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Simple Preparation of Sterically Congested 1,9-Disubstituted Dibenzothiophenes and Formation of Their Dithia Dications via Transannular S-S Interaction

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ABSTRACT

*4,6-Disubstituted thianthrene-5-oxides reacted with n-butyllithium to afford sterically crowded 1,9-disubstituted dibenzothiophenes (**3**) in moderate yields. The structures of the phenylthio derivative **3a** and its monooxide **6a** were determined by X-ray crystallographic analysis, which revealed that the distances between the two outer sulfur atoms are 3.012 Å (**3a**) and 3.016 Å (**6a**). 1,9-Disubstituted dibenzothiophenes **3** and their monooxides **6** afforded the corresponding dithia dications on dissolution in conc. sulfuric acid. The lower oxidation potentials of compounds **3** compared with other dibenzothiophene derivatives reveal evidence for strong transannular interaction between the two outer sulfur atoms.*

INTRODUCTION

It is well-known that sulfoxides react with organometallic reagents, such as butyllithium and Grignard reagents, to give ligand coupling products [1]. These reactions are believed to take place via the initial formation of a σ-sulfurane after nucleophilic attack of the carbanion on the sulfinyl sulfur atom. Earlier, Gilman reported that when thianthrene-5-oxide was treated with *n*-butyllithium, both ligand coupling and reduction took place simultaneously, in addition to the desired *o*-lithiation at the α-position of the sulfinyl group, to give dibenzothiophene and thianthrene as main products [2]. On the other hand, it has been reported that diaryl sulfoxides were *o*-lithiated in a regiospecific manner by treatment with organolithium reagents [3]. Recently, we found that the lithiation reactions of diphenyl and dipyridyl sulfoxides using lithium diisopropylamide (LDA) proceeded regiospecifically to afford the *o*-lithiated sulfinyl compounds which were converted to the *o*-substituted diaryl sulfoxides on treatment with electrophiles [3].

Interestingly, by using these reactions, sterically congested 1,9-disubstituted dibenzothiophenes (**3**) were synthesized in moderate yields from 4,6-disubstituted thianthrene-5-oxides (**2**) and *n*-butyllithium [4]. Since 1,9-bis(phenylthio) dibenzothiophene (**3a**) has two sulfur atoms in close proximity, as disclosed by X-ray crystallographic analysis, it should have a strong transannular interaction between these two sulfur atoms and is

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Dedicated to Prof. James Cullen Martin on the occasion of his sixty-fifth birthday.

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expected to form a new dicationic S-S σ-bond on oxidation [5]. Formation of dications or cation radicals via transannular interaction has often been observed between two heteroatoms that are arranged appropriately in one molecule [6]. For example, dications of 1,5-dithiacyclooctane [7] and 1,5-diselenacyclooctane [8] and their benzo derivatives [9] have been reported. In this article, we present a simple preparation of sterically crowded 1,9-disubstituted dibenzothiophenes (**3**) via the ligand coupling reaction of **2** and evidence for formation of dithia dications in conc. sulfuric acid-d_2 provided by ^{1}H NMR spectroscopy and fast atom bombardment mass spectrometry (FAB MS). Electrochemical oxidation of **3** by cyclic voltammetry also revealed the presence of the transannular interaction between the two sulfur atoms in **3**.

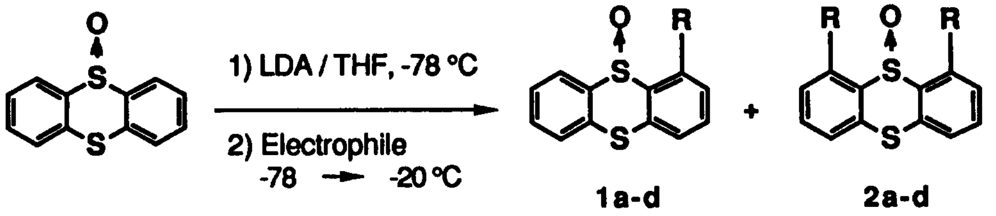
RESULTS AND DISCUSSION

In order to avoid the ligand coupling and the reduction observed in Gilman's lithiation [2], thianthrene-5-oxide was treated initially with LDA (2.2 eq) and, subsequently, with diphenyl disulfide to give both 4-(phenylthio) thianthrene-5-oxide (**1a**) and 4,6-bis(phenylthio)thianthrene-5-oxide (**2a**) in 25 and 61% yields, respectively (Equation 1) [4]. Similarly, dilithiated thianthrene-5-oxide was treated with other electrophiles to give a variety of 4-substituted or 4,6-disubstituted thianthrene-5-oxides in moderate to good yields, as shown in Table 1.

Furthermore, when **1** and **2** were allowed to react with *n*-butyllithium (Equation 2), concurrent ring contraction and ring opening reactions took place, affording the corresponding 1,9-disubstituted dibenzothiophenes **3** and 3,3′-disubstituted diphenyl sulfides **4**, probably via intermediary formation of the σ-sulfurane **5** (Table 2) [10].

The X-ray crystallographic analysis of **3a** revealed that the distance between the two sulfur atoms is 3.012 Å, which is less than the van der Waals contact of two sulfur atoms (3.70 Å) (Figure 1) [5,11]. The two phenyl rings are located at an antiorientation, and the dibenzothiophene ring is distorted from the usual planar form due to the steric repulsion of the two phenylthio substituents [12]. The sulfide **3a** was treated with an equimolar amount of *m*-chloroperbenzoic acid (mCPBA) to give the corresponding monooxide **6a** in a 78% yield. The X-ray crystallographic analysis of sulfoxide **6a** demonstrates that the S-S distance is 3.016 Å and the O-S-S angle is 158.8°, suggesting that the sulfenyl and the sulfinyl sulfur atoms interact transannularly.

When the sulfoxide **6a** was dissolved in conc. sulfuric acid, the color of the solution changed immediately to dark green. In order to characterize the products formed in the conc. sulfuric acid solution, the UV, ^{1}H NMR, ESR, and FAB MS spectra were determined. The UV spectrum of **6a** showed a bathochromic shift in the conc. sulfuric acid solution compared with that in dichloromethane solution, suggesting the formation of the dithia dication **7a** in conc. sulfuric acid [9,13]: λ_{max} nm (ϵ) (H_2SO_4) 223 (44,000), 240 (sh) (37,000), 278 (sh) (16,000), 322 (9900), 382 (12,000), 452 (sh) (8400), 674 (3100); λ_{max} nm (ϵ) (CH_2Cl_2) 219 (37,000), 306 (sh) (9400), 352 (4900), 366 (5400). The ^{1}H NMR spectrum of the compound **6a** was measured in conc. sulfuric acid-d_2 (Figure 2). On the other hand, the ^{1}H NMR spectrum of compound **3a** gave very weak and unidentified signals soon after dissolution in conc. sulfuric acid-d_2, but, after 24 hours, the spectrum of **3a** was found to be identical to that of **6a** in conc. sulfuric acid-d_2. In general, an NMR spectrum is influenced by a magnetic moment of a radical or a cation radical which gives broad signals in the spectrum [14]. The initial unidentified ^{1}H NMR spectrum of **3a** in conc. sulfuric acid-d_2 can be explained in terms of the formation of a radical cation from **3a** which was further oxidized to the dication after standing for an appropriate time interval. Therefore, the oxidation of **3a** to the dithia dication **7a** with conc. sulfuric acid should produce initially a dithia cation radical. In fact, in the ESR spectrum of **3a** in conc. sulfuric acid, one broad singlet was observed with g = 2.0058, but it degraded gradually at 25°C and disappeared after 1 week, while only a very weak ESR signal was observed for sulfoxide **6a** under similar conditions. These results suggest that the dithia dication **7a** is produced from **3a** and **6a** via different pathways. The dication **7a** was found to be stable



(1)

a: R=SPh, **b**: R=S^{p}Tol, **c**: R=S^{p}ClC$_6$H$_4$, **d**: R=SCH$_3$.

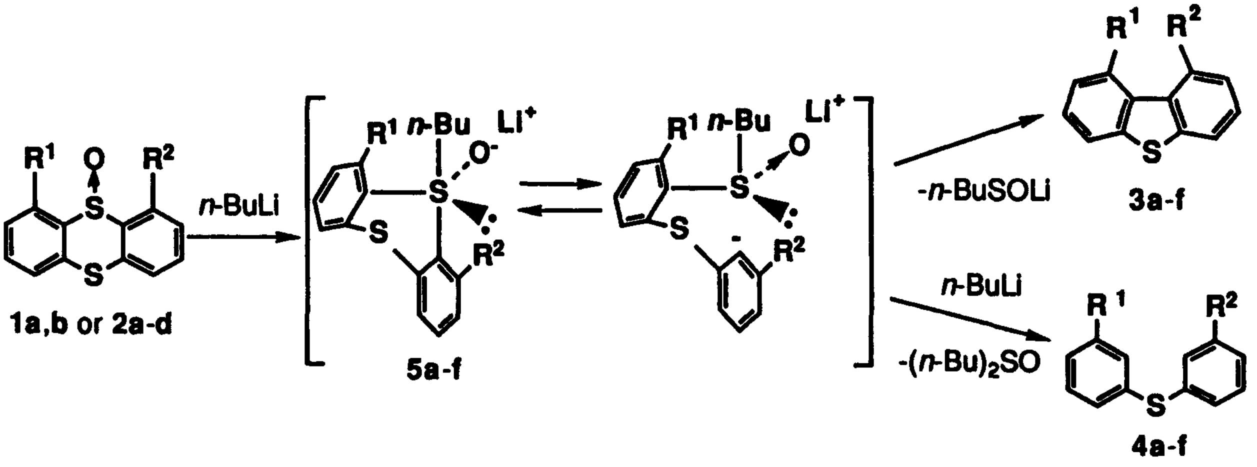
TABLE 1 Reaction of Thianthrene-5-Oxide with LDA and Electrophiles

LDA (eq)	Electrophile	R	Yield (%) 1	Yield (%) 2
1.1	$(PhS)_2$	PhS	61 (**1a**)	19 (**2a**)
2.2	$(PhS)_2$	PhS	25 (**1a**)	61 (**2a**)
1.1	$(p\text{-TolS})_2$	p-TolS	66 (**1b**)	21 (**2b**)
2.2	$(p\text{-TolS})_2$	p-TolS	26 (**1b**)	53 (**2b**)
1.1	$(p\text{-ClC}_6H_4S)_2$	$p\text{-ClC}_6H_4S$	55 (**1c**)	26 (**2c**)
2.2	$(p\text{-ClC}_6H_4S)_2$	$p\text{-ClC}_6H_4S$	29 (**1c**)	38 (**2c**)
2.2	S_8 + MeI	MeS	87 (**1d**)	trace(**2d**)
3.3	S_8 + MeI	MeS	trace (**1d**)	63 (**2d**)

in conc. sulfuric acid, and its NMR spectrum did not change at all, even on standing for 1 week at room temperature. The structure of the dication **7a** was further identified by FAB MS in a conc. sulfuric acid matrix, and the cationic peaks observed are as follows: (m/z) 595 (MH^+), 497 ($(M\text{-}HSO_4)^+$). When the dark green solutions of **3a** and **6a** were treated with ice water, the sulfoxide **6a** was obtained in a good yield together with small amounts of by-products. In the reactions of other arylthio derivatives **6**, similar results were obtained, as shown in Scheme 1.

It has been known that several cyclic compounds bearing two heteroatoms in close proximity have unusually low oxidation potentials due to transannular bond formation between the two atoms [9]. Accordingly, in order to investigate the nature of the S-S interaction, the oxidation potentials of the compounds **3** and other dibenzothiophene derivatives, 2,8-bis(methylthio)dibenzothiophene (**8**) and 2,8-bis(phenylthio)dibenzothiophene (**9**) were determined by cyclic voltammetry using a Pt electrode and Ag/(0.01 M)$AgNO_3$ as a reference electrode (scan rate: 200 mV/s) at 25°C in acetonitrile. These results are shown in Table 3. Apparently, the observed peak potentials of **3a,d**, lower than those of other dibenzothiophene derivatives, provide evidence supporting the transannular interaction between the two outer sulfur atoms in **3a,d** on electrochemical oxidation (Table 3).

When the ^1H NMR of sulfoxide **6d** was determined in conc. sulfuric acid-d_2, the two methyl protons of **6d** which appeared at δ 2.79 ($SOCH_3$) and 2.33 (SCH_3) in chloroform-d had shifted downfield and coalesced to a singlet at δ 3.04. When the solution was treated with ice water, the starting sulfoxide **6d** was recovered in 56% yield, together with demethylated disulfide **10** that was present in a trace amount [15]. Furthermore, when the deuterated sulfoxide **11** (D-content > 96%) was treated similarly with conc. sulfuric acid and then with ice water, a 1 : 1 mixture of **11** and **12** was obtained in 63% yield (Scheme 2). When ^{18}O-labeled sulfoxide **13** was prepared and treated in the same manner as described previously, nonlabeled sulfoxide **6d** was obtained in 70% yield (Scheme 2). On the other hand, since 1-(methylsulfinyl)dibenzothiophene (**14**) and 2-(methylsulfinyl)-8-(methylthio)dibenzothiophene (**15**) were unstable in conc. sulfuric acid, their ^1H NMR spectra could not be obtained in conc. sulfuric acid-d_2. The present results demonstrate clearly that a new dithia dication **7d** is formed and stabilized by the neighboring group interaction of the sulfenyl sulfur atoms. The sulfide **3d** was also oxidized in conc. sulfuric acid to give the sulfoxide **6d** in 58% yield, together with a trace amount of **10**, after treatment with ice water. The ^1H NMR



(2)

1a: R^1=SPh, R^2=H, **1b**: R^1=S^pTol, R^2=H; **2, 3, 4** and **5, a**: R^1=R^2=SPh, **b**: R^1=R^2=S^pTol, **c**: R^1=R^2=$S^pClC_6H_4$, **d**: R^1=R^2=SCH_3, **e**: R^1=SPh, R^2=H, **f**: R^1=S^pTol, R^2=H.

TABLE 2 Reactions of Substituted Thianthrene-5-Oxides with *n*-BuLi

Substrate	*R*^{1}	*R*^{2}	*Yield* (%) 3	4
2a	PhS	PhS	63 (**3a**)	25 (**4a**)
2b	*p*-TolS	*p*-TolS	46 (**3b**)	40 (**4b**)
2c	*p*-ClC$_6$H$_4$S	*p*-ClC$_6$H$_4$S	59 (**3c**)	30 (**4c**)
2d	MeS	MeS	22 (**3d**)	65 (**4d**)
1a	PhS	H	10 (**3e**)	70 (**4e**)
1b	*p*-TolS	H	10 (**3f**)	52 (**4f**)

spectrum of **3d** in conc. sulfuric acid-d_2 is the same as that of the sulfoxide **6d**.

Unexpectedly, in the ^{1}H NMR spectrum of the dication **7a** in conc. sulfuric acid-d_2, broadening of the resonances of the protons of the phenylthio groups was observed. Two protons had shifted to an unusually high field at δ 5.89 (2H) as a broad singlet compared with ^{1}H NMR spectra of **3a** and **6a** in chloroform-*d* (Figure 2) [5]. The signal at δ 5.89 was assigned to the two *o*-protons of the two phenylthio groups, since the intensity of the signals at δ 5.89 and 7.18 decreased in an ^{1}H NMR spectrum of 1,9-bis(*o*-monodeuterated phenylthio)dibenzothiophene (**3a**-d_2) in conc. sulfuric acid-d_2 [5,16]. The ^{1}H NMR spectra of **3a** and **6a** indicate clearly that the two phenyl rings attached to the sulfur atoms overhang the dibenzothiophene ring, and, thus, the protons at the *o,m*-positions become magnetically nonequivalent in the dithia dication **7a**. Other substituted dibenzothiophenes **3** show identical behaviors, and, particularly, in the 3,5-xylyl derivative **3j**, two sharp methyl singlets appear in the spectrum. These results demonstrate that the free rotation of the S–C (phenyl) bond should be restricted or that pyramidal inversion at the sulfonium sulfur atoms in **7** should be slow on the ^{1}H NMR time scale at 27°C. Attribution of these broadening phenomena of the ^{1}H NMR spectra to the presence of a cation radical was eliminated from consideration, since no ESR spectrum was observed in the reaction mixture of **6a** in conc. sulfuric acid. Dithia dication **7a** is unusually stable in conc. sulfuric acid, remaining for several hours even at 70°C. By elevating the temperature, the resonances of the two ortho protons coalesced into a singlet at δ 6.56 at 67°C. The spectrum returned to the original one by lowering the temperature to 27°C. Thus, the temperature-dependent spectrum is attributed to the free rotation of the phenyl rings. The free energy for the rotation is calculated to be $\Delta G^{\neq}$ = 63 kJmol^{-1} at 67°C. These results provide evidence for the formation of new types of dithia dication from the sterically congested 1,9-disubstituted dibenzothiophenes on chemical and electrochemical oxidation.

EXPERIMENTAL SECTION

The IR spectra were recorded on a JASCO FT/IR-5000 spectrometer. The NMR spectra were measured on a Hitachi R-600, a JEOL JNM-EX270, or a Bruker AM-500 spectrometer. Mass spectra were obtained with a Hitachi RMU-6MG or a JEOL JMX SX102 mass spectrometer. All reagents were obtained from Wako Pure Chemical Industries, Ltd., Kanto Chemical Co., or Aldrich Chemical Co. The reaction solvents were further purified by standard methods.

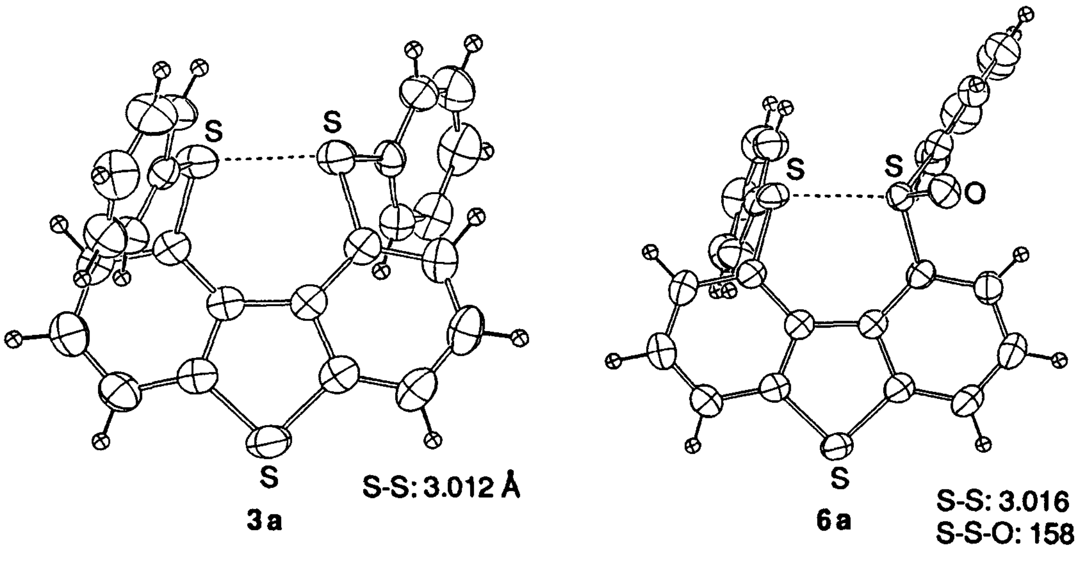


FIGURE 1 The X-ray crystallographic analysis of **3a** and **6a**.

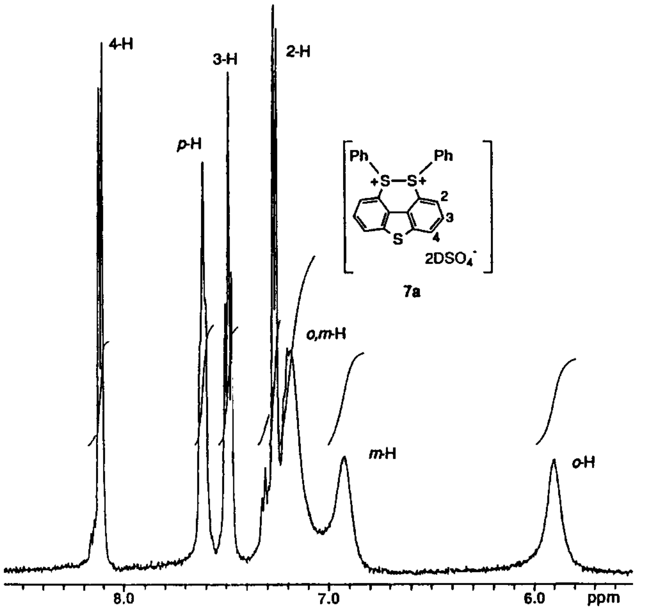
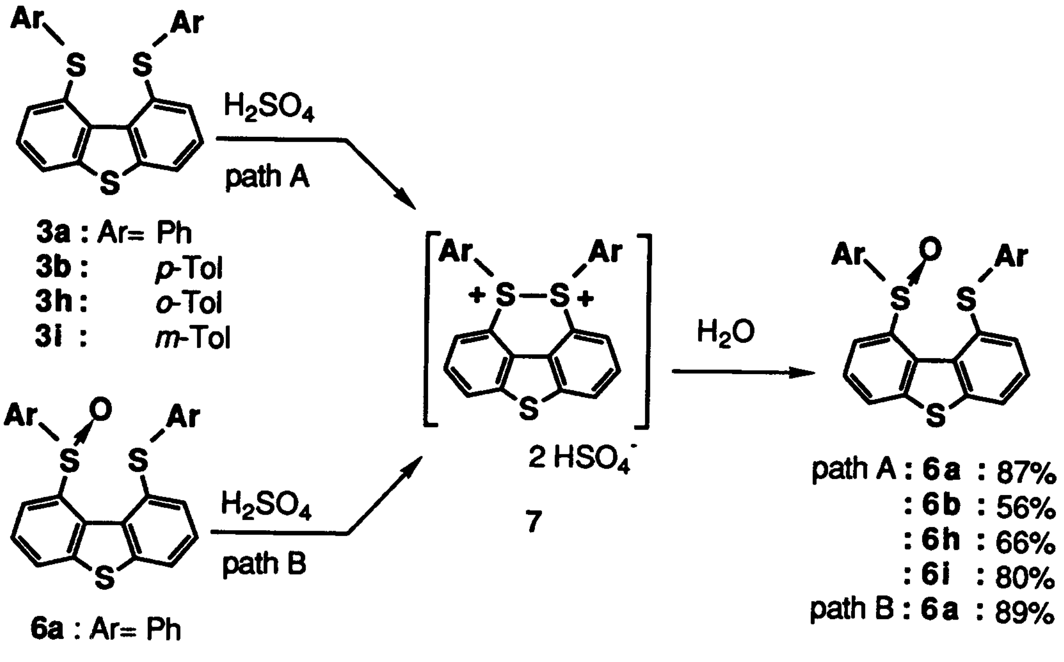


FIGURE 2 500 MHz ^{1}H NMR spectrum of dication **7a** in conc. D_2SO_4.

4-(p-Tolylthio)thianthrene-5-oxide (**1b**) *and 4,6-Bis(p-Tolylthio)thianthrene-5-oxide* (**2b**). Thianthrene-5-oxide (464 mg, 2 mmol) dissolved in THF (20 ml) was lithiated with 0.22 M LDA (10 ml, 2.2 mmol) at −78°C. To this solution was added di-*p*-tolyl disulfide (1.23 g, 5 mmol) in THF (10 ml). After the usual workup and purification by column chromatography (silica gel; CH_2Cl_2) and then preparative liquid chromatography, **1b** and **2b** were obtained in 66 and 21% yields, respectively. **1b**: mp 212–213.5°C; ^{1}H NMR ($CDCl_3$) δ 7.93–6.90 (m, 11H, Ar-H), 2.35 (s, 3H, CH_3); IR (KBr) 1025 cm^{-1}; MS (m/z) 354 (M^+). Anal. calcd for $C_{19}H_{14}OS_3$: C, 64.37; H, 3.98. Found: C, 64.42; H, 4.01. **2b**: mp 272–275°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.54 (dd, J_1 = 7.8 Hz, J_2 = 1.0 Hz, 2H, Ar-H), 7.38 (d, J = 7.8 Hz, 4H, Ar-H), 7.25 (t, J = 7.8 Hz, 2H, Ar-H), 7.10 (d, J = 7.8 Hz, 4H, Ar-H), 7.04 (dd, J_1 = 7.8 Hz, J_2 = 1.0 Hz, 2H, Ar-H), 2.37 (s, 6H, CH_3); IR (KBr) 1046 cm^{-1}; MS (m/z) 476 (M^+). Anal. calcd for $C_{26}H_{20}OS_4$: C, 65.51; H, 4.23. Found: C, 65.22; H, 4.15.

4-(Phenylthio)thianthrene-5-oxide (**1a**) *and 4,6-Bis(phenylthio)thianthrene-5-oxide* (**2a**). **1a**: mp 149–150°C; ^{1}H NMR ($CDCl_3$) δ 7.83–6.97 (m, 12H, Ar-H); IR (KBr) 1038 cm^{-1}; MS (m/z) 340 (M^+). Anal. calcd for $C_{18}H_{12}OS_3$: C, 63.50; H, 3.55. Found: C, 63.42; H, 3.49. **2a**: mp 210–211°C; ^{1}H NMR ($CDCl_3$) δ 7.82–6.83 (m, 16H, Ar-H); IR (KBr) 1027 cm^{-1}; MS (m/z) 448 (M^+). Anal. calcd for $C_{24}H_{16}OS_4$: C, 64.25; H, 3.59. Found: C, 64.07; H, 3.62.

4-(p-Chlorophenylthio)thianthrene-5-oxide (**1c**) *and 4,6-Bis(p-Chlorophenylthio)thianthrene-5-oxide* (**2c**). **1c**: mp 195.5°C; ^{1}H NMR ($CDCl_3$) δ 7.83–7.13 (m, 11H, Ar-H); IR (KBr) 1015 cm^{-1}; MS (m/z) 374 (M^+). Anal. calcd for $C_{18}H_{11}ClOS_3$: C, 57.66; H, 2.96. Found: C, 57.54; H, 2.98. **2c**: mp 259–261°C; ^{1}H NMR ($CDCl_3$) δ 7.90–7.03 (m, 14H, Ar-H); IR (KBr) 1015 cm^{-1}; MS (m/z) 516 (M^+). Anal. calcd for



SCHEME 1

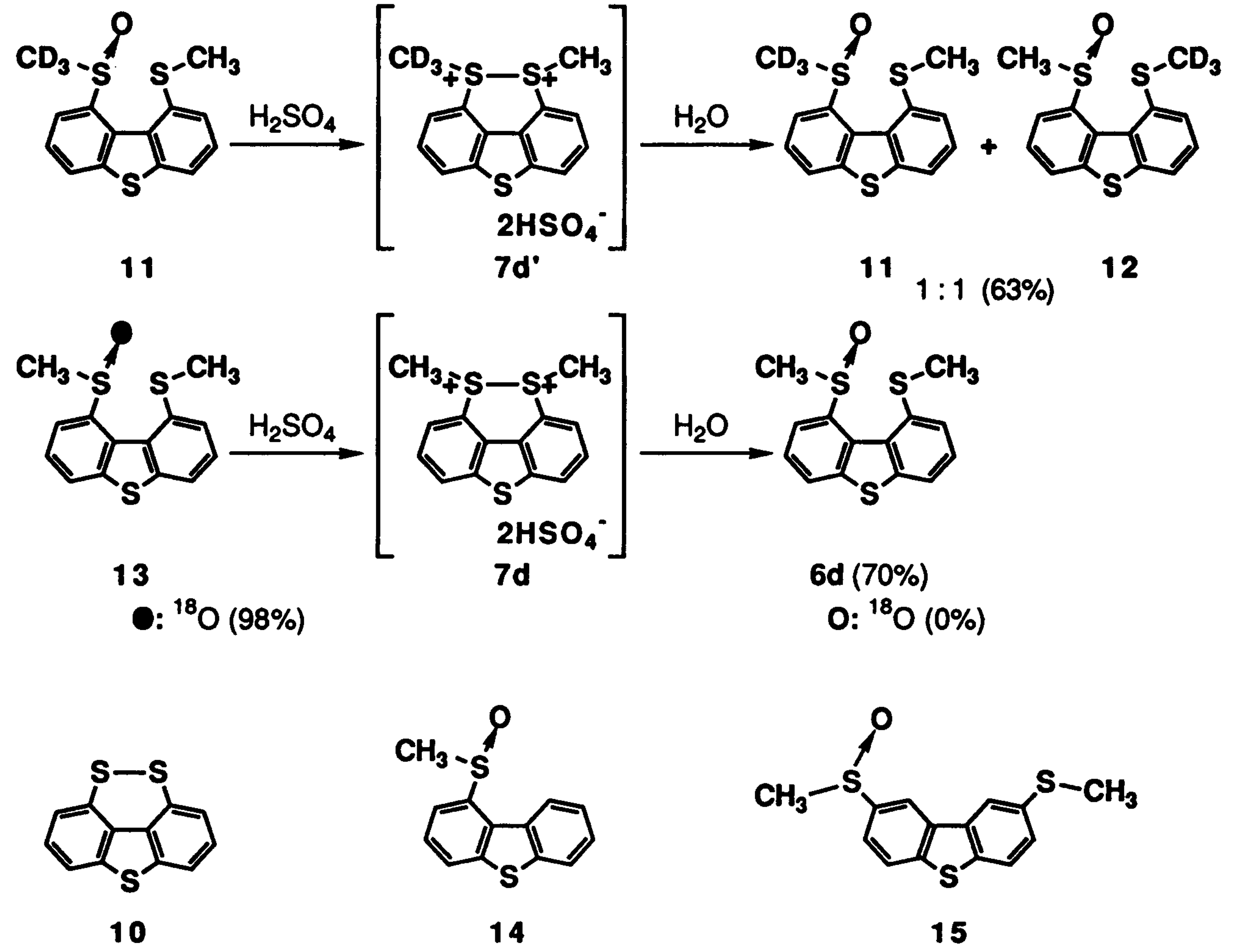
TABLE 3 Oxidation Potentials (Ep)

Compound	*Ep (V)*	*Compound*	*Ep (V)*
3a	0.86	**3d**	0.76
9	1.09	**8**	0.96
3e	1.12	**3g**	1.02
DS	1.21	TA	1.09
DT	1.31	**10**[a]	0.91

DS: diphenylsulfide, TA: thioanisole, DT: dibenzothiophene.
[a]Since compound **10** indicated a reversible cyclic voltammogram, its oxidation potential was $E_{1/2}$ (V).

$C_{24}H_{14}Cl_2OS_4$: C, 55.70; H, 2.73. Found: C, 55.61; H, 2.59.

4-(Methylthio)thianthrene-5-oxide (**1d**) *and 4,6-Bis(methylthio)thianthrene-5-oxide* (**2d**). Thianthrene-5-oxide (2.32 g, 10 mmol) dissolved in THF (70 ml) was lithiated with 0.63 M LDA (40 ml, 25 mmol) at −78°C. To this solution was added elemental sulfur (1.6 g, 50 mg-atm). After 12 hours, iodomethane (7 ml, 112 mmol) was added with a syringe and the solution was stirred for 6 hours. The reaction mixture was treated with H_2O and purified by column chromatography (silica gel; CH_2Cl_2) and then by preparative liquid chromatography to give **1d** in 87% yield together with a trace of **2d**. **1d**: mp 128°C; ^1H NMR ($CDCl_3$) δ 8.13–7.87 (m, 1H, Ar-H), 7.67–7.12 (m, 6H, Ar-H), 2.76 (s, 3H, CH_3). Anal. calcd for $C_{13}H_{10}OS_3$: C, 56.08; H, 3.62. Found: C, 56.39; H, 3.60. **2d**: mp 190.5–191.5°C; ^1H NMR ($CDCl_3$) δ 7.69–7.06 (m, 6H, Ar-H), 2.59 (s, 6H, CH_3); IR (KBr) 1020 cm^{-1}; MS (m/z) 324 (M^+). Anal. calcd for $C_{14}H_{12}OS_4$: C, 51.82; H, 3.73. Found: C, 51.96; H, 3.75.



SCHEME 2

4,6-Bis(o-Tolylthio)thianthrene-5-oxide (**2f**). Mp 221–222°C; ^{1}H NMR ($CDCl_3$) δ 7.64–6.67 (m, 14H, Ar-H), 2.44 (s, 6H, CH_3); IR (KBr) 1054 cm^{-1}; MS (m/z) 476 (M^+); Anal. calcd for $C_{26}H_{20}OS_4$: C, 65.51; H, 4.23. Found: C, 65.63; H, 4.25.

4,6-Bis(m-Tolylthio)thianthrene-5-oxide (**2g**). Mp 153°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.60–7.20 (m, 14H, Ar-H), 2.31 (s, 6H, CH_3); IR (KBr) 1031 cm^{-1}; MS (m/z) 476 (M^+). Anal. calcd for $C_{26}H_{20}OS_4$: C, 65.51; H, 4.23. Found: C, 65.27; H, 4.07.

4,6-Bis(3,5-Xylylthio)thianthrene-5-oxide (**2h**). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.57 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 2H, Ar-H), 7.29 (t, J = 7.8 Hz, 2H, Ar-H), 7.14 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 2H, Ar-H), 7.07 (s, 4H, *o*-Ph-H), 6.97 (s, 2H, *p*-Ph-H), 2.27 (s, 12H, CH_3); MS (m/z) 504 (M^+). Anal. calcd for $C_{28}H_{24}OS_4$: C, 66.63; H, 4.79. Found: C, 66.20; H, 4.74.

1,9-Bis(phenylthio)dibenzothiophene (**3a**) *and 3,3′-Bis(phenylthio)diphenyl Sulfide* (**4a**). **2a** (224 mg, 0.5 mmol) dissolved in THF (10 ml) was treated with *n*-butyllithium (1.3 ml, 2 mmol) at −78°C. After treatment with H_2O and purification by column chromatography (silica gel; CH_2Cl_2) and by preparative liquid chromatography, **3a** and **4a** were obtained in 63 and 25% yields. **3a**: mp 197.5–200°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, J_1 = 7.9 Hz, J_2 = 0.9 Hz, 2H, Ar-H), 7.53 (dd, J_1 = 7.9 Hz, J_2 = 0.9 Hz, 2H, Ar-H), 7.37 (t, J = 7.9 Hz, 2H, Ar-H), 7.16–7.06 (m, 6H, Ar-H), 7.01–6.95 (m, 4H, Ar-H); MS (m/z) 400 (M^+); UV (C_6H_{10}) λ_{max} (nm) ϵ 232 (39,000), 257 (41,000), 306 (sh) (11,000), 354 (6800), 369 (7800). Anal. calcd for $C_{24}H_{16}S_3$: C, 71.96; H, 4.03. Found: C, 72.06; H, 4.04; Crystal data for **3a**; monoclinic, space group $P2_1/n$, a = 17.862(2), b = 8.050(2), c = 13.594(2) Å, β = 95.74(1)°, V = 1938.4(5) Å^3, z = 4, D_x = 1.373 gcm^{-3}, μ (Mo-K_α) = 0.372 mm^{-1}, R = 0.0526 ($_wR$ = 0.0744). **4a**: ^{1}H NMR ($CDCl_3$) δ 7.33–6.98 (m, 18H, Ar-H). Found: m/z 402.0583. Calcd. for $C_{24}H_{18}S_3$: M, 402.0571.

1,9-Bis(p-Tolylthio)dibenzothiophene (**3b**) *and 3,3′-Bis(p-Tolylthio)diphenyl Sulfide* (**4b**). **3b**: mp 177°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.72 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 2H, Ar-H), 7.52 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 2H, Ar-H), 7.34 (t, J = 7.8 Hz, 2H, Ar-H), 6.96 (s, 8H, Ar-H), 2.24 (s, 6H, CH_3); MS (m/z) 428 (M^+). Anal. calcd for $C_{26}H_{20}S_3$: C, 72.85; H, 4.70. Found: C, 72.99; H, 4.74. **4b**: ^{1}H NMR ($CDCl_3$) δ 7.47–6.93 (m, 16H, Ar-H), 2.34 (s, 6H, CH_3). Found: m/z 430.0841. Calcd for $C_{26}H_{22}S_3$: 430.0884.

1,9-Bis(p-Chlorophenylthio)dibenzothiophene (**3c**) *and 3,3′-Bis(p-Chlorophenylthio)diphenyl Sulfide* (**4c**). **3c**: mp 158°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.80 (dd, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 2H, Ar-H), 7.50 (dd, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 2H, Ar-H), 7.41 (t, J = 7.6 Hz, 2H, Ar-H), 7.10 (dd, J_1 = 6.5 Hz, J_2 = 1.9 Hz, 4H, Ar-H), 6.89 (dd, J_1 = 6.5 Hz, J_2 = 1.9 Hz, 4H, Ar-H); MS (m/z) 468 (M^+). Anal. calcd for $C_{24}H_{14}Cl_2S_3$: C, 61.40; H, 3.01. Found: C, 61.23; H, 3.01. **4c**: ^{1}H NMR ($CDCl_3$) δ 7.26 (s, 8H, Ar-H), 7.17 (s, 8H, Ar-H). Found: m/z 469.9791. Calcd for $C_{24}H_{16}Cl_2S_3$: M, 469.9791.

1,9-Bis(methylthio)dibenzothiophene (**3d**) *and 3,3′-Bis(methylthio)diphenyl Sulfide* (**4d**). **3d**: mp 147.5–148°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.67 (d, J = 7.6 Hz, 2H, Ar-H), 7.59 (d, J = 7.6 Hz 2H, Ar-H), 7.46 (t, J = 7.6 Hz, 2H, Ar-H), 2.41 (s, 6H, CH_3); MS (m/z) 276 (M^+). Anal. calcd for $C_{14}H_{12}S_3$: C, 60.83; H, 4.38. Found: C, 60.83; H, 4.37. **4d**: ^{1}H NMR ($CDCl_3$) δ 7.37–6.93 (m, 8H, Ar-H), 2.44 (s, 6H, CH_3). Found: m/z 278.0273. Calcd for $C_{14}H_{14}S_3$: M, 278.0258.

1-(Phenylthio)dibenzothiophene (**3e**) *and 3-(Phenylthio)diphenyl Sulfide* (**4e**). **3e**: ^{1}H NMR ($CDCl_3$) δ 9.17–8.78 (m, 1H, Ar-H), 7.92–6.97 (m, 11H, Ar-H). Found: 292.0396. Calcd for $C_{18}H_{12}S_2$: M, 292.0380; **4e**: ^{1}H NMR ($CDCl_3$) δ 7.40–6.97 (m, 16H, Ar-H). Found: 294.0540. Calcd for $C_{18}H_{14}S_2$: M, 294.0537.

1-(p-Tolylthio)dibenzothiophene (**3f**) *and 3-(p-Tolylthio)diphenyl Sulfide* (**4f**). **3f**: mp 106°C; ^{1}H NMR ($CDCl_3$) δ 9.12–9.05 (m, 1H, Ar-H), 7.88–7.84 (m, 1H, Ar-H), 7.78–7.74 (m, 1H, Ar-H), 7.48–7.43 (m, 2H, Ar-H), 7.35–7.23 (m, 4H, Ar-H), 7.17–7.10 (m, 2H, Ar-H), 2.33 (s, 3H, CH_3); MS (m/z) 306 (M^+). Anal. calcd for $C_{19}H_{14}S_2$: C, 74.47; H, 4.58. Found: C, 74.15; H, 4.58. **4f**: ^{1}H NMR ($CDCl_3$) δ 7.47–6.80 (m, 13H, Ar-H), 2.33 (s, 3H, CH_3). Found: m/z 308.0686. Calcd for $C_{19}H_{16}S_2$: M, 308.0693.

1-(Methylthio)dibenzothiophene (**3g**). Mp 78.5–79°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.03–8.96 (m, 1H, Ar-H), 7.87–7.81 (m, 1H, Ar-H), 7.71–7.64 (m, 1H, Ar-H), 7.54–7.27 (m, 4H, Ar-H), 2.63 (s, 3H, CH_3); MS (m/z) 230 (M^+). Anal. calcd for $C_{13}H_{10}S_2$: C, 67.78; H, 4.38. Found: C, 67.53, H, 4.42.

1,9-Bis(o-Tolylthio)dibenzothiophene (**3h**). Mp 126°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 2H, Ar-H), 7.37 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 2H, Ar-H), 7.34 (t, J = 7.8 Hz, 2H, Ar-H), 7.08–6.98 (m, 8H, Ar-H) 2.06 (s, 6H, CH_3); MS (m/z) 428 (M^+). Anal. calcd for $C_{26}H_{20}S_3$: C, 72.85; H, 4.70. Found: C, 72.99; H, 4.74.

1,9-Bis(m-Tolylthio)dibenzothiophene (**3i**). Mp 131–132°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.76 (d, J = 7.8 Hz, 2H, Ar-H), 7.52 (d, J = 7.8 Hz, 2H, Ar-H), 7.37 (t, J = 7.8 Hz, 2H, Ar-H), 7.01 (t, J = 7.6 Hz, 2H, Ar-H), 6.91–6.90 (m, 4H, Ar-H), 6.74 (d, J

= 7.6 Hz, 2H, Ar-H), 2.20 (s, 6H, CH_3); MS (*m/z*) 428 (M^+). Anal. calcd for $C_{26}H_{20}S_3$: C, 72.85; H, 4.70. Found: C, 72.70; H, 4.67.

1,9-Bis(3,5-Xylylthio)dibenzothiophene (**3j**). Mp 184°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.75 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 2H, Ar-H), 7.51 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 2H, Ar-H), 7.36 (t, J = 7.8 Hz, 2H, Ar-H), 6.74 (s, 2H, *p*-Ph-H), 6.66 (s, 4H, *o*-Ph-H), 2.15 (s, 12H, CH_3); MS (*m/z*) 456 (M^+). Anal. calcd for $C_{28}H_{24}S_3$: C, 73.64; H, 5.30. Found: C, 73.29; H, 5.34.

1,9-Bis(o-Monodeuterated Phenylthio)dibenzothiophene (**3a**-d_2). **3a**-d_2 was prepared by the method similar to the synthesis of **3a** by using 2,2'-bisdeuterated diphenyl disulfide [5,16].

2,8-Bis(methylthio)dibenzothiophene (**8**). To a solution of 2,8-dibromodibenzothiophene [17] (684 mg, 2 mmol) in 30 ml THF, *n*-butyllithium (1.55 M) (3.2 ml, 5 mmol) was added at −78°C. The solution was stirred for 1 hour, and then dimethyl disulfide (0.9 ml, 10 mmol) was added with a syringe. After the usual workup and purification by column chromatography (silica gel; CCl_4), **8** was obtained in 81% yield: mp 142.5; ^{1}H NMR ($CDCl_3$) δ 8.02 (d, J = 2.4 Hz, 2H, Ar-H), 7.75 (d, J = 8.4 Hz, 2H, Ar-H), 7.39 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 2H, Ar-H), 2.59 (s, 6H, CH_3). Anal. calcd for $C_{14}H_{12}S_3$: C, 60.83; H, 4.38. Found: C, 60.70; H, 4.37.

2,8-Bis(phenylthio)dibenzothiophene (**9**). Mp 143–143.5; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.11 (d, J = 1.4 Hz, 2H, Ar-H), 7.77 (d, J = 8.6 Hz, 2H, Ar-H), 7.47 (dd, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 2H, Ar-H), 7.41–7.15 (m, 10H, Ph-H); MS (*m/z*) 400 (M^+). Anal. calcd for $C_{24}H_{16}S_3$: C, 71.96; H, 4.03. Found: C, 71.54; H, 4.21.

1-(Methylsulfinyl)-9-(Methylthio)dibenzothiophene (**6d**). To a solution of **3d** (321 mg, 1.16 mmol) in 50 ml CH_2Cl_2, mCPBA (286 mg, 1.16 mmol) dissolved in 50 ml CH_2Cl_2 was added at −20°C. The solution was stirred for 12 hours, and then ammonia gas was bubbled in for a few minutes at 25°C. A white solid was filtered off, and the filtrate was evaporated. The residue was purified by column chromatography (silica gel; CH_2Cl_2 and ethyl acetate) and **6d** was obtained in 92% yield: mp 158–160°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.36 (dd, J_1 = 7.6 Hz, J_2 = 1.1 Hz, 1 H, Ar-H), 7.99 (dd, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 1H, Ar-H), 7.82 (dd, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 1H, Ar-H), 7.76 (t, J = 7.8 Hz, 1H, Ar-H), 7.70 (dd, J_1 = 7.6 Hz, J_2 = 1.1 Hz, 1H, Ar-H), 7.47 (t, J = 7.6 Hz, 1H, Ar-H), 2.79 (s, 3H, $SOCH_3$), 2.33 (s, 3H, SCH_3); IR (KBr) 1021 cm^{-1}; MS (*m/z*) 292 (M^+). Anal. calcd for $C_{14}H_{12}OS_3$: C, 57.50; H, 4.14. Found: C, 57.65; H, 4.11.

1-(Phenylsulfinyl)-9-(Phenylthio)dibenzothiophene (**6a**). Mp 211–212°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00–6.57 (m, 16H, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0, 144.1, 141.3, 140.5, 138.7, 135.7, 133.8, 132.5, 130.5, 130.0, 128.8, 128.4, 128.3, 128.0, 127.8, 126.6, 126.1, 125.6, 125.2, 122.9; IR (KBr) 1031 cm^{-1}; MS (*m/z*) 416 (M^+). Anal. calcd for $C_{24}H_{16}OS_3$: C, 69.20; H, 3.87. Found: C, 69.16; H, 3.76. Crystal data for **6a**: monoclinic, space group $P2_1/n$, a = 9.972(4), b = 8.835(4), c = 21.915(9) Å, β = 92.21(4)°, V = 1929.4(1) Å^3, z = 4, D_x = 1.434 gcm^{-3}, μ (Cu-K_α) = 3.546 mm^{-1}, R = 0.028 (wR = 0.027).

1-(Trideuterated Methylsulfinyl)-9-(methylthio) dibenzothiophene (**11**). To a 29% solution of sodium deuteroxide in 5 ml D_2O, a solution of **6d** (150 mg, 0.51 mmol) in 2 ml THF was added at 0°C. The solution was stirred for 10 days at 67°C, and THF (2 ml) was added every 48 hours (4 × 2 ml). Then the solution was cooled to room temperature, and 5 N hydrochloric acid (20 ml) was added. After the usual workup and purification by column chromatography (silica gel; CH_2Cl_2 and ethyl acetate), **11** was obtained in 95% yield (D content > 96%).

^{18}O-Labeled 1-(Methylsulfinyl)-9-(methylthio)dibenzothiophene (**13**). To a solution of **3d** (138 mg, 0.5 mmol), pyridine (0.5 ml), and ^{18}O-labeled water (^{18}O content > 99%) (0.1 ml, 5.5 mmol) in 1.5 ml CH_2Cl_2, Br_2 (0.03 ml, 0.58 mmol) in 1 ml CH_2Cl_2 was added at 25°C under argon atmosphere. The solution was stirred for 1 hour, and sodium thiosulfate (248 mg, 1 mmol) was added. The reaction mixture was treated with H_2O and purified by column chromatography (silica gel; CH_2Cl_2 and ethylacetate) to give **13** in 95% yield (^{18}O content = 98%) [18].

Reaction of 1,9-Bis(methylthio)dibenzothiophene (**3d**) *with Conc. Sulfuric Acid.* **3d** was dissolved in conc. sulfuric acid, and the solution was stirred for 5 minutes. This solution was poured into ice water, and the aqueous solution was extracted with CH_2Cl_2. After evaporation and column chromatography, **6d** was obtained in 61% yield together with a trace of compound **10**.

Reaction of 1-(Methylsulfinyl)-9-(methylthio) dibenzothiophene (**6d**) *with Conc. Sulfuric Acid.* After treatment with conc. sulfuric acid, **6d** was recovered in 56% yield together with a trace of compound **10**. **6d**: ^{1}H NMR (500 MHz, D_2SO_4, DSS) δ 8.18 (d, J = 8.0 Hz, 2H, Ar-H), 7.87 (d, J = 8.0 Hz 2H, Ar-H), 7.59 (t, J = 8.0 Hz, 2H, Ar-H), 3.04 (s, 6H, CH_3).

Reaction of 1-(Trideuterated Methylsulfinyl)-9-(methylthio)dibenzothiophene (**11**) *with Conc. Sulfuric Acid.* **11** was dissolved in conc. sulfuric acid, and a 1:1 mixture of **11** and **12** was obtained in 63% yield.

Reaction of ^{18}O-Labeled 1-(Methylsulfinyl)-9-(methylthio)dibenzothiophene (**13**) *with Conc. Sulfuric Acid.* **13** was dissolved in conc. sulfuric acid, and nonlabeled **6d** was obtained in 70% yield.

Reaction of 1,9-Bis(phenylthio)dibenzothiophene (**3a**) with Conc. Sulfuric Acid. After treatment with conc. sulfuric acid and H_2O, **3a** and **6a** were obtained in 6% and 87% yields.

Reaction of 1-(Phenylsulfinyl)-9-(phenylthio)dibenzothiophene (**6a**) *with Conc. Sulfuric Acid.* **6a** was treated with conc. sulfuric acid and then with H_2O to give **3a** and **6a** in 5% and 89% yields. **6a**: ^{1}H NMR (500 MHz, D_2SO_4, DSS) δ 8.11 (d, J = 8.0 Hz, 2H), 7.64–7.56 (m, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.24–7.07 (m, 4H), 6.94 (brs, 2H), 5.90 (brs, 2H); ^{13}C NMR (125 MHz, D_2SO_4, DSS) δ 148.2, 146.4, 140.8, 136.1, 135.7, 134.0, 133.9, 130.8, 122.4, 112.2.

Reaction of 1,9-Bis(p-tolylthio)dibenzothiophene (**3b**) *with Conc. Sulfuric Acid.* Mp 218°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.9 Hz, 1H, Ar-H), 7.88 (d, J = 7.9 Hz, 1H, Ar-H), 7.84 (d, J = 7.9 Hz, 1H, Ar-H), 7.61 (t, J = 7.9 Hz, 1H, Ar-H), 7.60 (d, J = 7.9 Hz, 1H, Ar-H), 7.56 (d, J = 8.2 Hz, 2H, Ar-H), 7.44 (t, J = 7.9 Hz, 1H, Ar-H), 7.14 (d, J = 8.0 Hz, 2H, Ar-H), 6.94 (d, J = 8.0 Hz, 2H, Ar-H), 6.77 (d, J = 8.2 Hz, 2H, Ar-H), 2.34 (s, 3H, CH_3), 2.23 (s, 3H, CH_3); IR (KBr) 1031 cm^{-1}; MS (m/z) 444 (M^+). Anal. calcd for $C_{26}H_{20}OS_3$: C, 70.23; H, 4.53. Found: C, 69.82; H, 4.46.

Reaction of 1,9-Bis(o-tolylthio)dibenzothiophene (**3h**) *with Conc. Sulfuric Acid.* **6h**: Mp 197°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 7.9 Hz, 1H, Ar-H), 7.90 (d, J = 7.9 Hz, 1H, Ar-H), 7.85 (d, J = 7.8 Hz, 1H, Ar-H), 7.81 (d, J = 7.8 Hz, 1H, Ar-H), 7.59 (t, J = 7.9 Hz, 1H, Ar-H), 7.49 (d, J = 7.0 Hz, 1H, Ar-H), 7.42 (t, J = 7.8 Hz, 1H, Ar-H), 7.28–7.19 (m, 2H, Ar-H), 7.10–7.05 (m, 2H, Ar-H), 7.00–6.94 (m, 2H, Ar-H), 6.84 (d, J = 7.8 Hz, 1H, Ar-H), 2.07 (s, 3H, CH_3), 1.83 (s, 3H, CH_3); IR (KBr) 1021 cm^{-1}; MS (m/z) 444 (M^+). Anal. calcd for $C_{26}H_{20}OS_3$: C, 70.23; H, 4.53. Found: C, 70.05; H, 4.45.

Reaction of 1,9-Bis(m-tolylthio)dibenzothiophene (**3i**) *with Conc. Sulfuric Acid.* **6i**: Mp 163.5–165°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.9 Hz, 1H, Ar-H), 7.90 (d, J = 7.9 Hz, 1H, Ar-H), 7.86 (d, J = 7.9 Hz, 1H, Ar-H), 7.67 (d, J = 7.9 Hz, 1H, Ar-H), 7.62 (t, J = 7.9 Hz, 1H, Ar-H), 7.55 (s, 1H, Ar-H), 7.49 (t, J = 7.9 Hz, 1H, Ar-H), 7.47 (d, J = 7.5 Hz, 1H, Ar-H), 7.23 (t, J = 7.5 Hz, 1H, Ar-H), 7.19 (d, J = 7.5 Hz, 1H, Ar-H), 6.98 (t, J = 7.9 Hz, 1H, Ar-H), 6.88 (d, J = 7.9 Hz, 1H, Ar-H), 6.62 (s, 1H, Ar-H), 6.46 (d, J = 7.9 Hz, 1H, Ar-H), 2.25 (s, 3H, CH_3), 2.17 (s, 3H, CH_3); IR (KBr) 1035 cm^{-1}; MS (m/z) 444 (M^+). Anal. calcd for $C_{26}H_{20}OS_3$: C, 70.23; H, 4.53. Found: C, 70.34; H, 4.48.

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