Catalytic Asymmetric Sulfimidation

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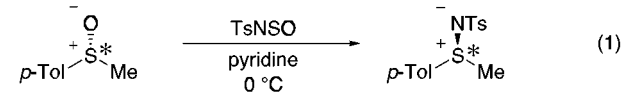
A direct catalytic imidation of sulfides to sulfimides with [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane (TsN═IPh) using a catalytic amount of copper triflate (CuOTf) has been developed. The reaction proceeds with a wide range of sulfides to give the corresponding sulfimides in 50−83% isolated yields. When the reaction is applied to allylic sulfides, the products are the corresponding sulfonamides produced via [2,3] sigmatropic rearrangement of the initially formed allylic sulfimides. In the presence of a chiral bis(oxazoline) as ligand, asymmetric induction occurs to afford the chiral sulfimides (up to 71% ee) and sulfonamides (up to 58% ee). Chloramine T (TsNClNa) can be used in place of TsN═IPh for asymmetric sulfimidation, but the ee's are much lower. Some mechanistic observations are described.

Introduction

Although the chemistry of chiral sulfoxides[1,2] and sulfonium ylides[3−5] has been investigated with a good deal of success, the study of their nitrogen analogues, sulfimides,[6] remains underdeveloped, partly as the methods for preparation of enantiomerically enriched sulfimides are limited to (a) the conversion of chiral sulfoxides to the corresponding enantiomerically pure sulfimides, as reported by Cram *et al.*,[7] and (b) the kinetic resolution of racemic sulfimides reported by Annunziata *et al.*,[8] as shown in eqs 1 and 2.



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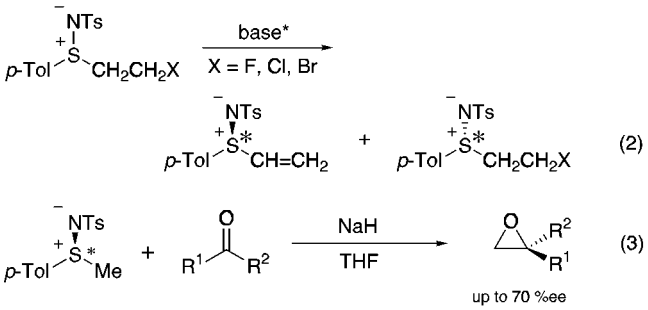
Very recently, chiral sulfimides were demonstrated by ourselves to be useful asymmetric methylidene transfer reagents to prochiral carbonyl groups in the presence of a base such as sodium hydride (eq 3),[9a] the products being



(2)

(3)

enantiomerically enriched epoxides (up to 70% ee). Furthermore, the analogous reaction of imines, to give chiral aziridines, has given some promising results.[9b] Development of a simple new method for asymmetric synthesis of sulfimides is thus most timely.

Recently, Evans reported that [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane (TsN═IPh) is an effective asymmetric nitrene transfer reagent to alkenes in the presence of a catalytic amount of a copper(I) salt and a chiral bis(oxazoline) ligand.[10] Jacobsen has investigated the mechanism of this reaction using (diimine)copper(I) catalysts and obtained strong evidence for a discrete copper(III)−nitrene complex as a reactive intermediate.[11] These

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

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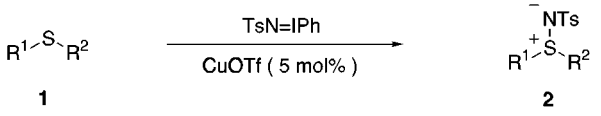
Table 1. Catalytic Sulfimidation of Sulfides 1[a]



1 2

entry	substrate	R^1	R^2	product	yield, %
1	**1a**	Tol	Me	**2a**[b]	83
2	**1b**	Ph	Me	**2b**	79
3	**1c**	Ph	*i*-Pr	**2c**	81
4	**1d**	Ph	Bn	**2d**	82
5	**1e**	4-$MeOC_6H_4$	Bn	**2e**	70
6	**1f**	2-$NO_2C_6H_4$	Bn	**2f**	53
7	**1g**	Ph	4-$NO_2C_6H_4CH_2$	**2g**	72
8	**1h**	1-naphthyl	Bn	**2h**	54
9	**1i**	Ph	Ph	**2i**[b]	79
10	**1j**	$PhCH_2CH_2$	Ph	**2j**[b]	50
11	**1k**	Et	Me	**2k**[c]	50
12	**1l**	EtO_2CCH_2	Me	**2l**	53

[a] All reactions were carried out in acetonitrile with 1.0 equiv (to TsN=IPh) of sulfide in the presence of 5 mol % Cu(I) catalyst at 25 °C for 48 h unless otherwise noted. [b] For 26 h. [c] For 28 h.

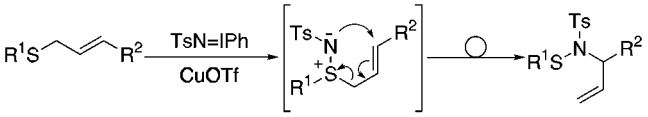
reports prompted us to apply this methodology to the synthesis of chiral sulfimides. We present here a simple method for the direct sulfimidation of a variety of sulfides to yield the corresponding sulfimides (and sulfonamides), either as racemates or enantiomerically enriched.[12]

Results and Discussion

Racemic Syntheses. First, we wished to explore a new method for imidation of sulfides with TsN=IPh[13] using a copper(I) salt as a catalyst.[14] All experiments were performed by stirring equimolar amounts of the sulfide and TsN=IPh in acetonitrile in the presence of 5 mol % catalyst; acetonitrile has been reported to be the solvent of choice in aziridination of alkenes with TsN=IPh.[14] The results are summarized in Table 1. The reaction proceeded well with a variety of sulfides to give the corresponding sulfimides in 50−83% isolated yields. Aromatic sulfides **1a**−**i** bearing either an electron-releasing or an electron-withdrawing moiety on the ring gave the products in higher yields than aliphatic sulfides **1j**−**l**. As this reaction is believed to proceed by a nitrene mechanism, we anticipate that it may have applications to substrates where conventional ionic sulfimidation methods fail.

When the reaction was applied to allylic sulfides **3**, the expected aziridination of the double bond[10,11,14] did not occur. Instead, a range of allylic sulfonamides **5** was obtained selectively in good yields. The results are summarized in Table 2. For example, treatment of allyl methyl sulfide (**3a**) with TsN=IPh at room temperature for 48 h afforded the corresponding sulfonamide **5a** in 78% isolated yield. Similarly, aromatic and aliphatic allylic sulfides could be converted smoothly to the corresponding sulfonamides in 35−82% isolated yields. It seems likely that the sulfimides **4** are formed as intermediates and that a [2,3] sigmatropic rearrangement follows.[15]

Table 2. Catalytic Synthesis of Sulfonamides 5[a]



3 4 5

entry	substrate	R^1	R^2	product	yield, %
1	**3a**	Me	H	**5a**	78
2	**3b**	allyl	H	**5b**	82
3	**3c**	Ph	Ph	**5c**	75
4	**3d**	2-$NO_2C_6H_4$	Ph	**5d**	35
5	**3e**	1-naphthyl	Ph	**5e**	80
6	**3f**	Ph	Me	**5f**	44
7	**3g**	1-naphthyl	Me	**5g**	55

[a] All reactions were carried out in acetonitrile with 1.0 equiv (to TsN=IPh) of allylic sulfide in the presence of 5 mol % Cu(I) catalyst at 25 °C for 48 h.

Asymmetric Syntheses. For the initial investigation of the asymmetric sulfimidation reaction, a variety both of chiral bis(oxazoline) ligands **6a**−**e** and of solvents were examined using either methyl *p*-tolyl sulfide (**1a**) or benzyl phenyl sulfide (**1d**) as a substrate. The ligand favored by Jacobsen for asymmetric aziridination[11] is, in our hands, ineffective for asymmetric sulfimidation.

All experiments were performed using 5−10 mol % of the catalyst derived from copper(I) triflate (CuOTf) and the indicated bis(oxazoline) ligand and proceeded smoothly to give the expected sulfimides in 56−80% yield. As can been seen in Table 3, asymmetric induction occurred, but the nature of the sulfide, the solvent, and the chiral ligand all had significant effects on the enantioselectivity. Asymmetric induction was poor in acetonitrile with all of the bis(oxazoline) ligands (less than 22% ee), but the change of the solvent from acetonitrile to toluene led to good enantioselectivities. The highest ee's were observed with **1d** (65% ee) using **6a** as a chiral ligand in toluene (entry 11). In toluene the reaction at 25 °C gave a similar result (entry 12). As to the effectiveness of ligands, **6a** gave the best result followed by **6e** and then **6b**, **6c**, and **6d** (entries 11, 21, 15, 17, and 19) in the imidation of **1d** with TsN=IPh in toluene.

Next, we examined the effect of the nature of copper salts upon both the yield and the enantioselectivity (Table 4). Among the copper salts investigated, a copper(I) salt, CuOTf, was revealed to give both the highest yield (78%) and ee (65% ee) in the sulfimidation process (entry 1). In the cases of other copper salts such as $CuPF_6(CH_3CN)_4$[16] and copper(II) triflate, the enantioselectivity was lower (entries 2 and 3).

From these results, the optimum conditions for asymmetric sulfimidation were judged to be copper(I) triflate with chiral ligand **6a** in toluene at 25 °C for 48 h. We then applied this condition to a variety of sulfides. The results are summarized in Table 5 and indicate that a higher enantioselectivity was generally obtained in the cases of diaryl sulfides than those of alkyl aryl sulfides and dialkyl sulfides. The highest enantioselectivity (71% ee) was obtained with the sulfide **1h**.

In the asymmetric reaction of allylic aryl sulfides **3**, the corresponding chiral allylic sulfonamides **5** were

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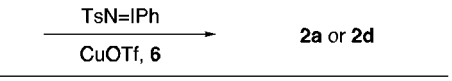
Table 3. Effect of Chiral Ligands and Solvent on Asymmetric Induction[a]



entry	substrate	chiral ligand	solvent	temp, °C	product[b]	ee, %[c]
1	**1a**	**6a**	MeCN	0	**2a**	<5
2	**1a**	**6a**	toluene	0	**2a**	16
3	**1a**	**6a**	toluene	25	**2a**	13
4	**1a**	**6b**	MeCN	0	**2a**	<5
5	**1a**	**6b**	toluene	0	**2a**	<5
6	**1a**	**6c**	MeCN	0	**2a**	<5
7	**1a**	**6c**	toluene	0	**2a**	<5
8	**1a**	**6d**	MeCN	0	**2a**	<5
9	**1a**	**6d**	toluene	0	**2a**	<10
10	**1d**	**6a**	MeCN	0	**2d**	12
11	**1d**	**6a**	toluene	0	**2d**	65
12	**1d**	**6a**	toluene	25	**2d**	64
13	**1d**	**6a**	CH_2Cl_2	0	**2d**	35
14	**1d**	**6b**	MeCN	0	**2d**	<5
15	**1d**	**6b**	toluene	0	**2d**	34
16	**1d**	**6c**	MeCN	0	**2d**	<5
17	**1d**	**6c**	toluene	0	**2d**	<5
18	**1d**	**6d**	MeCN	0	**2d**	<5
19	**1d**	**6d**	toluene	0	**2d**	<5
20	**1d**	**6e**	MeCN	0	**2d**	22
21	**1d**	**6e**	toluene	0	**2d**	55

[a] Sulfide (0.2 mmol), TsN=IPh (0.2 mmol),CuOTf (5 mol %), and chiral ligand **6** (6 mol %) were used. For 48 h. [b] The chemical yields of **2a** and **2d** are 56−80%. [c] Enantiomeric excesses were determined by HPLC using suitable chiral columns.

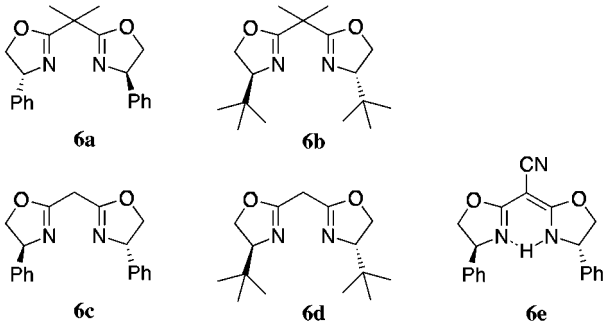
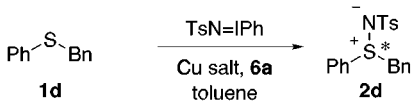


Table 4. Effect on Copper Salt on Asymmetric Induction[a]

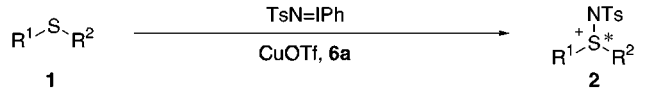


entry	copper salts	yield, %	ee, %[b]
1	$CuOTf(C_6H_6)_{0.5}$	78	64
2	$CuPF_6(CH_3CN)_4$	66	26
3	$Cu(OTf)_2$	74	25

[a] **1d** (0.2 mmol), TsN=IPh (0.2 mmol), Cu salt (5 mol %), **6a** (6 mol %), and toluene (1.0 mL) were used. At 25 °C for 48 h. [b] Enantiomeric excesses were determined by HPLC using suitable chiral columns.

obtained, indicating that chirality is transfered in the [2,3] sigmatropic rearrangement of the intermediate chiral allylic sulfimides.[17] The results are summarized in Table 6. Once again, the sulfide containing 1-naphthyl moiety gave the highest enantioselectivity (58% ee). As to the absolute configuration of the product, (−)-methyl *p*-tolyl sulfimide **2a** has been assigned to be the *S*-

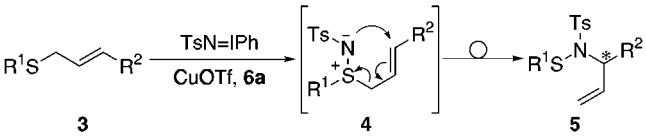
Table 5. Catalytic Asymmetric Sulfimidation of Sulfides 1[a]



entry	sub-strate	R^1	R^2	product	yield, %	ee, %[b]
1	**1a**	Tol	Me	**2a**	82	13[e]
2	**1b**	Ph	Me	**2b**	78	<10
3	**1c**	Ph	*i*-Pr	**2c**	44	23
4	**1d**	Ph	Bn	**2d**	78	64[e]
5	**1e**	4-$MeOC_6H_4$	Bn	**2e**	72	<10
6	**1f**	2-$NO_2C_6H_4$	Bn	**2f**	54	<10
7	**1g**	Ph	4-$NO_2C_6H_4CH_2$	**2g**	37	25
8	**1h**	1-naphthyl	Bn	**2h**	75	71
9	**1i**	$PhCH_2CH_2$	Ph	**2j**	63	22[c]
10	**1k**	Et	Me	**2k**	36	<10[c]
11	**1l**	EtO_2CCH_2	Me	**2l**	41	<10[c]
12	**1m**	Bn	Me	**2m**	70	15

[a] Sulfide (0.2 mmol), PhI=NTs (0.2 mmol), CuOTf (5 mol %), **6a** (6 mol %), and toluene (1.0 mL) were used. At 25 °C for 48 h. [b] Enantiomeric excesses were determined by HPLC using suitable chiral columns. [c] ^{1}H NMR analysis (270 MHz) in the presence of $Eu(hfc)_3$. [d] ^{1}H NMR analysis (400 MHz) in the presence of (trifluoromethyl)anthrylethanol. [e] Both methods *b* and *d*.

Table 6. Catalytic Asymmetric Imidation of Various Allylic Sulfides[a]



entry	substrate	R^1	R^2	product	yield, %	ee, %[b]
1	**3c**	Ph	Ph	**5c**	40	27
2	**3d**	2-$NO_2C_6H_4$	Ph	**5d**	37	43
3	**3e**	1-naphthyl	Ph	**5e**	80	58
4	**3f**	Ph	Me	**5f**	30	25[c]
5	**3g**	1-naphthyl	Me	**5g**	35	50[c]

[a] **3** (0.2 mmol), TsN=IPh (0.2 mmol), CuOTf (5 mol %), **6a** (6 mol %), and toluene (1.0 mL) were used. At 25 °C for 48 h. [b] Enantiomeric excesses were determined by HPLC using suitable chiral columns after products were converted to the corresponding amine by treatment with NaOH in MeOH. [c] Enantiomeric excess was determined by ^{1}H NMR analysis (270 MHz) in the presence of $Eu(hfc)_3$.

enantiomer.[7,18] Since our product has a (+) optical rotation, the absolute configuration of this imide is *R*. The absolute configuration of other sulfimides is not yet known,[19] but may well be *R* by analogy with **2a**.

Mechanistic Observations. There are a number of variables in the asymmetric sulfimidation reaction. Some mechanistic implications of the following will be discussed in detail: (1) the structure of the sulfide; (2) the structure of the chiral ligand; (3) the nitrene source; (4) the solvent; (5) the copper salt.

It should be noted that *in general* changing the temperature has only a limited effect on the yield and ee.

1. Structure of the Sulfide. We will first consider just three of the sulfides **1d**, **1e**, and **1f** and the ee for their sulfimidation with TsN=IPh (Table 5). There is clearly no variation in the steric environment of the sulfur centers, and it is difficult to explain the results

(17) Similar phenomena have been observed in chiral selenimides and tellurimides: (a) Nishibayashi, Y.; Chiba, T.; Ohe, K.; Uemura, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1243. (b) Nishibayashi, Y.; Srivastava, S. K.; Ohe, K.; Uemura, S. *Tetrahedron Lett.* **1995**, *36*, 6725.

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(19) Many attempts to obtain good crystals of enantiopure **2d** and **2h** for X-ray determination, which were obtained as colorless needles by one recrystallization from CH_2Cl_2−diethyl ether, were unsuccessful.

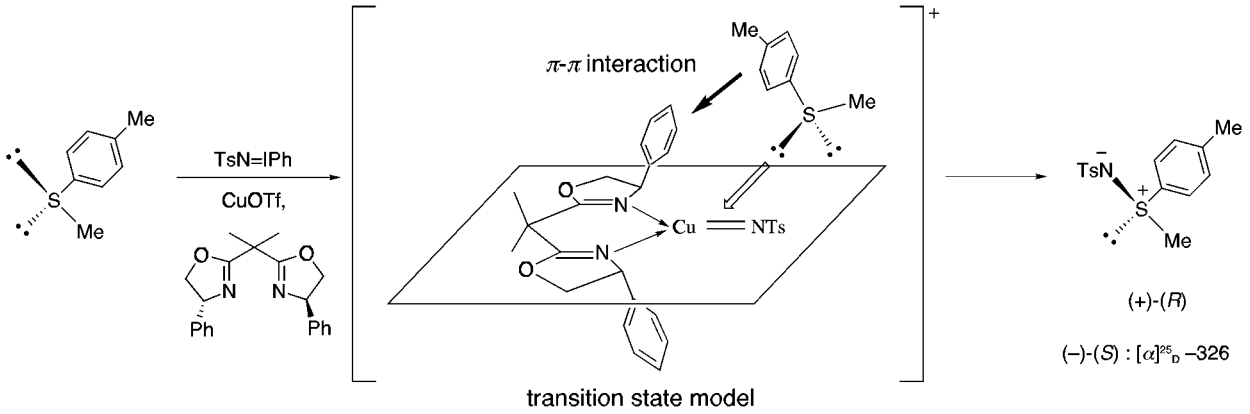


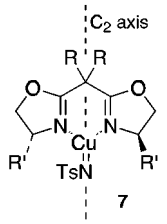
Figure 1. Proposed transition state model for asymmetric sulfimidation.

on electronic grounds. We therefore propose that the markedly lower ee's for **1e** and **1f** are due to competing coordination of copper by the methoxy and nitro groups, respectively. We will thus exclude **1e**, **1f**, **1g**, and **1l** from further discussion and concentrate on the remaining sulfides, in which sulfur is the only heteroatom.

When the remaining entries are studied, a counterintuitive conclusion emerges that the *highest ee's are found with two large groups*. In particular, methyl sulfides uniformly lead to very low ee's (entries 1, 2, 10, 11, and 12) and high ee's are observed for entries 4 and 8, which both have two large substituents, both of which have aromatic π systems. Possible implications of these observations are discussed in section 2.

2. Structure of the Ligand. Five different ligands, *all of C_2 symmetry*, have been employed in asymmetric sulfimidation, namely, compounds **6a**−**e**. It is interesting to compare the very similar **6a** and **6c** and also **6b** and **6d**. In all cases, the *gem*-dimethyl compounds **6a** and **6b** gave higher ee's than their methylene analogues. For example, in sulfimidation of benzyl phenyl sulfide (**1d**) the dimethyl ligand **6a** gave 65% ee, whereas **6c** gave 3% ee.

Considering this *gem*-dimethyl effect alongside the observation in section 1 that two large groups are required for high ee leads us to propose the following hypothesis. By analogy with Jacobsen's work,[11] we propose that the reaction proceeds *via* intermediates **7**.



7

To gain maximum asymmetric induction, it is important that the sulfide approaches the complex in such a way that its substituents interact with the substituents on the oxazolidine (phenyl or *tert*-butyl). We suggest that the bulky *gem*-dimethyl group in **6a** and **6b** will help to direct the sulfide into such an orientation and that this directing effect will be most marked with sulfides bearing two bulky substituents.

However, the above hypothesis is not consistent with the 55% ee observed for the sulfimidation of benzyl phenyl sulfide with **6e**, which does not have a *gem*-dimethyl bridging group. This leads us to consider another set of interactions, depicted in Figure 1. Thus, the approach of the sulfide to the nitrene complex may be favored from the side where a $\pi-\pi$ interaction between the aryl group of the substrate and the phenyl group of chiral ligand **6a** can occur. This may also explain why a higher ee was observed with the substrate having a 1-naphthyl group, where more efficient π-stacking is expected. However, it is difficult to explain why ligand **6b**, which has no phenyl substituents, is superior to ligand **6c** which does. Nevertheless, this model does predict the observed *R*-configuration for **2a**.

3. Nitrene Source. All the reactions described so far have employed TsN=IPh as the nitrene source. However, TsN=IPh requires a two-step preparation[13] and we therefore decided to try replacing it with Chloramine T, TsNClNa, which is commercially available and very cheap. Indeed, Chloramine T is the reagent routinely used in the uncatalysed racemic synthesis of sulfimides from sulfides.[6] In our hands, tosyl azide, which was the nitrene source used in the original report of copper-catalyzed sulfimidation,[20] gave unreliable results for asymmetric sulfimidation.

We investigated the use of Chloramine T in the asymmetric sulfimidation reaction with chiral ligands **6a** and **6c** in toluene. Comparison of the data with that from the corresponding TsN=IPh reactions revealed striking resemblances. In particular, ligand **6a** appeared once again to be superior to ligand **6c** and reaction times and yields were very similar. However, the ee's with Chloramine T were *much lower in all cases* (Table 7).

We concluded that the reaction mechanisms with both TsN=IPh and Chloramine T must be similar but that a subtle effect was leading to reduced enantioselectivity. We thus considered the byproducts of the reactions, namely, iodobenzene (from TsN=IPh) and sodium chloride (from TsNClNa). Indeed, it seemed feasible that the ionic sodium chloride would be more likely to interfere with the copper coordination complex than iodobenzene. In particular, the presence of chloride (from CuCl) has been noted by Evans to be detrimental to aziridination.[14]

To test this hypothesis we repeated the TsN=IPh reactions in the presence of 5 mol % sodium chloride. The yields and reaction times were very similar to those for salt-free reactions, but there was a drastic decrease in ee (e.g., 74% to <10 % for benzyl phenyl sulfide (**1d**)) (Table 7). We therefore conclude that commercially available Chloramine T is potentially as effective as the

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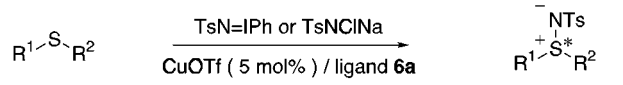
Table 7. Sulfimidation with TsN=IPh vs TsNClNa for Sulfides 1a, 1d, and 1m[a]



1 2

entry	TsN=X	substrate	R^1	R^2	time, h	yield, %	ee, %
1	TsN=IPh	**1a**	Tol	Me	48	81	14
2		**1d**	Ph	Bn	72	67	74
3		**1m**	Bn	Me	48	70	15
4	TsN=IPh	**1a**	Tol	Me	48	79	<10
5	+5 mol %	**1d**	Ph	Bn	72	66	<10
6	NaCl	**1m**	Bn	Me	48	68	<10
7	TsNClNa	**1a**	Tol	Me	48	80	<10
8		**1d**	Ph	Bn	72	61	<10
9		**1m**	Bn	Me	48	75	<10

[a] All reactions were carried out in toluene with 1.0 equiv (to TsN=X) of sulfide in the presence of 5 mol % Cu(I) catalyst and ligand **6a** at 0 °C.

less accessible TsN=IPh in the asymmetric sulfimidation reaction, if the detrimental effect of sodium chloride can be countered. The apparent mechanistic similarity of the reactions of TsN=IPh and Chloramine T suggests a common copper(III) nitrene intermediate, which is particularly interesting as nitrenes and nitrenoids are not usually invoked in the chemistry of Chloramine T.

4. Solvent. Copper(I) catalyzed sulfimidation occurs in a very wide range of solvents. However, as remarked earlier, acetonitrile is the solvent of choice for racemic sulfimidations with TsN=IPh but is detrimental to asymmetric sulfimidations, where toluene is preferred. The simplest explanation for these phenomena is that for efficient copper−nitrenoid formation additional nitrogen ligands are required. In the racemic reactions this role is fulfilled by acetonitrile, whereas in the asymmetric reactions it is the chiral ligand which is coordinated to copper. In the latter case, any acetonitrile present will compete for the ligand sites on copper, leading to lower ee's.

5. Copper Salt. Both $CuPF_6(CH_3CN)_4$ and copper(II) triflate have been shown by Evans and Jacobsen to be effective catalysts for aziridination.[10,11,14] However, as mentioned above, both were inferior to copper(I) triflate for asymmetric sulfimidation. We speculate that this may be due to interference from the acetonitrile ligands in the former case (see section 4) and due to the poorer solubility of the copper(II) salt in the latter.

Conclusion

Racemic catalytic sulfimidation of various sulfides with TsN=IPh in the presence of copper(I) triflate produced the corresponding sulfimides in 50 to 83% isolated yields, in acetonitrile as solvent. Using chiral bis(oxazoline) ligand **6a**, the first asymmetric sulfimidation was accomplished, in toluene as solvent. Enantioselectivities of 0−71% were observed; these were highest for sulfides with two aromatic (or partly aromatic) substituents. The reasons for this are unclear, but it appears that oxazolines which have the possibility of π-stacking interactions and which block approach in a plane containing the C_2 axis lead to highest ee's.

Chloramine T can also be used as a nitrene source, but the presence of the sodium chloride byproduct lowers the enantioselectivities. Similarly, other copper salts can be employed, but enantioselectivities are not as good.

With allylic sulfides, the initially produced allylic sulfimides are converted to the corresponding sulfonamides by [2,3] sigmatropic rearrangement; chirality transfer is observed when a chiral ligand is employed.

Experimental Section

General. ^1H and ^{13}C NMR spectra were measured at 270 and 400 MHz for solutions in $CDCl_3$ with Me_4Si as an internal standard: the following abbreviations are used; s, singlet; d, doublet; q, quartet; qui, quintet; m, multiplet. IR spectra were recorded on an FT-IR spectrometer. Melting points are uncorrected. HPLC analyses were performed at 40 °C. Elemental analyses were performed at Microanalytical Center of Kyoto University and at Warwick University. 4,4′-Disubstituted bis(oxazoline)s **6a**−**c**, $Eu(hfc)_3$, and (trifluoromethyl)anthrylethanol were purchased from Aldrich Chemical Co. Dichloromethane was distilled from CaH_2, and acetonitrile and toluene were distilled from P_2O_5 just before use.

Preparation of [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane.[13] Diacetoxyiodobenzene (10.6 g, 33 mmol) was added to an ice-cold stirring solution of *p*-toluenesulfonamide (5.65 g, 33 mmol) and potassium hydroxide (4.63 g, 83 mmol) in 115 mL of dry methanol. The solution was maintained at 0 °C for 30 min and then allowed to warm up to room temperature. Stirring was continued for 3 h, and then ice-cold H_2O (*ca.* 115 mL) was poured into the reaction mixture which was allowed to stand overnight to precipitate a yellow solid. The pale yellow precipitate (12.1 g) was collected by suction filtration and dissolved in hot dry methanol (60 mL). The solution was stood overnight at 0 °C, and the precipitated pale yellow solid was collected by suction filtration and thoroughly washed with the mother liquid to afford [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane (5.91 g, 15.8 mmol, 48%) as an off-white powdery solid: mp 104.0−105.0 °C dec (lit.[13] mp 102−104 °C, dec).

Typical Procedure for the Imidation of Sulfide. To a solution of CuOTf (2.59 mg, 0.010 mmol, 0.050 equiv) in 1.0 mL of acetonitrile were added first TsN=IPh (75.0 mg, 0.20 mmol, 1.0 equiv) and then the sulfide (0.20 mmol, 1.0 equiv), and the resulting mixture was stirred under nitrogen at 25 °C for appropriate time as shown in Tables 1 and 2. The mixture was then added with brine and extracted with dichloromethane. The extract was dried over anhydrous $MgSO_4$, and the evaporation of the solvent left a crude product. Purification by silica gel column chromatography gave the corresponding pure sulfimide or sulfonamide, representative spectroscopic and analytical data being shown below. The sulfimides (sulfilimines) **2f**, **2g**, **2h**, **2l**, and **2m** and the sulfonamides **5a**, **5d**, **5e**, **5f**, and **5g** are new compounds.

***S*-Methyl-*S*-*p*-tolyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2a):** colorless needles; 83% yield; eluent, Et_2O/MeOH = 25/1; mp 124.0−125.0 °C (lit.[21] mp 125−126 °C); ^1H NMR δ 2.34 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.81 (s, 3H, CH_3), 7.13−7.73 (m, 8H).

***S*-Methyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2b):** colorless needles; 79% yield; eluent, Et_2O/MeOH = 25/1; mp 131.5−132.0 °C (lit.[22] mp 131−132 °C); ^1H NMR δ 2.32 (s, 3H, CH_3), 2.81 (s, 3H, CH_3), 7.12−7.71 (m, 9H).

***S*-Isopropyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2c):** colorless needles; 81% yield; eluent, Et_2O/MeOH = 25/1; mp 96.0−97.0 °C (lit.[23] mp 98.5−99.5 °C); ^1H NMR δ 1.18 (t, J = 6.8 Hz, 6H, CH_3), 2.33 (s, 3H, CH_3), 3.16 (qui, J = 6.8 Hz, 1H, CH), 7.12−7.74 (m, 9H).

***S*-Benzyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2d):** colorless needles; 82% yield; eluent, hexane/Et_2O = 1/4; mp 147.0−148.0 °C (lit.[24] mp 146−147 °C); IR (KBr) 1278, 1087, 989, 964, 751, 742, 571, 551 cm^{-1}; ^1H NMR δ 2.32 (s, 3H, CH_3), 4.13 (d, J = 12.0 Hz, 1H), 4.34 (d, J = 12.0 Hz, 1H), 6.96−7.64 (m, 14H); ^{13}C NMR δ 21.6, 60.6, 126.2, 126.7, 127.5, 128.8, 129.1, 129.2, 129.6, 129.8, 130.8, 132.5, 133.7, 141.2, 141.4;

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EIMS (*m*/*z*) 369 (M^+), 214 (M^+ − Ts). Anal. Calcd for $C_{20}H_{19}NO_2S_2$: C, 65.01; H, 5.18; N, 3.79. Found: C, 64.96; H, 5.27; N, 3.73.

***S*-Benzyl-*S*-(4-methoxyphenyl)-*N*-(*p*-tolylsulfonyl)sulfilimine (2e):** [25] colorless needles; 70% yield; eluent, hexane/Et_2O = 1/4; mp 127.5−128.0 °C; ^{1}H NMR δ 2.31 (s, 3H, CH_3), 3.81 (s, 3H, CH_3), 4.10 (d, J = 12.5 Hz, 1H), 4.33 (d, J = 12.5 Hz, 1H), 6.86−7.62 (m, 13H).

***S*-Benzyl-*S*-(2-nitrophenyl)-*N*-(*p*-tolylsulfonyl)sulfilimine (2f):** colorless needles; 53% yield; eluent, CH_2Cl_2/MeOH = 70/1; mp 194.0−195.0 °C; IR (KBr) 1533 (NO_2), 1347 (NO_2), 1280, 1137, 1088, 1021, 1005 cm^{-1}; ^{1}H NMR δ 2.33 (s, 3H, CH_3), 4.17 (d, J = 11.9 Hz, 1H), 4.49 (d, J = 11.9 Hz, 1H), 6.98−8.62 (m, 13H); ^{13}C NMR δ 21.3, 60.0, 125.7, 125.9, 128.3, 128.8, 129.0, 129.2, 130.8, 132.8, 134.0, 136.0, 140.4, 141.4, 145.3. Anal. Calcd for $C_{20}H_{18}N_2O_4S_2$: C, 57.96; H, 4.38; N, 6.76. Found: C, 57.68; H, 4.44; N, 6.55.

***S*-(4-Nitrophenylmethyl)-*S*-phenyl-*N*-(*p*-tolylsulfonyl)-sulfilimine (2g):** colorless needles; 72% yield; eluent, CH_2Cl_2; mp 197.0−198.0 °C; IR (KBr) 1522 (NO_2), 1344 (NO_2), 1292, 1278, 1020, 1003, 988, 749 cm^{-1}; ^{1}H NMR δ 2.31 (s, 3H, CH_3), 4.28 (s, 2H, CH_2), 7.04−8.10 (m, 13H); ^{13}C NMR δ 21.2, 58.6, 123.5, 126.0, 126.3, 129.1, 130.0, 131.8, 132.9, 133.5, 134.5, 140.9, 141.9, 148.2. Anal. Calcd for $C_{20}H_{18}N_2O_4S_2$: C, 57.96; H, 4.38; N, 6.76. Found: C, 57.16; H, 4.47; N, 6.44.

***S*-Benzyl-*S*-(1-naphthalenyl)-*N*-(*p*-tolylsulfonyl)sulfilimine (2h):** colorless needles; 54% yield; eluent, hexane/Et_2O = 1/4; mp 153.5−154.5 °C; IR (KBr) 1281, 1149, 1140, 1086, 1021, 991, 967 cm^{-1}; ^{1}H NMR δ 2.42(s, 3H, CH_3), 4.07 (d, J = 12.9 Hz, 1H), 4.28 (d, J = 12.9 Hz, 1H), 6.88−7.95 (m, 16H); ^{13}C NMR δ 21.3, 59.2, 121.3, 125.7, 126.1, 127.0, 127.7, 128.0, 128.6, 128.9, 129.1, 130.6, 132.7, 133.5, 141.3; EIMS (*m*/*z*) 264 (M^+ − Ts). Anal. Calcd for $C_{24}H_{21}NO_2S_2$: C, 68.71; H, 5.04; N, 3.34. Found: C, 68.45; H, 5.28; N, 3.34.

***S,S*-Diphenyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2i):** colorless needles; 79% yield; eluent, hexane/Et_2O = 1/6; mp 109.0−109.5 °C (lit.[26] mp 111−112 °C); ^{1}H NMR δ 2.43 (s, 3H, CH_3), 7.29−7.83 (m, 14H).

***S*-Phenyl-*S*-(2-phenylethyl)-*N*-(*p*-tolylsulfonyl)sulfilimine (2j):** colorless needles; 50% yield; eluent, hexane/Et_2O = 1/4; mp 137.0−138.0 °C (lit.[21] mp 137−138 °C); ^{1}H NMR δ 2.34 (s, 3H, CH_3), 2.85−2.95 (m, 2H), 3.07−3.17 (m, 1H), 3.27−3.35 (m, 1H), 7.01−7.79 (m, 14H).

***S*-Ethyl-*S*-methyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2k):** colorless needles; 50% yield; eluent, Et_2O/MeOH = 4/1; mp 131.5−132.0 °C (lit.[27] mp 133 °C); ^{1}H NMR δ 1.25 (t, J = 7.4 Hz, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 2.88 (q, J = 7.4 Hz, 2H, CH_2), 7.25 (d, J = 7.4 Hz, 2H), 7.78 (d, J = 7.4 Hz, 2H).

***S*-[(Ethoxycarbonyl)methyl]-*S*-methyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2l):** colorless needles; 53% yield; eluent, CH_2Cl_2/MeOH = 40/1; mp 73.5−74.5 °C; IR (KBr) 1748 (C=O), 1282, 1134, 1086, 1000, 965, 749 cm^{-1}; ^{1}H NMR δ 1.28 (t, J = 7.1 Hz, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.86 (s, 3H, CH_3), 3.94 (s, 2H, CH_2), 4.01−4.24 (m, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H); ^{13}C NMR δ 13.9, 21.4, 34.5, 53.7, 62.9, 126.3, 129.3, 141.0, 142.1; EIMS (*m*/*z*) 303 (M^+); HRMS calcd for $C_{12}H_{17}NO_4S_2$ 303.0599; found 303.0589. Anal. Calcd for $C_{12}H_{17}NO_4S_2$: C, 47.51; H, 5.65; N, 4.62. Found: C, 47.42; H, 5.51; N, 4.62.

***S*-Benzyl-*S*-methyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2m):** colorless needles; 70% yield; eluent, EtOAc; ^{1}H NMR δ 2.33 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 4.21 (AB, J = 12.5, 38.9 Hz, 2H, CH_2), 7.10 (d, J = 8.1 Hz, 2H), 7.26 (m, 5H, Ph), 7.60 (d, J = 8.1 Hz, 2H). Anal. Calcd for $C_{15}H_{17}NO_2S_2$: C, 58.60; H, 5.57; N, 4.56. Found: C, 58.62; H, 5.55; N, 4.45.

***N*-Allyl-*N*-(methylthio)-*p*-toluenesulfonamide (5a):** colorless needles; 78% yield; eluent, hexane/Et_2O = 1/1; mp 68.5−69.5 °C; IR (KBr) 2991, 2919, 2852, 1435, 1345, 1333, 1160, 1089, 1067, 935, 826, 810, 661, 593, 546, 537 cm^{-1}; ^{1}H NMR δ 2.36 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.98 (d, J = 6.4 Hz, 2H, CH_2), 5.14 (dd, J = 17.0, 1.4 Hz, 1H, CH=C*H*H), 5.15 (dd, J = 10.0, 1.4 Hz, 1H, CH=CH*H*), 5.76 (ddt, J = 17.0, 10.0, 6.4 Hz, 1H, C*H*=CH_2), 7.24 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 21.6, 23.6, 56.4, 119.2, 127.8, 129.5, 133.2, 136.1, 143.8; EIMS (*m*/*z*) 257 (M^+), 102 (M^+ − Ts). Anal. Calcd for $C_{11}H_{15}NO_2S_2$: C, 51.34; H, 5.87; N, 5.44. Found: C, 51.27; H, 5.87; N, 5.37.

***N*-Allyl-*N*-(allylthio)-*p*-toluenesulfonamide (5b):** colorless needles; 82% yield; eluent, hexane/Et_2O = 7/1; mp 74.5−75.5 °C (lit.[15a] mp 72 °C); ^{1}H NMR δ 2.43 (s, 3H, CH_3), 3.53 (d, J = 7.4 Hz, 2H, CH_2), 4.07 (d, J = 6.3 Hz, 2H, CH_2), 5.16 (dd, J = 10.5, 1.4 Hz, 1H, CH=C*H*H), 5.18 (dd, J = 17.2, 1.4 Hz, 1H, CH=CH*H*), 5.19 (dd, J = 9.8, 1.4 Hz, 1H, CH=C*H*H), 5.21 (dd, J = 17.0, 1.4 Hz, 1H, CH=CH*H*), 5.74 (ddt, J = 17.0, 9.8, 7.4 Hz, 1H, C*H*=CH_2), 5.85 (ddt, J = 17.2, 10.5, 6.3 Hz, 1H, C*H*=CH_2), 7.30 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 8.5 Hz, 2H).

***N*-(1-Phenylallyl)-*N*-(phenylthio)-*p*-toluenesulfonamide (5c):** colorless needles; 75% yield; eluent, hexane/Et_2O = 7/1; mp 82.5−83.5 °C (lit.[15c] mp 88 °C); ^{1}H NMR δ 2.31 (s, 3H, CH_3), 5.03 (dd, J = 18.0, 1.1 Hz, 1H, CH=C*H*H), 5.16 (dd, J = 11.0, 1.1 Hz, 1H, CH=C*H*H), 5.99 (br. s, 1H), 6.05 (ddd, J = 18.0, 11.0, 6.5 Hz, 1H, C*H*=CH_2), 7.12−7.25 (m, 12H), 7.68 (br, 2H).

***N*-(1-Phenylallyl)-*N*-(2-nitrophenylthio)-*p*-toluenesulfonamide (5d):** colorless needles; 35% yield; eluent, hexane/Et_2O = 7/1; mp 162−163 °C; IR (KBr) 1593, 1513 (NO_2), 1344, 1335 (NO_2), 1310, 1161, 990, 885, 735, 705 cm^{-1}; ^{1}H NMR δ 2.33 (s, 3H, CH_3), 4.91 (d, J = 16.5 Hz, 1H), 5.10 (d, J = 10.2 Hz, 1H), 5.92−6.07 (m, 2H), 6.99−8.31 (m, 13H); ^{13}C NMR δ 21.6, 67.1, 119.1, 124.6, 125.5, 126.0, 127.7, 128.0, 128.2, 129.0, 129.3, 129.7, 134.2, 134.8, 136.9, 144.4; EIMS (*m*/*z*) 440 (M^+); HRMS calcd for $C_{22}H_{20}N_2O_4S_2$ 440.0864, found 440.0852. Anal. Calcd for $C_{22}H_{20}N_2O_4S_2$: C, 59.98; H, 4.58; N, 6.36. Found: C, 59.13; H, 4.55; N, 6.10.

***N*-(1-Phenylallyl)-*N*-(1-naphthalenylthio)-*p*-toluenesulfonamide (5e):** clear oil; 80% yield; eluent, hexane/Et_2O = 7/1; IR (neat) 1164, 1089, 933, 908, 812, 792, 769, 733, 702, 670, 594 cm^{-1}; ^{1}H NMR δ 2.35 (s, 3H, CH_3), 5.04 (dd, J = 16.2, 1.4 Hz, 1H, CH=C*H*H), 5.11 (dd, J = 10.2, 1.4 Hz, 1H, CH=CH*H*), 6.05 (d, J = 6.7 Hz, 1H, CH), 6.11 (ddd, J = 16.2, 10.2, 6.7 Hz, 1H, C*H*=CH_2), 7.03−7.89 (m, 16H); ^{13}C NMR δ 21.5, 60.0, 116.9, 125.3, 126.8, 127.9, 128.7, 129.5, 136.7, 137.2, 143.9; EIMS (*m*/*z*) 260 (M^+ − CH_2=$CH_2C_{10}H_7S$). Anal. Calcd for $C_{26}H_{23}NO_2S_2$: C, 70.08; H, 5.20; N, 3.14. Found: C, 70.04: H, 5.28; N, 3.08.

***N*-(1-Methylallyl)-*N*-(1-phenylthio)-*p*-toluenesulfonamide (5f):** colorless needles; 44% yield; eluent, hexane/Et_2O = 7/1; mp 63.5−64.5 °C; IR (KBr) 1350, 1166, 894, 819, 746, 670, 569, 550 cm^{-1}; ^{1}H NMR δ 1.26 (d, 3H, CH_3), 2.42 (s, 3H, CH_3), 4.90−5.00 (m, 3H), 5.60 (br s, 1H), 7.17−7.84 (m, 9H); ^{13}C NMR δ 21.5, 60.0, 116.9, 125.2, 126.2, 126.8, 127.9, 128.7, 129.5, 136.7, 137.2, 138.9, 143.9; EIMS (*m*/*z*) 333 (M^+). Anal. Calcd for $C_{17}H_{19}NO_2S_2$: C, 61.23; H, 5.74; N, 4.20. Found: C, 61.28; H, 5.81; N, 4.20.

***N*-(1-Methylallyl)-*N*-(1-naphthalenylthio)-*p*-toluenesulfonamide (5g):** clear oil; 55% yield; eluent, hexane/Et_2O = 7/1; IR (neat) 1354, 1165, 1089, 909, 769, 733, 669 cm^{-1}; ^{1}H NMR δ 1.18 (d, J = 6.6 Hz, 3H, CH_3), 2.38 (s, 3H, CH_3), 4.92−5.08 (m, 3H), 5.64 (ddd, J = 17.0, 10.5, 6.6 Hz, 1H, C*H*=CH_2), 7.23−7.98 (m, 11H); ^{13}C NMR δ 18.4, 21.4, 60.2, 117.0, 122.4, 123.1, 125.80, 125.85, 125.96, 126.52, 127.9, 128.5, 129.5, 133.3, 135.3, 136.6, 136.9, 144.0; EIMS (*m*/*z*) 383 (M^+); HRMS calcd for $C_{21}H_{21}NO_2S_2$ 383.1014, found 383.1011.

Typical Procedure for Asymmetric Imidation of Sulfide. To a solution of CuOTf (2.60 mg, 0.010 mmol, 0.050 equiv) and 4,4′-disubstituted bis(oxazoline) **6a** (4.11 mg, 0.012 mmol, 0.060 equiv) in 1.0 mL of toluene were added first TsN=IPh (75.0 mg, 0.20 mmol, 1.0 equiv) and then the sulfide (0.20 mmol, 1.0 equiv), and the resulting mixture was stirred under nitrogen at 25 °C for 48 h as shown in Tables 5 and 6. The mixture was then added with brine and extracted with dichloromethane. The extract was dried over anhydrous $MgSO_4$, and the evaporation of the solvent left a crude product. Purification by silica gel column chromatography gave the corresponding enantiopure sulfimide. Enantiomeric excesses

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were determined by HPLC usung a suitable chiral column or ^{1}H NMR analysis (270 MHz in the presence of Eu(hfc)$_3$ or 400 MHz in the presence of (trifluoromethyl)anthrylethanol) as shown below.

***S*-Methyl-*S*-*p*-tolyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2a):** colorless needles; 82% yield; 13% ee by Daicel chiralcel OB column with 25% 2-propanol/hexane and by ^{1}H NMR analysis in the presence of (trifluoromethyl)anthrylethanol; mp 124.0−125.0 °C (lit.[21] mp 125−126 °C).

***S*-Methyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2b):** colorless needles; 78% yield; <10% ee by Daicel chiralcel OJ column with 25% 2-propanol/hexane; mp 131.5−132.0 °C (lit.[22] mp 131−132 °C).

***S*-Isopropyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2c):** colorless needles; 44% yield; 23% ee by Daicel chiralcel OJ column with 25% 2-propanol/hexane; mp 96.0−97.0 °C (lit.[23] mp 98.5−99.5 °C).

***S*-Benzyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2d):** colorless needles; 78% yield; 64% ee by Daicel chiralcel OD column with 10% 2-propanol/hexane and by ^{1}H NMR analysis in the presence of (trifluoromethyl)anthrylethanol; mp 147.0−148.0 °C (lit.[24] mp 146−147 °C).

***S*-Benzyl-*S*-(4-methoxyphenyl)-*N*-(*p*-tolylsulfonyl)sulfilimine (2e):** [25] colorless needles; 72% yield; <10% ee by Daicel chiralcel OF column with 10% 2-propanol/hexane; mp 127.5−128.0 °C.

***S*-Benzyl-*S*-(2-nitrophenyl)-*N*-(*p*-tolylsulfonyl)sulfilimine (2f):** colorless needles; 54% yield; <10% ee by Daicel chiralcel OB column with 25% 2-propanol/hexane; mp 194.0−195.0 °C.

***S*-((4-Nitrophenyl)methyl)-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2g):** colorless needles; 37% yield; 25% ee by Daicel chiralcel OD column with 25% 2-propanol/hexane; mp 197.0−198.0 °C.

***S*-Benzyl-*S*-(1-naphthalenyl)-*N*-(*p*-tolylsulfonyl)sulfilimine (2h):** colorless needles; 75% yield; 71% ee by Daicel chiralcel OD column with 10% 2-propanol/hexane. One recrystallization from CH_2Cl_2−diethyl ether gave an enantiopure **2h** in ca. 40% yield: $[\alpha]^{25}_D$ +67.46 (*c* 0.25, acetone); mp 156.0−157.0 °C.

***S*-Phenyl-*S*-(2-phenylethyl)-*N*-(*p*-tolylsulfonyl)sulfilimine (2j):** white needles; 63% yield; 22% ee by ^{1}H NMR analysis in the presence of Eu(hfc)$_3$; mp 137.0−138.0 °C (lit.[21] mp 137−138 °C).

***S*-Ethyl-*S*-methyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2k):** white needles; 36% yield; <10% ee by ^{1}H NMR analysis in the presence of Eu(hfc)$_3$; mp 131.5−132.0 °C (lit.[27] mp 133 °C).

***S*-[(Ethoxycarbonyl)methyl]-*S*-methyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2l):** white needles; 41% yield; <10% ee by ^{1}H NMR analysis in the presence of Eu(hfc)$_3$; mp 73.5−74.5 °C.

***S*-Benzyl-*S*-methyl-*N*-(*p*-tolylsulfonyl)sulfilimine (2m):** white needles; 70% yield; 15% ee by ^{1}H NMR analysis in the presence of (trifluoromethyl)anthrylethanol.

***N*-(1-Phenylallyl)-*N*-(phenylthio)-*p*-toluenesulfonamide (5c):** white needles; 40% yield; 40% ee by Daicel chiralcel OD column with 10% 2-propanol/hexane after products were converted to the corresponding amine by treatment with NaOH in MeOH; mp 82.5−83.5 °C (lit.[15c] mp 88 °C).

***N*-(1-Phenylallyl)-*N*-((2-nitrophenyl)thio)-*p*-toluenesulfonamide (5d):** white needles; 37% yield; 43% ee by Daicel chiralcel OD column with 10% 2-propanol/hexane after products were converted to the corresponding amine by treatment with NaOH in MeOH; mp 162−163 °C.

***N*-(1-Phenylallyl)-*N*-(1-naphthalenylthio)-*p*-toluenesulfonamide (5e):** clear oil; 80% yield; 58% ee by Daicel chiralcel OD column with 10% 2-propanol/hexane after products were converted to the corresponding amine by treatment with NaOH in MeOH.

***N*-(1-Methylallyl)-*N*-(1-phenylthio)-*p*-toluenesulfonamide (5f):** white needles; 30% yield; 25% ee by ^{1}H NMR analysis in the presence of Eu(hfc)$_3$; mp 63.5−64.5 °C.

***N*-(1-Methylallyl)-*N*-(1-naphthalenylthio)-*p*-toluenesulfonamide (5g):** clear oil; 35% yield; 50% ee by ^{1}H NMR analysis in the presence of Eu(hfc)$_3$.

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