with iodide anion derived from *n*-Bu<sub>4</sub>NI affords the more reactive benzyl iodide in situ and the tetra-*n*-butylammonium cation may also play some role as a phase transfer catalyst to accelerate the reaction, although the details of the reaction mechanism are not yet clear. In a separate experiment, we confirmed that the BF<sub>4</sub><sup>-</sup> analogue of



**SCHEME 2** Asymmetric induction model.



**SCHEME 3** Reaction of sulfonium salt with benzaldehyde.

compound **1** (**3**), prepared separately, reacted with benzaldehyde in the presence of KOH (1.2 equiv) in  $\text{CH}_2\text{Cl}_2$  at room temperature for 1 h to afford a 37% yield of *trans*-stilbene oxide with 33% ee (S, S) (Scheme 3). The enantioselectivity obtained here was slightly lower than that of the catalytic reaction (Table 2, entries 1 and 2). This result may suggest that the counter anion of the sulfonium salt plays some role in the asymmetric induction.

In conclusion, we found that a  $C_2$  symmetric sulfide having a binaphthyl skeleton **1** worked as a chiral catalyst in the presence of *n*- $\text{Bu}_4\text{NI}$  for the asymmetric reaction between aromatic aldehydes and benzyl halides to give the corresponding *trans*-stilbene oxides in moderate to good yields (up to 79%) with moderate enantioselectivities (up to 55% ee).

## EXPERIMENTAL

### General

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on JEOL EX-400, JEOL JNM-AL300, and JEOL JNM-GSX270 spectrometers for solutions in  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$  as an internal standard. GLC analyses were carried out with a Shimadzu GC-14A instrument equipped with a CPB 10-S25-050 (Shimadzu, fused silica capillary column, 0.33 mm  $\times$  25 m, 5.0 mm film thickness) column using helium as the carrier gas. GLC yields were determined using biphenyl as an internal standard. HPLC analyses were carried out on a HITACHI L-7100 instrument with an L-7300 column oven and an L-7400 UV detector using a Daicel Chiralcel OD column. Column chromatographies were performed with Merck silica gel 60.

### Materials

Tetrahydrofuran (THF) was freshly distilled over sodium benzophenone ketyl just before use. Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and acetonitrile were distilled over calcium hydride under argon. Benzaldehyde was distilled under reduced pressure. Other commercially available organic and inorganic compounds were used without further purification. Benzyl iodide in benzene solution was prepared by ion exchange of benzyl chloride with sodium iodide.

(*R*)-4,5-Dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]thiepin (**1**) was prepared from (*R*)-BINOL according to the literature method [10].

### Preparation of (*R*)-2,6-Diphenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]thiepin (**2**)

This compound was prepared from (*R*)-3,3'-diphenylbinaphthol [12] according to the literature method [10]: A pale yellow solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.34 (d,  $J = 12.8$  Hz, 2H), 3.58 (d,  $J = 12.8$  Hz, 2H), 7.23–7.93 (m, 20H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.45 MHz):  $\delta$  29.3, 125.9, 126.0, 127.0, 127.3, 128.2, 129.7, 130.2, 131.1, 131.7, 132.4, 134.7, 139.2, 141.1; HRMS Calcd for  $\text{C}_{34}\text{H}_{24}\text{S}$   $m/z$  464.1599 ( $\text{M}^+$ ), Found 464.1614.

### General Procedure for Asymmetric Synthesis of Epoxides using Benzyl Iodide

After benzene was removed from a benzene solution of benzyl iodide (0.24 M; 1.0 ml, 0.24 mmol) under reduced pressure,  $\text{CH}_2\text{Cl}_2$  (0.4 ml) was added and the mixture was stirred at room temperature under nitrogen. The sulfide (0.02 mmol), *n*- $\text{Bu}_4\text{NI}$  (88.7 mg, 0.24 mmol), pulverized KOH (13.5 mg, 0.24 mmol), and the aldehyde (0.20 mmol) were added to the mixture and then the reaction mixture was stirred for 24 h. The resulting mixture was treated with water (10 ml), extracted with  $\text{CH}_2\text{Cl}_2$ , dried over  $\text{MgSO}_4$ , filtered, and the filtrate was evaporated. The residue was purified by column chromatography using hexane/ $\text{CH}_2\text{Cl}_2$  as an eluent.

*trans*-2,3-Diphenyloxirane. A White solid; mp 62–64°C (lit. 61–63°C) [13];  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.87 (s, 2H), 7.30–7.45 (m, 10H). The ee value was determined by HPLC analysis with a Daicel Chiralcel OD column (eluent: hexane/2-propanol = 95:5, flow rate: 1.0 ml/min, column temperature: 25°C, retention time: 7.3 min (S, S), 14.5 min (R, R)).

*trans*-2-(*p*-Chlorophenyl)-3-phenyloxirane [13]. A white solid; mp 86–88°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.82 (d,  $J = 1.8$  Hz, 1H), 3.84 (d,  $J = 1.8$  Hz, 1H), 7.24–7.42 (m, 9H). The ee value was determined by HPLC analysis with a Daicel Chiralcel OD column (eluent: hexane/2-propanol = 95:5, flow rate: 1.0 ml/min, column temperature: 25°C, retention time: 8.4 min (S, S), 10.4 min (R, R)).

*trans*-2-(*p*-Tolyl)-3-phenyloxirane. A white solid; mp 70–72°C (lit. 72–73°C) [13];  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  2.37 (s, 3H), 3.83 (d,  $J = 1.8$  Hz, 1H), 3.86 (d,  $J = 1.8$  Hz, 1H), 7.18–7.41 (m, 9H). The ee value was determined by HPLC analysis

with a Daicel Chiralcel OD column (eluent: hexane/2-propanol = 95:5, flow rate: 0.5 ml/min, column temperature: 25°C, retention time: 12.0 min (S, S), 18.2 min (R, R)).

*trans-2-(p-Nitrophenyl)-3-phenyloxirane*. A pale yellow solid; mp 75–77°C (lit. 73–75°C) [13]; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 3.85 (d, *J* = 1.5 Hz, 1H), 3.97 (d, *J* = 1.5 Hz, 1H), 7.25–7.45 (m, 5H), 7.52 (d, *J* = 8.7 Hz, 2H), 8.25 (d, *J* = 8.7 Hz, 2H). The ee value was determined by HPLC analysis with a Daicel Chiralcel OD column (eluent: hexane/2-propanol = 90:10, flow rate: 1.0 ml/min, column temperature: 25°C, retention time: 16.2 min, 20.7 min).

*trans-2-(1-Naphthyl)-3-phenyloxirane* [14]. A colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 3.86 (br s, 1H), 4.49 (s, 1H), 7.38–7.99 (m, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.45 MHz): δ 61.1, 62.0, 122.0, 122.9, 125.6, 125.9, 126.4, 128.2, 128.4, 128.7, 131.2, 133.2, 133.3, 137.2. The ee value was determined by HPLC analysis with a Daicel Chiralcel OD column (eluent: hexane/2-propanol = 95:5, flow rate: 1.0 ml/min, column temperature: 25°C, retention time: 14.4 min, 19.4 min).

*trans-2-(2-Naphthyl)-3-phenyloxirane* [15]. A white solid; mp 114–116°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 3.97 (d, *J* = 1.5 Hz, 1H), 4.04 (d, *J* = 1.5 Hz, 1H), 7.34–7.88 (m, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.45 MHz): δ 63.0, 63.1, 122.8, 125.0, 125.5, 126.2, 126.4, 127.79, 127.83, 128.36, 128.43, 128.6, 133.2, 133.4, 134.6, 137.1. The ee value was determined by HPLC analysis with a Daicel Chiralcel OD column (eluent: hexane/2-propanol = 98:2, flow rate: 1.0 ml/min, column temperature: 25°C, retention time: 30.9 min, 34.9 min).

### X-ray Structural Analysis of **1**

A single crystal of **1** (C<sub>22</sub>H<sub>16</sub>S) suitable for X-ray analysis was prepared by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-*n*-hexane. Diffraction data were collected on a Rigaku AFC-7R four-circle automated diffractometer with Mo-Kα (λ = 0.719 Å) radiation and a graphite monochromator at 23°C using the ω – 2θ scan technique. Details of the X-ray diffraction study are summarized in Table 3. For a structure analysis and refinement, computations were performed using the TEXAN [16] crystallographic software package of Molecular Structure. Neutral atom scattering factors were taken from Ref. [17]. Anomalous dispersion effects were included in *F*<sub>calc</sub> [18]; the values of Δ*f*' and Δ*f*'' were those of Ref. [19]. The

TABLE 3 Summary of Crystallographic Data of Compound **1**

Empirical formula	C <sub>22</sub> H <sub>16</sub> S
Formula weight	312.43
Crystal system	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (#19)
Crystal color	Colorless
Lattice parameters	
<i>a</i> (Å)	22.229 (10)
<i>b</i> (Å)	25.594 (8)
<i>c</i> (Å)	8.59 (2)
<i>V</i> (Å <sup>3</sup> )	4888 (9)
<i>Z</i>	12
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.273
μ (Mo Kα) (cm <sup>-1</sup> )	1.95
<i>F</i> (000)	1968.00
Diffractometer	Rigaku AFC7R
Radiation	Mo Kα (λ = 0.71069 Å) graphite monochromated
Temp. (°C)	23.0
Scan type	ω
Max. 2θ (°)	55.0
No. of reflections measured	5126
No. of observations ( <i>I</i> > 3.00σ( <i>I</i> ))	2200
Structure soln	Direct methods (SIR92)
Refinement	Full-matrix least squares
No. of variables	532
Reflection/parameter ratio	4.14
Residuals: <i>R</i> ; <i>R</i> <sub>w</sub>	0.067; 0.066
Goodness of fit (GOF)	1.15
Max shift/error in final cycle	6.61
Maximum peak in final diff map (e Å <sup>-3</sup> )	0.26
Minimum peak in final diff map (e Å <sup>-3</sup> )	-0.20

structure was solved by direct methods (SIR92). Three independent molecules of compound **1** occupy a unit cell. The structure of these three independent molecules are almost the same. The carbon atoms at C5-8 positions of the binaphthyl ring were refined isotropically. All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but not refined. The weighting scheme ω = 1/σ<sup>2</sup>(*F*<sub>0</sub>) with σ(*F*<sub>0</sub>) from counting statistics gave satisfactory agreement analyses.

### Preparation of Sulfonium Salt **3**

A mixture of optically active sulfide **1** (234 mg, 0.750 mmol) and benzyl bromide (0.09 ml, 0.75 mmol) was stirred in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) at room temperature under nitrogen. AgBF<sub>4</sub> (146 mg, 0.750 mmol) was added to the mixture and then the reaction mixture was stirred for 5 h. Removal of the precipitates from the mixture by use of Celite and evaporation of the solvent gave a crude solid product. The crude product was washed with Et<sub>2</sub>O to give a

white solid in 82% yield (304 mg, 0.620 mmol); mp 149–151°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  3.63 (d,  $J = 11.7$  Hz, 1H), 3.99 (d,  $J = 14.7$  Hz, 1H), 4.39 (d,  $J = 12.5$  Hz, 1H), 4.47 (d,  $J = 14.7$  Hz, 1H), 4.62 (d,  $J = 12.5$  Hz, 1H), 4.64 (d,  $J = 11.7$  Hz, 1H), 7.23–8.27 (m, 20H);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz):  $\delta$  39.3, 42.4, 44.4, 122.2, 126.1, 126.5, 126.7, 127.1, 127.31, 127.34, 127.5, 128.4, 129.7, 130.0, 130.1, 130.4, 130.5, 131.5, 135.9; HRMS Calcd for  $\text{C}_{29}\text{H}_{23}\text{S}$   $m/z$  403.1520 ( $\text{M}^+ - \text{BF}_4$ ), Found 403.1510.

### Reaction of Sulfonium Salt **3** with Benzaldehyde

A mixture of the sulfonium salt **3** (98 mg, 0.20 mmol) and pulverized KOH (13.5 mg, 0.240 mmol) was stirred in  $\text{CH}_2\text{Cl}_2$  (4 ml) at room temperature under nitrogen for 15 min. Benzaldehyde (20.3  $\mu\text{l}$ , 0.2 mmol) was added to the mixture and then the reaction mixture was stirred for 1 h. The resulting mixture was treated with water (10 ml), extracted with  $\text{CH}_2\text{Cl}_2$ , dried over  $\text{MgSO}_4$ , and filtered. The filtrate contained 2,3-diphenyloxirane in 37% GLC yield (14.5 mg, 0.074 mmol, biphenyl as internal standard). The filtrate was then evaporated to leave a residue which was purified by column chromatography using hexane/ $\text{CH}_2\text{Cl}_2$  as an eluent, the enantioselectivity of the product oxirane being 33% ee.

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