

Syntheses and Structures of Sulfilimine, Sulfone Diimine, and Sulfoximine Derivatives of a Monocyclic Thiophene, 3,4-Di-*tert*-butylthiophene

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ABSTRACT: The reaction of 3,4-di-*tert*-butylthiophene (**6a**) with *N*-[(*p*-tolylsulfonyl)imino]-phenyliodinane (*TsN* = *IPh*) in the presence of $\text{Cu}(\text{MeCN})_4\text{PF}_6$ in MeCN at room temperature provided 3,4-di-*tert*-butyl-1-[(*p*-tolylsulfonyl)imino]-1,1-dihydrothiophene (**3b**), 3,4-di-*tert*-butyl-1,1-bis[(*p*-tolylsulfonyl)imino]-1,1-dihydrothiophene (**5a**), and 1-(*p*-tolylsulfonyl)-3,4-di-*tert*-butylpyrrole (**7a**) as the principal products. The use of 20 molar amounts of **6a** gave **3b** in an increased yield of 61%. Treatment of 3,4-di-*tert*-butylthiophene 1-oxide (**1a**) with $(\text{CF}_3\text{CO})_2\text{O}$ or $(\text{CF}_3\text{SO}_2)_2\text{O}$, followed by reactions with RSO_2NH_2 , $\text{ROC}(=\text{O})\text{NH}_2$, or RCONH_2 , furnished a series of *S*-imino derivatives (**3b,c,e-h**) of **6a**, which carry an electron-withdrawing substituent on the imino nitrogen atom. Treatment of the *S*-imino derivative **3f** (substituent on the nitrogen atom = CO_2^tBu) with $\text{CF}_3\text{CO}_2\text{H}$ gave an aminosulfonium salt (**13**), whose deprotonation led to the parent *N*-unsubstituted 1-imide derivative (**3n**). Treatment of 2,4-di-*tert*-butylthiophene 1-oxide (**1b**) with *TsN* = *IPh* in the presence of $\text{Cu}(\text{MeCN})_4\text{PF}_6$ in MeCN at room

temperature provided 2,4-di-*tert*-butyl-1-[(*p*-toluene-sulfonyl)imino]-1,1-dihydrothiophene 1-oxide (**4e**) in 81% yield. Hydrolysis of **4e** by concentrated H_2SO_4 at room temperature furnished 2,4-di-*tert*-butyl-1-imino-1,1-dihydrothiophene 1-oxide (**4f**) in 89% yield. A pair of enantiomers of **4f** were separated by high-performance liquid chromatography (HPLC) on a chiral column, and their absolute configurations were determined by an X-ray crystallographic analysis. Structures of sulfilimine, sulfone diimine, and sulfoximine derivatives of monocyclic thiophenes, obtained in these ways, are discussed based on spectroscopies (IR and ^1H and ^{13}C NMR) and X-ray crystallographic analyses. © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:333–348, 2001

INTRODUCTION

The chemistry of thiophene 1,1-dioxides (**2**) has been extensively studied both experimentally and theoretically and is thus well documented [1]. A recent exhaustive literature survey has revealed that more than 300 articles have been published on the chemistry of **2** [1a]. Recently, thiophene 1-oxides (**1**) have been attracting much interest from the standpoints of syntheses, structures, synthetic applications, and biochemistry [1b,2]. Substitution of the oxygen atom of **1** by an imino group leads to sulfilimine derivatives (**3**). Substitution of one of the two oxygen atoms of **2** by an imino group provides sulfoximine deriv-

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atives (4), whereas substitution of both oxygen atoms by imino groups leads to the sulfone diimine derivatives (5) (Scheme 1). When we planned a synthetic study of 3–5 in 1997, the following had been reported on these compounds [3,4]. Meth-Cohn et al. obtained sulfilimines (3a) by thermolyses of azides in tetrachlorothiophene [3a], which were the only sulfilimine derivatives of monocyclic thiophenes, and they investigated the reactivities of these sulfilimines toward dienophiles in some detail [3c]. They also obtained the sulfoximine (4a) by oxidation of 3a ($R = \text{CO}_2\text{Et}$) [3b]. Sulfone diimines (5) were still unknown and had remained to be synthesized.

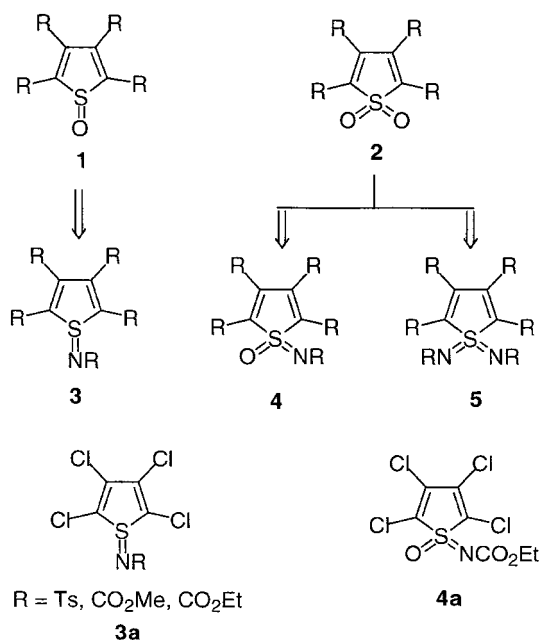
The parent thiophene 1,1-dioxide and monosubstituted thiophene 1,1-dioxides undergo very rapid $[4 + 2]$ self-dimerization, where one molecule acts as a diene and the other as a dienophile, and thus they are labile and are not isolated at room temperature [1b,5]. Many stable and isolable di-, tri- and tetra-substituted thiophene 1,1-dioxides are known [1]. Thiophene 1-oxides are much more reactive than the corresponding thiophene 1,1-dioxides [1b,2]. By analogy, nitrogen-substituted compounds 3–5 are expected to be labile species. Therefore, in order to obtain stable and isolable derivatives of 3–5, the double bonds of these compounds should be deactivated either kinetically or electronically. Taking this into account, we have chosen 3,4- and 2,4-di-*tert*-butylthiophenes (6a and 6b) as starting materials for our synthetic study since the double bonds of 3–5, derived from these compounds, would be stabilized ki-

netically by steric protection. Indeed, this strategy worked well to lead to the successful preparation of 3–5 [6]. Reported here are experimental details of this synthetic study. Structures of 3–5 are also discussed in some detail based on spectroscopies (IR and ^1H and ^{13}C NMR) and X-ray crystallographic analyses.

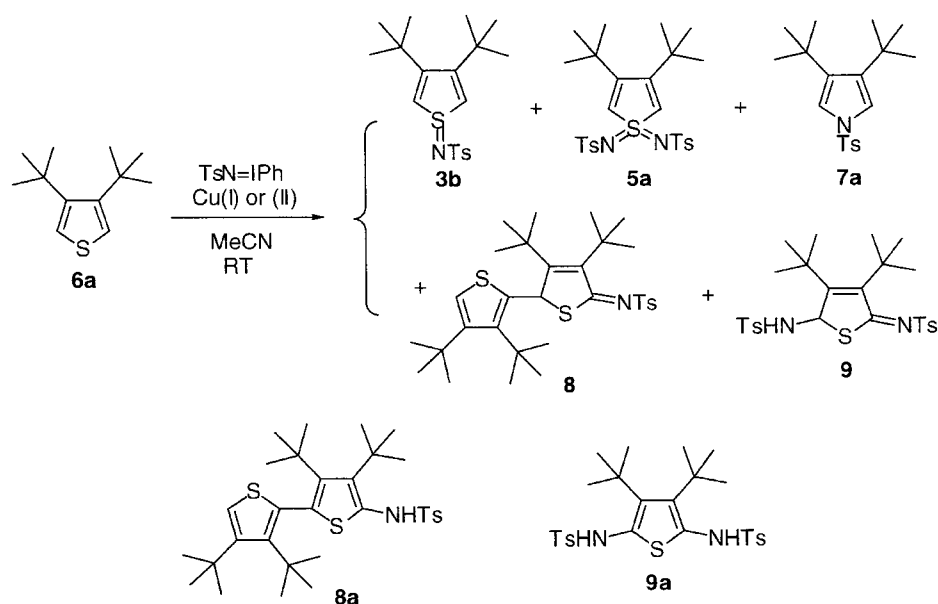
RESULTS AND DISCUSSION

Preparation of Sulfilimine and Sulfone Diimine Derivatives

Preparation of Sulfilimine and Sulfone Diimine Derivatives by Direct Imination of 3,4-Di-*tert*-butylthiophene. Thermolyses of organic azides in tetrachlorothiophene afforded the desired sulfilimines (3a) [3a]. Thermolyses in other thiophenes, however, all failed to give the corresponding sulfilimines [3a,7,8]. This would be at least partly due to the expected thermal instability of sulfilimines, which may not allow their survival under the thermolysis conditions ($130\text{--}150^\circ\text{C}$). Reportedly, *N*-[(*p*-tolylsulfonyl)imino]phenyliodinane ($\text{TsN}=\text{IPh}$) [9] generates the tosyl nitrene or its equivalent at a lower temperature in the presence of a Cu(I) or Cu(II) catalyst [10]. We therefore first examined the imination of 3,4-di-*tert*-butylthiophene (6a) by this reagent. Thus, 6a and $\text{TsN}=\text{IPh}$ were allowed to react in varying molar ratios in the presence of 5 mol % of $\text{Cu}(\text{MeCN})_4\text{PF}_6$ [Cu(I)] [11] or $\text{Cu}(\text{OTf})_2$ [Cu(II)] ($\text{Tf} = \text{SO}_2\text{CF}_3$) in MeCN. The reaction took place at room temperature in every case. Purification of the resulting complex mixtures provided the expected sulfilimine 3b, together with unexpected formation of the sulfone diimine 5a and the pyrrole 7a [8] (Scheme 2 and Table 1). Compounds 8, 9, and TsNH_2 were also isolated in small amounts. Structures of 3b, 5a, and 9 were established by X-ray crystallographic analyses. Better total yields of the products were obtained by using the Cu(I) catalyst rather than the Cu(II) (entries 2 and 3, Table 1). The yield of 3b, based on $\text{TsN}=\text{IPh}$, increased with an increasing molar ratio of 6a; a satisfactory yield of 61% was attained by use of 20 molar amounts of 6a. The sulfilimine 3b was more stable thermally than we had initially expected and melted at $130\text{--}131^\circ\text{C}$ without decomposition. Compound 5a provided the first example of a sulfone diimine derivative of a thiophene. It was also thermally stable and had a melting point of $155.0\text{--}155.5^\circ\text{C}$. As for the structures of 8 and 9, the corresponding tautomeric forms 8a and 9a are possible. However, compound 8 exists exclusively in the imino form, as revealed by IR and NMR spectral analyses, at the sacrifice of the aromaticity of one of the thiophene



SCHEME 1



SCHEME 2

TABLE 1 Reactions of **6a** with TsN = IPh under a Variety of Conditions

Entry	Molar Ratio (6a /TsN = IPh)	Catalyst ^a	Isolated Yield (%) ^b				
			3b	5a	7a	8	9
1	2.5	Cu(I)	23	9	9	2	+ ^c
2	5.0	Cu(I)	38	18	10	3	+ ^c
3	5.0	Cu(II)	32	8	4	3	3
4	7.5	Cu(I)	50	9	10	4	+ ^c
5	20	Cu(I)	61	7	5	3	4

^aCu(I) = Cu(MeCN)₄PF₆, Cu(II) = Cu(OTf)₂.^bBased on TsN = IPh.^cNo effort was made to isolate **9** (detected by TLC).

rings. Release from steric repulsions between the two thiophene rings that carry bulky *tert*-butyl groups serves to explain the existence of **8** in the imino form. Previously, we reported that the two thiophene rings of 3,4,3',4'-tetra-*tert*-butyl-2,2'-bithiophene are nearly perpendicular to each other to avoid steric repulsions. Compound **9** exists in the amino-imino form, as revealed by X-ray crystallographic analysis, to avoid steric repulsions among the substituents. Any evidence for the existence of the diamino form **9a** in solution was also not found by ¹H and ¹³C NMR spectral analyses. Thus, **8** and **9** contradict the fact that 2-amino derivatives of thiophene generally exist in the amino form [12].

The sulfilimine **3b** would be formed by addition of the tosyl nitrene to the thiophene **6a**. The sulfur atom of **3b**, whose thiophene ring is not aromatic as

discussed later, would be more reactive than that of **6a** toward the nitrene or TsN = IPh. Therefore, **3b** would react further to give the sulfone diimine **5a**. A separate reaction of **3b** with an equimolar amount of TsN = IPh in the presence of 5 mmol % of the Cu(I) catalyst gave **5a** in 10% yield with recovered **3b** in 48% yield; the pyrrole **7a** and TsNH₂ were also formed in 18 and 43% yields, respectively (Scheme 3). The formation of sulfone diimines by reaction of sulfides with TsN = IPh is unprecedented to our knowledge. Previously, we reported that the pyrrole **7a** is formed in a low yield by thermolysis of tosyl azide in **6a** at 150°C [8]. At that time, we thought that **7a** would be formed by the secondary self-reaction of the initial product **3b** as one of the plausible pathways. However, this pathway might now be ruled out because the sulfilimine **3b** was not converted to **7a** by heating its benzene solution at 160°C for 3 hours in a sealed tube. Also, the conversion of **3b** to **7a** was not brought about by the action of the Cu(I) catalyst at room temperature. These observations lead to a conclusion that **7a** is formed by reaction of **3b** with TsN = IPh. In order to look into the mechanism of the formation of **7a**, **3b** was allowed to react with PhSO₂N = IPh in the presence of the Cu(I) catalyst. The reaction gave sulfone diimine **5b** in 6% yield and a mixture of pyrroles **7a** and **7b** in 14% yield in the ratio 15:85, with recovery of **3b** in 72% yield (Scheme 3). The predominant formation of **7b** over **7a** is suggestive of the mechanism. One of the plausible mechanisms, based on this observation, involves the 1,4-addition of the benzenesulfonyl nitrene to **3b**. The resulting adduct (**10**) would produce

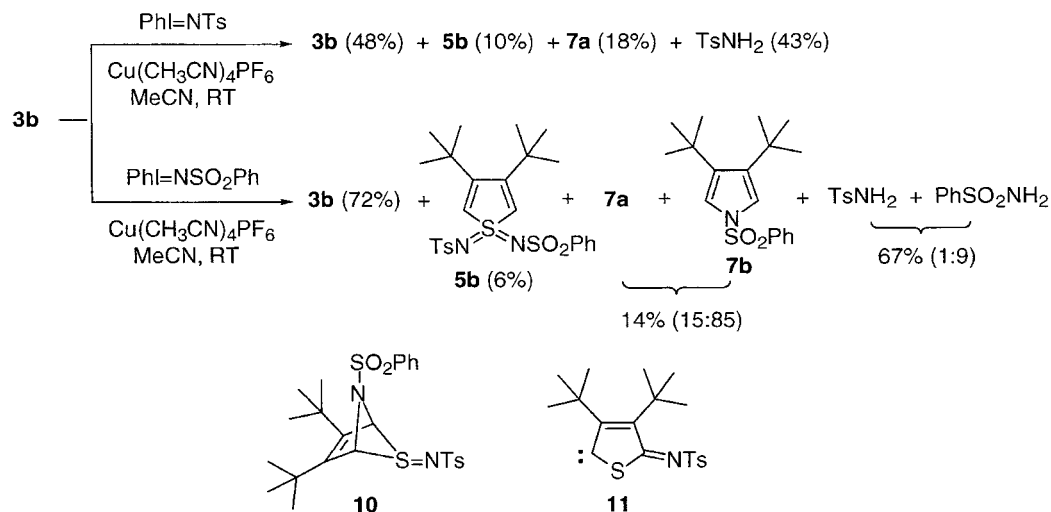
7b with extrusion of $\text{TsN}=\text{S}$, although the concomitant formation of **7a** in a small amount still remains to be explained.

Mechanisms of the formation of **8** and **9** are not clear, although many tentative explanations are possible. For example, the simplest explanation would be provided by insertion of a carbene (**11**) into the $\text{C}_\alpha\text{-H}$ bond of the thiophene **6a** and into the N-H bond of TsNH_2 , which affords **8** and **9**, respectively, although it is not easy to explain how **11** was produced.

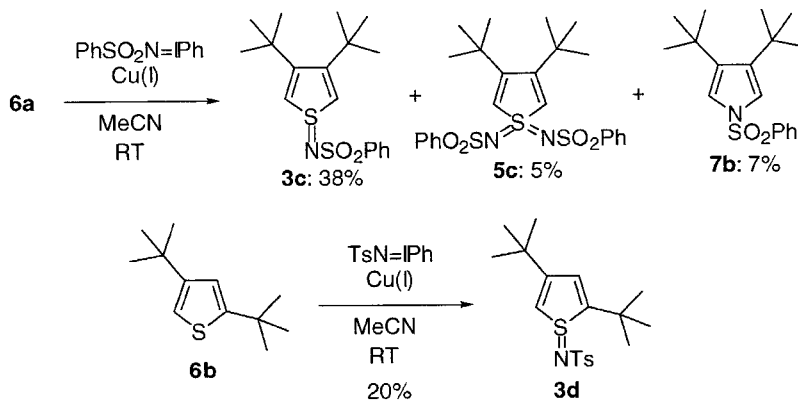
The reactions of **6a** with $\text{PhSO}_2\text{N}=\text{IPh}$ and of 2,4-di-*tert*-butylthiophene (**6b**) with $\text{TsN}=\text{IPh}$ were also examined, though not in great detail (Scheme 4). The former reaction gave sulfilimine (**3c**), sulfone diimine (**5c**), pyrrole (**7b**); and PhSO_2NH_2 in 38, 5, 7, and 33% yields, respectively, by use of five molar amounts of **6a** and the Cu(I) as the catalyst. The lat-

ter reaction gave a complex mixture from which a sulfilimine (**3d**) was isolated in 20% yield.

*Preparation of Sulfilimine Derivatives from 3,4-Di-*tert*-butylthiophene 1-Oxide.* The synthesis, described previously, required the use of 20 molar amounts of the thiophene **6a** to obtain **3b** in 61% yield. Another drawback to this method is that **3b** cannot be converted to the N-unsubstituted derivative by conventional methods of detosylation [13]. These considerations prompted us to develop an alternative synthesis of S-iminated thiophenes. Previously, we reported that the oxidation of **6a** with *m*-chloroperbenzoic acid (MCPBA) in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ affords the corresponding thiophene 1-oxide (**1a**) in good yield [14]. We therefore examined the conversion of **1a** to **3b** and the related sulfilimines [15].



SCHEME 3



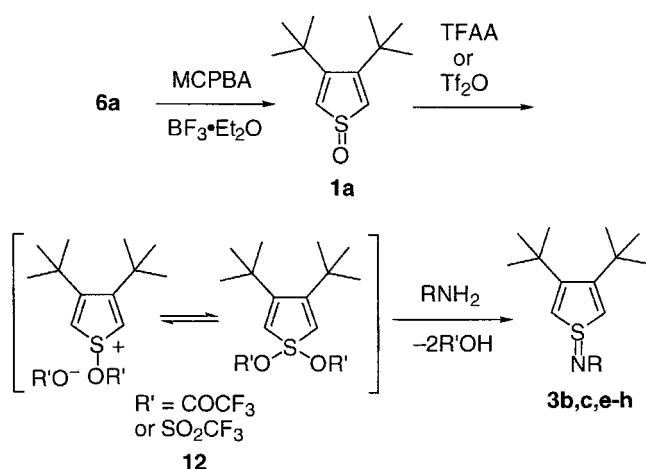
SCHEME 4

The thiophene 1-oxide **1a** was allowed to react with two molar amounts of $(\text{CF}_3\text{CO})_2\text{O}$ (TFAA) at -78°C to form a sulfonium salt or a sulfurane (**12**) ($\text{R}' = \text{COCF}_3$), which was treated in situ with two molar amounts of TsNH_2 at the same temperature (Scheme 5). The mixture was warmed slowly to room temperature, and the reaction was quenched by addition of water. Purification of the mixture gave **3b** in 86% yield (Table 2, run 1). The reaction, in which $(\text{CF}_3\text{SO}_2)_2\text{O}$ (Tf_2O) was used instead of TFAA, under similar conditions, also afforded **3b** in 79% yield (run 2). In these ways, a series of sulfilimines **3b,c,e-h** were synthesized in satisfactory yields, as shown in Table 2.

Although the previous synthesis seemed to be quite general and unsatisfactory, but interesting, exceptions were found. Thus, treatment of **1a** with TFAA and then with H_2NCN yielded the trifluoroacetyl derivative (**3i**) in 85% yield, but not the expected cyano derivative (**3j**) (Scheme 6). Similarly, treatment of **1a** with TFAA, and then with H_2NCONH_2 , also gave **3i** in 83% yield. Neither of the

expected compounds **3k** or **3l** was formed. In these cases, the initial products **3j** and **3k** are probably converted to **3i** by the action of TFAA or $\text{CF}_3\text{CO}_2\text{H}$. An analogy is found in the reaction of DMSO with TFAA, followed by treatment with H_2NCONH_2 in CH_2Cl_2 , which gave $\text{Me}_2\text{S}=\text{NCOCF}_3$ in 80% yield [15e]. The reaction of **1a** with MeNH_2 , after treatment with TFAA, also failed to give the expected sulfilimine (**3m**), with quantitative recovery of **1a** being realized. Conversion of **3b** to **3e** was done in 85% yield by treatment of **3b** with TFAA and then with 10 molar amounts of $\text{H}_2\text{NCO}_2\text{Et}$. Thus, desirable mutual conversions between sulfilimine derivatives seem possible.

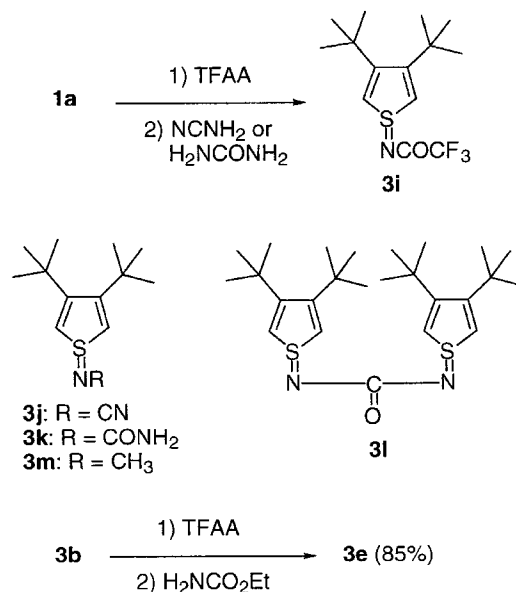
In order to obtain the parent N-unsubstituted compound (**3n**), the N-Boc substituted **3f** was treated with $\text{CF}_3\text{CO}_2\text{H}$ [16]. The reaction satisfactorily yielded an aminosulfonium salt (**13**) quantitatively, which provided the first example of aminosulfonium salt of a monocyclic thiophene. Treatment of a solution of **13** in CH_2Cl_2 with aqueous NaOH gave the expected sulfilimine **3n** and the thiophene **6a** in the ratio 30:1 in a quantitative total yield, whereas treatment of **13** with NaH in ether gave **3n** and **6a** in the ratio 58:42 (Scheme 7). The formation of **6a**, in addition to **3n**, indicates that the nucleophiles attack not only the amino hydrogen atom but also the amino nitrogen atom as depicted in Figure 1; in other words, **13** possesses the potential to serve as an amination reagent. The compound **3n** provides the first example of an N-unsubstituted sulfilimine of a thiophene. It is converted to **3b** in 84% yield by



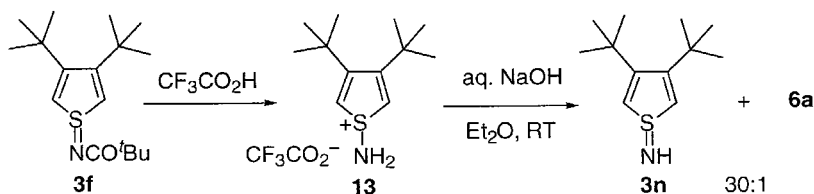
SCHEME 5

TABLE 2 Preparation of a Variety of N-Substituted 1-Imino Derivatives **3b,c,e-h** from 3,4-Di-*tert*-butylthiophene 1-Oxide (**1a**)

Run	1-Imino Derivative	R	Acid Anhydride	Yield (%)
1	3b	$\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3(\text{p})$	TFAA	86
2	3b	$\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3(\text{p})$	Tf_2O	79
3	3c	$\text{SO}_2\text{C}_6\text{H}_5$	Tf_2O	74
4	3e	CO_2Et	TFAA	90
5	3f	CO_2tBu	TFAA	82
6	3g	COCH_3	TFAA	53
7	3h	$\text{COC}_6\text{H}_4\text{CH}_3(\text{p})$	TFAA	74



SCHEME 6



SCHEME 7

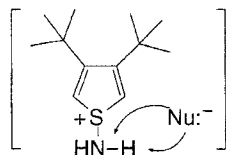


FIGURE 1

treatment with TsCl (Scheme 8). Thus, it seems possible to derive a variety of sulfilimine derivatives from **3n** by alkylation and acylation. The sulfilimine **3n** is storable at below -20°C at least for one month without any appreciable decomposition, but it was converted to the thiophene **6a** quantitatively through hydrolysis by contaminating water, when its CDCl_3 solution was heated at 50°C for 6 hours. The hydrolysis probably involves an aminosulfonium ion (**14**).

Preparation of Sulfoximines by Imination of 2,4- and 3,4-Di-tert-butylthiophene 1-Oxides

A great number of sulfoximines have been synthesized, and their chemistry has been attracting much interest from a variety of standpoints, such as structures, stereochemistry, reactivities, and applications to organic syntheses [17]. However, synthetic study of sulfoximine derivatives of thiophenes has been surprisingly neglected. To our knowledge, the sulfoximine (**4a**) [**3b**] is the only sulfoximine derivative of a monocyclic thiophene ever synthesized [**4a**]. Described in the following paragraphs is our synthetic study.

The reaction of the thiophene 1-oxide **1a** with TsN=IPh (1.2 molar amounts) proceeded smoothly in the presence of the Cu(I) catalyst $[\text{Cu}(\text{MeCN})_4\text{PF}_6]$ in MeCN at room temperature to furnish the expected thiophene sulfoximine (**4b**) in 67% yield. These results show that the imination of **1a** takes place more effectively than that of the corresponding 1-imide **3b**. A conventional method, which employs tosyl azide (three molar amounts) in the presence of an activated copper powder in refluxing methanol [18], worked only in a sluggish way to produce **4b** in a moderate yield of 35%. The tosyl group of **4b** was eliminated by hydrolysis with concentrated H_2SO_4

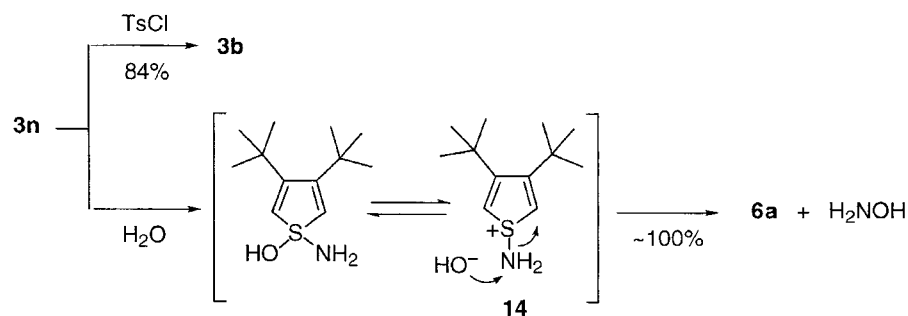
[**13a,b**] to form the parent sulfoximine (**4c**) in 95% yield. Treatment of **4c** with $\text{Me}_3\text{O}^+\text{BF}_4^-$ gave the N-methylated compound **4d** in 43% yield, with a 40% yield recovery of **4c**.

Similarly, the unsymmetrically substituted thiophene 1-oxide (**1b**) also afforded the sulfoximine (**4e**) in 81% yield on reaction with TsN=IPh in the presence of the Cu(I) catalyst. Treatment of **4e** with concentrated H_2SO_4 gave the parent sulfoximine (**4f**) in 89% yield. Both **4c** and **4f** were not very stable thermally; **4c** decomposed completely, when heated in boiling toluene for several hours, to give at least 10 products.

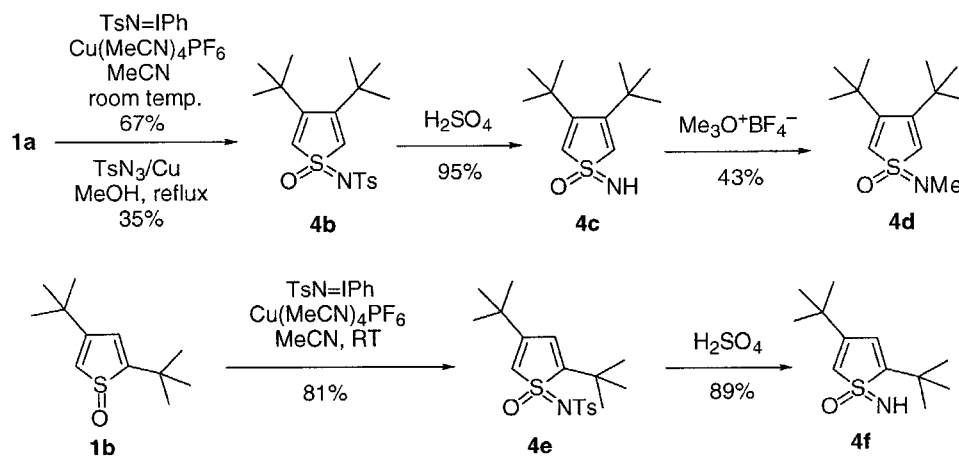
Spectroscopies and X-Ray Crystallographic Analyses of Sulfilimine, Sulfone Diimine, and Sulfoximine

^1H and ^{13}C NMR Spectra. Table 3 summarizes chemical shift values of a series of S-substituted derivatives of 3,4-di-tert-butylthiophene (**6a**). The chemical shift values of the α -hydrogen atoms of the thiophene ring in ^1H NMR and those of the α - and β -carbon atoms in ^{13}C NMR spectra are given. For comparison, the chemical shift values of 3,4-di-tert-butylthiophene 1,1-dioxide (**2a**) [19] are also included.

The thiophene 1-oxide **1a** and the sulfilimine **3n** are isoelectronic to each other, and their ring α -hydrogen atoms resonate at δ 6.93 and 6.81, respectively, upper fields than those of the parent thiophene **6a**, which resonate at δ 7.16. The observed upfield shift ongoing from **6a** to **1a** and **3n** is indicative of the disappearance of the ring current effect of the thiophene ring in **1a** and **3n**, namely, the loss of aromaticity. The resonance of the α -hydrogen atoms of **3n** at an upper field than that of **1a** by 0.12 ppm would be due to the smaller electronegativity of the nitrogen atom than that of the oxygen atom. The α -hydrogen atoms of N-acyl substituted sulfilimines **3g-i** resonate in the range δ 7.10–7.22, comparable values with those of **6a**, δ 7.16. This reflects that the α -carbon atoms of **3g-i** are more electron deficient, thus, the hydrogen atoms attached to them are more acidic than those of the other sulfilimines due to the contribution of the canonical structure (**15**); need-



SCHEME 8



SCHEME 9

TABLE 3 Relevant ^1H and ^{13}C NMR Data for a Series of S-Substituted Derivatives of 3,4-Di-*tert*-butylthiophene (**6a**).^a

Compounds	^1H NMR	^{13}C NMR	
	α -Hydrogens	α -Carbons	β -Carbons
6a	7.16	134.4	150.6
1a	6.93	122.3	158.4
3n	6.81	135.1	158.4
3b	6.70	^b	160.4
3c	6.70	^b	162.0
3e	6.92	128.5	162.4
3f	6.92	128.8	162.2
3g	7.10	129.1	162.7
3h	7.22	^b	162.4
3i	7.15	125.2	164.7
13	6.97	126.5	165.7
2a	6.44	127.5	156.8
4c	6.53	129.4	155.0
4b	6.92	^b	158.9
4d	6.57	126.5	155.4
5a	7.13	^b	160.4

^aChemical shifts are given in δ values with TMS as the internal standard and with CDCl_3 as the solvent.^bNot assigned.

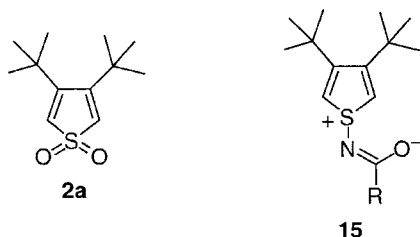
less to say, this does not mean that these compounds are aromatic.

The α -hydrogen atoms of the aminosulfonium salt **13** resonate at an upper field of δ 6.97 than those of **6a** by 0.19 ppm. The thiophene ring of **13**, in which the sulfur atom has tetrahedral hybrid orbitals, also would not be aromatic.

The thiophene 1,1-dioxide **2a**, the sulfoximine **4c**, and the sulfone diimine **5a**, in which two pairs of lone-pair electrons on the sulfur atom are consumed for bond formation with heteroatoms, are isoelectronic to each other and are also not aromatic. Interestingly, the α -hydrogen atoms of **2a** and **4c** resonate at δ 6.44 and 6.53, respectively, upper fields than those of the thiophene 1-oxide **1a** and the sulfilimine **3n**, despite the fact that their sulfur atom carries two electronegative heteroatoms. The α -hydrogen atoms of the sulfone diimine **5a** resonates at a lower field of δ 7.13.

The α -carbon atoms of a series of S-substituted compounds resonate in the range δ 122.3–129.4, which is at a higher field than those of the thiophene

6a, δ 134.4. An exception is the α -carbon atoms of the sulfilimine 3n, which resonate at δ 135.1. On the contrary, the β -carbon atoms of S-substituted compounds, which carry a bulky *tert*-butyl group, resonate at lower fields, δ 155.4–165.7, than those of the thiophene 6a, δ 150.6, without any exception.



Infrared Spectra. Table 4 summarizes the C=O stretching vibrations of sulfilimines 3e–i. The C=O stretching frequencies of 3e,f and those of 3g–i are more than 50 cm^{-1} smaller than the corresponding carbamates ($\text{R}_2\text{NCO}_2\text{R}'$) and amides ($\text{R}_2\text{NCOR}'$) [20], respectively, suggesting that the canonical structure 15 is the principal contributor of 3e–i, in accordance with the same conclusion reached by ^1H NMR spectral analysis.

Here it would be worthy of mention that $\text{C}(\text{sp}^2)\text{--H}$ stretching vibrations of the sulfilimines 3e–i, particularly of 3g,h, appeared abnormally enhanced. Figure 2 shows the infrared spectrum of 3g, in which a very intense $\text{C}(\text{sp}^2)\text{--H}$ stretching vibration is observed at 3097 cm^{-1} ; consider that there exist only two $\text{C}(\text{sp}^2)\text{--H}$ bonds in 3g, whereas the number of

TABLE 4 Carbonyl Stretching Vibrations of Sulfilimines 3e–i in the IR Spectra

Compounds	3e	3f	3g	3h	3i
$\nu_{\text{C=O}}$ (cm^{-1}) ^a	1636	1639	1573	1541	1627

^aTaken for KBr disks.

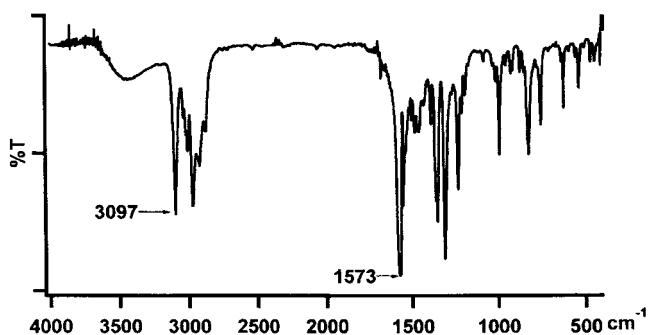
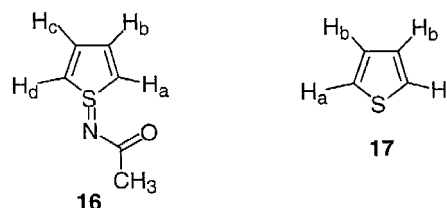


FIGURE 2 Infrared Spectrum of 3g.

$\text{C}(\text{sp}^3)\text{--H}$ bonds is 21. These findings prompted us to carry out ab initio calculations (B3LYP/6-31G*) on the infrared spectrum of the simplest sulfilimine (16) [21]. The calculations predicted that the C--H_a stretching vibration of 16 appears at 3181 cm^{-1} (scaling factor, 0.96) and 5.8 times enhanced, compared to the C--H_a stretching vibration of the parent thiophene (17), while the C--H_d stretching vibration of 16 appears at 3159 cm^{-1} , only 1.8 times enhanced. Therefore, the very intense absorption of 3g at 3097 cm^{-1} would be assigned to the stretching vibration of the C--H_a bond that faces to the carbonyl side. Although the reason for the enhanced absorption is not clear, it is certainly related to the presence of the C=O group since such enhancement was not observed with 3b,c [22].



X-Ray Crystallographic Analyses. An ORTEP structure of 3b is given in Figure 3, along with the relevant bond lengths and angles data. For comparison, the outline structure of 3b and that of 1a [14], which is isoelectronic with the former, are also shown in Figure 3. Crystal data of 3b are summarized in Table 5. The geometry of 3b is similar to that of 1a with a pyramidal configuration at the sulfur atom. In both 3b and 1a, although four carbon atoms of the thiophene ring form a quasi-plane, the sulfur atom is placed out of the plane. Their C2–C3 bond lengths, 1.53–1.54 Å, and C1–C2 (C3–C4) bond lengths, 1.33–1.34 Å, are almost equal to the common single and double bond lengths [23], respectively, revealing a bond alternation. Pyramidal geometry of the sulfur atom, nonplanar structure of the thiophene ring, and the bond alternation data lead to the conclusion that both 3b and 1a are not aromatic, in agreement with the conclusion reached by ^1H NMR data analyses. Interestingly, the benzene and thiophene rings of 3b exist in a face-to-face conformation. If this conformation is the preferred one in solution, the shielding effect by the benzene ring would explain the fact that the thiophene ring α -hydrogen atoms of 3b and 3c resonate at a higher field δ 6.70 than do the corresponding hydrogens of 3n, δ 6.81 (Table 3). In this connection, we are currently investigating how this conformation influences the π -face selectivity in cycloadditions of 3b.

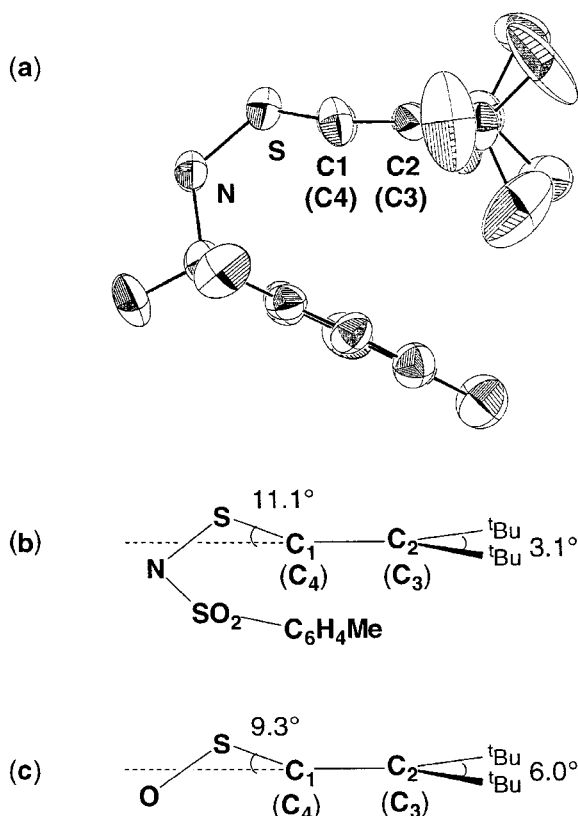


FIGURE 3 (a) ORTEP structure of **3b**. (b) Outline structure of **3b**. (c) Outline structure of **1a**. Selected bond lengths data of **3b**: S–N, 1.595(7); S–C1, 1.744(7); S–C4, 1.742(8); C1–C2, 1.332(11); C2–C3, 1.535(10); C3–C4, 1.329(10). Bond angles data of **3b** (°): C1–S–C4, 90.7(4); S–C1–C2, 113.6(6); C1–C2–C3, 109.9(7); C2–C3–C4, 111.7(7); C3–C4–S, 112.6(6).

An ORTEP structure of **5a** and its outline structure are given in Figure 4, along with the relevant bond lengths and angles data. Crystal data of **5a** are summarized in Table 5. The thiophene ring of the sulfone diimine **5a** is nearly planar as is true of most thiophene 1,1-dioxides [24]. The S–N1 and S–N2 bond lengths are 1.55 Å and are nearly equal to the bond length (1.54 Å) of the common S–N bonds [23] that are conventionally expressed by a double bond. The bond alternation in the thiophene ring is evident from the bond lengths data: C1–C2, 1.34; C2–C3, 1.52 Å.

An ORTEP structure of **9** is shown in Figure 5, along with the relevant bond lengths and angles data. Crystal data of **9** are summarized in Table 5. The ORTEP structure shows that **9** exists in the amino-imino form in the solid state. Thus, C4–N2 is typical of a double bond with a bond length of 1.29 Å, while the C1–N1 is typical of a single bond with a bond length of 1.46 Å [23].

The tetracoordinated sulfur atom of **4f** is chiral; thus, an effort was made to separate a pair of enantiomers. High-performance liquid chromatography (HPLC) on a chiral column gave two well-separated peaks due to a pair of enantiomers and allowed us their easy separation. Both enantiomers, on slow evaporation of a hexane solution, provided good crystals for an X-ray crystallographic analysis. The analysis disclosed that the second-eluted enantiomer has an (*S*)-configuration with the η value defined by Rogers [25] being 1.03(6) [26]. The (*R*) configuration is therefore assigned to the first-eluted enantiomer. An ORTEP structure of (*S*)-**4f** is given in Figure 6, along with the relevant bond lengths and bond angles data. Crystal data of (*S*)-**4f** are summarized in Table 5. The thiophene ring of the compound is planar, as in many thiophene 1,1-dioxides [24], as well as in the sulfone diimine **5a**, which is isoelectronic with **4f**. The bond length data (1.32 Å for C2–C3 and C4–C5, 1.49 Å for C3–C4) are indicative of a bond alternation, that is, nonaromaticity of the thiophene ring. The S–O and S–N bond lengths are 1.45 and 1.54 Å, respectively, and are comparable with those of other sulfoximides [26]. The O–S–N bond angle of 119° is larger than those of acyclic sulfoximides. The sulfur atom of **1b** is also chiral. However, attempted separation of a pair of enantiomers was fruitless because of the low inversion barrier that is characteristic of the sulfur atom in monocyclic thiophene 1-oxides [27]. Attempted separation of a pair of enantiomers of **3d** also failed, probably because of the same reason as that for **1b**.

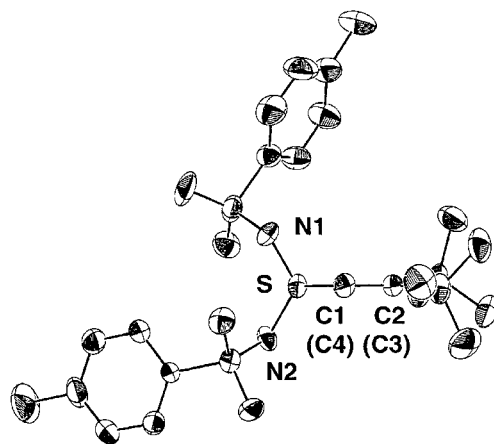
(*R*)-**4f** and (*S*)-**4f** both had a melting point of 114–115°C, which was much higher than that of the racemate **4f** (m.p. 82.5–83.5°C), and showed specific rotations of -48.6° and $+48.6^\circ$ (c 0.10 g/100 mL, CHCl₃, 26°C), respectively. The UV–vis spectrum of the racemate **4f** showed absorption maxima at ca. 315 (sh), 279, and 245 nm (Figure 7). Thus, (–)-(*R*)-**4f** showed the negative first Cotton effect at 315, the positive second one at 279, and the negative third one at 236 nm in the circular dichroism (CD) spectrum, while (+)-(*S*)-**4f** gave the exactly reverse pattern (Figure 7).

The present study has developed rather general syntheses of sulfilimine and sulfoximine derivatives of monocyclic thiophenes. These compounds are not aromatic but are cyclic dienes. In addition, they show equally characteristic properties of sulfilimines and sulfoximines. Taking these properties into account, a special emphasis of the future study of these compounds should be placed on their applications to organic syntheses to open a new field of heterocyclic and heteroatom chemistry. Particularly, their

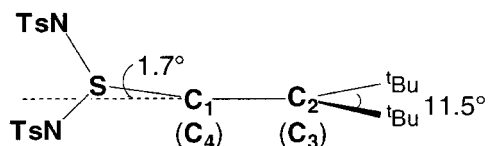
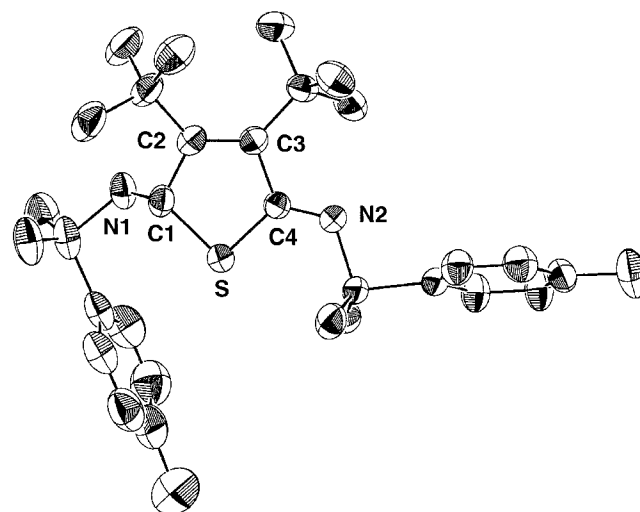
TABLE 5 Crystal Data of **3b**, **5a**, **9**, and (S)-**4f**

	3b	5a	9	(S)- 4f
Chemical formula	C ₁₉ H ₂₇ NO ₂ S ₂	C ₂₆ H ₃₄ N ₂ O ₄ S ₃	C ₂₆ H ₃₄ N ₂ O ₄ S ₃	C ₁₂ H ₂₁ NOS
Formula weight	365.56	534.77	534.77	227.40
Crystal form	Needles	Needles	Needles	Needles
Crystal size (mm ³)	0.29 × 0.08 × 0.08	0.16 × 0.08 × 0.08	0.34 × 0.15 × 0.15	0.58 × 0.16 × 0.10
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	9.696(1)	10.246(2)	12.355(1)	13.491(3)
<i>b</i> (Å)	14.071(3)	11.848(1)	17.297(1)	17.019(4)
<i>c</i> (Å)	15.614(4)	22.677(3)	13.864(1)	5.802(1)
α (°)	105.811(9)			
β (°)	100.32(1)	95.132(7)	108.502(4)	
γ (°)	98.07(1)			
<i>V</i> (Å ³)	1975.9(7)	2741.8(6)	2809.7(3)	1332.2(5)
<i>Z</i>	4	4	4	4
<i>D</i> _{calc} (Mg m ⁻³)	1.229	1.295	1.264	1.133
No. of measured reflections	8212	7608	7380	1553
No. of independent reflections	3087	2859	5060	1361
No. of observed reflections (<i>I</i> > 2σ(<i>I</i>))	6639	5953	6702	1450
No. of parameters	487	350	452	192
<i>R</i>	0.079	0.071	0.047	0.055
<i>R</i> _w	0.075	0.060	0.051	0.065
GOF	2.045	1.714	1.396	1.526
$\Delta\rho_{\max}$	0.61	0.41	0.55	0.41
$\Delta\rho_{\min}$	−0.44	−0.69	−0.42	−0.46

(a)



(b)

**FIGURE 4** (a) ORTEP structure of **5a**. (b) Outline structure of **5a**. Selected bond lengths (Å): S–N1, 1.551(6); S–N2, 1.557(5); S–C1, 1.737(7); S–C4, 1.728(7); C1–C2, 1.339(10); C2–C3, 1.524(11); C3–C4, 1.343(9). Bond angles (°): N1–S–N2, 121.5(3); C1–S–C4, 93.1(4); S–C1–C2, 111.7(5); C2–C3–C4, 111.7(6); C3–C4–S, 111.7(5).**FIGURE 5** ORTEP structures of **9**. Selected bond length (Å): N1–C1, 1.455(2); C1–C2, 1.521(3); C2–C3, 1.359(2); C3–C4, 1.485(2); C4–N2, 1.292(2); C1–S, 1.815(2); S–C4, 1.730(2). Bond angles (°): N1–C1–C2, 109.6(2); N1–C1–S, 113.3(2); S–C1–C2, 108.4(1); C1–C2–C3, 113.7(2); C2–C3–C4, 110.3(2); C3–C4–S, 113.7(1); C3–C4–N2, 121.3(2); S–C4–N2, 124.8(2).

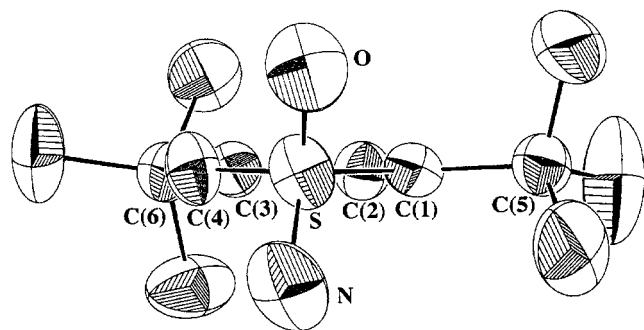


FIGURE 6 ORTEP structure of (+)-(S)-**4f**. Selected bond lengths (Å): S–O, 1.445(3); S–N, 1.536(3); S–C1, 1.796(3); S–C4, 1.739(3); C1–C2, 1.321(3); C2–C3, 1.492(3); C3–C4, 1.319(4); C1–C5, 1.520(4); C3–C6, 1.507(4). Bond angles (°): O–S–N, 119.3(2); C1–S–C4, 92.9(2); S–C1–C2, 107.3; C1–C2–C3, 116.4(2); C2–C3–C4, 111.5(3); C3–C4–S, 111.9(2); S–C1–C5, 123.2(2); C2–C3–C6, 121.5(2).

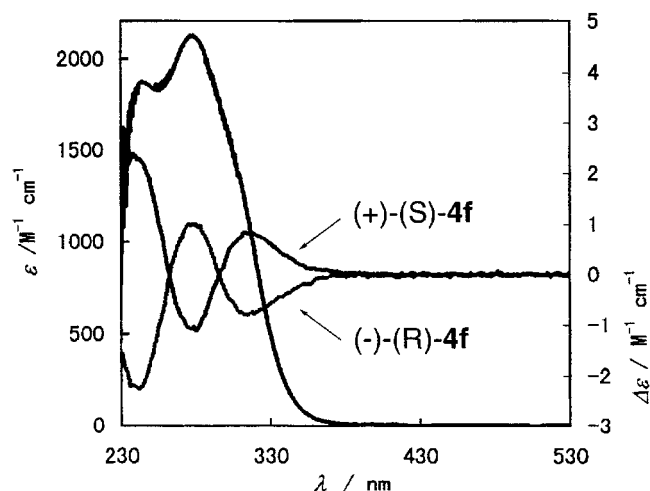


FIGURE 7 CD Spectra of (–)-(R)- and (+)-(S)-**4f** (c 0.010 g/100 mL, CH₂Cl₂) and UV–vis Spectrum of the Racemate **4f** (CH₂Cl₂)

cycloaddition chemistry would be of much interest in comparison with those of thiophene 1-oxides and 1,1-dioxides.

EXPERIMENTAL

Solvents were purified and dried in the usual manner. All of the reactions were carried out under argon. Silica-gel column chromatography was performed on silica gel 7734 (Merck, 70–230 mesh). Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Bruker ARX400, a Bruker AM400, or a Bruker AM300 spectrometer using CDCl₃ as the solvent with TMS as the internal standard. IR spectra were taken on a Hitachi 270-50

or a Perkin Elmer System 2000 FT-IR spectrometer. UV–vis spectra were determined on a JASCO V-560 spectrophotometer. CD spectra were determined on a JASCO J-600 spectropolarimeter. Mass spectra were recorded on a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode. Elemental analyses were performed by the Chemical Analysis Center of Saitama University.

Imination of 3,4-Di-*tert*-butylthiophene (**6a**) by *N*-[(*p*-tolylsulfonyl)imino]phenyliodinane (TsN=IPh)

Cu(MeCN)₄PF₆ as the Catalyst. The thiophene **6a** and TsN=IPh in a variety of molar ratios were allowed to react in the presence of 5 mol % of Cu(MeCN)₄PF₆. The following are experimental details of the 20:1 molar ratio reaction. A mixture of 3.92 g (20 mmol) of **6a**, 373 mg (1 mmol) of TsN=IPh, and 20 mg (0.05 mmol) of Cu(MeCN)₄PF₆ in 25 mL of MeCN was stirred for 3 hours at room temperature. The reaction was quenched by addition of water. The resulting mixture was extracted with ether (50 mL). The extract was washed with water, dried over MgSO₄, and evaporated. Chromatography was performed on the residue on a column of silica gel (100 g). The column was first eluted with hexane to remove excess **6a** and iodobenzene. The column was then eluted with a 9:1 mixture of hexane and CH₂Cl₂ to give 18 mg (5%) of **7a** and 17 mg (3%) of **8**, in that order. The column was further eluted with CH₂Cl₂ to give 10 mg (4%) of **9**, 18 mg (7%) of **5a**, TsNH₂, and 238 mg (61%) of **3b** in that order. Separation of all of these products by single column chromatography was not complete, and thus repurification of the mixture parts by further column chromatography was required in many cases.

Compound 3b: m.p. 130–131°C (from cyclohexane); ¹H NMR (400 MHz, CDCl₃) δ = 1.37 (s, 18H), 2.40 (s, 3H), 6.70 (s, 2H), 7.24 (d, *J* = 8 Hz, 2H), 7.76 (d, *J* = 8 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ = 21.4 (CH₃), 31.8 (CH₃), 36.4 (C), 127.0 (CH), 128.4 (CH), 129.2 (CH), 140.3 (C), 142.2 (C), 161.8 (C). Anal. calcd for C₁₉H₂₇NO₂S₂: C, 62.43; H, 7.45; N, 3.83. Found: C, 62.37; H, 7.44; N, 3.81.

Compound 5a: m.p. 155.0–155.5°C (from Et₂O/hexane); ¹H NMR (400 MHz, CDCl₃) δ = 1.38 (s, 18H), 2.40 (s, 6H), 7.13 (s, 2H), 7.21 (d, *J* = 8 Hz, 4H), 7.72 (d, *J* = 8 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃) δ = 21.6 (CH₃), 31.3 (CH₃), 36.7 (C), 125.9 (CH), 126.9 (CH), 129.3 (CH), 139.6 (C), 143.2 (C), 160.4 (C). Anal. calcd for C₂₆H₃₄N₂O₄S₃: C, 58.40; H, 6.41; N, 5.24. Found: C, 58.47; H, 6.42; N, 5.34.

Compound 8: m.p. 140–141°C (from pentane); ¹H NMR (400 MHz, CDCl₃) δ = 1.34 (s, 9H), 1.47 (s,

9H), 1.51 (s, 9H), 1.63 (s, 9H), 2.42 (s, 3H), 6.57 (s, 1H), 7.07 (s, 1H), 7.29 (d, $J = 8$ Hz, 2H), 7.85 (d, $J = 8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 21.6$ (CH_3), 31.7 (CH_3), 33.3 (CH_3), 34.58 (CH_3), 34.61 (CH_3), 36.9 (C), 37.1 (C), 37.3 (C), 38.6 (C), 57.2 (CH), 121.3 (CH), 127.0 (CH), 129.3 (CH), 137.5 (C), 138.2 (C), 143.2 (C), 145.7 (C), 149.0 (C), 152.1 (C), 167.0 (C), 183.8 (C). Anal. calcd for $\text{C}_{31}\text{H}_{45}\text{NO}_2\text{S}_3$: C, 66.50; H, 8.10; N, 2.50. Found: C, 66.67; H, 8.20; N, 2.40.

Compound 9: m.p. $> 167^\circ\text{C}$ (dec) (from Et_2O /hexane); ^1H NMR (400 MHz, CDCl_3) $\delta = 1.37$ (s, 9H), 1.47 (s, 9H), 2.42 (s, 3H), 2.50 (s, 3H), 4.38 (d, $J = 12$ Hz, 1H), 6.04 (d, $J = 12$ Hz, 1H), 7.27 (d, $J = 8$ Hz, 2H), 7.40 (d, $J = 8$ Hz, 2H), 7.74 (d, $J = 8$ Hz, 2H), 7.76 (d, $J = 8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 21.6$ (CH_3), 21.8 (CH_3), 31.6 (CH_3), 32.3 (CH_3), 36.9 (C), 37.7 (C), 67.0 (CH), 127.1 (CH), 127.8 (CH), 129.4 (CH), 130.4 (CH), 135.5 (C), 137.3 (C), 143.7 (C), 145.3 (C), 149.9 (C), 163.5 (C), 181.2 (C); IR (KBr) 3216 cm^{-1} (N-H). Anal. calcd for $\text{C}_{26}\text{H}_{34}\text{N}_2\text{O}_4\text{S}_3$: C, 58.40; H, 6.41; N, 5.24. Found: C, 58.44; H, 6.41; N, 5.17.

Cu(OTf)₂ as the Catalyst. A mixture of 500 mg (2.5 mmol) of **6a**, 200 mg (0.54 mmol) of TsN=IPh , and 15 mg (0.04 mmol) of Cu(OTf)_2 in 5 mL of MeCN was stirred for 2 hours at room temperature. The reaction mixture was worked up in a manner similar to that described previously give 64 mg (32%) of **3b**, 12 mg (8%) of **5a**, 7 mg (4%) of **7a**, 9 mg (3%) of **8**, and 4 mg (3%) of **9**.

Imination of 3,4-Di-tert-butylthiophene (6a) by N-[(benzenesulfonyl)imino]phenyliodinane ($\text{PhSO}_2\text{N=IPh}$)

A mixture of 1.00 g (5 mmol) of **6a**, 0.36 g (1 mmol) of $\text{PhSO}_2\text{N=IPh}$, and 18 mg (0.05 mmol) of $\text{Cu(MeCN)}_4\text{PF}_6$ in 20 mL of MeCN was stirred at room temperature for 1 hour. The resulting reaction mixture was purified in a manner similar to that of the reaction of **6a** with TsN=IPh to give 133 mg (38%) of the sulfilimine **3c**, 12 mg (5%) of the sulfone diimine **5c**, 22 mg (7%) of the pyrrole **7b**, and 52 mg (33%) of PhSO_2NH_2 .

Compound **3c**: m.p. $133\text{--}135^\circ\text{C}$; colorless crystals (from cyclohexane); ^1H NMR (CDCl_3 , 400 MHz) δ 1.37 (s, 18H), 6.70 (s, 2H), 7.43–7.53 (m, 3H), 7.88–7.90 (m, 2H); ^{13}C NMR (CDCl_3 , 100.6 MHz) δ 31.8, 36.5, 126.9, 128.3, 128.6, 131.6, 143.2, 162.0. Anal. calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_2\text{S}_2$: C, 61.50; H, 7.17; N, 3.99. Found: C, 61.39; H, 7.15; N, 3.93.

Compound **5c**: m.p. $184\text{--}187^\circ\text{C}$; colorless crystals (from hexane); ^1H NMR (CDCl_3 , 400 Hz) δ 1.38 (s, 18H), 7.15 (s, 2H), 7.42–7.46 (m, 4H), 7.52–7.55

(m, 2H), 7.83–7.85 (m, 4H). ^{13}C NMR (CDCl_3 , 100.6 MHz) δ 31.3, 36.7, 125.8, 126.8, 128.8, 132.6, 142.3, 160.7. Anal. calcd for $\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_4\text{S}_3$: C, 56.89; H, 5.97; N, 5.53. Found: C, 56.62; H, 5.89; N, 5.37.

Compound **7b**: m.p. $147\text{--}148^\circ\text{C}$; colorless crystals (from hexane); ^1H NMR (CDCl_3 , 400 MHz) δ 1.32 (s, 18H), 6.95 (s, 2H), 7.48–7.52 (m, 2H), 7.57–7.61 (m, 1H), 7.80–7.82 (m, 2H); ^{13}C NMR (CDCl_3 , 100.6 MHz) δ 32.3, 32.6, 118.6, 126.6, 129.2, 133.4, 138.2, 139.4. Anal. calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_2\text{S}$: C, 67.67; H, 7.89; N, 4.38. Found: C, 67.59; H, 7.88; N, 4.32.

Imination of 2,4-Di-tert-butylthiophene (6b) by N-[(p-tolylsulfonyl)imino]phenyliodinane (TsN=IPh)

A mixture of 400 mg (2 mmol) of **6b**, 373 mg (1 mmol) of TsN=IPh , and 20 mg (0.05 mmol) of $\text{Cu(MeCN)}_4\text{PF}_6$ in 10 mL of MeCN was stirred at room temperature for 1 hour. The resulting mixture was purified by silica-gel column chromatography to give 76 mg (20%) of the sulfilimine **3d**. Structures of other products, which were obtained in small amounts or in pure form, could not be elucidated.

Compound **3d**: m.p. $111\text{--}113^\circ\text{C}$; colorless crystals (from ether/hexane); ^1H NMR (CDCl_3 , 400 MHz) δ 1.21 (s, 9H), 1.35 (s, 9H), 2.40 (s, 3H), 6.12 (d, $J = 1$ Hz, 1H), 6.57 (d, $J = 1$ Hz, 1H), 7.25 (d, $J = 8$ Hz, 2H), 7.80 (d, $J = 8$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100.6 MHz) δ 21.4, 28.3, 30.6, 34.3, 35.9, 120.3, 126.7, 127.0, 129.2, 140.7, 142.0, 158.7, 161.4. Anal. calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_2\text{S}_2$: C, 62.43; H, 7.45; N, 3.83. Found: C, 62.35; H, 7.49; N, 3.78.

Reaction of Sulfilimine 3b with TsN=IPh

A mixture of 183 mg (0.5 mmol) of **3b**, 183 mg (0.5 mmol) of TsN=IPh , and 9 mg (0.03 mmol) of $\text{Cu(MeCN)}_4\text{PF}_6$ in 5 mL of MeCN was stirred for 5 hours at room temperature. Purification of the mixture by silica-gel column chromatography gave 26 mg (10%) of **5a**, 88 mg (48%) of **3b**, 28 mg (18%) of **7a**, and 37 mg (43%) of TsNH_2 .

Reaction of Sulfilimine 3b with $\text{PhSO}_2\text{N=IPh}$

A mixture of 366 mg (1.0 mmol) of **3b**, 360 mg (1.0 mmol) of $\text{PhSO}_2\text{N=IPh}$, and 20 mg (0.05 mmol) of $\text{Cu(MeCN)}_4\text{PF}_6$ in 10 mL of MeCN was stirred for 8 hours at room temperature. Purification of the mixture by silica-gel column chromatography gave 45 mg (14%) of a mixture of pyrroles **7a** and **7b** in the ratio of 15:85, 32 mg (6%) of sulfone diimine **5b**, 102 mg (67%) of a mixture of PhSO_2NH_2 and TsNH_2 in the ratio of 9:1, and 264 mg (72%) of sulfilimine **3b**.

Compound **5b**: m.p. 124–126°C; colorless crystals (from hexane); ^1H NMR (400 MHz, CDCl_3) δ 1.37 (s, 18H), 2.39 (s, 3H), 7.20 (d, J = 8.0 Hz, 2H), 7.41–7.45 (m, 2H), 7.51–7.55 (m, 1H), 7.70–7.73 (m, 2H), 7.85 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 21.5, 31.3, 36.7, 125.9, 126.82, 126.84, 128.7, 129.3, 132.5, 139.5, 142.4, 143.3, 160.5. Anal. calcd for $\text{C}_{25}\text{H}_{32}\text{N}_2\text{O}_4\text{S}_3$: C, 57.66; H, 6.19; N, 5.38. Found: C, 57.79; H, 6.24; N, 5.22.

Preparation of Sulfilimines **3b,c,e–h** from 3,4-Di-*tert*-butylthiophene 1-Oxide (**1a**)

By Use of $(\text{CF}_3\text{CO})_2\text{O}$. To a solution of 210 mg (1.0 mmol) of $(\text{CF}_3\text{CO})_2\text{O}$ in 5 mL of CH_2Cl_2 , cooled at -78°C was added 105 mg (0.5 mmol) of **1a** all at once. After the mixture had been stirred for 10 minutes at -78°C , 171 mg (1.0 mmol) of TsNH_2 was added quickly. The mixture was warmed slowly to room temperature. The reaction was quenched by addition of ice water. The organic layer was separated, washed with water, and then with aqueous NaHCO_3 , dried over MgSO_4 , and evaporated. The resulting residue was purified by passing it through a short column of silica gel to give 156 mg (86%) of **3b**. Sulfilimines **3c,e–h** were prepared in similar manners. In the case of **3g**, the reaction was quenched at -20°C ; quenching of the reaction at room temperature may result in a decrease of the yield because of partial decomposition of the product.

Compound **3e**: viscous oil; ^1H NMR (400 MHz, CDCl_3) δ 1.27 (t, J = 7.1 Hz, 3H), 1.42 (s, 18H), 4.13 (q, J = 7.1 Hz, 2H), 6.92 (s, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 14.7, 32.0, 36.5, 62.1, 128.5, 162.4, 166.0. HRMS calcd for $\text{C}_{15}\text{H}_{25}\text{NO}_2\text{S}$ m/z 283.1606 (M^+); Found, 283.1597. **3f**: m.p. 129–131°C (from hexane); ^1H NMR (400 MHz, CDCl_3) δ 1.42 (s, 18H), 1.49 (s, 9H), 6.92 (s, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 28.4, 32.0, 36.4, 79.4, 128.8, 162.2, 165.6. Anal. calcd for $\text{C}_{17}\text{H}_{29}\text{NO}_2\text{S}$: C, 65.55; H, 9.38; N, 4.50. Found: C, 65.63; H, 9.35; N, 4.49.

Compound **3g**: m.p. 90–91°C (from hexane); ^1H NMR (400 MHz, CDCl_3) δ 1.44 (s, 18H), 2.14 (s, 3H) 7.10 (s, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 23.4, 31.9, 36.5, 12.9, 162.7, 182.1. Anal. calcd for $\text{C}_{14}\text{H}_{23}\text{NOS}$: C, 66.36; H, 9.15; N, 5.53. Found: C, 66.55; H, 9.34; N, 5.48.

Compound **3h**: m.p. 110–111°C (from hexane); ^1H NMR (400 MHz, CDCl_3) δ 1.46 (s, 18H), 2.37 (s, 3H), 7.16 (d, J = 8 Hz, 2H), 7.22 (s, 2H), 7.97 (d, J = 8 Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 21.5, 32.1, 36.6, 127.4, 128.6, 128.8, 132.8, 141.0, 162.4, 177.4. Anal. calcd for $\text{C}_{26}\text{H}_{34}\text{N}_2\text{O}_4\text{S}_3$: C, 72.90; H, 8.26; N, 4.25. Found: C, 72.63; H, 8.35; N, 4.23.

By Use of $(\text{CF}_3\text{SO}_2)_2\text{O}$. To a solution of 170 mg (0.6 mmol) of $(\text{CF}_3\text{SO})_2\text{O}$ in 10 mL of CH_2Cl_2 , cooled at 0°C , was added 106 mg (0.5 mmol) of **1a** all at once. After the mixture had been stirred for 10 minutes at 0°C , a solution of 103 mg (0.6 mmol) of TsNH_2 in 10 mL of CH_2Cl_2 was added. The mixture was warmed slowly to room temperature. The reaction was quenched by addition of ice water. The organic layer was separated, washed with water and then with aqueous NaHCO_3 , dried over MgSO_4 , and evaporated. The resulting residue was purified by passing it through a short column of silica gel to give 144 mg (79%) of **3b**. Sulfilimine **3c** was also prepared in a similar manner.

Preparation of Sulfilimine **3i**

To a solution of 210 mg (1.0 mmol) of $(\text{CF}_3\text{CO})_2\text{O}$ in 10 mL of CH_2Cl_2 , cooled at -78°C , was added 106 mg (0.5 mmol) of **1a** all at once. After the mixture had been stirred for 1 hour at -78°C , a solution of 42 mg (1.0 mmol) of NCNH_2 in 10 mL of CH_2Cl_2 was added. The mixture was stirred at the same temperature for 2 hours and then warmed slowly to room temperature. The reaction was quenched by addition of ice water. The organic layer was separated, washed with water and then with aqueous NaHCO_3 , dried over MgSO_4 , and evaporated. The resulting crystalline residue was purified by passing it through a short column of silica gel to give 130 mg (85%) of **3i**: m.p. 158–160°C (from cyclohexane); ^1H NMR (400 MHz, CDCl_3) δ 1.46 (s, 18H), 7.15 (s, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 31.8, 36.9, 117.0 (q, $^1J(\text{C},\text{F})$ = 286 Hz), 125.2 (dt, $^5J(\text{C},\text{F})$ = 19, 86 Hz), 164.7, 167.3 (q, $^2J(\text{C},\text{F})$ = 35 Hz). Anal. calcd for $\text{C}_{14}\text{H}_{20}\text{F}_3\text{NOS}$: C, 54.71; H, 6.56; N, 4.56. Found: C, 54.80; H, 6.56; N, 4.44.

In a similar manner, 128 mg (83%) of **3i** was obtained from 106 mg (0.5 mmol) of **1a** and 50 mg (0.8 mmol) of H_2NCONH_2 .

Mutual Conversion between Sulfilimines: Conversion of **3b** to **3e**

To a solution of 105 mg (0.5 mmol) of $(\text{CF}_3\text{CO})_2\text{O}$ in 5 mL of CH_2Cl_2 , cooled at -78°C , was added 92 mg (0.25 mmol) of **3b** all at once. After the mixture had been stirred for 10 minutes at -78°C , a solution of 225 mg (2.5 mmol) of $\text{H}_2\text{NCO}_2\text{Et}$ in 5 mL of CH_2Cl_2 was added. The mixture was warmed slowly to -10°C . The reaction was quenched by addition of ice water. The organic layer was separated, washed with aqueous NaHCO_3 , and evaporated. The resulting residue was dissolved in 10 mL of ether, and the solution was washed with 2M NaOH , dried over

MgSO₄, and evaporated. The resulting residue was purified by passing it through a short column of silica gel to give 60 mg (85%) of **3e**.

Preparation of the Aminosulfonium Salt **13**

To a solution of 156 mg (0.5 mmol) of **3f** in 2.5 mL of CH₂Cl₂ was added 0.5 mL of CF₃CO₂H. After stirring for 3 hours, the volatiles were removed by evaporation. Dilution of the residue by 3 mL of cold ether gave 107 mg (66%) of the aminosulfonium salt **13**: m.p. 123–126°C (decomp.); colorless needles (from ether/hexane); ¹H NMR (400 MHz, CDCl₃) δ 1.44 (s, 18H), 6.97 (s, 2H), 7.16 (broad s, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 31.7, 37.0, 116.7 (q, ¹J(C,F) = 294 Hz), 126.5, 161.8 (q, ²J(C,F) = 34 Hz), 165.7. Anal. calcd for C₁₄H₂₂F₃NO₂S: C, 51.68; H, 6.82; N, 4.31. Found: C, 51.67; H, 6.79; N, 4.31.

Preparation of the Sulfilimine **3n**

To a suspension of 110 mg (0.34 mmol) of **13** in 10 mL of ether was added 10 mL of 0.1 M NaOH at room temperature. The mixture was stirred for 3 minutes, and the organic layer was separated, washed with water, dried over MgSO₄, and evaporated. The resulting residue was washed with pentane to give 63 mg (88%) of **3n** as a viscous oil that solidified in a refrigerator; ¹H NMR (400 MHz, CDCl₃) δ 1.44 (s, 18H), 2.34 (broad s, 1H, NH), 6.81 (s, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 32.1, 35.9, 135.1, 158.4. HRMS calcd for C₁₂H₂₁NS *m/z* 211.1395 (M⁺); Found, 211.1392.

Conversion of **3n** to **3b** (Tosylation of **3n**)

To a stirred and ice-cooled solution of 63 mg (0.3 mmol) of **3n** in 5 mL of CH₂Cl₂ was added dropwise a solution of 86 mg (0.5 mmol) of tosyl chloride in 5 mL of CH₂Cl₂. The mixture was warmed slowly to room temperature and stirred for 2 hours. The reaction was quenched by addition of ice water. The organic layer was separated, washed with aqueous NaHCO₃, dried over MgSO₄, and evaporated. The resulting residue was purified by passing it through a short column of silica gel to give 92 mg (84%) of **3b**.

Preparation of Sulfoximines **4b** and **4e** from **1a** and **1b**, respectively, by Treatment with TsN=IPh

A mixture of 103 mg (0.49 mmol) of **1a**, 215 mg (0.58 mmol) of TsN=IPh, and 4.8 mg (0.01 mmol) of Cu(MeCN)₄PF₆ in 4 mL of MeCN was stirred for 15 minutes at room temperature. AcOEt (30 mL) was

added to the reaction mixture, and the resulting mixture was washed with brine, dried over Na₂SO₄, and evaporated. Chromatography was performed on the residue on a column of silica gel (15 g). Elution of the column with a 1:3 mixture of AcOEt and hexane gave 124 mg (67%) of **4b**: m.p. 140.0–140.5°C; colorless needles (from hexane); ¹H NMR (400 MHz, CDCl₃) δ 1.41 (s, 18H), 2.41 (s, 3H), 6.92 (s, 2H), 7.29 (d, *J* = 8 Hz, 2H), 7.89 (d, *J* = 8 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 21.5, 31.5, 36.2, 126.6, 126.7, 129.4, 140.5, 143.0, 158.9; IR (KBr) 3110, 2867, 1316, 1303, 1266, 1222, 1153, 1081, 1061, 831, 745, 657 cm⁻¹. Anal. calcd for C₁₉H₂₇NO₃S₂: C, 59.81; H, 7.13; N, 3.67. Found: C, 59.97; H, 7.14; N, 3.67.

The sulfoximine **4e** was prepared in 81% yield by stirring a mixture of 212 mg (1 mmol) of **1b**, 453 mg (1.2 mmol) of TsN=IPh, and 8.7 mg of Cu(MeCN)₄PF₆ in 5 mL of MeCN for 20 minutes at room temperature.

Compound **4e**: m.p. 124.5–126.0°C; colorless needles (from hexane); ¹H NMR (300 MHz, CDCl₃) δ 1.19 (s, 9H), 1.36 (s, 9H), 2.42 (s, 3H), 6.55 (d, *J* = 1 Hz, 1H), 6.96 (d, *J* = 1 Hz, 1H), 7.29 (d, *J* = 8 Hz, 2H), 7.89 (d, *J* = 8 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 21.5, 27.6, 29.5, 33.7, 35.6, 121.3, 124.9, 126.5, 129.3, 141.0, 142.7, 153.3, 153.9. Anal. calcd for C₁₉H₂₇NO₃S₂: C, 59.81; H, 7.13; N, 3.67. Found: C, 59.83; H, 7.20; 3.66.

Preparation of Sulfoximine **4b** from **1a** and TsN₃

Activated copper, prepared from 2.11 g of CuSO₄ · 5H₂O and 0.78 g of zinc powder, was washed with 2 M HCl, water, and MeOH successively, and suspended in 20 mL of MeOH. To this suspension were added 213 mg (1.0 mmol) of **1a** and 591 mg (2.9 mmol) of TsN₃. The mixture was heated at reflux for 3 hours and filtered while hot. The insoluble materials were washed with CH₂Cl₂. The filtrate and washings were combined, washed with water, dried over Na₂SO₄, and evaporated. The resulting residue was chromatographed on a column of silica gel (50 g) with CH₂Cl₂ as the eluent to give 138 mg (35%) of **4b**.

Conversion of Sulfoximines **4b** and **4e** to the Corresponding *N*-Unsubstituted Sulfoximines **4c** and **4f**

Sulfoximine **4b** (77 mg, 0.20 mmol) was added to 1.0 mL of concentrated H₂SO₄ under stirring. The resulting homogeneous mixture was added slowly to 20 mL of a 20% NaOH solution under ice-cooling. The mixture was extracted with CH₂Cl₂, and the ex-

tract was washed with water, dried over Na_2SO_4 , and evaporated to give 43 mg (95%) of the N-unsubstituted sulfoximine **4c**: m.p. 95.5–96.0°C; colorless needles (from hexane); ^1H NMR (400 MHz, CDCl_3) δ 1.40 (s, 18H), 2.97 (broad s, 1H, NH), 6.53 (s, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 31.6, 35.4, 129.4, 155.0; IR (KBr) 3156 (NH), 3112, 2964, 1238, 1222, 1210, 1006 (SO), 994 cm^{-1} . Anal. calcd for $\text{C}_{12}\text{H}_{21}\text{NOS}$: C, 63.39; H, 9.31; 6.16. Found: C, 63.49; H, 9.41; N, 6.15.

The N-unsubstituted sulfoximine **4f** was prepared in 89% yield by treatment of 299 mg of **4e** with 3 mL of concentrated H_2SO_4 .

Compound **4f**: m.p. 82.5–83.5°C (racemate); colorless needles (from hexane); ^1H NMR (400 MHz, CDCl_3) δ 1.17 (s, 9H), 1.42 (s, 9H), 2.96 (broad s, 1H, NH), 6.12 (d, $J = 1$ Hz, 1H), 6.29 (d, $J = 1$ Hz, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 27.7, 29.6, 33.1, 35.1, 120.1, 122.8, 152.7, 156.0; UV-vis (CH_2Cl_2) λ_{max} (ϵ) 245 (1880), 279 (2130), 315 nm (sh). Anal. calcd for $\text{C}_{12}\text{H}_{21}\text{NOS}$: C, 63.39; H, 9.31; 6.16. Found: C, 63.56; H, 9.42; N, 6.12.

Preparation of **4d**: N-Methylation of **4b**

A mixture of 62 mg (0.27 mmol) of **4b** and 81 mg (0.55 mmol) of $\text{Me}_3\text{O}^+\text{BF}_4^-$ in 6 mL of CH_2Cl_2 was stirred overnight at room temperature. Since the progress of the methylation was sluggish, an additional 81 mg (0.55 mmol) of $\text{Me}_3\text{O}^+\text{BF}_4^-$ was added, and the mixture was stirred for an additional 8 hours. The reaction was quenched by addition of water. The organic layer was washed with water, dried over Na_2SO_4 , and evaporated. The residue was purified by preparative thin-layer chromatography (TLC) with a 1:1 mixture of AcOEt and hexane as the eluent to give 28 mg (43%) of **4d** and 25 mg (40%) of **4b**.

Compound **4d**: m.p. 117–118°C; yellow powder (from hexane); ^1H NMR (400 MHz, CDCl_3) δ 1.23 (s, 18H), 2.95 (s, 3H), 6.57 (s, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 31.1, 31.7, 35.5, 126.5, 155.4. Anal. calcd for $\text{C}_{13}\text{H}_{23}\text{N}_2\text{S}$: C, 64.68; H, 9.60; N, 5.80. Found: C, 64.78; H, 9.69; N, 5.76.

Optical Resolution of (R)-**4f** and (S)-**4f**

Optical resolution was done by HPLC on a chiral column CHIRALPAK AD (4.6 mm i.d. $\times$ 250 mm; Daicel Chemical Industries, Ltd.) using a UV detector of 254 nm. A 1.3 mg sample of **4f** was charged, with a 98.5:1.5 mixture of hexane and ethanol being used as the eluent at a flow rate of 1.0 mL/min. Under these conditions, retention times of (R)-**4f** and (S)-**4f** were 44 and 54 minutes, respectively. Many runs

were carried out to collect enough samples for determination of CD spectra and X-ray crystallographic analysis.

X-Ray Crystallographic Analyses of **3b**, **5a**, **9**, and (S)-**4f**

Crystal data are for **3b**, **5a**, **9**, and (S)-**4f** are given in Table 5.

The crystal data for **3b**, **5a**, and **9** were recorded on a Mac Science DIP3000 diffractometer equipped with a graphite monochromator. Oscillation and nonscreen Weissenberg photographs were recorded on the imaging plates of the diffractometer by using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å), and the data reduction was made by the MAC DENZO program system. Cell parameters were determined and refined by using the MAC DENZO for all observed reflections. The structure was solved by direct methods using SIR in the CRYSTAN-GM program system. The atomic coordinates and anisotropic thermal parameters of the non-H atoms were refined by full-matrix least squares.

The crystal data for (S)-**4f** was recorded on a Mac Science MXC3K diffractometer, Cu $\text{K}\alpha$ radiation ($\lambda = 1.54178$ Å) with a graphite crystal monochromator in the incident beam. The unit cell dimensions were obtained by a least-squares fit of 22 automatically centered reflections in the range of $56.5 < 2\theta < 59.9^\circ$. Intensity data were collected using ω - 2θ scan method in the range $3 < 2\theta < 40^\circ$. The scan width, $\Delta\omega$, for each reflection was $2.34 + 0.2\tan\theta$, with a scan speed of $6.0^\circ \text{ min}^{-1}$. The structure was solved by direct methods using SIR92 [28] in the CRYSTAN-GM program system. The atomic coordinates and the anisotropic thermal parameters of the non-H atoms were refined by full-matrix least squares [29] to minimize functions $\sum w(|F_o| - |F_c|)^2$.

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