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Catalytic asymmetric Payne oxidation under the catalysis of *P*-spiro chiral triaminoiminophosphorane: Application to the synthesis of *N*-sulfonyl oxaziridines

Daisuke Uraguchi^a, Ryosuke Tsutsumi^a and Takashi Ooi^{a, b, *}

^a Institute of Transformative Bio-Molecules (WPI-ITbM) and Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho B2-3(611), Chikusa, Nagoya 464-8603, Japan

^b CREST, Japan Science and Technology Agency (JST), Chikusa, Nagoya 464-8603, Japan

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Catalytic asymmetric Payne oxidation under the catalysis of *P*-spiro chiral triaminoiminophosphorane: Application to the synthesis of *N*-sulfonyl oxaziridines

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^a Institute of Transformative Bio-Molecules (WPI-ITbM) and Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho B2-3(611), Chikusa, Nagoya 464-8603, Japan

^b CREST, Japan Science and Technology Agency (JST), Chikusa, Nagoya 464-8603, Japan

ARTICLE INFO

Article history:

Received
Received in revised form
Accepted
Available online

Keywords:

asymmetric catalysis
hydrogen peroxide
imine
organocatalysis
oxaziridine

ABSTRACT

The studies on the development of a highly enantioselective oxidation of *N*-sulfonyl imines with hydrogenperoxide-trichloroacetonitrile system utilizing *P*-spiro chiral triaminoiminophosphoranes as an organic base catalyst are detailed. This method is general and scalable, and exhibits unique chemoselectivity, providing a practical stereoselective route to structurally diverse *N*-sulfonyl oxaziridines. The mechanistic investigations reveal that the reaction proceeds through the Payne-type oxidation pathway. The synthetic utility of the optically active *N*-sulfonyl oxaziridines as versatile organic oxidants and chiral building blocks is also demonstrated.

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1. Introduction

Organic peroxy acids, such as peracetic acid, *m*-chloroperbenzoic acid (*m*-CPBA), and magnesium monoperoxyphthalate, are convenient yet reactive oxidizing agents in synthetic chemistry and are frequently used for the oxidation of organic functional groups and low-valent metal species.¹ The primary factors responsible for their competent reactivity are vulnerability of the oxygen–oxygen bond and good leaving ability of the acyloxy moiety. At the same time, however, these characteristics are tightly linked with their thermal instability and potentially explosive nature, thus impeding the application to large-scale operations. Therefore, the development of a reliable method for the *in situ* catalytic generation of a peroxy acid or its equivalent is desirable to reduce hazardousness of this synthetically useful oxidation process.

Besides the practical issues associated with the reactivity, stereoselectivity control is another important subject of interest in peroxy acid-mediated oxidations. Although substrate-directed stereospecific oxidations have been well established, asymmetric catalysis using peroxy acids as a source of active oxygen atom has scarcely been developed.^{2,3} The landmark thesis was released from Miller group in 2007, wherein a small peptide architecture was elaborated as a catalytic promoter with remarkable performance.^{3a} A free carboxylic acid moiety of an aspartic acid

residue in the catalyst was condensed with hydrogen peroxide (H₂O₂) with the aid of a stoichiometric amount of carbodiimide to repetitively generate the requisite chiral peroxy acid for the enantioselective epoxidation of unactivated olefins with a secondary carbamate as the directing group. The effectiveness of this approach was also demonstrated in the Baeyer–Villiger oxidation of cyclic ketones and the hydroxylation of substituted indoles.^{3c,d} On the other hand, a method for controlling the stereochemical outcome of the oxidation with an *in situ*-generated achiral peroxy acid by a catalytic quantity of a chiral molecule remains virtually unknown and is considered to be rather problematic. This is partially because the corresponding carboxylic acid is inevitably formed as the side product in this type of oxidation, preventing the selective activation of the peroxy acid by the chiral catalyst.

In this context, the Payne oxidation, where the active oxidant is an *in situ*-generated peroxyimide acid, appears to be a uniquely attractive system.⁴ This reaction was originally discovered in the study directed toward the epoxidation of acrylonitrile with H₂O₂ and was subsequently applied to the epoxidation of simple olefins.^{4a} The oxidation process is initiated by the addition of H₂O₂ to a nitrile in the presence of excess base to afford the peroxyimide acid intermediate that instantly transfers active oxygen to the substrate (Scheme 1), forming the corresponding amide as the side product unlike the carboxylic acid produced in the standard peroxy acid-mediated oxidations.

* Corresponding author. Tel.: +81-52-798-4501; fax: +81-52-789-3338; e-mail: tooi@apchem.nagoya-u.ac.jp

Because the pK_a of the resulting amide ion is expected to be higher than H_2O_2 , it could regenerate a hydroperoxide ion (OOH^-). This notion clearly indicates the inherent feasibility of rendering the Payne oxidation catalytic in base. However, such a system has never been developed, much less the catalytic asymmetric variant, probably because of the lack of an appropriate chiral base catalyst.

Scheme 1. Mechanism of the Payne Oxidation.

As a part of our research program aiming at the molecular design and synthetic applications of *P*-spiro chiral tetraaminophosphonium salts as organic ion-pair catalysts,⁵ we have demonstrated the potential of their conjugate bases, triaminoiminophosphoranes of type **1** (Fig. 1),^{6,7} as chiral organic superbases through the development of a series of highly stereoselective transformations.⁸ In particular, iminophosphorane **1a** catalyzes the stereoselective glycolate aldol reaction that involves the *P*-Brook rearrangement of α -hydroxy phosphonates triggered by their deprotonation with **1a** (Scheme 2).^{8c} The ability of iminophosphorane **1** to generate the aminophosphonium alkoxide in this direct aldolization hinted at the possibility that **1**, upon treatment with H_2O_2 , could catalytically generate the corresponding hydroperoxide **1**·HOOH, which would be sufficiently reactive for the facile addition to nitrile to form the aminophosphonium peroxyimide as the key intermediate for achieving the catalytic asymmetric Payne-type oxidation. Herein, we describe the details of our endeavor to substantiate this hypothesis in the establishment of the catalytic, highly enantioselective oxidation of *N*-sulfonyl imines as a broadly applicable method for the synthesis of optically active *N*-sulfonyl oxaziridines.⁹

Figure 1. *P*-Spiro Chiral Triaminoiminophosphoranes **1**.

Scheme 2. Chiral Iminophosphorane **1a**-Catalyzed Glycolate Aldol Reaction.

2. Results and Discussion

2.1. Optimization of the reaction conditions

The feasibility of the asymmetric Payne-type oxidation under the catalysis of the iminophosphorane was investigated in the oxidation of *N*-sulfonyl imines to chiral *N*-sulfonyl oxaziridines.^{10–18} Chiral *N*-sulfonyl oxaziridine is one of the unique organic oxidants in synthetic chemistry and used for the oxygen-transfer reactions to electron-rich functional groups such as enolates and heteroatoms.^{15,16} While diastereoselective oxidation of *N*-sulfonyl imines with a chiral backbone has been utilized for the preparation of stereochemically defined *N*-sulfonyl oxaziridines, a reliable method for their enantioselective synthesis is rather underdeveloped.^{15,16} In 2011, Jørgensen pioneered the catalytic asymmetric oxidation of *N*-sulfonyl imines with *m*-CPBA using a cinchona alkaloid derivative as the chiral base catalyst.¹² Although this protocol requires over-stoichiometric amount of peroxy acid, a variety of aromatic and aliphatic imines can be converted into the corresponding *N*-sulfonyl oxaziridines with moderate-to-excellent enantioselectivity. Yamamoto also succeeded in the catalytic oxidation of *N*-sulfonyl imines by the combined use of a chiral hafnium(IV)-complex, which was originally introduced as an effective catalyst for the epoxidation of *N*-sulfonyl allylic amines, and cumenhydroperoxide.¹³ Excellent enantioselectivity was observed not only for aldimines but also for a ketimine, although the scope of this system was not fully studied. Our approach was based on the catalytic formation of chiral aminophosphonium peroxyimide **1**·HOOC(=NH)R as the key intermediate by the reaction of aminophosphonium hydroperoxide **1**·HOOH, generated from iminophosphorane **1** and H_2O_2 , with an appropriate nitrile (RCN) as illustrated in Figure 2. The nucleophilic peroxyimide ion of this chiral ion pair subsequently attacks electrophilic imine **2** enantioselectively followed by an expected smooth ring closure owing to the high leaving ability of the amidate ion $RCONH^-$ to afford the three-membered product and aminophosphonium amidate **1**·H₂NC(=O)R. The amidate ion is basic enough to abstract a proton from aminophosphonium ion **1**·H to regenerate parent iminophosphorane **1**, thus completing the catalytic cycle.

Initially, we chose trichloroacetonitrile (Cl₃CCN) as a requisite stoichiometric promoter, and carried out the oxidation

Figure 2. Working Hypothesis.

of *N*-Ts-4-nitrobenzalimine **2a** (Ts = tosyl) with an aqueous solution of H₂O₂ in the presence of Cl₃CCN and iminophosphorane **1a** (5 mol%) in toluene at 0 °C, which resulted in the quantitative isolation of the desired *N*-sulfonyl oxaziridine **3a** as anticipated, but with moderate enantioselectivity (Table 1, entry 1). An attempt without Cl₃CCN led to complete suppression of the reaction probably because leaving ability of the hydroxide ion was insufficient for *N*-sulfonyl amidate ion, a soft nucleophile, to attack the nearby oxygen atom in intermediate **a** (Fig. 2) for the rapid ring closure (entry 2).¹⁹ The formation of only a trace amount of **3a** was detected in the reactions with other electron-deficient nitriles (entry 3). These results demonstrate not only the crucial role of Cl₃CCN as a uniquely effective promoter but also the operation of the Payne-type oxidation mechanism. We then pursued the structural modification of the iminophosphorane for the improvement in the enantioselectivity (entries 4–10). With the L-valine-derived iminophosphoranes, the steric and electronic properties of the aromatic substituents (Ar) had a significant influence on the selectivity profile. In particular, the introduction of halogen atoms to the appropriate position of the aromatic nuclei was found to be beneficial; **1g** with a 3,5-dichlorophenyl substituent allowed for the production of **3a** in 86% yield with 94% ee (entry 9). The identity of the parent amino acid of the diamine backbone was also responsible for the stereocontrolling ability of iminophosphorane **1**, and L-isoleucine-derived **1i** was

Table 1. Optimization of the Catalyst Structure^a

Entry	1	imine	G	additive	Yield (%) ^b	ee (%) ^c	prod.
1	1a	2a	Ts	Cl ₃ CCN	99	68	3a
2	1a	2a	Ts	none	trace	—	—
3	1a	2a	Ts	R'CN ^d	trace	—	—
4	1b	2a	Ts	Cl ₃ CCN	88	44	3a
5	1c	2a	Ts	Cl ₃ CCN	83	74	3a
6	1d	2a	Ts	Cl ₃ CCN	84	65	3a
7	1e	2a	Ts	Cl ₃ CCN	94	85	3a
8	1f	2a	Ts	Cl ₃ CCN	89	70	3a
9	1g	2a	Ts	Cl ₃ CCN	86	94	3a
10	1h	2a	Ts	Cl ₃ CCN	88	91	3a
11	1i	2a	Ts	Cl ₃ CCN	89	98	3a
12	1i	4a	Mts ^e	Cl ₃ CCN	75	99	5a
13	1i	6	Mtr ^e	Cl ₃ CCN	87	97	7
14	1i	8	Bs	Cl ₃ CCN	89	97	9
15	1i	10	Ms	Cl ₃ CCN	86	93	11

^a Unless otherwise noted, reactions were performed on 0.1 mmol scale with 1.2 equiv of a 35% aqueous solution of H₂O₂, 1.2 equiv of Cl₃CCN, and 5 mol% of **1** in toluene (2.0 mL) at 0 °C.

^b Isolated yields were reported.

^c Enantiomeric excess was analyzed by chiral stationary phase HPLC. Absolute configuration of **3a** was assigned according to the literature data.¹²

^d R' = Me, Ph, C₆F₅, 3,5-(CF₃)₂C₆H₃

^e Mts = mesitylenesulfonyl, Mtr = 4-methoxy-2,3,6-trimethylbenzenesulfonyl. For this type of abbreviation for multi-substituted benzenesulfonyl groups, see ref 21.

singled out as the best catalyst (entry 11). It is noteworthy that over 1 g of **2a** was quantitatively converted into **3a** with virtually complete enantiocontrol in the presence of only 1 mol% of **1i** under otherwise similar conditions, demonstrating the scalability of this asymmetric oxidation (Scheme 3).²⁰ Furthermore, we confirmed that the variation in the *N*-sulfonyl group of the imines was feasible (entries 12–15); the asymmetric catalysis of **1i** accommodated imines **4a** and **6** bearing sterically demanding mesitylenesulfonyl (Mts) and 4-methoxy-2,3,6-trimethylbenzenesulfonyl (Mtr) groups, respectively (entries 12 and 13)²¹ and imine **10** with the smallest methanesulfonyl (Ms) group (entry 15).

Scheme 3. Catalytic Asymmetric Payne Oxidation on Practical Scale.

2.2. Generality

With the optimal catalyst structure, we thoroughly evaluated the generality of this **1i**-catalyzed asymmetric Payne oxidation of *N*-sulfonyl imines, and the results are summarized in Table 2. This system is applicable to a wide range of aromatic *N*-Ts imines with substituents of different steric and electronic attributes and the corresponding *N*-sulfonyl oxaziridines were obtained with uniformly excellent enantioselectivity (entries 1–11). Notably, potentially oxidizable furyl and thienyl functionalities were tolerated (entries 12 and 13), indicating the nucleophilic nature of the intermediary formed aminophosphonium peroxyimide **1i**-HOOC(N=H)CCl₃ (Fig. 2 and 3). With α,β -unsaturated aldimines, the 1,2-addition of the peroxyimide ion occurred exclusively with rigorous stereocontrol, leaving the olefin moiety intact (entry 14). In the oxidation of aliphatic imines, slight modifications of the reaction conditions were necessary for attaining high chemical yield except for α -quaternary imines (entries 15 and 16). When *N*-Ts-cyclohexylaldimine **2r** was exposed to the standard conditions using **1i** as the catalyst, the starting material was smoothly consumed, while only a trace amount of the desired oxaziridine **3r** was detected in the ¹H NMR spectrum of the crude aliquot. The major product was assigned as a diastereomeric mixture of dimeric peroxide **12** (R¹ = cyclo-hexyl) with dr = 1.7:1 (*vide infra*). This outcome could be attributed to the considerable effect of the inherent steric and electronic differences between the aromatic and aliphatic imines on the equilibrium in the addition of [•]OOH to the imine (Fig. 2). Although this problem was overcome by simply performing the reaction in dichloromethane at ambient temperature in the case of α -branched imines, installation of the bulky Mts group on the imine nitrogen was critical for promoting the enantioselective oxidation of α -unsubstituted imines with high efficiency (entries 17–23).²² In addition, *N*-Mts imines **4e** and **4f** with non-conjugated, electron-rich olefins were oxidized to the enantioenriched oxaziridines **5e** and **5f** without any difficulties (entries 22 and 23).

2.3. Kinetic resolution of α -chiral aldimines

Because this protocol for the catalytic asymmetric Payne oxidation was remarkably effective for a broad structural range of *N*-sulfonyl imines, we were interested in the application to the oxidative kinetic resolution of racemic α -chiral imines (Scheme

Table 2. Substrate Scope of the Payne Oxidation^a

<div> </div>							
Entry	R ¹	G	2	Time (h)	Yield (%) ^b	ee (%) ^c	3
1	Ph	Ts	2b	2.5	90	95	3b
2	2-FC ₆ H ₄	Ts	2c	4	83	95	3c
3	2-ClC ₆ H ₄	Ts	2d	3.5	72	95	3d
4	2-BrC ₆ H ₄	Ts	2e	3.5	78	95	3e
5	2-MeC ₆ H ₄	Ts	2f	2.5	86	96	3f
6	3-BrC ₆ H ₄	Ts	2g	2	84	97	3g
7	3-MeOC ₆ H ₄	Ts	2h	3.5	99	95	3h
8	4-ClC ₆ H ₄	Ts	2i	1.5	89	96	3i
9	4-BrC ₆ H ₄	Ts	2j	4	86	96	3j
10	4-MeC ₆ H ₄	Ts	2k	4.5	91	95	3k
11	2-naphthyl	Ts	2l	4.5	99	90	3l
12	3-furyl	Ts	2m	4	96	93	3m
13	3-thienyl	Ts	2n	2.5	91	94	3n
14	(<i>E</i>)-PhCH=CH	Ts	2o	3.5	85	96	3o
15	Me ₃ C	Ts	2p	2	85	98	3p
16	CH ₂ =CHCH ₂ C(Me) ₂	Ts	2q	3	79	98	3q
17 ^d	<i>cyclo</i> -hexyl	Ts	2r	1	91	98	3r
18 ^d	Me ₂ CH	Ts	2s	1	78	95	3s
19 ^d	Me ₂ CHCH ₂	Mts	4b	1	92	95	5b
20 ^d	Ph(CH ₂) ₂	Mts	4c	0.5	87	96	5c
21 ^d	Me(CH ₂) ₄	Mts	4d	1	87	94	5d
22 ^d	CH ₂ =CH(CH ₂) ₂	Mts	4e	1	83	96	5e
23 ^d	(<i>Z</i>)-EtCH=CH(CH ₂) ₂	Mts	4f	1	76	95	5f

^a Unless otherwise noted, reactions were performed on 0.1 mmol scale with 1.2 equiv of a 35% aqueous solution of H₂O₂, 1.2 equiv of Cl₃CCN, and 5 mol% of **1i** in toluene (2.0 mL) at 0 °C.

^b Isolated yields were reported.

^c Enantiomeric excesses were analyzed by chiral stationary phase HPLC. Absolute configurations of oxaziridines were assigned to be *R* by analogy to the known compounds.¹²

^d Reaction was conducted at 25 °C in dichloromethane (2.0 mL).

Scheme 4. Kinetic Resolution of α -Chiral Imines.

4). If aminophosphonium peroxyimide intermediate **1i**-HOOC(N=H)CCl₃ could discriminate the chirality of a stereogenic carbon at the α -position of the aliphatic imine, one of the enantiomers would be preferentially oxidized to afford a single diastereomer of four possible diastereomeric products. This possibility was explored in the reaction of the racemic

mixture of α -*tert*-butyldimethylsiloxy propanalimine (**4g**) under the reaction conditions similar to those optimized for the *N*-Mts-aliphatic aldimines except for the use of *rac*-**4g** in double the amount. Indeed, one of the diastereomers of the corresponding oxaziridine **5g** formed predominantly with high enantioselectivity, proving the prominent ability of the chiral peroxyimide to recognize the stereocenter in the starting imine.

2.4. Mechanistic study

As described above, when aliphatic *N*-Ts aldimine **2** was employed as the substrate in the **1i**-catalyzed Payne oxidation in toluene at 0 °C, a diastereomeric mixture of dimeric peroxides **12** was generally identified as the major products in the ¹H NMR spectrum of a crude mixture (Fig. 3). The formation of **12** could be accounted for by the fact that the aminophosphonium hydroperoxide first reacts with imine **2** to give a tautomeric mixture of peroxyhemiaminal intermediates **a** and **a'** and the peroxyanion form **a'** instantly attacks another imine **2**. This interpretation prompted us to consider another mechanism (path B), where key intermediate **b** is generated by the addition of **a'** to Cl₃CCN, in parallel with the Payne-type mechanism (path A).

Figure 3. Two Possible Reaction Pathways of Oxaziridination.

To elucidate the actual reaction pathway, the cross-over experiments were conducted, in which the predominant pathway could be determined by comparing the reactivities of imine **2** and peroxyhemiaminal **a**·H under the influence of **1i** and Cl₃CCN. Thus, a CDCl₃ solution of peroxyhemiaminal **4b'** was prepared by the treatment of *N*-Mts-isovaleraldimine **4b** with an ethereal solution of H₂O₂²³ in the presence of a catalytic quantity of iminophosphorane **1i** at ambient temperature; the ¹H NMR analysis showed that **4b** was instantly converted to **4b'** (Fig. 4a). After the simultaneous addition of *N*-Mts-hydrocinnalalimine **4c** and excess amount of Cl₃CCN to the reaction mixture, the ¹H NMR spectral analysis revealed almost exclusive formation of **5c** in 63% yield with 97% ee (Scheme 5, top and Fig. 4b), suggesting the dominant contribution of path A. Importantly, **5b** predominantly formed by switching the roles of **4b** and **4c** (Scheme 5, bottom and Fig. 4d). These observations clearly demonstrated that hydroperoxide ion rather than the peroxyhemiaminal ion preferentially attacked Cl₃CCN with the aid of **1i**-H to afford the oxaziridines **3**. Moreover, the enantiomeric excesses of **5b** and **5c** thus obtained were the same

Scheme 5. Cross-Over Experiments Using Aliphatic Imines.

Figure 4. ^1H NMR Analysis of Cross-Over Experiment.

Scheme 6. Oxaziridination of Aliphatic *N*-Mts Imines in the $\text{CDCl}_3/\text{Et}_2\text{O}$ Solvent System.

with those of the products obtained from the independent reactions with **4b** and **4c** under similar conditions (Scheme 6). Although the intervention of path B could not be completely

excluded, the experimental results strongly supported that iminophosphorane selectively catalyzes this asymmetric oxazirination via the initially proposed path A.

2.5. Derivatization

The synthetic utility of this catalytic imine oxidation protocol was highlighted through the fruitful derivatization of the chiral oxaziridines (Scheme 7). With the expectation of intramolecular oxygen-transfer reaction on the basis of the intrinsic character of the oxaziridine as an organic oxidant,^{24–26} **5e** (96% ee) was simply heated at 60 °C in chloroform and indeed transformed into the corresponding epoxy imine **13e**. The subsequent Lewis acid-promoted reduction of the C–N double bond triggered the 5-*exo-tet* cyclization to furnish the pyrrolidine methanol derivative **14e** in good yield with 95% ee (Scheme 7a). The conservation of enantiomeric purity throughout this process reflects the cyclic transition state (TS) at the oxygen-transfer stage. The result of the cross-over experiment shown in Scheme 8 also suggests the participation of the intramolecular oxygen-transfer process. In a similar manner, chiral secondary alcohol **14f** was prepared from **5f** (95% ee) via *N*-sulfonyl imine **13f** with an internal *cis*-epoxide moiety (Scheme 7b). Finally, enantioenriched aromatic oxaziridine **3b** (95% ee) was subjected to the Yoon's conditions for the copper salt-catalyzed oxyamination of *N*-acetyl indole, taking the advantage of the recent progress in methodology development for utilizing oxaziridines as versatile intermediates; tricyclic indoline derivative **15** was obtained without loss of enantiomeric excess (Scheme 7c).^{25j}

Scheme 7. Derivatization of Chiral Oxaziridines.

3. Conclusion

The first catalytic asymmetric Payne oxidation of *N*-sulfonyl imines was developed under the catalysis of *P*-spiro chiral triaminoiminophosphoranes. This protocol is applicable to structurally diverse aromatic and aliphatic imines, which makes the chiral oxaziridines easily accessible yet synthetically valuable reagents and building blocks. Furthermore, the success in the

Scheme 8. Cross-Over Experiment at the Oxygen-transfer Reaction.

catalytic use of a chiral base for the Payne oxidation would stimulate further research on the asymmetric oxidations based on the H_2O_2 -nitrile system.

4. Experimental

4.1. General

Infrared spectra were recorded on a Shimadzu IRAffinity-1 spectrometer. ^1H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) or a Bruker AVANCE III-OneBasy500 (500 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane (0.0 ppm) resonance as the internal standard (CDCl_3). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 (101 MHz) or a Bruker AVANCE III-OneBasy500 (126 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard (CDCl_3 ; 77.36 ppm, C_6D_6 ; 128.06 ppm). ^{31}P NMR spectra were recorded on a JEOL JNM-ECS400 (162 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from H_3PO_4 (0.0 ppm) resonance as the external standard. ^{19}F NMR spectra were recorded on a JEOL JNM-ECS400 (376 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from benzotrifluoride (−64.0 ppm) resonance as the external standard. Optical rotations were measured on a HORIBA SEPA-500 polarimeter. The high resolution mass spectra were conducted on Thermo Fisher Scientific Exactive. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm). Flash column chromatography was performed on PSQ60AB (spherical, av. 55 μm ; Fuji Silysia Chemical Ltd.). Enantiomeric excesses were determined by HPLC analysis using chiral columns [$\square$ 4.6 mm x 250 mm, DAICEL CHIRALCEL OD-3 (OD3), CHIRALCEL OJ-3 (OJ3), CHIRALPAK AD-3 (AD3), CHIRALPAK IB (IB), and CHIRALPAK IC-3 (IC3)] with *n*-hexane (H), 2-propanol (IPA), and ethanol (EtOH) as eluent. Toluene and dichloromethane (CH_2Cl_2) were supplied from Kanto Chemical Co., Inc. as “Dehydrated” and further purified by passing through neutral alumina under nitrogen atmosphere. Aminophosphonium chlorides **1**·HCl,^{8f} iminophosphoranes **1**,^{8f} and *N*-sulfonyl imines **2**²⁷ were prepared by following the literature procedures. Trifluoroacetic acid (TFA) and trifluoromethanesulfonic acid (TfOH) were kindly supplied from Asahi Glass Co., Ltd. and Central Glass Co., Ltd., respectively. Other simple chemicals were purchased and used as such.

4.2. Experimental Procedures and Characterization

4.2.1. Characterization of Chiral Iminophosphorane **1i**

1i·HCl: White solid; mp 204–206 °C (decomp); ^1H NMR (400 MHz, CD_3OD) δ 7.72 (4H, brd, J = 1.6 Hz), 7.61 (2H, t, J = 1.6 Hz), 7.55 (2H, t, J = 1.6 Hz), 7.40 (4H, br), 4.23 (2H, dd, $J_{\text{P-H}}$

= 20.4 Hz, $J_{\text{H-H}}$ = 4.3 Hz), 2.07 (6H, d, $J_{\text{P-H}}$ = 10.0 Hz), 1.85–1.72 (2H, m), 1.53–1.40 (2H, m), 1.16–1.01 (2H, m), 0.90 (6H, t, J = 7.3 Hz), 0.79 (6H, d, J = 6.9 Hz), N-H protons were missing due to deuterium exchange; ^{13}C NMR (101 MHz, CD_3OD) δ 151.4, 143.6 (d, $J_{\text{P-C}}$ = 12.6 Hz), 137.5, 136.6, 129.9, 129.6, 127.4, 126.7, 72.8 (d, $J_{\text{P-C}}$ = 10.6 Hz), 71.0 (d, $J_{\text{P-C}}$ = 11.6 Hz), 37.8, 33.0 (d, $J_{\text{P-C}}$ = 5.8 Hz), 26.3, 18.8, 12.2; ^{31}P NMR (162 MHz, CD_3OD) δ 35.5; IR (film) 2970, 2930, 2874, 1568, 1558, 1420, 1356, 1179, 1005, 862, 856, 802 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{38}\text{H}_{40}\text{N}_4^{35}\text{Cl}_8\text{P}^+$ ($[\text{M}-\text{Cl}]^+$) 863.0493. Found 863.0495; $[\alpha]_{\text{D}}^{22}$ −158.1 (c = 1.00, CH_2Cl_2).

1i: White solid; mp 133–135 °C (decomp); ^1H NMR (400 MHz, CD_3OD) δ 7.72 (4H, d, J = 1.7 Hz), 7.47 (4H, br), 7.44 (2H, t, J = 1.7 Hz), 7.39 (2H, t, J = 1.7 Hz), 3.93 (2H, dd, $J_{\text{P-H}}$ = 19.5 Hz, $J_{\text{H-H}}$ = 3.9 Hz), 2.02–1.87 (2H, m), 1.96 (6H, d, $J_{\text{P-H}}$ = 9.1 Hz), 1.43–1.29 (2H, m), 1.13–0.98 (2H, m), 0.83 (6H, t, J = 7.3 Hz), 0.77 (6H, d, J = 7.3 Hz), N-H proton was missing due to deuterium exchange; ^{13}C NMR (101 MHz, CD_3OD) δ 154.9, 147.6, 136.5, 135.9, 128.4, 128.3, 127.8, 127.1, 74.0 (d, $J_{\text{P-C}}$ = 15.5 Hz), 72.0 (d, $J_{\text{P-C}}$ = 7.7 Hz), 38.5, 32.9 (d, $J_{\text{P-C}}$ = 4.8 Hz), 26.2, 19.3, 12.4; ^{31}P NMR (162 MHz, CD_3OD) δ 42.2; IR (film) 2968, 2930, 2872, 1558, 1418, 1204, 1136, 1121, 854 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{38}\text{H}_{40}\text{N}_4^{35}\text{Cl}_8\text{P}^+$ ($[\text{M}+\text{H}]^+$) 863.0493. Found 863.0499; $[\alpha]_{\text{D}}^{22}$ −218.9 (c = 1.00, CH_2Cl_2).

4.2.2. Characterization of *N*-Sulfonyl Imines

2h: White solid; mp 71–72 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.99 (1H, s), 7.89 (2H, d, J = 8.5 Hz), 7.50–7.46 (1H, m), 7.45 (1H, d, J = 7.7, 1.1 Hz), 7.40 (1H, t, J = 7.7 Hz), 7.35 (2H, d, J = 8.5 Hz), 7.16 (1H, ddd, J = 7.7, 2.7, 1.1 Hz), 3.84 (3H, s), 2.44 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 170.5, 160.4, 145.0, 135.3, 134.0, 130.4, 130.1, 128.5, 125.7, 122.6, 113.5, 55.9, 22.0; IR (film) 3003, 2938, 2833, 1576, 1321, 1302, 1273, 1155, 1086, 1040, 806 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{15}\text{NNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 312.0665. Found 312.0663.

2m: Off-white solid; mp 126–127 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.00 (1H, s), 8.09 (1H, t, J = 1.4 Hz), 7.86 (2H, d, J = 8.2 Hz), 7.50 (1H, t, J = 1.4 Hz), 7.34 (2H, d, J = 8.2 Hz), 6.84 (1H, d, J = 1.4 Hz), 2.44 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 162.1, 152.4, 145.7, 144.9, 35.4, 130.1, 128.3, 123.6, 108.3, 22.0; IR (film) 3130, 3026, 2970, 1601, 1315, 1283, 1150, 1086, 870, 827, 808 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_{11}\text{NNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 272.0352. Found 272.0350.

2q: White solid; mp 57–58 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.44 (1H, s), 7.79 (2H, d, J = 8.4 Hz), 7.33 (2H, d, J = 8.4 Hz), 5.64 (1H, ddt, J = 17.1, 10.4, 7.3 Hz), 5.03 (1H, dq, J = 10.4, 1.0 Hz), 5.01 (1H, dq, J = 17.1, 1.0 Hz), 2.45 (3H, s), 2.24 (2H, dt, J = 7.3, 1.0 Hz), 1.12 (6H, s); ^{13}C NMR (126 MHz, CDCl_3) δ 184.0, 144.9, 135.2, 133.1, 130.1, 128.4, 119.3, 44.2, 41.2, 23.9, 22.0; IR (film) 2974, 2928, 1628, 1468, 1323, 1159, 1092, 922, 804 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{19}\text{NNaO}_2\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 288.1029. Found 288.1028.

4a: Pale yellow solid; mp 178–179 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.13 (1H, s), 8.34 (2H, d, J = 8.7 Hz), 8.11 (2H, d, J = 8.7 Hz), 7.01 (1H, s), 2.71 (6H, s), 2.33 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 166.6, 151.4, 144.3, 140.9, 138.0, 132.4, 132.1, 131.4, 124.5, 23.4, 21.4; IR (film) 1593, 1522, 1342, 1317, 1215, 1155, 1036, 854, 839 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{NaO}_4\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 355.0723. Found 355.0723.

4e: Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 8.60 (1H, t, J = 4.2 Hz), 6.97 (2H, s), 5.79 (1H, ddt, J = 17.1, 10.2, 6.9 Hz), 5.04 (1H, dq, J = 17.1, 1.3 Hz), 5.01 (1H, dq, J = 10.2, 1.3 Hz), 2.66–2.58 (2H, m), 2.63 (6H, s), 2.39 (2H, q, J = 6.9 Hz), 2.31

(3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 176.6, 143.8, 140.7, 136.2, 132.2, 131.7, 116.6, 35.2, 29.0, 23.3, 21.4; IR (film) 2978, 2939, 1628, 1443, 1317, 1155, 1055, 916, 853 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_2\text{S}^+$ ($[\text{M}+\text{H}]^+$) 266.1209. Found 266.1203.

6: Yellow solid; mp 191–192 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.11 (1H, s), 8.33 (2H, d, $J = 8.7$ Hz), 8.11 (2H, d, $J = 8.7$ Hz), 6.64 (1H, s), 3.87 (3H, s), 2.72 (3H, s), 2.66 (3H, s), 2.17 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 165.9, 160.9, 151.3, 141.1, 140.4, 138.2, 132.0, 126.5, 126.0, 124.5, 112.6, 56.0, 24.5, 19.0, 12.3; IR (film) 1593, 1520, 1342, 1315, 1275, 1150, 1121, 839 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_5\text{S}^+$ ($[\text{M}+\text{H}]^+$) 363.1009. Found 363.1009.

8: Pale yellow solid; mp 190–191 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.14 (1H, s), 8.34 (2H, d, $J = 8.8$ Hz), 8.13 (2H, d, $J = 8.8$ Hz), 8.04 (2H, d, $J = 7.8$ Hz), 7.69 (1H, t, $J = 7.8$ Hz), 7.60 (2H, t, $J = 7.8$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 168.1, 151.6, 137.7, 137.5, 134.5, 132.3, 129.7, 128.7, 124.6; IR (film) 1597, 1522, 1348, 1321, 1217, 1161, 1088, 843 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{NaO}_4\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 313.0253. Found 313.0252.

10: White solid; mp 186–187 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 9.14 (1H, s), 8.39 (2H, d, $J = 8.6$ Hz), 8.16 (2H, d, $J = 8.6$ Hz), 3.20 (3H, s); ^{13}C NMR (126 MHz, CDCl_3) δ 169.5, 151.7, 137.4, 132.2, 124.7, 40.6; IR (film) 1618, 1593, 1522, 1346, 1310, 1217, 1146, 864, 841 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_8\text{H}_8\text{N}_2\text{NaO}_4\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 251.0097. Found 251.0096.

4.2.3. General Procedure 1 for Catalytic Asymmetric Payne Oxidation of Aromatic *N*-Sulfonyl Imines

To a solution of chiral iminophosphorane **1i** (4.33 mg, 0.0050 mmol, 0.05 equiv), *N*-sulfonyl imine **2** (0.100 mmol, 1 equiv), and Cl_3CCN (12.0 μL , 0.120 mmol, 1.2 equiv) in toluene (2.0 mL) was added an aqueous 35% solution of H_2O_2 (10.5 μL , 1.2 equiv, titrated by using KMnO_4) at 0 $^\circ\text{C}$ under Ar atmosphere. After being stirred for indicated time, the reaction was quenched by the addition of a saturated aqueous solution of Na_2SO_3 (5 mL). The aqueous phase was extracted with ethyl acetate (EA, 2×10 mL). The combined organic extracts were dried over Na_2SO_4 . After filtration, the organic phase was concentrated under reduced pressure. The residue thus obtained was purified by column chromatography on silica gel (H/EA as eluent) to afford oxaziridine **3**. The enantiomeric excess of **3** was determined by HPLC analysis.

4.2.4. General Procedure 2 for Catalytic Asymmetric Payne Oxidation of Aliphatic *N*-Sulfonyl Imines

A solution of chiral iminophosphorane **1i** (4.33 mg, 0.0050 mmol, 0.05 equiv), *N*-sulfonyl imine **4** (0.100 mmol, 1.0 equiv), and Cl_3CCN (12.0 μL , 0.120 mmol, 1.2 equiv) in CH_2Cl_2 (2.0 mL) was treated with an aqueous 35% solution of H_2O_2 (10.5 μL , 1.2 equiv, titrated by using KMnO_4) at 25 $^\circ\text{C}$ under Ar atmosphere. The resulting reaction mixture was stirred for indicated time and then, remaining peroxides were quenched by the addition of a saturated aqueous solution of Na_2SO_3 (5 mL). After extraction of the aqueous phase with EA (2×10 mL), the combined organic extracts were dried over Na_2SO_4 and filtered. The organic phase was concentrated and the residual crude mixture was purified by column chromatography on silica gel (H/EA as eluent) to afford oxaziridine **5**. The enantiomeric excess of **5** was determined by HPLC analysis.

4.2.5. Characterization of *N*-Sulfonyl Oxaziridines

3a¹²: Prepared from *N*-Ts-4-nitrobenzalimine **2a** (1.52 g, 5.00 mmol, 1 equiv) by *General Procedure 1* as a white solid (1.54 g, 4.82 mmol, 96%) with 98% ee as determined by HPLC analysis; HPLC OJ3, H/IPA = 60:40, flow rate = 1.0 mL/min, $\lambda = 232$ nm, 32.8 min (major isomer), 42.1 min (minor isomer); mp 121–123 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.27 (2H, d, $J = 8.3$ Hz), 7.93 (2H, d, $J = 8.2$ Hz), 7.63 (2H, d, $J = 8.7$ Hz), 7.46 (2H, d, $J = 8.7$ Hz), 5.56 (1H, s), 2.52 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 150.1, 147.2, 137.6, 131.4, 130.5, 129.8, 129.7, 124.2, 74.7, 22.2; IR (film) 1595, 1529, 1346, 1298, 1188, 1175, 1161, 1109, 1068, 827 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{NaO}_5\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 343.0359. Found 343.0360.; $[\alpha]_{\text{D}}^{22} +74.3$ ($c = 1.00$, CHCl_3).

5a: Prepared from *N*-Mts-4-nitrobenzalimine **4a** (32.2 mg, 0.0968 mmol, 1 equiv) by *General Procedure 1* as a white solid (25.4 mg, 0.0729 mmol, 75%) with 99% ee as determined by HPLC analysis; HPLC AD3, H/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 22.6 min (major isomer), 28.3 min (minor isomer); mp 137–139 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.27 (2H, d, $J = 8.6$ Hz), 7.65 (2H, d, $J = 8.6$ Hz), 7.06 (2H, s), 5.60 (1H, s), 2.73 (6H, s), 2.36 (3H, s); ^{13}C NMR (126 MHz, CDCl_3) δ 150.0, 145.6, 142.4, 138.0, 132.6, 129.7, 129.5, 124.2, 74.1, 23.5, 21.5; IR (film) 2922, 1715, 1603, 1524, 1458, 1344, 1238, 1163, 1107, 1040, 826 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{NaO}_5\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 371.0672. Found 371.0671.; $[\alpha]_{\text{D}}^{21} +81.6$ ($c = 1.00$, CHCl_3).

7: Prepared from *N*-Mtr-4-nitrobenzalimine **6** (36.3 mg, 0.100 mmol, 1 equiv) by *General Procedure 1* as a white solid (32.8 mg, 0.0867 mmol, 87%) with 97% ee as determined by HPLC analysis; HPLC AD3, H/IPA = 80:20, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 19.0 min (minor isomer), 24.2 min (major isomer); mp 128–129 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.27 (2H, d, $J = 8.7$ Hz), 7.66 (2H, d, $J = 8.7$ Hz), 6.67 (1H, s), 5.61 (1H, s), 3.90 (3H, s), 2.73 (3H, s), 2.70 (3H, s); ^{13}C NMR (126 MHz, CDCl_3) δ 161.7, 150.0, 142.4, 142.2, 138.2, 129.7, 126.3, 124.5, 124.2, 112.7, 74.2, 56.0, 24.5, 19.1, 12.4; IR (film) 1582, 1560, 1528, 1447, 1339, 1315, 1238, 1184, 1153, 1125, 1015, 827 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{NaO}_5\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 401.0778. Found 401.0779.; $[\alpha]_{\text{D}}^{21} +60.2$ ($c = 1.00$, CHCl_3).

9: Prepared from *N*-Bs-4-nitrobenzalimine **8** (29.3 mg, 0.101 mmol, 1 equiv) by *General Procedure 1* as a white solid (27.5 mg, 0.0898 mmol, 89%) with 97% ee as determined by HPLC analysis; HPLC OJ3, H/IPA = 60:40, flow rate = 1.0 mL/min, $\lambda = 258$ nm, 37.4 min (major isomer), 46.6 min (minor isomer); mp 105–107 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.27 (2H, d, $J = 8.7$ Hz), 8.06 (2H, dd, $J = 7.7$, 1.2 Hz), 7.80 (1H, tt, $J = 7.7$, 1.2 Hz), 7.66 (2H, t, $J = 7.7$ Hz), 7.65 (2H, d, $J = 8.7$ Hz), 5.60 (1H, s); ^{13}C NMR (126 MHz, CDCl_3) δ 150.2, 137.5, 135.7, 134.7, 129.9, 129.8, 129.7, 124.3, 74.9; IR (film) 1609, 1520, 1449, 1346, 1294, 1240, 1184, 1165, 1084, 827 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{NaO}_5\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 329.0203. Found 329.0202.; $[\alpha]_{\text{D}}^{21} +84.1$ ($c = 1.01$, CHCl_3).

11: Prepared from *N*-Ms-4-nitrobenzalimine **10** (22.6 mg, 0.0990 mmol, 1 equiv) by *General Procedure 1* as a white solid (20.8 mg, 0.0852 mmol, 86%) with 93% ee as determined by HPLC analysis; HPLC OJ3, H/IPA = 60:40, flow rate = 1.0 mL/min, $\lambda = 257$ nm, 52.7 min (major isomer), 59.0 min (minor isomer); mp 122–124 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.30 (2H, d, $J = 8.9$ Hz), 7.69 (2H, d, $J = 8.9$ Hz), 5.55 (1H, s), 3.26 (3H, s); ^{13}C NMR (126 MHz, CDCl_3) δ 150.2, 137.2, 129.7, 124.3, 74.0, 38.7; IR (film) 2922, 1709, 1609, 1524, 1339, 1296, 1240, 1157, 1107, 968, 822 cm^{-1} ; HRMS (ESI) Calcd for

$\text{C}_8\text{H}_8\text{N}_2\text{NaO}_5\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 267.0046. Found 267.0044.; $[\alpha]_{\text{D}}^{21} +156.9$ ($c = 1.00$, CHCl_3).

3b¹²: Prepared from *N*-Ts-benzaldimine **2b** (25.7 mg, 0.0991 mmol, 1 equiv) by *General Procedure 1* as a white solid (24.6 mg, 0.0894 mmol, 90%) with 95% ee as determined by HPLC analysis; HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 7.6 min (major isomer), 10.4 min (minor isomer); mp 85–87 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (2H, d, $J = 8.4$ Hz), 7.48–7.37 (7H, m), 5.55 (1H, s), 2.49 (3H, s); ^{13}C NMR (101 MHz, CDCl_3): δ 146.7, 131.8, 131.7, 130.9, 130.4, 129.8, 129.1, 128.6, 76.7, 22.2; IR (film) 2922, 2851, 1593, 1460, 1341, 1296, 1244, 1159, 1086, 814, 802 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{13}\text{NNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 298.0508. Found 298.0507.; $[\alpha]_{\text{D}}^{23} +110.2$ ($c = 1.00$, CHCl_3).

3c¹²: Prepared from *N*-Ts-2-fluorobenzaldimine **2c** (27.0 mg, 0.0974 mmol, 1 equiv) by *General Procedure 1* as a white solid (23.6 mg, 0.0805 mmol, 83%) with 95% ee as determined by HPLC analysis; HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda = 227$ nm, 6.2 min (major isomer), 7.0 min (minor isomer); mp 81–83 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (2H, d, $J = 8.4$ Hz), 7.43 (2H, d, $J = 8.7$ Hz), 7.45–7.40 (1H, m), 7.26 (1H, ddd, $J_{\text{H-H}} = 8.0$, 1.3 Hz, $J_{\text{F-H}} = 6.0$ Hz), 7.15 (1H, t, $J = 7.4$ Hz), 7.11 (1H, dd, $J_{\text{H-H}} = J_{\text{F-H}} = 9.4$ Hz), 5.79 (1H, s), 2.50 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 162.9 (d, $J_{\text{F-C}} = 256.4$ Hz), 146.9, 133.2 (d, $J_{\text{F-C}} = 7.7$ Hz), 131.5, 130.4, 129.9, 128.8, 124.9, 118.6 (d, $J_{\text{F-C}} = 11.6$ Hz), 116.0 (d, $J_{\text{F-C}} = 20.3$ Hz), 71.3 (d, $J_{\text{F-C}} = 6.8$ Hz), 22.2; ^{19}F NMR (376 MHz, CDCl_3): δ -120.3; IR (film) 1592, 1491, 1395, 1346, 1254, 1188, 1177, 1161, 1094, 1086, 837, 814 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{12}\text{FNNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 316.0414. Found 316.0413.; $[\alpha]_{\text{D}}^{22} +85.0$ ($c = 1.01$, CHCl_3).

3d: Prepared from *N*-Ts-2-chlorobenzaldimine **2d** (29.3 mg, 0.100 mmol, 1 equiv) by *General Procedure 1* as a white solid (22.3 mg, 0.0720 mmol, 72%) with 95% ee as determined by HPLC analysis; HPLC OJ3, H/IPA = 80:20, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 18.0 min (major isomer), 24.2 min (minor isomer); mp 78–80 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (2H, d, $J = 8.2$ Hz), 7.46–7.33 (4H, m), 7.32–7.22 (2H, m), 5.85 (1H, s), 2.49 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 146.9, 135.3, 132.3, 131.3, 130.4, 130.0, 129.0, 128.8, 127.6, 74.1, 22.2, one carbon was missing probably due to overlapping; IR (film) 2916, 1595, 1352, 1240, 1186, 1175, 1163, 1090, 1053 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{12}^{35}\text{ClNNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 332.0119. Found 332.0118.; $[\alpha]_{\text{D}}^{22} +23.0$ ($c = 1.01$, CHCl_3).

3e¹²: Prepared from *N*-Ts-2-bromobenzaldimine **2e** (33.9 mg, 0.100 mmol, 1 equiv) by *General Procedure 1* as a white solid (27.5 mg, 0.0776 mmol, 78%) with 95% ee as determined by HPLC analysis; HPLC OJ3, H/IPA = 4:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 20.5 min (major isomer), 25.7 min (minor isomer); mp 82–84 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.94 (2H, d, $J = 8.5$ Hz), 7.59 (1H, dd, $J = 6.6$, 2.5 Hz), 7.43 (2H, d, $J = 8.5$ Hz), 7.34–7.22 (3H, m), 5.80 (1H, s), 2.49 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 146.9, 133.2, 132.5, 131.2, 130.6, 130.4, 130.0, 129.1, 128.2, 124.4, 76.4, 22.2; IR (film) 2924, 2857, 1695, 1587, 1435, 1342, 1236, 1186, 1161, 1084, 1026, 812 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{12}^{79}\text{BrNNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 375.9613. Found 375.9613.; $[\alpha]_{\text{D}}^{23} +44.3$ ($c = 1.01$, CHCl_3).

3f¹²: Prepared from *N*-Ts-2-tolualdimine **2f** (27.8 mg, 0.102 mmol, 1 equiv) by *General Procedure 1* as a white solid (25.5 mg, 0.0881 mmol, 86%) with 96% ee as determined by HPLC analysis; HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda = 229$ nm, 6.7 min (major isomer), 11.0 min (minor isomer); mp 52–54 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (2H, d, $J = 8.4$ Hz),

7.42 (2H, d, $J = 8.4$ Hz), 7.32 (1H, ddd, $J = 8.8$, 7.4, 1.4 Hz), 7.24 (1H, d, $J = 7.8$ Hz), 7.21–7.17 (2H, m), 5.67 (1H, s), 2.51 (3H, s), 2.49 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 146.5, 137.9, 131.6, 130.7, 130.6, 130.1, 129.5, 128.9, 126.8, 126.4, 74.7, 21.9, 18.6; IR (film) 2924, 1595, 1491, 1464, 1342, 1250, 1186, 1165, 1088, 812 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{15}\text{NNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 312.0665. Found 312.0662.; $[\alpha]_{\text{D}}^{22} +58.0$ ($c = 1.19$, CHCl_3).

3g¹²: Prepared from *N*-Ts-3-bromobenzaldimine **2g** (33.9 mg, 0.100 mmol, 1 equiv) by *General Procedure 1* as a white solid (29.9 mg, 0.0844 mmol, 84%) with 97% ee as determined by HPLC analysis; HPLC OJ3, H/IPA = 80:20, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 18.2 min (major isomer), 28.0 min (minor isomer); mp 104–106 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (2H, d, $J = 8.4$ Hz), 7.59 (1H, ddd, $J = 8.0$, 2.0, 1.0 Hz), 7.55 (1H, t, $J = 1.7$ Hz), 7.44 (2H, d, $J = 8.1$ Hz), 7.40 (1H, dt, $J = 8.0$, 1.4 Hz), 7.29 (1H, d, $J = 7.7$ Hz), 5.41 (1H, s), 2.50 (3H, s); ^{13}C NMR (101 MHz, CDCl_3): δ 147.0, 134.8, 133.2, 131.6, 131.4, 130.6, 130.5, 129.8, 127.4, 123.2, 75.6, 22.2; IR (film) 1595, 1437, 1350, 1238, 1188, 1173, 1092, 1086, 1070, 814 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{12}^{79}\text{BrNNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 375.9613. Found 375.9614.; $[\alpha]_{\text{D}}^{22} +86.8$ ($c = 1.04$, CHCl_3).

3h: Prepared from *N*-Ts-3-anisaldimine **2h** (28.6 mg, 0.0988 mmol, 1 equiv) by *General Procedure 1* as a colorless oil (29.8 mg, 0.0976 mmol, 99%) with 95% ee as determined by HPLC analysis; HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 8.9 min (major isomer), 11.5 min (minor isomer); ^1H NMR (400 MHz, CDCl_3) δ 7.93 (2H, d, $J = 8.2$ Hz), 7.42 (2H, d, $J = 8.2$ Hz), 7.30 (1H, t, $J = 8.0$ Hz), 7.06 (1H, dt, $J = 8.0$, 1.3 Hz), 6.99 (1H, ddd, $J = 8.0$, 2.7, 1.3 Hz), 6.90 (1H, dd, $J = 2.7$, 1.3 Hz), 5.42 (1H, s), 3.78 (3H, s), 2.49 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 160.2, 146.8, 132.3, 131.7, 130.4, 130.1, 129.8, 121.2, 118.2, 112.6, 76.6, 55.7, 22.2; IR (film) 2963, 2926, 2841, 1595, 1493, 1348, 1267, 1167, 1090, 1040, 906 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{15}\text{NNaO}_4\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 328.0614. Found 328.0611.; $[\alpha]_{\text{D}}^{20} +103.9$ ($c = 2.27$, CHCl_3).

3i¹²: Prepared from *N*-Ts-4-chlorobenzaldimine **2i** (29.5 mg, 0.100 mmol, 1 equiv) by *General Procedure 1* as a white solid (27.5 mg, 0.0888 mmol, 89%) with 96% ee as determined by HPLC analysis; HPLC OJ3, H/IPA = 80:20, flow rate = 1.0 mL/min, $\lambda = 234$ nm, 19.6 min (major isomer), 23.7 min (minor isomer); mp 85–87 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (2H, d, $J = 8.0$ Hz), 7.43 (2H, d, $J = 8.4$ Hz), 7.38–7.37 (4H, m), 5.43 (1H, s), 2.49 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 146.9, 137.9, 131.7, 130.4, 129.9, 129.8, 129.4, 75.9, 22.2, one carbon was missing probably due to overlapping; IR (film) 1597, 1495, 1356, 1344, 1186, 1180, 1157, 1016, 816 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{12}^{35}\text{ClNNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 332.0119. Found 332.0118.; $[\alpha]_{\text{D}}^{22} +88.5$ ($c = 1.05$, CHCl_3).

3j¹²: Prepared from *N*-Ts-4-bromobenzaldimine **2j** (33.6 mg, 0.0993 mmol, 1 equiv) by *General Procedure 1* as a white solid (30.2 mg, 0.0853 mmol, 86%) with 96% ee as determined by HPLC analysis; HPLC OJ3, H/IPA = 80:20, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 19.6 min (major isomer), 23.6 min (minor isomer); mp 92–93 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (2H, d, $J = 8.5$ Hz), 7.54 (2H, d, $J = 8.5$ Hz), 7.43 (2H, d, $J = 8.5$ Hz), 7.30 (2H, d, $J = 8.5$ Hz), 5.42 (1H, s), 2.49 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 146.9, 132.4, 131.6, 130.4, 130.1, 130.0, 129.7, 126.3, 76.0, 22.2; IR (film) 1505, 1350, 1188, 1176, 1161, 1094, 1086, 1070, 1013, 816 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{12}^{79}\text{BrNNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 375.9613. Found 375.9613.; $[\alpha]_{\text{D}}^{23} +70.9$ ($c = 1.06$, CHCl_3).

3k¹²: Prepared from *N*-Ts-4-tolualdimine **2k** (27.3 mg, 0.0999 mmol, 1 equiv) by *General Procedure 1* as a white solid (26.2 mg, 0.0905 mmol, 91%) with 95% ee as determined by HPLC analysis; HPLC OJ3, H/IPA = 80:20, flow rate = 1.0 mL/min, λ = 230 nm, 24.0 min (major isomer), 28.0 min (minor isomer); mp 77–79 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.92 (2H, d, J = 8.4 Hz), 7.41 (2H, d, J = 8.4 Hz), 7.32 (2H, d, J = 8.4 Hz), 7.19 (2H, d, J = 8.1 Hz), 5.41 (1H, s), 2.48 (3H, s), 2.36 (3H, s); ¹³C NMR (101 MHz, CDCl₃) δ 146.7, 142.1, 131.9, 130.4, 129.8, 128.5, 127.9, 76.8, 22.2, 21.8, one carbon was missing probably due to overlapping; IR (film) 1593, 1385, 1348, 1236, 1186, 1171, 1159, 1119, 1094, 1088, 816 cm⁻¹; HRMS (ESI) Calcd for C₁₅H₁₅NNaO₃S⁺ ([M+Na]⁺) 312.0665. Found 312.0663; [α]_D²³ +95.3 (c = 1.00, CHCl₃).

3l¹²: Prepared from *N*-Ts-2-naphthaldimine **2l** (31.1 mg, 0.100 mmol, 1 equiv) by *General Procedure 1* as a white solid (32.4 mg, 0.096 mmol, 99%) with 90% ee as determined by HPLC analysis; HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 230 nm, 10.0 min (major isomer), 10.8 min (minor isomer); mp 92–93 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.02 (1H, s), 7.96 (2H, d, J = 8.5 Hz), 7.90–7.82 (3H, m), 7.58–7.50 (2H, m), 7.44 (2H, d, J = 8.5 Hz), 7.39 (1H, dd, J = 8.5, 1.4 Hz), 5.62 (1H, s), 2.50 (3H, s); ¹³C NMR (101 MHz, CDCl₃) δ 146.7, 135.0, 132.8, 131.7, 130.3, 130.0, 129.7, 129.1, 128.6, 128.2, 128.1, 127.9, 127.1, 123.7, 76.9, 22.1; IR (film) 1593, 1344, 1202, 1171, 1088, 822 cm⁻¹; HRMS (ESI) Calcd for C₁₈H₁₅NNaO₃S⁺ ([M+Na]⁺) 348.0665. Found 348.0664. [α]_D²³ +59.4 (c = 0.504, CHCl₃).

3m: Prepared from *N*-Ts-3-furaldimine **2m** (24.8 mg, 0.0995 mmol, 1 equiv) by *General Procedure 1* as a colorless oil (25.3 mg, 0.0954 mmol, 96%) with 93% ee as determined by HPLC analysis; HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 227 nm, 8.3 min (major isomer), 9.8 min (minor isomer); ¹H NMR (400 MHz, CDCl₃) δ 7.91 (2H, d, J = 8.4 Hz), 7.78 (1H, d, J = 0.8 Hz), 7.42 (2H, d, J = 8.4 Hz), 7.41 (1H, s), 6.36 (1H, d, J = 0.8 Hz), 5.48 (1H, s), 2.49 (3H, s); ¹³C NMR (101 MHz, CDCl₃) δ 146.8, 145.4, 144.6, 131.6, 130.4, 129.7, 118.4, 108.6, 71.5, 22.2; IR (film) 3140, 2918, 1595, 1508, 1344, 1163, 1088, 1016, 874, 808 cm⁻¹; HRMS (ESI) Calcd for C₁₂H₁₁NNaO₄S⁺ ([M+Na]⁺) 288.0301. Found 288.0301; [α]_D²⁰ +80.5 (c = 0.670, CHCl₃).

3n: Prepared from *N*-Ts-3-thienylaldimine **2n** (26.6 mg, 0.100 mmol, 1 equiv) by *General Procedure 1* as a white solid (25.5 mg, 0.0906 mmol, 91%) with 94% ee as determined by HPLC analysis; HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 10.3 min (major isomer), 17.2 min (minor isomer); mp 55–57 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (2H, d, J = 8.5 Hz), 7.66 (1H, dd, J = 3.0, 1.1 Hz), 7.42 (2H, d, J = 8.5 Hz), 7.32 (1H, dd, J = 5.3, 3.0 Hz), 7.05 (1H, dd, J = 5.3, 1.1 Hz), 5.53 (1H, s), 2.48 (3H, s); ¹³C NMR (101 MHz, CDCl₃) δ 146.8, 133.2, 131.8, 130.4, 129.8, 129.4, 127.5, 126.2, 73.1, 22.2; IR (film) 3103, 2920, 1597, 1495, 1400, 1373, 1155, 1121, 1030, 1003, 812 cm⁻¹; HRMS (ESI) Calcd for C₁₂H₁₁NNaO₃S₂⁺ ([M+Na]⁺) 304.0073. Found 304.0071; [α]_D²³ +51.8 (c = 1.65, CHCl₃).

3o: Prepared from *N*-Ts-(*E*)-cinnamaldimine **2o** (28.4 mg, 0.0995 mmol, 1 equiv) by *General Procedure 1* as a white solid (25.5 mg, 0.0846 mmol, 85%) with 96% ee as determined by HPLC analysis; HPLC OD3, H/IPA = 19:1, flow rate = 1.0 mL/min, λ = 258 nm, 22.9 min (major isomer), 25.2 min (minor isomer); mp 67–68 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (2H, d, J = 8.2 Hz), 7.48–7.38 (4H, m), 7.38–7.30 (3H, m), 7.12 (1H, d, J = 16.4 Hz), 5.88 (1H, dd, J = 16.4, 7.9 Hz), 5.15 (1H, d, J = 7.9 Hz), 2.48 (3H, s); ¹³C NMR (101 MHz, C₆D₆) δ 145.8, 142.0, 134.9, 133.0, 130.0, 129.5, 129.4, 128.8, 127.6, 120.2, 77.6, 21.2; IR (film) 2922, 2851, 1595, 1344, 1186, 1163, 1123, 1090,

974, 812 cm⁻¹; HRMS (ESI) Calcd for C₁₆H₁₅NNaO₃S⁺ ([M+Na]⁺) 324.0665. Found 324.0664; [α]_D²² +152.3 (c = 2.03, CHCl₃).

3p¹²: Prepared from *N*-Ts-pivalaldimine **2p** (23.9 mg, 0.0999 mmol, 1 equiv) by *General Procedure 1* as a white solid (21.7 mg, 0.0842 mmol, 85%) with 98% ee as determined by HPLC analysis; HPLC OD3, H/IPA = 99:1, flow rate = 1.0 mL/min, λ = 226 nm, 6.6 min (minor isomer), 8.1 min (major isomer); mp 67–68 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.86 (2H, d, J = 8.4 Hz), 7.40 (2H, d, J = 8.0 Hz), 4.43 (1H, s), 2.48 (3H, s), 0.97 (9H, s); ¹³C NMR (101 MHz, CDCl₃) δ 146.4, 132.1, 130.3, 129.6, 84.1, 32.1, 24.4, 22.1; IR (film) 2972, 1597, 1481, 1346, 1225, 1211, 1165, 1090, 868, 814 cm⁻¹; HRMS (ESI) Calcd for C₁₂H₁₇NNaO₃S⁺ ([M+Na]⁺) 278.0821. Found 278.0820; [α]_D²³ +118.5 (c = 1.55, CHCl₃).

3q: Prepared from *N*-Ts-2,2-dimethylpent-4-en-1-ylaldimine **2q** (26.4 mg, 0.0995 mmol, 1 equiv) by *General Procedure 1* as a colorless oil (22.2 mg, 0.0789 mmol, 79%) with 98% ee as determined by HPLC analysis; HPLC OD3, H/IPA = 99:1, flow rate = 1.0 mL/min, λ = 210 nm, 6.7 min (minor isomer), 8.1 min (major isomer); ¹H NMR (400 MHz, CDCl₃) δ 7.76 (2H, d, J = 8.7 Hz), 7.39 (2H, d, J = 8.7 Hz), 5.78 (1H, ddt, J = 14.8, 10.6, 7.6 Hz), 5.11 (2H, dd, J = 10.6, 1.4 Hz), 5.10 (2H, dd, J = 14.8, 1.4 Hz), 4.47 (1H, s), 2.47 (3H, s), 2.12 (2H, d, J = 7.6 Hz), 0.93 (3H, s), 0.92 (3H, s); ¹³C NMR (101 MHz, CDCl₃) δ 146.5, 133.1, 132.1, 130.3, 129.6, 119.2, 83.6, 43.1, 35.1, 22.1, 21.8, 21.7; IR (film) 2976, 1632, 1597, 1472, 1402, 1346, 1236, 1165, 1090, 997, 920, 866, 814 cm⁻¹; HRMS (ESI) Calcd for C₁₄H₂₀NO₃S⁺ ([M+H]⁺) 282.1158. Found 282.1157; [α]_D²¹ +91.5 (c = 1.81, CHCl₃).

3r¹²: Prepared from *N*-Ts-cyclohexanecarbaldimine **2r** (26.7 mg, 0.101 mmol, 1 equiv) by *General Procedure 2* as a white solid (26.0 mg, 0.0924 mmol, 91%) with 98% ee as determined by HPLC analysis; HPLC OD3, H/IPA = 95:5, flow rate = 0.5 mL/min, λ = 226 nm, 12.3 min (major isomer), 13.2 min (minor isomer); mp 32–33 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.85 (2H, d, J = 8.2 Hz), 7.39 (2H, d, J = 8.2 Hz), 4.47 (1H, s), 2.47 (3H, s), 1.80–1.71 (4H, m), 1.70–1.63 (1H, m), 1.62–1.55 (1H, m), 1.29–1.09 (5H, m); ¹³C NMR (101 MHz, CDCl₃) δ 146.4, 132.1, 130.3, 129.5, 81.5, 38.9, 27.4, 27.2, 26.2, 25.3, 22.1; IR (film) 2928, 2855, 1595, 1450, 1344, 1165, 1090, 858, 814 cm⁻¹; HRMS (ESI) Calcd for C₁₄H₁₉NNaO₃S⁺ ([M+Na]⁺) 304.0978. Found 304.0976; [α]_D²³ +104.9 (c = 1.70, CHCl₃).

3s¹²: Prepared from *N*-Ts-isobutyraldimine **2s** (22.3 mg, 0.0990 mmol, 1 equiv) by *General Procedure 2* as a white solid (18.8 mg, 0.0777 mmol, 78%) with 95% ee as determined by HPLC analysis; HPLC OD3, H/IPA = 19:1, flow rate = 0.5 mL/min, λ = 226 nm, 11.0 min (minor isomer), 12.1 min (major isomer); ¹H NMR (400 MHz, CDCl₃) δ 7.86 (2H, d, J = 8.2 Hz), 7.39 (2H, d, J = 8.2 Hz), 4.48 (1H, d, J = 6.5 Hz), 2.47 (3H, s), 1.89 (1H, octet, J = 6.5 Hz), 1.03 (3H, d, J = 6.5 Hz), 1.01 (3H, d, J = 6.5 Hz); ¹³C NMR (101 MHz, CDCl₃) δ 146.5, 132.0, 130.3, 129.5, 82.3, 29.9, 22.1, 16.9, 16.8; IR (film) 2970, 2934, 1597, 1470, 1346, 1188, 1163, 1090, 854, 814 cm⁻¹; HRMS (ESI) Calcd for C₁₁H₁₅NNaO₃S⁺ ([M+Na]⁺) 264.0665. Found 264.0664; [α]_D²³ +112.1 (c = 2.07, CHCl₃).

5b: Prepared from *N*-Mts-isovaleraldimine **4b** (26.4 mg, 0.0987 mmol, 1 equiv) by *General Procedure 2* as a colorless oil (25.8 mg, 0.0910 mmol, 92%) with 95% ee as determined by HPLC analysis; HPLC IC3, H/IPA = 98:2, flow rate = 1.0 mL/min, λ = 210 nm, 9.4 min (major isomer), 10.6 min (minor isomer); ¹H NMR (400 MHz, CDCl₃) δ 7.00 (2H, s), 4.73 (1H, t, J = 5.4 Hz), 2.70 (6H, s), 2.32 (3H, s), 1.93 (1H, nonet, J = 6.7

Hz), 1.70 (1H, ddd, $J = 14.3, 6.7, 5.4$ Hz), 1.66 (1H, ddd, $J = 14.3, 6.7, 5.4$ Hz), 1.01 (6H, t, $J = 6.7$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 142.0, 132.4, 76.9, 39.9, 25.3, 23.4, 23.1, 22.8, 21.5, one carbon atom was missing probably due to overlapping; IR (film) 2959, 1603, 1468, 1406, 1342, 1165, 1055, 1034, 853 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{21}\text{NNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 306.1134. Found 306.1131.; $[\alpha]_{\text{D}}^{22} +120.6$ ($c = 2.25$, CHCl_3).

5c: Prepared from *N*-Mts-hydrocinnamaldimine **4c** (31.0 mg, 0.0982 mmol, 1 equiv) by *General Procedure 2* as a white solid (28.4 mg, 0.0856 mmol, 87%) with 96% ee as determined by HPLC analysis; HPLC IC3, H/IPA = 98:2, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 17.3 min (major isomer), 19.0 (minor isomer); ^1H NMR (400 MHz, CDCl_3) δ 7.29 (2H, t, $J = 7.2$ Hz), 7.21 (1H, t, $J = 7.2$ Hz), 7.18 (2H, d, $J = 7.2$ Hz), 7.00 (2H, s), 4.77 (1H, t, $J = 4.7$ Hz), 2.78 (2H, t, $J = 8.1$ Hz), 2.68 (6H, s), 2.33 (3H, s), 2.23–2.08 (2H, m); ^{13}C NMR (101 MHz, CDCl_3) δ 145.0, 142.0, 140.1, 132.4, 129.8, 129.0, 128.6, 126.7, 76.9, 32.7, 29.9, 23.5, 21.5; IR (film) 2918, 2849, 1603, 1456, 1340, 1231, 1165, 1055, 1034, 856, 837 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{21}\text{NNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 354.1134. Found 354.1135.; $[\alpha]_{\text{D}}^{23} +87.6$ ($c = 1.69$, CHCl_3).

5d: Prepared from *N*-Mts-caproaldimine **4d** (24.9 mg, 0.0885 mmol, 1 equiv) by *General Procedure 2* as a colorless oil (23.0 mg, 0.0773 mmol, 87%) with 94% ee as determined by HPLC analysis; HPLC IC3, H/IPA = 99:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 14.7 min (major isomer), 17.1 (minor isomer); ^1H NMR (400 MHz, CDCl_3) δ 7.00 (2H, s), 4.71 (1H, t, $J = 5.0$ Hz), 2.70 (6H, s), 2.32 (3H, s), 1.85–1.77 (2H, m), 1.49 (2H, quintet, $J = 7.4$ Hz), 1.39–1.25 (4H, m), 0.89 (3H, t, $J = 6.9$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 142.1, 132.4, 130.0, 77.6, 31.5, 31.0, 23.6, 23.4, 22.7, 21.5, 14.2; IR (film) 2928, 2860, 1603, 1560, 1456, 1404, 1342, 1227, 1186, 1165, 1034, 853 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{23}\text{NNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 320.1291. Found 320.1290.; $[\alpha]_{\text{D}}^{24} +90.4$ ($c = 1.09$, CHCl_3).

5e: Prepared from *N*-Mts-4-pentenylaldimine **4e** (26.7 mg, 0.101 mmol, 1 equiv) by *General Procedure 2* as a colorless oil (24.0 mg, 0.0835 mmol, 83%) with 96% ee as determined by HPLC analysis; HPLC IC3, H/IPA = 99:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 17.2 min (major isomer), 19.2 min (minor isomer); ^1H NMR (400 MHz, CDCl_3) δ 7.00 (2H, s), 5.80 (1H, ddt, $J = 17.3, 10.3, 6.9$ Hz), 5.08 (1H, dq, $J = 17.3, 1.4$ Hz), 5.03 (1H, dq, $J = 10.3, 1.4$ Hz), 4.75 (1H, t, $J = 4.9$ Hz), 2.69 (6H, s), 2.32 (3H, s), 2.23 (2H, q, $J = 4.9$ Hz), 2.00–1.85 (2H, m); ^{13}C NMR (101 MHz, CDCl_3) δ 176.6, 144.4, 140.6, 136.2, 132.2, 131.7, 116.7, 35.2, 29.0, 23.3, 21.4; IR (film) 2980, 2941, 1603, 1449, 1344, 1165, 1055, 1034, 918, 854 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{19}\text{NNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 304.0978. Found 304.0975.; $[\alpha]_{\text{D}}^{22} +108.4$ ($c = 4.41$, CHCl_3).

5f: Prepared from *N*-Mts-(*Z*)-4-heptenylaldimine **4f** (29.1 mg, 0.0992 mmol, 1 equiv) by *General Procedure 2* as a colorless oil (23.3 mg, 0.0753 mmol, 76%) with 95% ee as determined by HPLC analysis; HPLC IC3, H/IPA = 99:1, flow rate = 1.0 mL/min, $\lambda = 210$ nm, 14.2 min (major isomer), 15.3 min (minor isomer); ^1H NMR (400 MHz, CDCl_3) δ 7.00 (2H, s), 5.45 (1H, tt, $J = 7.3, 1.4$ Hz), 5.31 (1H, tt, $J = 7.3, 1.4$ Hz), 4.74 (1H, t, $J = 4.8$ Hz), 2.69 (6H, s), 2.33 (3H, s), 2.22 (2H, q, $J = 7.3$ Hz), 2.04 (2H, quintet, $J = 7.3$ Hz), 1.89 (1H, dtd, $J = 14.7, 7.3, 4.8$ Hz), 1.86 (1H, dtd, $J = 14.7, 7.3, 4.8$ Hz), 0.96 (3H, t, $J = 7.6$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 142.1, 134.0, 132.4, 130.0, 126.5, 77.3, 31.3, 23.5, 21.7, 21.5, 20.8, 14.5; IR (film) 2970, 2934, 1628, 1603, 1560, 1456, 1339, 1319, 1155, 1055, 1034, 853 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{23}\text{NNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 332.1291. Found 332.1294.; $[\alpha]_{\text{D}}^{24} +7.3$ ($c = 1.00$, CHCl_3).

4.2.6. General Procedure for Kinetic Resolution of α -Chiral Imines

To a solution of chiral iminophosphorane **1i** (4.33 mg, 0.0050 mmol, 0.025 equiv), *N*-sulfonyl imine **4g** (72.0 mg, 0.20 mmol, 1 equiv), and Cl_3CCN (12.0 μL , 0.120 mmol, 0.6 equiv) in CH_2Cl_2 (4.0 mL) was added an aqueous 35% solution of H_2O_2 (8.8 μL , 0.5 equiv, titrated by using KMnO_4) at 25 °C under Ar atmosphere. After being stirred for 1 h, the reaction was quenched by the addition of a saturated aqueous solution of Na_2SO_3 (5 mL). The aqueous phase was extracted with EA (2 $\times$ 10 mL). The combined organic extracts were dried over Na_2SO_4 and filtered. The organic phase was concentrated under reduced pressure. The residue thus obtained was purified by column chromatography on silica gel (H/EA = 50/1 as eluent) to afford a diastereomeric mixture of oxaziridine **5g** as colorless oil (34.4 mg, 0.0897 mmol, 46%). The diastereomeric ratio of **5g** was determined by HPLC analysis (dr = 87.9:0.2:7.2:4.7). **5g**: HPLC IC3, H/IPA = 99:1, flow rate = 0.5 mL/min, $\lambda = 210$ nm, 10.9 min (major diastereomer of (1'*S*)-isomer), 12.3 min (minor diastereomer of (1'*R*)-isomer), 15.5 min (major diastereomer of (1'*R*)-isomer), 16.5 min (minor diastereomer of (1'*S*)-isomer); ^1H NMR (400 MHz, CDCl_3) *major isomer* δ 7.01 (2H, s), 4.59 (1H, d, $J = 6.3$ Hz), 3.66 (1H, quintet, $J = 6.3$ Hz), 2.69 (6H, s), 2.33 (3H, s), 1.28 (3H, d, $J = 6.3$ Hz), 0.88 (9H, s), 0.05 (6H, s); ^{13}C NMR (101 MHz, CDCl_3) *major isomer* δ 145.1, 142.2, 132.4, 129.6, 79.3, 69.0, 26.0, 23.5, 21.5, 19.4, 18.4, -4.4, -4.6; IR (film) 2954, 2930, 2859, 1602, 1464, 1350, 1254, 1188, 1173, 1115, 988, 835 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{31}\text{NNaO}_4\text{SSi}^+$ ($[\text{M}+\text{Na}]^+$) 403.1635. Found 408.1634.

4.3. Mechanistic Study

4.3.1. Preparation of an Ethereal Solution of H_2O_2 ²³

A 35% aqueous solution of H_2O_2 (titrated by using KMnO_4) was extracted with Et_2O . The ethereal phase was separated and dried over MgSO_4 . The concentration of the ethereal solution of H_2O_2 thus obtained was determined to be 1.5–1.7 M by titration with KMnO_4 .

4.3.2. Cross-Over Experiment (Fig. 4)

Chiral iminophosphorane **1i** (0.87 mg, 0.0010 mmol) and *N*-Mts-isovaleralaldimine **4b** (5.35 mg, 0.0200 mmol) were placed into a test tube and CDCl_3 (0.45 mL) was introduced to the tube at room temperature. An ethereal solution of H_2O_2 (27.0 μL)²³ was then added with stirring. After 5 min (The ^1H NMR analysis at this stage gave a spectrum (a).), a solution of *N*-Mts-hydrocinnamaldimine **4c** (6.31 mg, 0.0200 mmol) and Cl_3CCN (20.0 μL , 0.200 mmol) in CDCl_3 (0.10 mL) was rapidly added. Subsequent ^1H NMR analysis (400 MHz) gave a spectrum (b). The work-up and purification according to the general procedure gave oxaziridine **5c**. The enantiomeric excess of **5c** thus obtained was determined to be 96% by HPLC analysis. In a similar way, to the solution of **4c** and **1i** in CDCl_3 were sequentially added ethereal H_2O_2 (The ^1H NMR analysis at this stage gave a spectrum (c).) and a solution of **4b** and Cl_3CCN . Subsequent ^1H NMR analysis gave a spectrum (d). The enantiomeric excess of **5b** thus obtained was 97%.

4.3.3. Oxaziridination of Aliphatic *N*-Mts Imines in the $\text{CDCl}_3/\text{Et}_2\text{O}$ Solvent System

To a solution of **1i** (0.87 mg, 0.0050 mmol), **4b** (5.35 mg, 0.0200 mmol), and Cl_3CCN (20.0 μL , 0.200 mmol) in $\text{CDCl}_3/\text{Et}_2\text{O}$ (0.55 mL, 27.0 μL) were added an aqueous 35% solution of H_2O_2 (3.5 μL , titrated by using KMnO_4) at room temperature. The work-up and purification according to the general procedure gave oxaziridine **5b**. The enantiomeric excess

of **5b** thus obtained was determined to be 96% by HPLC analysis. Oxaziridine **5c** was obtained by the same procedure and its enantiomeric excess was 97%.

4.4. Derivatizations

4.4.1. Intramolecular Oxygen Atom-Transfer Reaction of **5e**

A solution of oxaziridine **5e** (21.0 mg, 0.0731 mmol) in CHCl_3 (3.0 mL) was stirred for 77 h at 60 °C under Ar atmosphere. After cooling to room temperature, all volatiles were evaporated off to give crude epoxy imine **13e**. The imine **13e** was used for the following reaction without further purification.

4.4.2. Reductive Cyclization to *N*-Mts Pyrrolidine Methanol **14e**

To a solution of the crude imine **13e** in CH_2Cl_2 (0.70 mL) was added $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (12.0 μL , 0.095 mmol) at –78 °C under Ar. Then, Et_3SiH (26.0 μL , 0.21 mmol) was slowly added over 5 min, and the reaction mixture was stirred for 0.5 h at –78 °C and for 2.5 h at room temperature. The reaction was quenched by the addition of a saturated aqueous solution of NaHCO_3 . The aqueous phase was extracted with EA twice and organic extracts were washed with brine. The combined organic extracts were dried over Na_2SO_4 and filtered. After concentration, the resulting residue was purified by column chromatography on silica gel (H/EA = 60/40 as an eluent) to afford **14e** in 74% yield (15.3 mg, 0.0540 mmol). **14e**: HPLC AD3, H/EtOH = 95:5, flow rate = 1.0 mL/min, λ = 210 nm, 44.9 min (minor isomer), 48.1 min (major isomer); ^1H NMR (400 MHz, CDCl_3) δ 6.97 (2H, s), 4.00 (1H, dq, J = 9.6, 4.6 Hz), 3.59 (1H, dd, J = 11.4, 5.0 Hz), 3.53 (1H, dd, J = 11.4, 5.0 Hz), 3.32 (1H, dt, J = 10.1, 6.9 Hz), 3.08 (1H, dt, J = 10.1, 6.4 Hz), 2.66 (6H, s), 2.40 (1H, brs), 2.31 (3H, s), 2.12–2.00 (1H, m), 1.94–1.81 (3H, m); ^{13}C NMR (101 MHz, CDCl_3) δ 143.3, 140.5, 132.6, 132.4, 65.5, 60.9, 49.0, 29.5, 24.9, 23.3, 21.3; IR (film) 3503 (br), 2974, 2940, 1603, 1456, 1308, 1194, 1148, 1059, 1043, 854 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{21}\text{NNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 306.1134. Found 306.1129; $[\alpha]_D^{20}$ –5.3 (c = 1.80, CHCl_3).

14f: HPLC AD3, H/EtOH = 95:5, flow rate = 1.0 mL/min, λ = 210 nm, 20.1 min (minor isomer), 24.5 min (major isomer); ^1H NMR (400 MHz, CDCl_3) δ 6.97 (2H, s), 3.93 (1H, dq, J = 8.2, 4.4 Hz), 3.45 (1H, dt, J = 11.0, 6.5 Hz), 3.37 (1H, td, J = 7.1, 4.4 Hz), 2.98 (1H, dt, J = 11.0, 6.9 Hz), 2.77 (1H, brs), 2.67 (6H, s), 2.30 (3H, s), 2.04 (1H, dq, J = 12.4, 7.4 Hz), 1.93–1.78 (2H, m), 1.78–1.64 (1H, m), 1.54 (1H, dqd, J = 15.1, 7.8, 2.7 Hz), 1.37–1.24 (1H, m), 0.96 (3H, t, J = 7.4 Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 143.3, 140.6, 132.5, 132.2, 75.1, 64.2, 49.1, 29.1, 26.5, 25.5, 23.4, 21.3, 10.1; IR (film) 3505, 2920, 1603, 1558, 1454, 1400, 1333, 1290, 1142, 1055, 962, 860 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{25}\text{NNaO}_3\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 334.1447. Found 334.1445; $[\alpha]_D^{21}$ +0.66 (c = 1.00, CHCl_3).

4.4.3. Preparation of Authentic Sample of **14e** from Commercially Available (*S*)-Pyrrolidine Methanol

To a solution of L-prolinol (18.4 mg, 0.182 mmol) in CH_2Cl_2 (1.0 mL) were added a 50% aqueous solution of KOH (0.2 mL) and MesSO_2Cl (133.2 mg, 0.609 mmol) at room temperature. An ordinary work-up and subsequent purification by column chromatography on silica gel yielded **14e** (37.9 mg, 0.127 mmol) as a colorless oil.

4.4.4. Oxyamination of *N*-Acyl Indole with **3b**^{25j}

A 0.02 M solution of copper(II) chloride and tetra-*n*-butylammonium chloride in CH_2Cl_2 (0.50 mL, 0.010 mmol), prepared by following the literature procedure,^{25j} was added to a

solution of *N*-acetyl indole (32.3 mg, 0.203 mmol) in CH_2Cl_2 (0.50 mL) at room temperature. Oxaziridine **3b** (103.3 mg, 0.404 mmol) was added and the reaction mixture was stirred for 21.5 h under Ar. The mixture was concentrated and the diastereomeric ratio of the products was determined by ^1H NMR analysis of the crude residue in CDCl_3 . Subsequent purification by flash column chromatography on silica gel (CHCl_3/EA = 99:1 as an eluent) gave **15** as a mixture of diastereomers in 76% yield (67.0 mg, 0.154 mmol). Diastereomers were partially separated by using PTLC for spectroscopic assignments. **15**: HPLC IB, H/EtOH = 95:5, flow rate = 0.5 mL/min, λ = 210 nm, 60.5 min (major isomer of major diastereomer), 65.9 min (minor isomer of minor diastereomer), 84.8 min (minor isomer of major diastereomer), 88.8 min (major isomer of minor diastereomer); ^1H NMR (400 MHz, CDCl_3) *major isomer* δ 8.24 (1H, d, J = 7.8 Hz), 7.92 (1H, J = 7.3 Hz), 7.40 (2H, t, J = 8.2 Hz), 7.26–7.19 (2H, m), 7.17–7.10 (3H, m), 7.10–7.04 (2H, m), 6.99 (2H, d, J = 8.2 Hz), 6.25 (1H, d, J = 6.0 Hz), 6.12 (1H, d, J = 6.0 Hz), 5.58 (1H, s), 2.38 (3H, s), 2.35 (3H, s); *minor isomer* δ 7.88 (2H, d, J = 8.2 Hz), 7.68 (1H, d, J = 8.2 Hz), 7.43 (2H, d, J = 8.2 Hz), 7.35 (1H, d, J = 7.3 Hz), 7.16–7.06 (3H, m), 7.06–6.97 (3H, m), 6.93 (1H, t, J = 7.3 Hz), 6.63 (1H, s), 5.69 (1H, d, J = 6.4 Hz), 5.63 (1H, d, J = 6.4 Hz), 2.51 (3H, s), 2.34 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) *major isomer* δ 170.1, 143.7, 143.6, 137.6, 131.4, 130.9, 130.0, 129.3, 128.0, 127.8₁, 127.8₂, 126.1, 125.2, 116.4, 89.6, 89.5, 64.2, 24.3, 21.8, one carbon was missing probably due to overlapping; *minor isomer* δ 169.4, 145.3, 141.9, 137.4, 134.7, 130.6, 130.3, 128.5, 128.2, 127.9, 126.4, 125.8, 125.7, 124.6, 116.5, 92.6, 91.5, 63.7, 24.2, 22.1; IR (film) *major isomer* 3034, 2926, 2893, 1684, 1479, 1395, 1354, 1339, 1157, 1092, 1057 cm^{-1} ; *minor isomer* 3034, 2926, 1680, 1479, 1395, 1356, 1281, 1165, 1090, 1038 cm^{-1} ; HRMS (ESI) *major isomer* Calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{NaO}_4\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 457.1192. Found 457.1192; *minor isomer* Calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{NaO}_4\text{S}^+$ ($[\text{M}+\text{Na}]^+$) 457.1192. Found 457.1193.

Acknowledgements

This work was supported by NEXT program, CREST-JST, a Grant-in-Aid for Scientific Research on Innovative Areas "Advanced Molecular Transformations by Organocatalysts" from MEXT, Program for Leading Graduate Schools "Integrative Graduate Education and Research Program in Green Natural Sciences" in Nagoya University, the Asahi Glass foundation, and Grants of JSPS for Scientific Research. R.T. acknowledges JSPS for financial support.

References and Notes

- Lawesson, S.-O.; Schroll, G., In *The Chemistry of Carboxylic Acids and Esters*, Patai, S. Ed., John Wiley & Sons, New York, **1969**, Chapter 14, pp 669–703.
- (a) Shu, L.; Shi, Y. *Tetrahedron Lett.* **1999**, *40*, 8721. (b) Shu, L.; Shi, Y. *Tetrahedron* **2001**, *57*, 5213. (c) Wang, Z.-X.; Shu, L.; Frohn, M.; Tu, Y.; Shi, Y. *Org. Synth.* **2003**, *80*, 9.
- (a) Peris, G.; Jakobsche, C. E.; Miller, S. J. *J. Am. Chem. Soc.* **2007**, *129*, 8710. (b) Jakobsche, C. E.; Peris, G.; Miller, S. J. *Angew. Chem. Int. Ed.* **2008**, *47*, 6707. (c) Peris, G.; Miller, S. J. *Org. Lett.* **2008**, *10*, 3049. (d) Kolundzic, F.; Noshi, M. N.; Tjandra, M.; Movassaghi, M.; Miller, S. J. *J. Am. Chem. Soc.* **2011**, *133*, 9104.
- For leading references on epoxidation using $\text{RCN-H}_2\text{O}_2$, see: (a) Payne, G. B.; Deming, P. H.; Williams, P. H. *J. Org. Chem.* **1961**, *26*, 659. (b) Payne, G. B. *Tetrahedron* **1962**, *18*, 763. (c) Bach, R. D.; Knight, J.

- W. *Org. Synth.* **1981**, 60, 63. (d) Arias, L. A.; Adkins, S.; Nagel, C. J.; Bach, R. D. *J. Org. Chem.* **1983**, 48, 888.
5. For reviews on phosphonium salt catalyses, see: (a) Werner, T. *Adv. Synth. Catal.* **2009**, 351, 1469. (b) Enders, D.; Nguyen, T. V. *Org. Biomol. Chem.* **2012**, 10, 5327.
 6. For a review on organic base catalysis, see: Palomo, C.; Oiarbide, M.; López, R. *Chem. Soc. Rev.* **2009**, 38, 632.
 7. Triaminoiminophosphoranes are also known as a P1-phosphazenes, which was developed by Schwesinger, see: (a) Schwesinger, R.; Schlemper, H. *Angew. Chem. Int. Ed. Engl.* **1987**, 26, 1167. For review, see: (b) In *Superbases for Organic Synthesis: Guanidines, Amidines, Phosphazenes and Related Organocatalysts*; Ishikawa, T. Ed.; John Wiley & Sons: West Sussex, U.K., 2009.
 8. (a) Uraguchi, D.; Ooi, T. *J. Synth. Org. Chem. Jpn.* **2010**, 68, 1185. (b) Uraguchi, D.; Nakamura, S.; Ooi, T. *Angew. Chem. Int. Ed.* **2010**, 49, 7562. (c) Uraguchi, D.; Ueki, Y.; Ooi, T. *Angew. Chem. Int. Ed.* **2011**, 50, 3681. (d) Uraguchi, D.; Ueki, Y.; Ooi, T. *Chem. Sci.* **2012**, 3, 842. (e) Corbett, M. T.; Uraguchi, D.; Ooi, T.; Johnson, J. S. *Angew. Chem. Int. Ed.* **2012**, 51, 4685. (f) Uraguchi, D.; Yoshioka, K.; Ueki, Y.; Ooi, T. *J. Am. Chem. Soc.* **2012**, 134, 19370. (g) Uraguchi, D.; Ueki, Y.; Sugiyama, A.; Ooi, T. *Chem. Sci.* **2013**, 4, 1308.
 9. Uraguchi, D.; Tsutsumi, R.; Ooi, T. *J. Am. Chem. Soc.* **2013**, 135, 8161.
 10. For examples of the oxaziridine synthesis, see: (a) Emmons, W. D. *J. Am. Chem. Soc.* **1956**, 78, 6208. (b) Boyd, D. R.; Malone, J. F.; McGuckin, M. R.; Jennings, W. B.; Rutherford, M.; Saket, B. M. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1145. (c) Martiny, L.; Jørgensen, K. A. *J. Chem. Soc., Perkin Trans. 1* **1995**, 699. (d) Damavandi, J. A.; Karami, B.; Zolfiğol, M. A. *Synlett* **2002**, 933.
 11. For the imine oxidations by means of RCN-H₂O₂ system, see: (a) Schirmann, J.-P.; Weiss, F. *Tetrahedron Lett.* **1972**, 13, 633. (b) Kraïem, J.; Kacem, Y.; Khiari, J.; Ben Hassine, B. *Synth. Commun.* **2001**, 31, 263. (c) Kraïem, J.; Ben Othman, R.; Ben Hassine, B. *C. R. Chim.* **2004**, 7, 1119. (d) Tka, N.; Kraïem, J.; Ben Hassine, B. *Synth. Commun.* **2012**, 42, 2994.
 12. Lykke, L.; Rodríguez-Esrich, C.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2011**, 133, 14932.
 13. Olivares-Romero, J. L.; Li, Z.; Yamamoto, H. *J. Am. Chem. Soc.* **2012**, 134, 5440.
 14. Dong, S.; Liu, X.; Zhu, Y.; He, P.; Lin, L.; Feng, X. *J. Am. Chem. Soc.* **2013**, 135, 10026.
 15. For review on asymmetric hydroxylation of enolates with *N*-sulfonyloxaziridines, see: Davis, F. A.; Chen, B. C. *Chem. Rev.* **1992**, 92, 919.
 16. (a) Davis, F. A.; Nadir, U. K.; Kluger, E. W. *J. Chem. Soc., Chem. Commun.* **1977**, 25. (b) Davis, F. A.; Jenkins, R., Jr.; Yocklovich, S. G. *Tetrahedron Lett.* **1978**, 19, 5171. (c) Davis, F. A.; Harakal, M. E.; Awad, S. B. *J. Am. Chem. Soc.* **1983**, 105, 3123. (d) Davis, F. A.; Billmers, J. M.; Gosciniak, D. J.; Towson, J. C.; Bach, R. D. *J. Org. Chem.* **1986**, 51, 4240. (e) Davis, F. A.; Sheppard, A. C. *Tetrahedron* **1989**, 45, 5703. (f) Davis, F. A.; Chen, B.-C. *Chem. Rev.* **1992**, 92, 919. (g) Petrov, V. A.; Resnati, G. *Chem. Rev.* **1996**, 96, 1809. (h) Andreae, S.; Schmitz, E. *Synthesis* **1991**, 327.
 17. Anderson, D. R.; Woods, K. W.; Beak, P. *Org. Lett.* **1999**, 1, 1415.
 18. Brodsky, B. H.; Du Bois, J. *J. Am. Chem. Soc.* **2005**, 127, 15391.
 19. Instead of the desired oxaziridine **3a**, the corresponding peroxyhemiaminal of type **a** (Figs. 2 and 3) was obtained. The stereoselectivity of this simple addition of hydroperoxide ion was not determined because of the instability of the peroxyhemiaminal.
 20. Iminophosphorane **1i** can be recovered as corresponding hydrogen chloride salt **1i**·HCl during purification procedure.
 21. For this type of abbreviation for multi-substituted benzenesulfonyl groups, see, for example: (a) Ramage, R.; Green, J.; Blake, A. J. *Tetrahedron* **1991**, 47, 6353. (b) Ooi, T.; Uematsu, Y.; Fujimoto, J.; Fukumoto, K.; Maruoka, K. *Tetrahedron Lett.* **2007**, 48, 1337.
 22. When α -unsubstituted aliphatic *N*-Ts aldimine **2** ($R^1 = \text{Ph}(\text{CH}_2)_2$) was subjected to the standard conditions (*General Procedure 2*), the corresponding oxaziridine was obtained with high enantioselectivity (94% ee) albeit in moderate chemical yield (57%).
 23. (a) Saito, I.; Nagata, R.; Yuba, K.; Matsuura, T. *Tetrahedron Lett.* **1983**, 24, 1737. (b) Sasakura, N.; Nakano, K.; Ichikawa, Y.; Kotsuki, H. *RSC Adv.* **2012**, 2, 6135.
 24. For review on aminohydroxylation of olefins using oxaziridines, see: Knappke, C. E. I.; von Wangelin, A. *J. ChemCatChem* **2010**, 2, 1381.
 25. For recent examples of transformations of *N*-sulfonyl oxaziridines, see: (a) Michaelis, D. J.; Shaffer, C. J.; Yoon, T. P. *J. Am. Chem. Soc.* **2007**, 129, 1866. (b) Partridge, K. M.; Anzovino, M. E.; Yoon, T. P. *J. Am. Chem. Soc.* **2008**, 130, 2920. (c) Michaelis, D. J.; Ischay, M. A.; Yoon, T. P. *J. Am. Chem. Soc.* **2008**, 130, 6610. (d) Michaelis, D. J.; Williamson, K. S.; Yoon, T. P. *Tetrahedron* **2009**, 65, 5118. (e) Benkovics, T.; Du, J.; Guzei, I. A.; Yoon, T. P. *J. Org. Chem.* **2009**, 74, 5545. (f) Allen, C. P.; Benkovics, T.; Turek, A. K.; Yoon, T. P. *J. Am. Chem. Soc.* **2009**, 131, 12560. (g) Partridge, K. M.; Guzei, I. A.; Yoon, T. P. *Angew. Chem., Int. Ed.* **2010**, 49, 930. (h) Williamson, K. S.; Yoon, T. P. *J. Am. Chem. Soc.* **2010**, 132, 4570. (i) DePorter, S. M.; Jacobsen, A. C.; Partridge, K. M.; Williamson, K. S.; Yoon, T. P. *Tetrahedron Lett.* **2010**, 51, 5223. (j) Benkovics, T.; Guzei, I. A.; Yoon, T. P. *Angew. Chem. Int. Ed.* **2010**, 49, 9153. (k) Williamson, K. S.; Yoon, T. P. *J. Am. Chem. Soc.* **2012**, 134, 12370.
 26. (a) Kraïem, J.; Grosvalet, L.; Perrin, M.; Ben Hassine, B. *Tetrahedron Lett.* **2001**, 42, 9131. (b) Fabio, M.; Ronzini, L.; Troisi, L. *Tetrahedron* **2007**, 63, 12896. (c) Motiwala, H. F.; Gülgeze, B.; Aubé, J. *J. Org. Chem.* **2012**, 77, 7005. (d) Richy, N.; Ghoraf, M.; Vidal, J. *J. Org. Chem.* **2012**, 77, 10972.

27. (a) Lu, K.; Kwon, O. *Org. Synth.* **2009**, 86, 212. (b) Chemla, F.; Hebbe, V.; Normant, J.-F. *Synthesis* **2000**, 75.