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Sulfimides

Enantioselective Nitrene Transfer to Sulfides Catalyzed by a Chiral Iron Complex**

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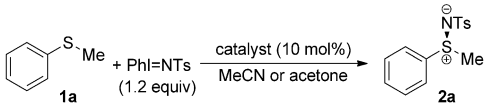
Sulfimides are nitrogen analogues of sulfoxides.[1] In organic synthesis, they serve as useful intermediates[1,2] and have been applied as efficient ligands for metal catalysts.[3] Because of their unique biological properties,[1a,4] sulfimides have also gained considerable attention in agricultural science and medicinal chemistry. As sulfoxides, sulfimides are chiral and have a stereogenic center at the sulfur atom if they originate from unsymmetrically substituted sulfides. Although sulfimides can be easily synthesized by various means,[1,5] their preparation in enantioenriched form is still challenging. The most prominent strategies involve the use of chiral auxiliaries[3a,6] or reagents.[7] All of those, however, require stoichiometric amounts of chiral compounds that are usually prepared by multi-step syntheses.

The field of catalytic asymmetric sulfimidation is scarcely explored, and only very few catalyst systems have been documented. For example, Uemura, Taylor and their coworkers disclosed the use of chiral copper(I)/bis(oxazoline) catalysts.[8] However, only sterically hindered aryl benzyl sulfides gave satisfying results. Subsequently, Katsuki and coworkers introduced chiral manganese(III)/salen[9] and ruthenium(II)/salen[10] (or salalen)[11] complexes as asymmetric sulfimidation catalysts. Excellent results were achieved, but the synthesis of salen ligands proved cumbersome.

Inspired by the early work of Bach[5a,b] and encouraged by our findings that simple iron(II) and iron(III) compounds could effectively catalyze non-asymmetric sulfide imidations,[5h–j] we decided to focus our search on chiral iron complexes for asymmetric versions of such reactions. Herein, we report that iron(III)/PyBOX combinations are highly effective catalysts for the aforementioned transformations. Noteworthy, this is the first iron-catalyzed enantioselective sulfimidation reported to date, despite many other breakthroughs in asymmetric iron catalysis.[12,13]

The asymmetric imidation of thioanisole (**1a**) with *N*-(*p*-tolylsulfonyl)imino phenyliodinane (PhI=NTs) in acetonitrile was selected as the benchmark reaction for our preliminary screening. Various catalysts formed in situ from chiral ligands and iron(III) acetylacetonate ([Fe(acac)$_3$], **3a**) were tested. Although in most cases the reaction proceeded smoothly to give the desired product **2a**, only (*S*,*S*)-2,6-bis(4-phenyl-2-oxazolinyl)pyridine ((*S*,*S*)-Ph-PyBOX, **L1**) led to a promising enantiomeric ratio (e.r.) of 77:23 (Table 1, entry 1). Some other PyBOX ligands were also evaluated (Table 1, entries 2–5), but the reactions proceeded with poor enantiocontrol, implying that the phenyl groups in **L1** were crucial for achieving the observed enantioselectivity. Although the use of iron(II) acetylacetonate ([Fe(acac)$_2$]) instead of [Fe(acac)$_3$] gave almost the same e.r. (75:25), the reactivity was reduced (Table 1, entry 6). Essentially racemic products were obtained with Fe(ClO$_4$)$_2$ and Fe(OTf)$_2$ (Table 1, entries 7 and 8).[13] The same was true when other metal acetylacetonates ([Cu-

Table 1: Optimization of reaction conditions.[a]

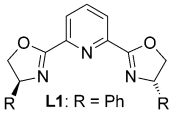


1a 2a

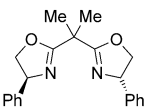
Entry	Metal compound	Ligand	*t*	Yield [%]	e.r.[b]
1	[Fe(acac)$_3$] (**3a**)	(*S*,*S*)-**L1**	3 h	88	77:23
2	[Fe(acac)$_3$] (**3a**)	(*S*,*S*)-**L2**	12 h	90	57:43
3	[Fe(acac)$_3$] (**3a**)	(*S*,*S*)-**L3**	12 h	94	56:44
4	[Fe(acac)$_3$] (**3a**)	(*S*,*S*)-**L4**	5 h	99	50:50
5	[Fe(acac)$_3$] (**3a**)	(*S*,*S*)-**L5**	22 h	90	50:50
6	[Fe(acac)$_2$]	(*S*,*S*)-**L1**	14 h	75	75:25
7	Fe(ClO$_4$)$_2$	(*S*,*S*)-**L1**	1 h	71	52:48
8	Fe(OTf)$_2$	(*S*,*S*)-**L1**	10 min	89	51:49
9	[Cu(acac)$_2$]	(*S*,*S*)-**L1**	14 h	63	52:48
10	[Mn(acac)$_3$]	(*S*,*S*)-**L1**	4 h	24	52:48
11	[Ru(acac)$_3$]	(*S*,*S*)-**L1**	17 h	45	55:45
12	**3b**	(*S*,*S*)-**L1**	1 h	97	82:18
13	**3c**	(*S*,*S*)-**L1**	6 h	99	86:14
14	**3d**	(*S*,*S*)-**L1**	6 h	96	90:10
15[c]	**3d**	**(*S*,*S*)-L1**	**2 h**	**99**	**91:9**
16[c,d]	**3d**	**(*R*,*R*)-L1**	**16 h**	**98**	**7:93**

[a] Reaction conditions: **1a** (0.1 mmol), PhI=NTs (0.12 mmol), ligand (0.01 mmol), metal compound (0.01 mmol), MeCN (1.0 mL), at 0 °C (no exclusion of air and moisture). [b] The enantiomeric ratios (e.r.) were determined by high-performance liquid chromatography (HPLC) analysis using a chiral stationary phase. [c] Acetone was used as solvent. [d] The reaction was run at −20 °C. The absolute configuration of the major enantiomer was determined to be (*S*) by comparing the specific rotation with the reported value after transforming **2a** to sulfoximine **4a** (Scheme 4).

3a: R = Me, X = H
3b: R = Me, X = Cl
3c: R = *i*Pr, X = H
3d: R = *i*Pr, X = Cl



L1: R = Ph
L2: R = Bn
L3: R = *t*Bu
L4: R = *i*Pr



L5

(*S*,*S*) configurations shown for **L1**–**L5**

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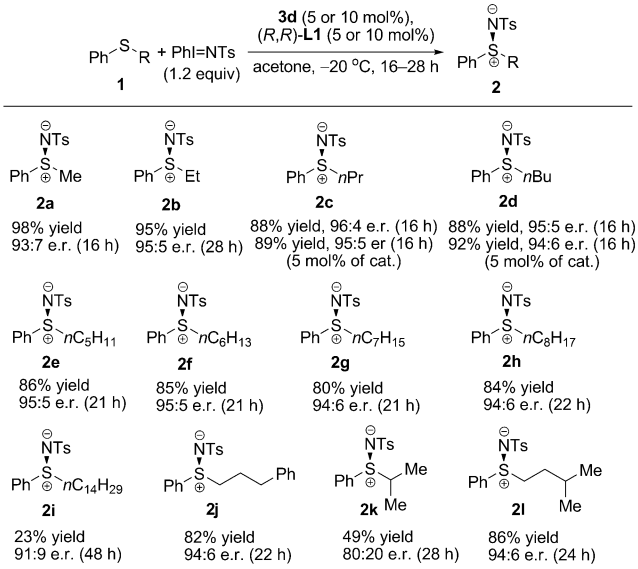
$(acac)_2$], [Mn(acac)$_3$], and [Ru(acac)$_3$]) were applied (Table 1, entries 9–11).

Next, a series of iron(III) acetylacetonate derivatives (**3b**–**d**) were prepared and investigated (Table 1, entries 12–14). As expected, the enantioselectivity in the formation of **2a** depended on both the steric and electronic properties of the acetylacetonate ligand. Finally, iron(III) 4-chloro-2,6-dimethyl-3,5-heptanedionate ([Fe(dmhdCl)$_3$], **3d**) proved optimal, providing **2a** with an e.r. of 90:10 in 96% yield (Table 1, entry 14).[14] Switching to acetone as a solvent showed its slight superiority over acetonitrile (Table 1, entry 15 versus entry 14). The enantioselectivity was further improved by lowering the reaction temperature to −20 °C (Table 1, entry 16).[15] Pleasingly, the reaction could be performed in air, and no particular protection from moisture was necessary. Varying the concentration, applying additives, or using some other iminoiodinane reagents[16] did not lead to improvements of yield and e.r. Thus, the optimal reaction conditions involved: [Fe(dmhdCl)$_3$] (10 mol%), (*R*,*R*)-Ph-PyBOX (10 mol%), sulfide (1.0 equiv), PhI=NTs (1.2 equiv), acetone (0.1M), −20 °C (without exclusion of moisture and air).[17]

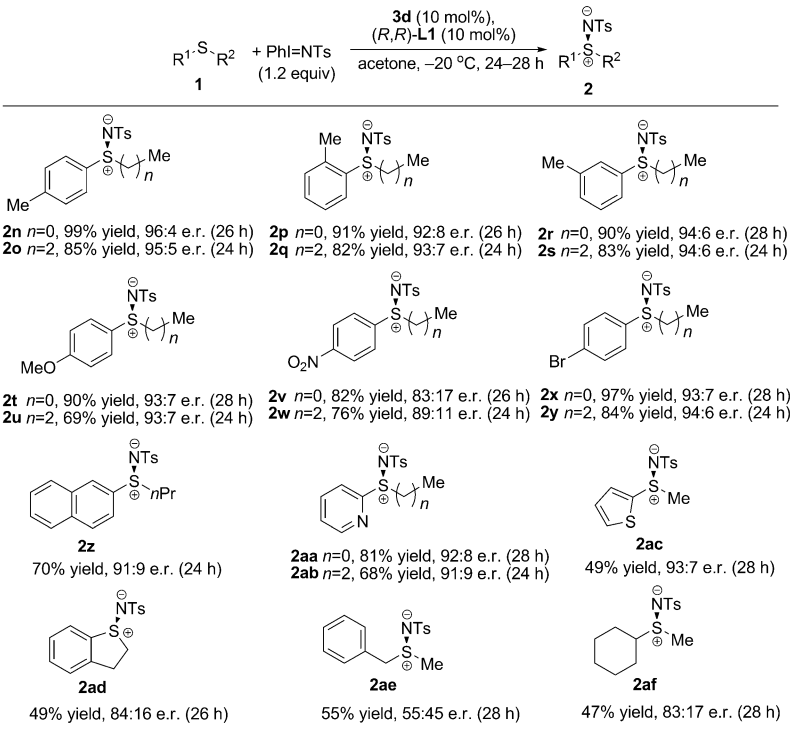


Scheme 1. Investigation of the substrate scope (part one).

To evaluate the substrate scope, various alkyl phenyl sulfides with linear alkyl chains were first subjected to the optimized reaction conditions (Scheme 1). In general, both the e.r. values (up to 96:4) and the yields (> 80–98%) were high. The data remained essentially constant when the length of the alkyl chain was varied from C_1 (methyl) to C_8 (octyl). The asymmetric imidation of phenyl tetradecanyl sulfide (**1i**) to give sulfimide **2i** (e.r. of 91:9; 23% yield) was less effective with respect to the yield, which was probably due to the poor solubility of the sulfide under the reaction conditions. A terminal phenyl group at an *n*-propyl substituent (as in **1j**) had no negative effect, and the corresponding product **2j** was obtained with an e.r. of 94:6 in 82% yield. As exemplified by the asymmetric imidation of sulfides **1c** and **1d**, a reduction of the catalyst loading from 10 mol% to 5 mol% was tolerated. Comparable yields and slightly decreased enantioselectivities in the respective formation of **2c** and **2d** were observed.

Finally, branched-alkyl phenyl sulfides were tested in this series. While 3-methylbutyl phenyl sulfide (**1l**) was imidated to give **2l** with an e.r. value and yield in the expected range (94:6; 86%), the nitrene transfer to isopropyl phenyl sulfide (**1k**) appeared to be hampered by the branching at the α position leading to sulfimide **2k** with an e.r. of only 80:20. This value as well as the moderate yield (49%) indicate the significant influence of steric effects during the asymmetric imidation by the chiral iron catalyst.

Next, various alkyl aryl sulfides bearing electron-donating or electron-withdrawing substituents on the arene were tested (Scheme 2). As revealed by the results of reactions with *ortho*-, *meta*-, or *para*-tolyl alkyl sulfides **1n**–**s**, the catalyst tolerated all substitution patterns. Generally, electronic properties only slightly affected the enantiocontrol of the reaction. However, the presence of the strongly electron-withdrawing nitro group in sulfide **1v** resulted in a lower enantioselectivity in the formation of the corresponding sulfimide **2v** (e.r. of 83:17). The reduced electron density around the sulfur atom caused by the nitro group could be partially compensated by a positive inductive effect achieved by chain extension of the alkyl substituent. Thus, compared with the formation of methyl-substituted **2v**,

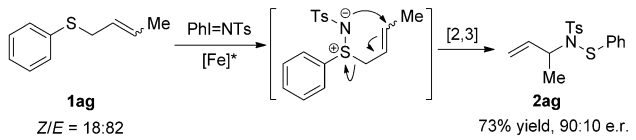


Scheme 2. Investigation of the substrate scope (part two).

a higher enantioselectvity was observed in the imidation of *n*-propyl-bearing sulfide **1w** to give **2w** (e.r. of 83:17 vs. e.r. of 89:11).

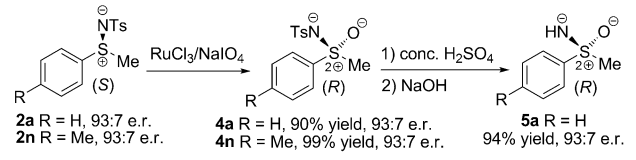
Finally, condensed aromatic, heteroaryl, and sterically constrained substrates were investigated. 2-Naphthyl *n*-propyl sulfide (**1z**) could be converted to sulfimide **2z** with an e.r. of 91:9 in 70% yield. To our delight, 2-(alkylthio)pyridines **1aa** and **1ab** were also applicable, affording the corresponding sulfimides **2aa** and **2ab** with an e.r. of 92:8 and an e.r. of 91:9, respectively.[18] Although the yield (49%) was only moderate because of a competing imidation of the sulfur atom in the thiophene ring, 2-(methylthio)thiophene (**1ac**) was converted to **2ac** with high enantioselectivity (e.r. of 93:7). Catalyses using 2,3-dihydrobenzothiophene (**1ad**), benzyl methyl sulfide (**1ae**), and cyclohexyl methyl sulfide (**1af**) as starting materials gave the corresponding products in low to moderate yields and enantioselectivities.

In accord with previous findings,[8a,b,10b,c] imidation of crotyl phenyl sulfide (**1ag**) resulted in a product that underwent immediate [2,3]-sigmatropic rearrangement to afford sulfenamide **2ag** (26 h; e.r. of 90:10; 73% yield; Scheme 3).[19]



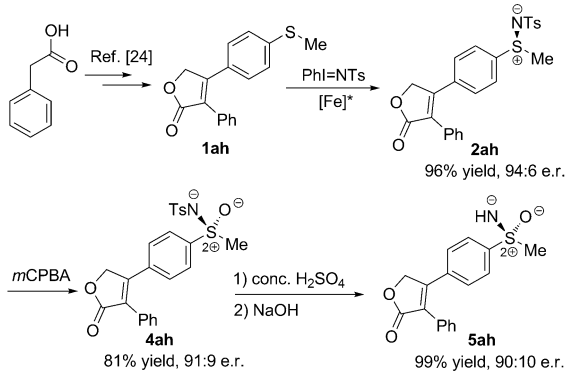
Scheme 3. Asymmetric imidation of crotyl phenyl sulfide (**1ag**) followed by an immediate [2,3]-sigmatropic rearrangement to give **2ag**.

In order to establish the stereochemical path of the asymmetric catalysis and to demonstrate the synthetic utility of the method, a few transformations of the sulfimide products were investigated. Cram and co-workers had oxidized sulfimide **2n** with *m*CPBA and isolated the corresponding sulfoximine **4n** in modest yield (65%) after 24 h.[20] With the goal to improve the yield and hoping to shorten the reaction time, we applied $NaIO_4$ as oxidant and a catalytic amount of $RuCl_3$ for the same transformation, starting from **2n**, which was obtained from the catalysis with Fe^{III}/(*R*,*R*)-**L1**.[21] Product **4n** was formed stereospecifically, and the yield was essentially quantitative (Scheme 4). Comparing the optical rotations of **2n** and **4n** with the respective reported values proved that the oxidation had proceeded with retention of configuration. Hence, sulfimide (*S*)-**2n** resulted in sulfoximine (*R*)-**4n** and for both the e.r. was 93:7. Sulfimide **2a**, prepared from thioanisole (**1a**), was elaborated to N-tosyl-protected sulfoximine **4a** in the same manner. Treatment of this product with concentrated sulfuric acid (followed by basification with sodium hydroxide) gave N-unprotected sulfoximine **5a** in 94% yield.[22] Analyzing the e.r. values of each compound confirmed the stereospecificity of both synthetic steps, the oxidation and the deprotection.[20]



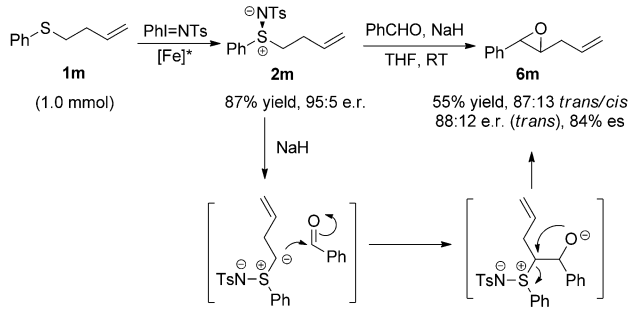
Scheme 4. Transformation of sulfimides to the corresponding NTs and NH sulfoximines.

Recently, we prepared a series of bioactive sulfoximines and demonstrated their potential applications in medicinal chemistry.[23] It was shown that the biological response significantly depended on the absolute configuration of the stereogenic sulfur atom.[23c] For obtaining those results, racemic compounds were prepared, which subsequently had to be resolved by HPLC using a chiral stationary phase. We now utilized our newly devised protocol for the iron-catalyzed asymmetric imidation in the synthesis of enantioenriched Vioxx analogue **5ah** (Scheme 5). To our delight, the enantioselective sulfimidation of **1ah**[24] proceeded smoothly, generating sulfimide **2ah** with high enantioselectivity (e.r. of 94:6) in excellent yield (28 h, 96%). Because the oxidation of sulfimide **2ah** to sulfoximine **4ah** with $NaIO_4$/$RuCl_3$ proved problematic (because of partial C=C bond oxidation), *m*CPBA was applied as oxidant. In this manner, sulfoximine **4ah** was formed chemoselectively in 81% yield. Removal of the tosyl group with concentrated H_2SO_4 occurred effortlessly without affecting any other functional groups, furnishing the desired sulfoximine **5ah** with an e.r. of 90:10 in 99% yield (Scheme 5).



Scheme 5. Asymmetric synthesis of sulfoximine-based Vioxx analogue **5ah**.

Another application of the iron-catalyzed asymmetric imidation was illustrated by the enantioselective synthesis of unsaturated epoxide **6m** (Scheme 6).[25] Starting from homoallyl phenyl sulfide (**1m**), the corresponding sulfimide **2m** was obtained with high enantioselectivity (e.r. of 95:5) in 87% yield after 28 h. The absence of an aziridine confirmed the full chemoselectivity of the nitrogen transfer (sulfur atom vs. double bond).[26] Treatment of a mixture of **2m** and benzaldehyde with NaH gave epoxide **6m** with good diastereoselectivity (*trans*:*cis* = 87:13) and enantioselectivity (e.r. of 88:12 for the *trans* isomer). Thus, the chirality transfer from the stereogenic sulfur atom to the two newly generated stereogenic carbon centers took place with high enantiospecificity (es = 84%).[27]



Scheme 6. Synthesis of the enantioenriched allyl epoxide **6m**.

In summary, we have developed the first iron-catalyzed asymmetric imidation of sulfides with a broad substrate scope. A variety of optically active sulfimides were prepared in good yields and enantioselectivities. Both ligand and iron precatalyst are readily available. Acetone is used as a cheap solvent with low toxicity. The reaction is easy to manipulate, as air and moisture do not have to be excluded. Finally, applications of the new protocol to the preparation of synthetically relevant products were demonstrated.

Experimental Section

Procedure for the iron(III)-catalyzed asymmetric sulfimidation: $[Fe(dmhdCl)_3]$ (0.01 mmol, 6.2 mg), (*R*,*R*)-Ph-PyBOX (0.01 mmol, 3.7 mg), and acetone (1 mL) were placed in a test tube equipped with a magnetic stir bar. The mixture was stirred at room temperature for 30 min. Then, the sulfide (0.1 mmol) was added by syringe. After the mixture was cooled to −20 °C, PhI=NTs (45 mg, 0.12 mmol) was added in one portion as a solid. The reaction mixture was stirred at −20 °C and monitored by thin-layer chromatography (TLC). When the reaction was finished, the solvent was removed under reduced pressure, and the sulfimide was purified by column chromatography on silica gel (60–200 μm). The enantiomeric ratio was determined by HPLC analysis using a chiral stationary phase.

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[14] Attempts to prepare $[Fe(t\text{BuCOCClCO}t\text{Bu})_3]$ failed. As $[Fe(PhCOCHCOPh)_3]$ gave an inferior result (24 h, 97% yield, e.r. of 80:20) compared with $[Fe(i\text{PrCOCHCO}i\text{Pr})_3]$ (6 h, 99% yield, e.r. of 86:14) in MeCN at 0 °C, the use of $[Fe(PhCOCClCOPh)_3]$ was not investigated.

[15] Further lowering of the reaction temperature to −30 °C did not enhance the enantioselectivity, but dramatically reduced the reaction rate.

[16] Under the reaction conditions shown in Table 1, entry 16, use of $4\text{-}NO_2C_6H_4SO_2N{=}IPh$ gave the corresponding product in 52% yield and an e.r. of 84:16. When $4\text{-}t\text{BuC}_6H_4SO_2N{=}IPh$ was

applied, the product was obtained in 60% yield and an e.r. of 90:10. Generating PhI=NTs in situ by combining PhI=O and $TsNH_2$ at −20 °C led to a similar enantioselectivity, but a lower reactivity, which was attributed to an inefficient formation of PhI=NTs under those conditions.

[17] No background reaction was observed in the absence of the chiral iron(III) catalyst at −20 °C.

[18] With 4-(*n*-propylthio)pyridine as substrate, the catalysis was almost inhibited, which was attributed to a strong coordination of the sterically unshielded basic pyridine nitrogen atom to the iron(III) catalyst.

[19] Although sulfenamide **2ag** possesses two stereochemical elements, namely a) a stereogenic carbon center and b) an axis of chirality because of the S–N bond (L. Craine, M. Raban, *Chem. Rev.* **1989**, *89*, 689), only one pair of peaks was observed when an HPLC analysis of a racemic sample of **2ag** was conducted on a chiral stationary phase at 20 °C. This result implies that the torsional barrier of the S–N bond was easily overcome at that temperature. In line with this result is the observed broadening of some peaks in ^{1}H NMR and ^{13}C NMR spectra recorded at 25 °C.

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[27] The enantiospecificity was calculated according to the following equation: es [%] = (enantiomeric excess of epoxide **6m**/enantiomeric excess of sulfimide **2m**) × 100%. For the first use of this term, see: S. E. Denmark, T. Vogler, *Chem. Eur. J.* **2009**, *15*, 11737.

