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COMMUNICATION

N-Sulfonyl α-Imino Ester-Derived Chiral Oxaziridines: Catalytic Asymmetric Synthesis and Application as a Modular Chiral Organic Oxidant†

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A novel class of chiral *N*-sulfonyl oxaziridines is introduced for use as structurally modifiable chiral oxidants. These oxaziridines are readily prepared from *N*-sulfonyl α-imino esters in a highly enantioenriched form by oxidation with hydrogen peroxide using L-isoleucine-derived triaminoiminophosphorane as a catalyst. The distinct advantage of their structural modularity is demonstrated through the identification of an optimal oxaziridine that exhibits high reactivity and enantiospecificity in the asymmetric oxidations of a silyl enol ether and *N*-sulfonyl allylic and homoallylic amines.

Oxaziridines are three-membered heterocycles consisting of oxygen, nitrogen and carbon atoms (Fig. 1a). The ring strain and weakness of the N–O bond allow oxaziridines to transfer their oxygen or nitrogen atoms to other nucleophilic functionalities.[1] The position of the nucleophilic attack on an oxaziridine depends on the electronic properties of the substituent on the 2-nitrogen atom. The presence of an electron-withdrawing group increases the leaving ability of the nitrogen atom and directs a nucleophile to the oxygen atom, endowing the oxaziridine with the character of a neutral organic oxidant. For example, perfluorinated oxaziridines, bearing perfluoroalkyl groups on their 2-nitrogen atoms, show greater oxidizing ability than the corresponding nonfluorinated congener, while preparation and handling of those fluorinated oxaziridines are somewhat difficult.[2] *N*-Sulfonyl oxaziridines, wherein strongly electron-withdrawing sulfonyl groups are attached on the 2-nitrogen atom, also have moderate oxygen-transfer ability. These are regarded as the most commonly utilized class of oxaziridines owing to their stability and ease of preparation.[1,3] *N*-Sulfonyl oxaziridines have been applied to various electrophilic oxidations such as epoxidation of olefins, α-hydroxylation of carbonyl compounds via metal enolates, and oxidation of heteroatoms.[4] Although enantioselective oxidations have been achieved using chiral, non-racemic, *N*-sulfonyl oxaziridines, their structures are practically confined to those derived from natural products,[5] primarily due to the lack of reliable methods for the asymmetric construction of the oxaziridine ring core. This limitation not only renders the design and preparation of an oxaziridine capable of oxidizing a given substrate with a high degree of enantioselectivity difficult, but also hampers the fine tuning of the inherent reactivity of the oxaziridine.[6] Hence, the potential utility of *N*-sulfonyl oxaziridines as structurally modifiable chiral organic oxidants remains unexplored.

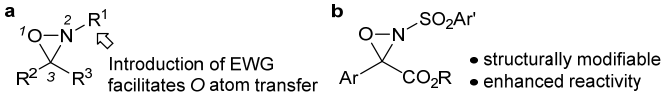
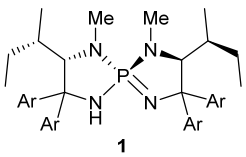


Figure 1. (a) General structure of oxaziridines (b) Structure of oxazridines designed in this study

Under these circumstances, catalytic systems for the asymmetric synthesis of *N*-sulfonyl oxaziridines by the oxidation of parent *N*-sulfonyl imines were independently reported by Jørgensen and Yamomoto's groups.[7–9] We also developed a broadly applicable, preparative method for the imine oxidation based on the use of chiral *P*-spiro triaminoiminophosphoranes of type **1**[10-15] as catalysts (Fig. 2).[16] The emergence of these methodologies unlocks the door to access a diverse range of optically active *N*-sulfonyl oxaziridines. This would ensure an otherwise unattainable possibility of their structural modification for precisely tuning the reactivity and selectivity in the application to asymmetric oxidations. In exploring the synthetic potential of such tailor-made chiral organic oxidants, we became



1a: Ar = Ph
1b: Ar = 4-MeC_6H_4
1c: Ar = 4-FC_6H_4
1d: Ar = 3-MeC_6H_4
1e: Ar = 3-FC_6H_4
1f: Ar = 3-$CF_3C_6H_4$

Figure 2. *P*-Spiro chiral triaminoiminophosphoranes

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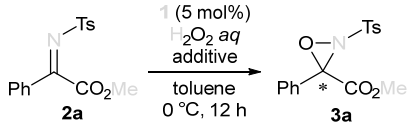
interested in the structural features of oxaziridines derived from *N*-sulfonyl α-arylimino esters for the following reasons: 1) the presence of the electron-withdrawing alkoxycarbonyl group would be beneficial in facilitating the oxygen atom-transfer event; 2) the steric and electronic attributes of the aromatic substituent (Ar) could be manipulated for rigorous control of the stereochemical outcome of the oxidation (Fig. 1b).[17] Herein, we report a catalytic enantioselective preparation of this novel class of *N*-sulfonyl oxaziridines and demonstrate their utility as modular chiral oxidants in the asymmetric oxidations of a silyl enol ether (Rubottom oxidation) and *N*-sulfonyl allylic and homoallylic amines.

At the outset of our investigation, we chose methyl (*Z*)-2-phenyl-2-(tosylimino)acetate (**2a**) as a precursor and exposed it to each two equivalents of 35% aqueous hydrogen peroxide (H_2O_2) and trichloroacetonitrile (Cl_3CCN) in toluene at 0 °C in the presence of a catalytic amount of L-isoleucine-derived triaminoiminophosphorane **1a** (5 mol%), which are the optimal conditions for the asymmetric oxidation of *N*-sulfonyl aldimines.[16a] The reaction proceeded smoothly to afford the corresponding *N*-sulfonyl oxaziridine **3a** in good yield with moderate enantioselectivity (Table 1, entry 1).[18] To our surprise,

Table 1. Optimization of Catalyst[a]



entry	1	additive	yield (%)[b]	ee (%)[c]
1[d]	**1a**	Cl_3CCN	73	69
2	**1a**	none	78	96
3	**1b**	none	59	94
4	**1c**	none	78	95
5	**1d**	none	80	94
6	**1e**	none	82	97
7	**1f**	none	69	95

[a] The reaction was performed with 0.2 mmol of **2a**, 2 equiv of 35% aqueous H_2O_2, and 5 mol% of **1** in toluene (4.0 mL) at 0 °C. [b] Isolated yield. [c] Enantiomeric excesses were analyzed by chiral stationary phase HPLC. [d] 2 equiv of Cl_3CCN was added as an additive.

however, the oxygen atom transfer from H_2O_2 occurred with comparable efficiency even in the absence of Cl_3CCN, yielding **3a** with a substantially higher enantiomeric excess (entry 2). This observation suggests that the catalytically generated aminophosphonium hydroperoxide provides a chiral environment superior to that created by the peroxyimidate counterpart for discriminating prochiral faces of **2a** in the nucleophilic attack by the hydroperoxide ion. In addition, the subsequent intramolecular N–O bond formation is facilitated probably because of the *geminal* substitution on the 3-carbon atom of **2a** (Thorpe-Ingold effect), despite the poor leaving ability of the hydroxide ion.[19] This initial yet intriguing finding led us to modify the structure of iminophosphorane catalyst **1**, specifically with respect to the aromatic substituents (Ar), for further selectivity enhancement (entries 3–7). While a slight decrease in enantioselectivity was observed with **1b** and **1d**, bearing *para*- and *meta*-tolyl groups, respectively, as catalysts (entries 3 and 5), the introduction of an electronegative fluoro appendage to the aromatic nucleus, particularly at the 3-position (**1e**), enabled the isolation of **3a** in 82% yield with 97% ee (entry 6). We also confirmed that the incorporation of a strongly electron-withdrawing trifluoromethyl group, instead of a fluoro functionality, was ineffective in terms of both catalytic activity and stereoselectivity (entry 7).

With the simple asymmetric oxidation protocol and optically active **3a** (97% ee) in hand, we sought to evaluate the performance of **3a** as a chiral oxidant. For this purpose, we selected the Rubottom oxidation of ketone-derived silyl enol ether **4** as a model system (Chart 1).[20] Upon treatment of **4** with

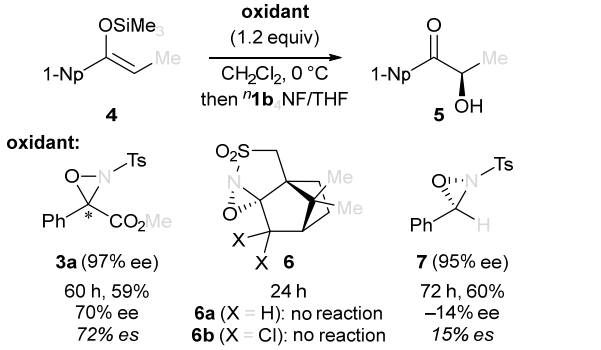


Chart 1. A Comparison of Reactivity and Selectivity of Representative Chiral Oxaziridines in the Rubottom Oxidation of Silyl Enol Ether **4** (1-Np = 1-naphthyl)

3a (1.2 equiv) in dichloromethane at 0 °C, oxygen atom transfer occurred smoothly to furnish α-hydroxy ketone **5** in 59% yield after desilylation with tetrabutylammonium fluoride ($^nBu_4NF$). The enantiomeric excess of **5** was determined to be 70% ee by chiral stationary phase HPLC, and the enantiospecificity of the oxidation process was calculated to be 72% es (es = [% ee of **5**]/[% ee of **3**]*100). In sharp contrast, no formation of the intended product was detected in the reaction with oxaziridines **6** derived from D-(+)-10-camphorsulfonic acid, and **5** was formed, but with much less enantiospecificity, when benzaldehyde-derived **7** was employed as an oxidant.[1,3,16a] These results reveal the superior reactivity and enantio-differentiating ability of **3a** compared to the previously accessible, representative chiral oxaziridines.

An additional salient feature of **3** as a chiral oxidant is its structural modularity, allowing us to pursue modification of the aromatic and ester substituents for improving the enantiospecificity of the present oxidation. Since the basis for taking full advantage of this possibility is the sufficient generality of the catalytic method for the asymmetric preparation of **3**, various α-arylimino esters **2** with different aromatic and ester substituents were subjected to oxidation with a chiral triaminoiminophosphorane **1e**-H_2O_2 system (Table 2, eq 1). As listed in Table 2, the corresponding oxaziridines **3** were obtained generally in good chemical yields with a high level of enantiocontrol, irrespective of the mode of substitution on the aromatic moiety of **2** (entries 1–11). The trends to be noted include slightly diminished enantioselectivity observed with **2**, having highly electron-deficient aromatic substituents (entries 9 and 10), and insensitivity of the stereochemical outcome to the steric bulk of the ester moiety (entry 3 vs. entry 12–14). The library of enantioenriched oxaziridines **3** thus obtained was

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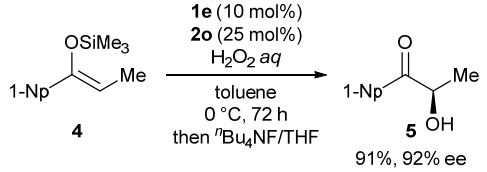
Table 2. Substrate Scope of **1e**-Catalyzed Asymmetric Oxaziridine Synthesis and Enantiospecificity of the Resulting Oxaziridine in the Rubottom Oxidation[a]

				eq 1			eq 2			
entry	Ar'	R	**2**	yield (%)[b]	ee (%)[c] of **3**	**3**	time (h)	yield (%)[b]	ee (%)[c] of **5**	es (%)[d]
1	4-MeC_6H_4	Me	**2b**	68	98	**3b**	50	37	77	79
2	4-FC_6H_4	Me	**2c**	71	95	**3c**	50	88	83	87
3	4-ClC_6H_4	Me	**2d**	79	96	**3d**	12	95	87	91
4	4-BrC_6H_4	Me	**2e**	77	97	**3e**	12	88	85	88
5	3-MeC_6H_4	Me	**2f**	73	96	**3f**	72	75	74	77
6	3-MeOC_6H_4	Me	**2g**	67	97	**3g**	72	37	74	76
7	3-FC_6H_4	Me	**2h**	63	95	**3h**	50	85	79	83
8	3-ClC_6H_4	Me	**2i**	58	95	**3i**	12	82	82	86
9	3-$CF_3C_6H_4$	Me	**2j**	62	85	**3j**	15	82	71	84
10	3,5-$F_2C_6H_3$	Me	**2k**	52	82	**3k**	12	99	71	87
11	2-MeC_6H_4	Me	**2l**	85	99	**3l**	72	<5	–	–
12	4-ClC_6H_4	Et	**2m**	70	95	**3m**	12	95	88	93
13	4-ClC_6H_4	^{i}Pr	**2n**	75	95	**3n**	12	90	90	95
14	4-ClC_6H_4	^{t}Bu	**2o**	77	96	**3o**	12	90	92	96

[a] The reaction 1 was performed with 0.2 mmol of **2**, 2 equiv of 35% aqueous H_2O_2, and 5 mol% of **1e** in toluene (4.0 mL) at 0 °C. The reaction 2 was conducted with **3** which was isolated from the reaction 1, 1 equiv of **4** in CH_2Cl_2 (0.1 M) at 0 °C, and then, whole reaction mixture was treated with a solution of ^{n}Bu$_4$NF in THF (1.2 equiv, 1.0 M) at 0 °C for 0.5 h. [b] Isolated yield. [c] Enantiomeric excesses were analyzed by chiral stationary phase HPLC. [d] es = 100*[% ee of **5**]/[% ee of **3**]

utilized for facile assessment of the structure-reactivity/selectivity relationship in the Rubottom oxidation of **4** (Table 2, eq 2). As expected, the electronic nature of **3** was found to be responsible for the reaction profile, and **3**, possessing an electron-deficient aromatic group, exerted higher reactivity and stereoselectivity (entries 1–10). The position of the substituents on the aromatic ring also appeared critical, as oxaziridines **3** prepared from 4-substituted α-arylimino esters gave **5** consistently with better enantioselectivity and the steric hindrance caused by the *ortho*-tolyl group completely suppressed the oxidation (entry 11). Importantly, however, an increase in the steric demand of the ester substituent led to a significant improvement in enantioselectivity without any detrimental impact on the reactivity, and **3o** with a *tert*-butyl ester substituent was identified as the optimal oxidant capable of transferring an oxygen atom to **4** with excellent enantiospecificity (entries 12–14).

The stereoselective Rubottom oxidation relies on the electrophilic nature of chiral oxaziridine **3o** that is converted into parent α-imino ester **2o** after transferring an oxygen atom to the electron-rich substrate **4**. Considering this aspect and the nucleophilic character of aminophosphonium hydroperoxide, the key reactive species in the asymmetric oxidation of **2o** with the chiral iminophosphorane **1e**-H_2O_2 system, we reasoned that these two oxidation processes could be merged through the establishment of a dual catalysis using H_2O_2 as a stoichiometric oxygen source.[21] Indeed, treatment of silyl enol ether **4** with H_2O_2 in the presence of each catalytic quantity of **1e** and **2o** in toluene at 0 °C resulted in the production of α-hydroxy ketone **5** in high yield with rigorous enantiocontrol (Scheme 1). This *catalytic* Rubottom oxidation involves the conversion of **2o** into **3o** by the action of the **1e**-H_2O_2 system (nucleophilic asymmetric oxidation) and subsequent stereoselective oxygen atom transfer from the *in situ* generated **3o** to **4** (electrophilic asymmetric oxidation), with the concomitant regeneration of **2o**, thus highlighting the distinctive feature of our approach.



Scheme 1. Dual Catalytic System for Asymmetric Oxidation of Silyl Enol Ether **4** by *in situ*-Generated Chiral Oxaziridine **3o**[22]

The potential utility of oxaziridine **3o** (96% ee) was further demonstrated in the application to the oxidation of more challenging substrates such as non-activated olefins (Chart 2).

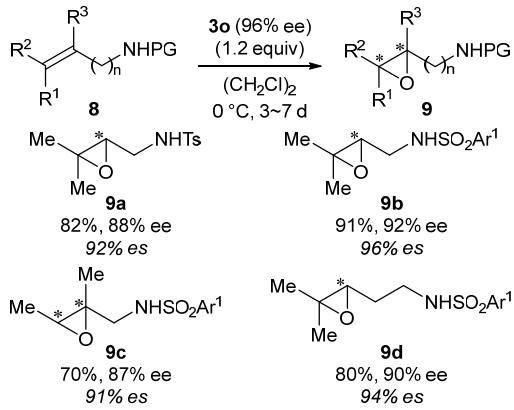


Chart 2. Asymmetric Oxidation of Simple Olefins **8** possessing *N*-Sulfonylated Amines by Chiral Oxaziridine **3o** (Ar^1 = 3,5-$(CF_3)_2C_6H_3$)[22]

For instance, **3o** acted as a prominent chiral oxidant for the epoxidation of prenyl amine derivatives **8a** and **8b**, giving rise to the desired epoxides **9a** and **9b** with excellent enantiospecificity. Not only *N*-sulfonyl tiglic amine **8c** but also *N*-sulfonyl homoprenyl amine **8d** were also epoxidized by **3o** with satisfactory levels of efficiency and stereochemical control. Although three alkyl substituents on a double bond are essential for ensuring adequate conversion, this represents a rare example of the highly enantioselective epoxidation of simple olefins by chiral oxaziridines.[8,23]

In summary, we have introduced a novel class of chiral *N*-sulfonyl oxaziridines as uniquely reactive and modular chiral organic oxidants that can be readily prepared by the asymmetric oxidation of α-imino esters with H_2O_2 using *P*-spiro chiral triaminoiminophosphoranes as catalysts. The ample generality of this practical method for the synthesis of the enantioenriched oxaziridines offers an unprecedented opportunity of the fine tuning of the oxaziridine structure, thereby enabling facile identification of an optimal chiral oxidant for the enantioselective oxidation of a silyl enol ether (Rubottom oxidation). Notably, a catalytic Rubottom oxidation has also been developed based on the *in situ* generation of the requisite chiral oxaziridine by the oxidation of a catalytic quantity of the parent α-imino ester under the catalysis of the iminophosphorane with H_2O_2 as a stoichiometric terminal oxidant. The synthetic utility of this class of chiral *N*-sulfonyl oxaziridines is further demonstrated in achieving the highly enantioselective epoxidation of *N*-sulfonyl allylic and homoallylic amines. We believe that this study opens a door to a new avenue for the use of optically active oxaziridines as tailor-made chiral oxidants in implementing selective chemical synthesis.

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