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# Asymmetric Oxidation and Determination of the Configurations of an Optically Pure Sulfoxide and an *l*-Menthoxysulfonium Salt of 1,9-Bis(methylthio)dibenzothiophene by X-ray Crystallographic Analysis

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## ABSTRACT

*1,9-Bis(methylthio)dibenzothiophene (**1a**) was treated with one equivalent of bromine and pyridine in the presence of l-menthol and then with aqueous sodium hydroxide to give optically active 1-(methylsulfinyl)-9-(methylthio)dibenzothiophene (**2a**) enriched by the S isomer (ee: 57%). The configuration of optically pure sulfoxide (**2a**) was determined by X-ray crystallographic analysis to be the S configuration at the sulfinyl sulfur atom. On the other hand, 1-(methyl-l-menthoxysulfonio)-9-(methylthio)dibenzothiophene tetrafluoroborate (**4a**) was isolated as an intermediate of this asymmetric oxidation in an optically pure form, as yellow crystals. The absolute configuration of this sulfonium salt (**4a**) was verified by X-ray crystallographic analysis as the R configuration. Optically pure sulfonium salt (**4a**) also gave partially optically active sulfoxide (**2a**) with net inversion on its hydrolysis. It was suggested that the hydrolysis reaction of the sulfonium salt (**4a**) accordingly proceeds, not only via a sulfurane having a simple $S_N2$ type of geometry but also by a front side attack of hydroxide anion, with respect to the l-menthoxy group, on sulfur, and the sequential elimination of the l-menthoxy group from the tetracoordinated intermediate.* © *1996 John Wiley & Sons, Inc.*

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## *INTRODUCTION*

Preparation of optically active sulfoxides by asymmetric induction has been an important subject of research in organic synthesis, and hence the asymmetric oxidation of organic sulfur compounds has become of great interest to organic chemists [1]. As one procedure for preparation of optically active diaryl or alkyl aryl sulfoxides from the corresponding sulfides, it has been reported that an asymmetric induction was achieved by oxidation of sulfides with halogenating reagents in the presence of *l*-menthol as a chiral auxiliary [2]. The *l*-menthoxysulfonium salts produced initially as intermediates in the reaction are readily hydrolyzed in aqueous sodium hydroxide to the corresponding optically active sulfoxides. The hydrolysis of the optically pure alkoxysulfonium salts with sodium hydroxide solution (or with several alkoxides) proceeds quantitatively via a sulfurane having an $S_N2$ type of geometry, accompanied by complete inversion of the configuration of the sulfur atom [3]. On the other hand, an E2 type of reaction of *l*-menthoxysulfonium salts by thermolysis gives the optically active sulfoxides with retention of the configuration [2]. Interestingly, retention of the configuration was observed in the acid catalyzed alcoholysis of optically active *N,N*-diisopropyl *p*-toluensulfinamide, and the result was ascribed to the formation of a sulfurane as an intermediate that undergoes rapid pseudorotation prior



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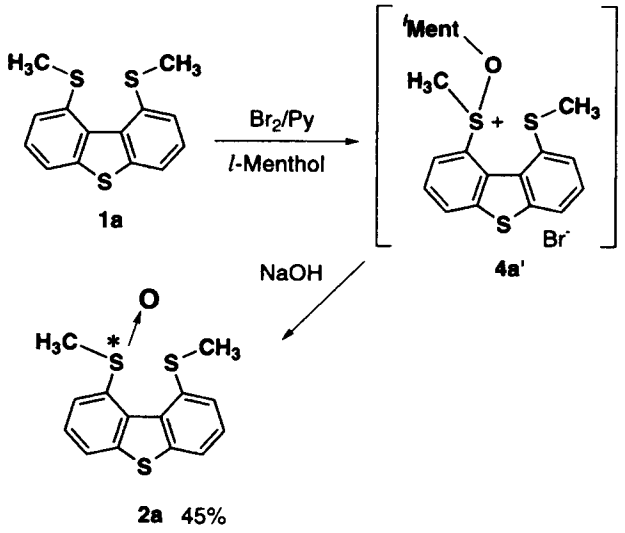



**SCHEME 1**

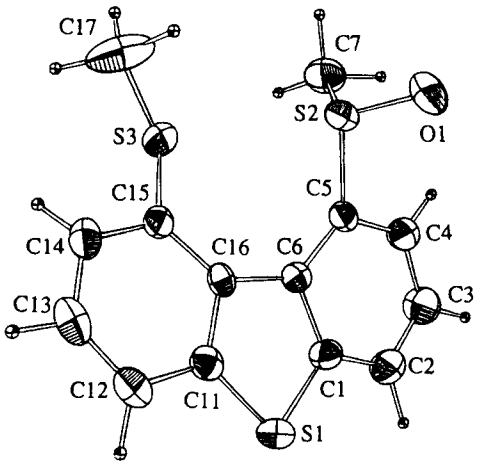



**FIGURE 1** ORTEP drawing of optically pure **2a**.

to completion of the reaction [4]. Recently, we have reported the preliminary results of the asymmetric oxidation of 1,9-bis(alkylthio)dibenzothiophenes to produce optically active sulfoxides [5]. To investigate the influence of a neighboring substituent in the asymmetric oxidation of sulfides and hydrolysis of alkoxysulfonium salts, 1,9-bis(alkylthio)dibenzothiophenes and their analogs were oxidized with bromine, and then the alkoxysulfonium salts obtained were hydrolyzed in aqueous sodium hydroxide solution. In this article, we describe the preparation of optically pure 1-(methylsulfinyl)-9-(methylthio)dibenzothiophene (**2a**) together with determination of the configuration by X-ray crystallographic analysis as the *S* configuration, while the optically pure *l*-menthoxysulfonium salt, 1-(methyl-*l*-menthoxysulfonio)-9-(methylthio) dibenzothiophene tetrafluoroborate (**4a**) was found to have the *R* configuration.

## *RESULTS AND DISCUSSION*

Typically, 1,9-bis(methylthio)dibenzothiophene (**1a**) was oxidized with one equivalent of bromine in the presence of pyridine and 10 equivalents of *l*-menthol in dichloromethane at −20°C under argon for 2 hours (Scheme 1). Then the *l*-menthoxysulfonium salt produced was treated with aqueous sodium hydroxide for 12 hours to give optically active sulfoxide **2a** in 45% chemical yield and in 57% ee. The sulfoxide **2a** was purified by recrystallization from dichloromethane and ethanol to produce optically pure **2a**, $[\alpha]_D^{23} = -433°$ (c = 0.406, $CHCl_3$), and its enantiomeric excess was determined by 500 MHz $^1H$ NMR spectroscopy using a shift reagent, $Eu(tfc)_3$ as ee > 99%. In order to determine the absolute configuration of the sulfoxide **2a**, the X-ray crystallographic analysis of optically pure **2a** was performed by Cu Kα radiation. The ORTEP drawing of sulfoxide **2a** is shown in Figure 1.

In the structure of **2a**, the distance between the S2 and S3 atoms is 3.11 Å, which is shorter than the van der Waals S–S contact distance (3.70 Å) [6]. Furthermore, the angle at the O1–S2–S3 position, and the torsional angle at the C5–C6–C16–C15 position of **2a** are 168.8° and 22.1°, respectively, revealing that the dibenzothiophene ring is distorted from the normal planar structure due to the steric or electronic repulsion between the methylsulfinyl and the methylthio substituents at the 1,9-positions [7]. As shown in Figure 1, the sulfoxide **2a** has an *S* configuration at the sulfinyl sulfur atom. When the coordinations of positional parameters *X*, *Y*, and *Z* are shifted to (1 − *X*), (1 − *Y*), and (1 − *Z*), the *R* values of **2a** changed from R = 0.04018 ($R_w$ = 0.04327) to *R* = 0.04765 ($R_w$ = 0.05022). Therefore, the *S* configuration of optically pure sulfoxide **2a** is correct, and its enantiomeric structure, i.e., *R* configuration, could be rationally eliminated at the 0.005 significance level [8].

On the other hand, asymmetric oxidations of 1,9-bis(*i*-propylthio)dibenzothiophene (**1b**), 1,9-bis(methylthio)dibenzofuran (**1c**), 1-(methylthio)dibenzothiophene (**1d**), and 1,8-bis(methylthio) naphthalene were similarly performed by the method described earlier to produce the corresponding optically active sulfoxides, 1-(*i*-propylsulfinyl)-9-(*i*-propylthio)dibenzothiophene (**2b**) 1-(methylsulfinyl)-9-(methylthio)dibenzofuran (**2c**), 1-(methylsulfinyl)dibenzothiophene (**2d**), and 1-(methylsulfinyl)-8-(methylthio)naphthalene (**3**) in

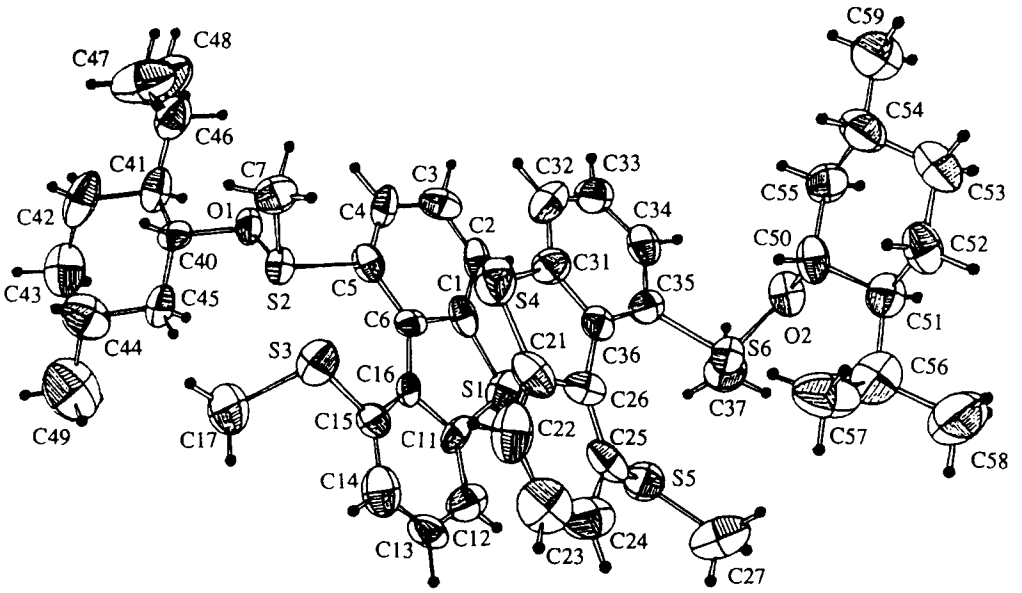
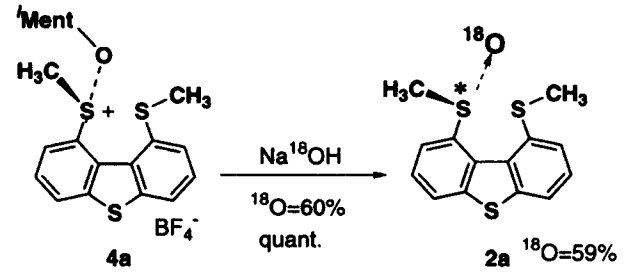



**FIGURE 2** ORTEP drawing of optically pure **4a**, except for $BF_4$ and $C_6H_6$.

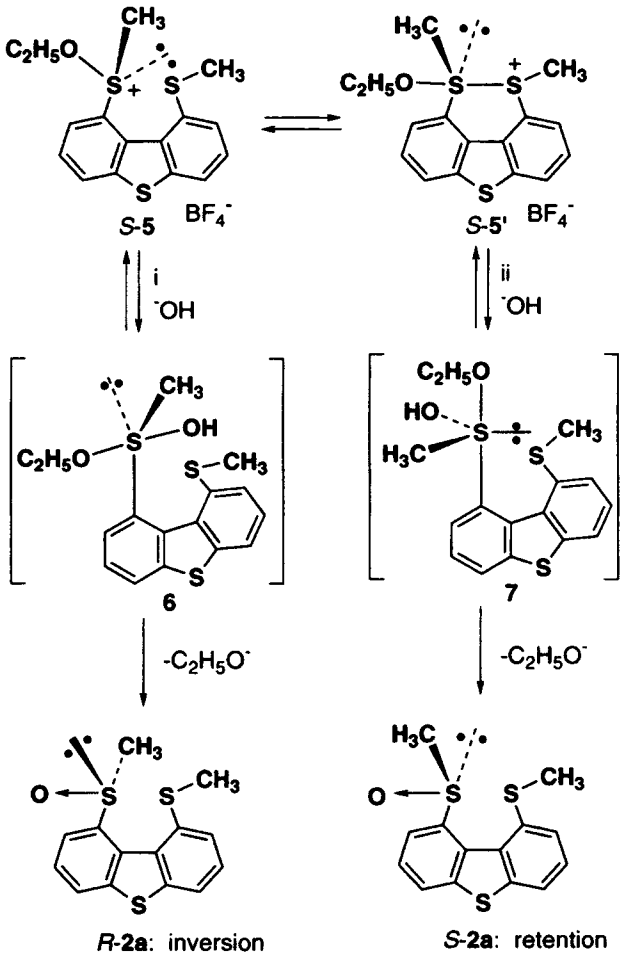
21% (ee = 17%), 57% (ee = 27%), 65% (ee = 17%), and 56% (ee = 33%) yields, respectively.

Although several *l*-menthoxysulfonium salts have been obtained as intermediates in asymmetric oxidations of sulfides with halogenating reagents and *l*-menthol, the salts were very hygroscopic, and hence, their structures have never been determined in detail. Therefore, we tried to isolate the compound **4a** as an intermediate of the asymmetric oxidation of 1,9-bis(methylthio)dibenzothiophene and to verify the configuration by X-ray crystallographic analysis. The isolation of the salt **4a** was successfully achieved by treatment of the intermediate *l*-menthoxysulfonium bromide **4a'** with silver tetrafluoroborate in dichloromethane to obtain the corresponding tetrafluoroborate **4a** as yellow crystals in 40% yield (de = 52%). The sulfonium salt **4a** is unstable to water and decomposes gradually in the presence of moisture to give the corresponding sulfoxide **2a**. The optically pure sulfonium salt **4a** was obtained by recrystallization from benzene and ether, and the optical purity of **4a** was determined by 500 MHz $^1$H NMR spectroscopy by comparing the integral ratio of the methylsulfonio proton to that of its diastereoisomer (de = 96%). Accordingly, the structure of optically pure *l*-menthoxysulfonium salt **4a** was determined by X-ray crystallographic analysis. As shown in Figure 2, the configuration of the sulfonium sulfur atom of **4a** was determined to be the *R* configuration by comparison with that of the *l*-menthoxy group in **4a** as a reference of chirality. In the structures of compound **4a**, the bond lengths of S2–O1 and S6–O2 are 1.63 and 1.61 Å, respectively, and the bond angles around the sulfonium sulfur atom are 95.8° (O1–S2–C5), 99.4° (O1–S2–C7), and 102.8° (C5–S2–C7), and 103.6° (O2–S6–C35), 92.4° (O2–S6–C37), and 105.0° (C35–S6–C37), respectively. The S–S distances at the S2–S3 and S5–S6 positions and the torsional angles at the C5–C6–C16–C15 and C25–C26–C36–C35 positions of compound **4a** were found to be 2.85 and 2.85 Å, and −16.1° and −15.6°, which are shorter lengths and smaller angles than those of the corresponding values of sulfoxide **2a**. Furthermore, upon use of two equivalents of bromine for the asymmetric oxidation of **1a**, the yield of sulfoxide **2a** was not changed, and the corresponding bissulfoxide and sulfone were not produced in the reaction [9]. These results suggest that the lone pair repulsion between the two sulfur atoms should decrease in the *l*-menthoxysulfonium salt **4a** due to the oxidation of one sulfur atom of **1a**.

Since the hydrolysis of optically pure sulfonium salt **4a** was performed with aqueous 2 M sodium hydroxide at 0°C for 12 hours to produce sulfoxide **2a** in 99% yield, but with an ee of 76%, with net inversion, the hydrolysis reaction would appear to proceed, not only via a sulfurane having the usual $S_N2$ type of reaction geometry but also by either or both an elimination of menthone or a substitution reaction involving nucleophilic attack of hydroxide anion at the sulfonium sulfur atom from the front side with reference to the *l*-menthoxy group and subsequent elimination of the *l*-menthoxy group from this hypervalent intermediate. Therefore, *l*-menthoxysulfonium salt **4a** was treated with $^{18}$O-enriched aqueous sodium hydroxide ($^{18}$O content = 60%). In the




SCHEME 2




i: Back side attack; ii: Front side attack.

SCHEME 3

hydrolysis of the sulfonium salt **4a**, the sulfoxide obtained was found to contain $^{18}O$ atom at the sulfinyl oxygen ($^{18}O$ content = 59%), indicating that the reaction proceeds, not via an elimination reaction of menthone, but mainly via a nucleophilic substitution reaction at the sulfonium sulfur atom (Scheme 2). Furthermore, trideuteriated ethoxysulfonium salt **5**-$D_3$ was prepared from 1-(trideuterated methylsulfinyl)-9-(methylthio)dibenzothiophene (**2a**-$D_3$) on treatment with $(C_2H_5)_3O \cdot BF_4$, and was treated with sodium hydroxide solution at $-20°C$ to give the starting sulfoxide **2a**-$D_3$ quantitatively. These tracer experiments demonstrate clearly that the nucleophilic attack of hydroxide anion proceeds only at the sulfonium sulfur atom at the 1 position and not at the sulfenyl sulfur atom at the 9 position of compound **5**, although these two sulfur atoms are located in close proximity and interact strongly with each other. On the other hand, the optically pure sulfoxide **2a** was treated with $(C_2H_5)_3O \cdot BF_4$ similarly to give optically active ethoxysulfonium salt **5**. After hydrolysis of the optically pure ethoxysulfonium salt **5**, the optical rotation of the sulfoxide obtained in quantitative yield decreased to $[\alpha]_D^{25} = +316°$ (76% ee). Therefore, the hydrolysis reaction of the sulfonium salts **4a** and **5** proceeds with net inversion, with the ratio of inversion (88%) and retention (12%).

Recently, Martin reported that the hydrolysis of an optically active tetracoordinated chlorosulfurane proceeded by treatment with water in the presence of several amines to give an optically active sulfoxide and the configurations of the chlorosulfurane and sulfoxide were found to be both of the *S* configuration at the sulfur atoms [10]. As shown in Figure 2, the configuration around the sulfonium sulfur atom of compound **4a** is similar to a trigonal-bipyramidal structure, although the distance between the two sulfur atoms at the 1,9-positions is longer than that of a usual S–S bond. In fact, the angles around the sulfonium sulfur atom are 169.0° (O1–S2–S3), 86.4° (S3–S2–C7), 92.0° (S3–S2–C7), 168.8° (O2–S6–S5), 88.2° (S5–S6–C37), and 88.0° (S5–S6–C35), respectively. Therefore, the electronic attractive force between the two sulfur atoms at the 1,9-positions strongly affect each other. This through-space attractive force in the alkoxysulfonium salts **4a** and **5** should play important roles with respect to the retention of configuration of the sulfur atom in the hydrolysis. Inversion of the configuration has been observed in the hydrolysis when the hydroxide anion approaches the sulfonium sulfur atom from the backside of the ethoxy group (the apical position), and the ethoxy group leaves from another apical position of the $\sigma$-sulfurane intermediate (**6**) (Scheme 3). If the hydrolysis of the sulfonium salts having the *S* configuration proceeded at the sulfur atom via the attack of the hydroxide anion from the back and elimination of the alkoxide group from the front, it should produce the optically active sulfoxide having the *R* configuration. On the other hand, if the hydroxide anion attacks the sulfonium sulfur atom at the apical side relative to the alkoxy group in the

sulfurane type structure of 5′, avoiding the steric hindrance of the methylsulfenyl group, then the structure changes to the sulfurane intermediate (7), which has the putative leaving ethoxy group and one of the aromatic carbons in the dibenzothiophene ring at the apical positions. Subsequently, the intermediate decomposes immediately to produce optically active sulfoxide having the *S* configuration. Although the stereochemistry is predominantly an inversion in the hydrolysis of *l*-menthoxysulfonium salt **4a** and ethoxy sulfonium salt **5**, this hydrolysis reaction of **4a** and **5** bearing two sulfur atoms in close proximity may involve new dual type of substitution reactions on the sulfonio sulfur atom, namely, a colinear type of reaction involving the nucleophilic attack of hydroxide anion at the back of the sulfonium sulfur atom and elimination of the alkoxy group from the front to give the sulfoxide with retention of the configuration. There are only a few known substitution reactions at sulfur with retention of configuration. Our present result reveals an additional example that should be investigated in detail.

## EXPERIMENTAL

### General

Infrared spectra were recorded on a JASCO FT/IR-5000 spectrometer. The NMR spectra were measured in $CDCl_3$ solution on a JEOL JNM EX270 or a Bruker AM-500 spectrometer. Mass spectra were obtained with a JEOL JMX SX102 and Shimadzu QP-2000 mass spectrometer. X-ray data collection was performed on an Enraf-Nonius CAD4 computer-controlled kappa axis diffractometer, and calculations for structure solution and refinement were performed on a VAX computer using MolEN.

## PREPARATION

### 4,6-Bis(*i*-propylthio)thianthrene 5-Oxide

Thianthrene 5-oxide (5.00 g, 21.5 mmol) dissolved in THF (80 mL) was lithiated with 0.284 M LDA (250 mL, 71 mmol) for 3 hours at −78°C. To this solution was added elemental sulfur (8.0 g, 267 mmol), and the solution was stirred for 3 hours at −20°C. After addition of isopropyl iodide (21.5 mL, 215 mmol), the solution was stirred for 10 hours at 25°C, then treated with water (5 mL). The solvent was evaporated, and the residue was extracted with $CH_2Cl_2$ (3 × 150 mL). The extract was washed with saturated $Na_2S_2O_3$ solution and water and dried with $MgSO_4$. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, $CH_2Cl_2$: ethyl acetate = 5:1). Recrystallization gave 4,6-bis(*i*-propylthio)thianthrene 5-oxide (5.9 g, 72%); mp 115–116°C (ethanol); $^1H$ NMR (270 MHz) $\delta$ 1.33 (d, $J$ = 6.7 Hz, 6H, $CH_3$), 1.42 (d, $J$ = 6.7, 6H, $CH_3$), 3.53 (sept, $J$ = 6.7 Hz, 2H, CH), 7.39 (t, $J$ = 7.8 Hz, 2H), 7.53 (dd, $J$ = 7.8, 1.3 Hz, 2H), 7.65 (dd, $J$ = 7.8 Hz, 1.3 Hz, 2H); MS (*m/z*) 380 ($M^+$); anal. calcd for $C_{18}H_{20}OS_4$: C, 56.80; H, 5.30. Found: C, 56.62; H, 5.13.

### 1,9-Bis(*i*-propylthio)dibenzothiophene (**1b**)

To a THF (300 mL) solution of 1,9-bis(*i*-propylthio)thianthrene 5-oxide (3.8 g, 10 mmol), 1.0 M $C_2H_5MgBr$/THF (100 mL, 100 mmol) was added dropwise. The solution was stirred for 1 hour, anhydrous $CuCl_2$ (20.2 g, 150 mmol) was added, and the solution was stirred for 42 hours. The solution was treated with water (3 mL), and aqueous-saturated $NH_4Cl$ solution was added. After evaporation of the solvent, the solution was treated with 2 M NaOH solution and was extracted with $CH_2Cl_2$ (3 × 200 mL). The extract was dried with $MgSO_4$, and then the solvent was evaporated. The residue was purified by column chromatography (silica gel, $CCl_4$) and with recrystallization (cyclohexane) to give **1b** (2.5 g, 76%); mp 117–118°C; $^1H$ NMR (270 MHz) $\delta$ 0.89 (d, $J$ = 6.5 Hz, 12 H), 3.11 (sept, $J$ = 6.5 Hz, 2H), 7.44 (t, $J$ = 7.8 Hz, 2H), 7.68 (dd, $J$ = 7.8, 1.1 Hz, 2H), 7.72 (dd, $J$ = 7.8, $J$ = 1.1 Hz, 2H); MS (*m/z*) 332 ($M^+$); anal. calcd for $C_{18}H_{20}S_3$: C, 65.01; H, 6.06. Found: C, 64.67; H, 6.03.

### 1,9-Bis(methylthio)dibenzothiophene (**1a**), 1,9-Bis(methylthio)dibenzofuran (**1c**), and 1-(Methylthio)dibenzothiophene (**1d**)

These compounds were prepared from 4,6-bis-(methylthio)thianthrene 5-oxide, 1,9-bis(methylthio)phenoxathiin 10-oxide, and 4-(methylthio) thianthrene 5-oxide [11].

### Asymmetric Oxidation 1-(Methylsulfinyl)-9-(methylthio)dibenzothiophene (**2a**)

1,9-Bis(methylthio)dibenzothiophene (279 mg, 1.0 mmol) was treated with $Br_2$ (0.4 M in $CH_2Cl_2$, 2.5 mL, 1.0 mmol) and pyridine (1.0 mL, 12 mmol) in the presence of *l*-menthol (1.56 g, 10 mmol) in $CH_2Cl_2$ (5.6 mL) at −20°C under argon for 2 hours. Then 3.3 M aqueous sodium hydroxide (3 mL, 10 mmol) was added, and the solution was stirred for 12 hours. After treatment with 2 M HCl solution, the reaction mixture was extracted with $CH_2Cl_2$ (3 × 30 mL) and dried with $MgSO_4$. Then $CH_2Cl_2$ was evaporated, and

the residue was purified by column chromatography (silica gel, $CH_2Cl_2$:ethylacetate = 1:1) to give optically active sulfoxide **2a** in 45% yield, $[\alpha]_D^{23} = -215°$ (c = 0.446, $CHCl_3$); mp 182–183°C (Ref. 150–151°C) [2]; $^1H$ NMR (270 MHz) $\delta$ 2.35 (s, 3H), 2.85 (s, 3H), 7.49 (t, $J$ = 7.8 Hz, 1H), 7.71 (dd, $J$ = 7.8, 1.1 Hz, 1H), 7.76 (t, $J$ = 7.8 Hz, 1H), 7.82 (dd, $J$ = 7.8, 1.1 Hz, 1H), 8.00 (dd, $J$ = 7.8, 1.1 Hz, 1H), 8.37 (dd, $J$ = 7.8, 1.1 Hz, 1H).

*Crystal Data.* Orthorhombic, $P2_12_12_1$; a = 8.839 (1), b = 17.333 (1), c = 8.445 (3) Å; V = 1293.9 Å$^3$; $Z$ = 4, $\rho$ = 1.50 g/cm$^3$, $\mu$(Cu $K\alpha$) = 50.3 cm$^{-1}$, 1365 with $Fo^2 > 3.0\sigma(Fo^2) = I > 3.0\sigma(I)$; $R$ = 0.040 ($R_w$ = 0.043).

### *1-(i-Propylsulfinyl)-9-(i-propylthio) dibenzothiophene* (2b)

Yield: 21%; mp 107–108°C; $^1H$ NMR (500 MHz) $\delta$ 0.42 (d, $J$ = 6.5 Hz, 3H, $CH_3$), 0.82 (d, $J$ = 6.5 Hz, 3H, $CH_3$), 1.20 (d, $J$ = 6.5 Hz, 3H, $CH_3$), 1.38 (d, $J$ = 6.5 Hz, 3H, $CH_3$), 2.86 (sept, $J$ = 6.5 Hz, 1H, SCH) 2.96 (sept, $J$ = 6.5 Hz, 1H, SOCH), 7.47 (t, $J$ = 7.8 Hz, 1H), 7.73 (t, $J$ = 7.8 Hz, 1H), 7.74 (dd, $J$ = 7.8, 1.4 Hz, 1H), 7.87 (dd, $J$ = 7.8, 1.4 Hz, 1H), 7.98 (dd, $J$ = 7.8, 1.4 Hz, 1H), 8.29 (dd, $J$ = 7.8, 1.4 Hz, 1H); IR (KBr) 1046 cm$^{-1}$ (SO); MS ($m/z$) 348 ($M^+$); $[\alpha]_D^{23} = -26°$ (c = 0.17, $CHCl_3$, ee = 17%); anal. calcd for $C_{18}H_{20}OS_3$: C, 62.03; H, 5.78. Found: C, 61.92; H, 5.76.

### *1-(Methylsulfinyl)-9-(methylthio)dibenzofuran* (2c)

Yield: 57%; mp 141–143°C; $^1H$ NMR (270 MHz) $\delta$ 2.58 (s, 3H), 2.82 (s, 3H), 7.48–7.55 (m, 3H), 7.59–7.71 (m, 2H), 8.24–8.28 (m, 1H); IR (KBr) 1040 cm$^{-1}$ (SO); MS ($m/z$) 276 ($M^+$); $[\alpha]_D^{23} = -276°$ (c = 0.346, $CHCl_3$, ee = 27%); anal. calcd for $C_{14}H_{12}O_2S_2$: C, 60.84; H, 4.38. Found: C, 60.57; H, 4.36.

### *1-(Methylsulfinyl)dibenzothiophene* (2d)

Yield: 65%; mp 116.5–117.5°C; $^1H$ NMR (270 MHz) $\delta$ 2.85 (s, 3H), 7.50–7.54 (m, 2H), 7.97 (t = 7.8 Hz, 1H), 7.91–7.94 (m, 1H), 8.00 (dd, $J$ = 7.8, 1.6 Hz, 1H), 8.19–8.22 (m, 1H), 8.29 (dd, $J$ = 7.8, 1.6 Hz, 1H); IR (KBr) 1050 cm$^{-1}$ (SO); MS ($m/z$) 246 ($M^+$); $[\alpha]_D^{23} = -107°$ (c = 0.20, $CHCl_3$, ee = 17%); anal. calcd for $C_{13}H_{10}OS_2$: C, 63.38; H, 4.09. Found: C, 63.42; H, 4.14.

### *1-(Methylsulfinyl)-8-(methylthio)naphthalene* (3)

Compound **3** was prepared in a similar manner to that described earlier for 1,8-bis(methylthio) naphthalene [12] in 56% yield; mp 94–95°C; $^1H$ NMR (270 MHz) $\delta$ 2.44 (s, 3H), 2.90 (s, 3H), 7.50 (t, $J$ = 8.3 Hz, 1H), 7.73 (t, $J$ = 8.3 Hz, 1H), 7.86 (d, $J$ = 8.3 Hz, 1H), 7.93 (d, $J$ = 8.3 Hz, 1H), 8.01 (d, $J$ = 8.3 Hz, 1H), 8.63 (d, $J$ = 8.3 Hz, 1H); IR (KBr) 1038 cm$^{-1}$ (SO); MS ($m/z$) 236 ($M^+$); $[\alpha]_D^{23} = -145°$ (c = 0.524, $CHCl_3$, ee = 33%); anal. calcd for $C_{12}H_{12}OS_2$: C, 60.98; H, 5.12. Found: C, 60.94; H, 5.06.

### *Isolation of l-menthoxysulfonium Salt* (4a)

To a solution of (**1b**) (276 mg, 1.0 mmol), pyridine (1.0 mL, 12 mmol), and *l*-menthol (1.56 g, 10.0 mmol) in 5.6 mL of $CH_2Cl_2$ was added 0.97 M $Br_2$/$CH_2Cl_2$ (1.0 mL, 1 mmol) at −20°C under argon. The solution was stirred for 4 hours at −20°C and treated with $AgBF_4$ (194 mg, 1.0 mmol). The solution was filtered off, and ether (25 mL) was added to the yellow solution to produce yellow precipitates. Then the solvent was removed by a syringe, and the residue was washed with ether for 3 times to give **4a** in 42% yield (217 mg); mp 98–103°C; $^1H$ NMR (500 MHz) $\delta$ 0.44–0.37 (m, 4H, *l*-ment), 0.62–0.55 (m, 4H, *l*-ment), 0.92–0.79 (m, 7H, *l*-ment), 1.24–1.17 (m, 4H, *l*-ment), 1.56–1.49 (m, 1H, *l*-ment), 1.92–1.90 (m, 1H, *l*-ment), 2.69 (s, 3H, $SCH_3$), 4.05 (s, 3H, $SOCH_3$), 4.16–4.10 (m, 1H, *l*-ment), 7.64 (t, $J$ = 8.1 Hz, 1H), 7.76 (d, $J$ = 8.1 Hz, 1H), 7.91 (t, $J$ = 8.1 Hz, 1H), 7.92 (d, $J$ = 8.1 Hz, 1H), 8.22 (d, $J$ = 8.1 Hz, 1H), 8.28 (d, $J$ = 8.1 Hz, 1H); $^{13}C$ NMR (125 MHz) $\delta$ 15.9, 20.7, 21.3, 21.5, 23.0, 25.7, 31.2, 33.2, 38.1, 41.0, 48.5, 89.0, 123.5, 126.1, 128.9, 129.0, 129.3, 129.6, 131.20, 131.24, 132.4, 132.5, 141.4, 142.0; $[\alpha]_D^{25} = +316°$ (c = 0.12, $CHCl_3$); anal. calcd for $C_{24}H_{31}OS_3BF_4 \cdot 1/2C_6H_6$: C, 58.16; H, 6.15. Found: C, 57.98; H, 6.12.

*Crystal Data.* $C_{24}H_{31}OS_3BF_4 \cdot 1/2C_6H_6$, monoclinic, $P2_1$, a = 10.216 (2), b = 23.076 (7), c = 12.906 (2) Å, $\beta$ = 108.87 (1)°, V = 2879.1 Å$^3$, Z = 4, $\rho_x$ = 1.20 g/cm$^3$, $\mu$(Mo $K\alpha$) = 2.8 cm$^{-1}$, $R$ = 0.058 ($R_w$ = 0.060).

### *Hydrolysis of* 4a

The optically pure **4a** was treated with aqueous 2M NaOH at 0°C for 12 hours to give the sulfoxide **2a** in 99% yield; $[\alpha]_D^{25} = -319°$ (c = 0.30, $CHCl_3$).

### *Treatment of* 4a *with* $Na^{18}OH$

The optically pure **4a** was treated with aqueous $Na^{18}OH$ ($^{18}O$ = 60%) at 0°C for 12 hours to give the sulfoxide **2a** in 98% yield ($^{18}O$ = 59%).

### *Preparation of Ethoxysulfonium Salt* (5)

To a solution of **2a** (292 mg, 1.0 mmol) in 2 mL of $CH_2Cl_2$ was added 1 M $(C_2H_5)_3O \cdot BF_4/CH_2Cl_2$ (1.0 mL,

1 mmol) at 25°C under argon. The solution was stirred at 25°C for 24 hours, and ether (25 mL) was added to produce yellow precipitates. Then the solvent was removed by a syringe, and the residue was washed with ether 3 times to give **5** in 70% yield (285 mg); mp 141–144°C; $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 1.18 (t, $J$ = 7.0 Hz, 3H, $CH_3$), 2.83 (s, 3H, $SCH_3$), 3.76 (dq, $J$ = 7.0, 2.4 Hz, 1H, $CH_2$), 4.05 (s, 3H, $SOCH_3$), 4.28 (dq, $J$ = 7.0, 2.4 Hz, 1H, $CH_2$), 7.63 (t, $J$ = 7.8 Hz, 1H), 7.72 (d, $J$ = 7.8 Hz, 1H), 7.89 (t, $J$ = 7.8 Hz, 1H), 7.91 (d, $J$ = 7.8 Hz, 1H), 8.21 (d, $J$ = 7.8 Hz, 1H), 8.23 (d, $J$ = 7.8 Hz, 1H); anal. calcd for $C_{16}H_{17}OS_3BF_4$: C, 47.07; H, 4.20. Found: C, 46.86; H, 4.19.

### *1-(Trideuteriated methylsulfinyl)-9-(methylthio)dibenzothiophene* (**2a**-$D_3$)

Preparation of **2a**-$D_3$ was performed by treatment of **2a** (292 mg, 1.0 mmol) with $CH_3ONa$ (6 mmol) in $CH_3OD$ (3 mL) at reflux temperature under Ar for 48 hours in 89% yield (D content = 99%); $^1$H NMR (270 MHz) $\delta$ 2.35 (s, 3H), 7.49 (t, $J$ = 7.8 Hz, 1H), 7.71 (dd, $J$ = 7.8, 1.1 Hz, 1H), 7.76 (t, $J$ = 7.8 Hz, 1H), 7.82 (dd, $J$ = 7.8, 1.1 Hz, 1H), 8.00 (dd, $J$ = 7.8, 1.1 Hz, 1H), 8.37 (dd, $J$ = 7.8, 1.1 Hz, 1H).

### *Trideuteriated Ethoxysulfonium Salt* (**5**-$D_3$)

Preparation of **5**-$D_3$ was performed by a similar procedure to that described earlier using (**2a**-$D_3$) (70% yield, D content = 99%); $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 1.18 (t, $J$ = 7.0 Hz, 3H, $CH_3$), 2.83 (s, 3H, $SCH_3$), 3.76 (dq, $J$ = 7.0 Hz, 2.4 Hz, 1H, $CH_2$), 4.28 (dq, $J$ = 7.0 Hz, 2.4 Hz, 1H, $CH_2$), 7.63 (t, $J$ = 7.8 Hz, 1H), 7.72 (d, $J$ = 7.8 Hz, 1H), 7.89 (t, $J$ = 7.8 Hz, 1H), 7.91 (d, $J$ = 7.8 Hz, 1H), 8.21 (d, $J$ = 7.8 Hz, 1H), 8.23 (d, $J$ = 7.8 Hz, 1H).

### *Hydrolysis of Trideuteriated Ethoxysulfonium Salt* (**5**-$D_3$)

Trideuteriated ethoxysulfonium salt (**5**-$D_3$) was treated with aqueous 2 M NaOH at −20°C to give (**2a**-$D_3$) quantitatively (D content = 99%).

### *Optically Active Ethoxysulfonium Salt* (**5**)

Preparation of optically active **5** was achieved in 70% yield by using optically pure **2a**.

### *Hydrolysis of Optically Active* (**5**)

The optically active **5** was treated with aqueous 2 M NaOH solution at −20°C to give **2a** quantitatively (ee: 76%), $[\alpha]_D^{25}$ = +316° ($CHCl_3$).

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