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Construction of Robust Ruthenium(salen)(CO) Complexes and Asymmetric Aziridination with Nitrene Precursors in the Form of Azide Compounds That Bear Easily Removable *N*-Sulfonyl Groups

Hirotoshi Kawabata, Kazufumi Omura, Tatsuya Uchida, and Tsutomu Katsuki*[a]

Abstract: We synthesized new Ru(salen)(CO) complexes of high durability and achieved aziridination with good to excellent enantioselectivity by using azide compounds that contain an easily removable *N*-sulfonyl group, such as the 2-(trimethylsilyl)ethanesulfonyl group, as a nitrene precursor. Aziridination of less-reactive α,β-unsaturated esters (and amides) proceeded with excellent enantioselectivities, from which it is inferred that an electrophilic species is the active species of this reaction. The present asymmetric aziridination provides a useful tool for introducing optically active nonprotected amine groups.

Keywords: asymmetric catalysis · azides · aziridination · ruthenium · salen ligands

Introduction

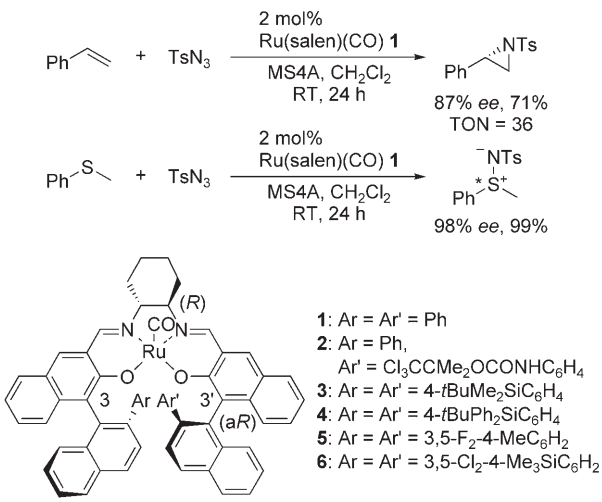
Aziridines are nitrogen equivalents of epoxides, which are useful synthetic intermediates. The former, however, are less reactive than the latter, thus the use of aziridines in organic synthesis is limited. On the other hand, aziridines that carry an electron-withdrawing group, such as the arylsulfonyl group, as the N-protective group undergo various types of nucleophilic ring-opening reactions; this makes them as useful as epoxides as synthetic intermediates.[1] In particular, optically active aziridines serve as useful chiral building blocks for the construction of chiral nitrogen compounds. Thus, much effort has been directed toward the development of synthetic methods for N-protected optically active aziridines. Among the various methods examined thus far, asymmetric aziridination, especially metal-catalyzed nitrene-transfer reactions that transform olefins into optically active aziridines protected by an electron-withdrawing group in a single step, has attracted much attention.[2] Many chiral metal catalysts such as metalloporphyrin,[3] Mn–salen,[4] Ru–salen,[5] Cu–bis(oxazoline),[6] Rh–bis(oxazoline),[7] Rh–bis-naphtholphosphate,[8] Cu–chiral diimine,[9] and Cu–diamine complexes[10] (salen = *N*,*N*′-ethylenebis(salicylideneiminato)) have been developed for asymmetric aziridination, and high enantioselectivity was achieved in some cases. However, their utility is impaired mainly by the following two problems. First, most of the reactions use N-substituted iminoiodinanes such as *N*-(arylsulfonylimino)(phenyl)iodinanes as the nitrene precursor, which inevitably generate a stoichiometric amount of iodobenzene as the waste co-product. This badly reduces the atom efficiency and diminishes the ecological benignity of the reactions. The second problem is concerned with the N-protecting group. The N-protecting group of a nitrene precursor is introduced onto the resulting aziridine and serves not only as the protecting but also as the activating group of the aziridine. However, the N-protecting group must be removed from the aziridine after it has been converted into the desired compound. Nonetheless, the previously reported asymmetric aziridinations have mostly used nitrene precursors carrying simple arylsulfonyl groups such as the *p*-toluenesulfonyl (Ts) group, deprotection of which needs harsh conditions. On the other hand, it has been reported that certain groups such as the *p*-nitro- and *o*-nitrobenzenesulfonyl (*p*-Ns and *o*-Ns) groups[11] and the 2-(trimethylsilyl)ethanesulfonyl (SES) group[12] can be removed under mild conditions. Although asymmetric aziridination with nitrene precursors that contain an easily removable *N*-sulfonyl group has been reported, most of the precursors are iminoiodinane derivatives of low atom efficiency,[6e–g,i,k,8] with the exception of one example in which *p*-NsN_3 was used under UV irradiation as the precursor, albeit with modest enantioselectivity.[8,14] Still, there is a strong demand for the introduction of a new catalyst that allows

[a] Dr. H. Kawabata, K. Omura, Dr. T. Uchida, Prof. Dr. T. Katsuki
Department of Chemistry, Faculty of Science
Graduate School, Kyushu University
Hakozaki, Higashi-ku, Fukuoka 812-8581 (Japan)
Fax: (+81) 92-642-2607
E-mail: katsuscc@mbox.nc.kyushu-u.ac.jp

highly enantioselective asymmetric aziridination by using an atom-efficient nitrene precursor carrying an easily removable N-protecting group.

Azide compounds are ideal nitrene precursors in terms of atom efficiency and ecological benignity, because they can generate the necessary nitrenoid species simply by dissociating innocuous and eco-friendly molecular nitrogen. Thus, nitrene-transfer reactions with azide compounds as precursors have been studied continuously.[13] However, azides are not very reactive, and their previous use as precursor needed harsh conditions such as heating or UV irradiation. In 1995, Jacobsen and co-workers reported a seminal study on asymmetric aziridination with TsN_3 in the presence of a chiral Cu–diimine catalyst.[9c] Müller et al. also reported a reaction with *p*-NsN_3 catalyzed by a chiral Rh–bisnaphtholphosphate complex.[8,14] Both reactions needed UV irradiation, and the enantioselectivity was modest. Still, construction of a catalyst that can convert azide compounds into an active species in a highly asymmetric atmosphere under mild conditions is necessary to make asymmetric aziridination a truly valuable synthetic tool.

Recently, we disclosed that chiral Ru(salen)(CO) complex **1** was able to catalyze nitrene-transfer reactions such as imidation of sulfides[15] and aziridination of olefins[16] with azide compounds in a highly enantioselective manner at room temperature (Scheme 1). Notably, neither heating nor UV irradiation was required. However, the complex was not very robust, and its turnover number (TON) in the aziridination of styrene with TsN_3 was found to be 36. The spectroscopic analysis of a stoichiometric reaction of **1** with 2,2,2-trichloro-1,1-dimethylethyloxycarbonyl azide revealed that a phenyl group on the binaphthyl moieties of the salen ligand was aminated by an intramolecular C–H nitrene-transfer reaction, and catalytically inactive complex **2** was generated.[17] This explains the unsatisfactory TON of the catalyst. Although we could not determine the exact location of the aminated carbon atom in **2** due to the intricacy of its ^{1}H NMR spectrum, we assumed that the *m*-carbon atom of the phenyl group might be aminated based on the X-ray structure of **1**, in which the *m*- and *o*-carbon atoms, especially the former, are close to the apical ligand. Thus, we anticipated that the durability of **1** would be enhanced by somehow protecting the *m*-carbon atoms in particular. For this purpose, we explored two approaches: 1) steric protection of the *m*-carbon atoms by introducing a bulky substituent such as the *tert*-butyldimethylsilyl or *tert*-butyldiphenylsilyl group at the *p*-carbon atom of the phenyl group, and 2) substitution of the *m*-hydrogen atom with an inert atom such as halogen. Herein, we report a full account of our recent investigations for the preparation of robust Ru(salen)(CO) complexes and their application to asymmetric aziridination of olefins with azide compounds that contain an easily removable N-substituent as the nitrene precursor.[18]



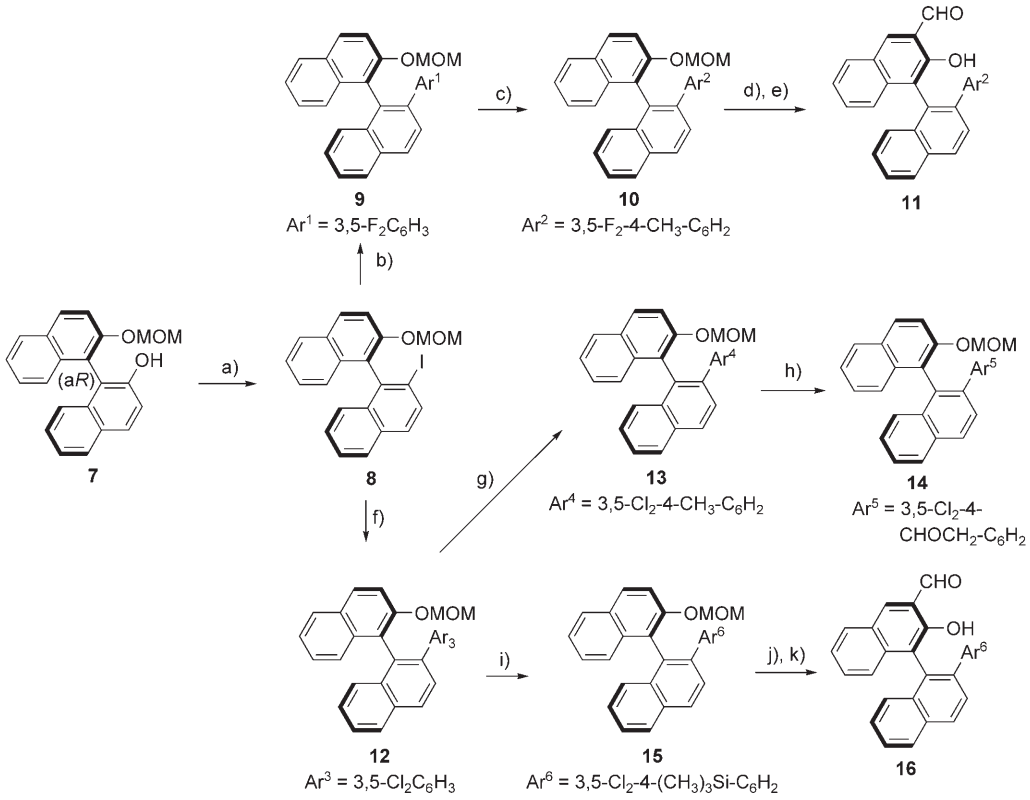
Scheme 1. Asymmetric nitrene-transfer reactions with the Ru(salen)(CO)/TsN_3 system. MS4A = 4-Å molecular sieves.

Results and Discussion

Along the lines described above, we newly synthesized chiral Ru(salen)(CO) complexes **3**–**6**. Aldehydes used for synthesizing **3** and **4** were prepared according to the reported procedure.[19] On the other hand, **5** and **6** are different from those originally designed, because the synthesis of the planned aldehydes, which bear a di-*m*-halogenated phenyl group at C2′, was impossible owing to the undesired *o*-lithiation; it was necessary for us to prepare aldehydes that bear a di-*m*-halogenated and *p*-substituted phenyl group at C2′, which were used for the construction of **5** and **6**. The synthesis of the aldehydes started with monomethoxymethylated (*R*)-binaphthol **7**, which was converted into iodobinaphthyl **8** according to the Yamamoto procedure (Scheme 2).[20] Suzuki–Miyaura coupling reactions of **8** with 3,5-difluoro- or 3,5-dichlorobenzeneboronic acid proceeded smoothly to give the corresponding 2′-arylated compounds **9** and **12**, respectively. We next attempted a methoxymethoxy (MOMO)-group-directed *o*-lithiation, followed by formylation. However, the lithiation directed by the two halogen atoms took place in preference to the desired *o*-lithiation, and the formylation occurred at the *p*-position of the 2′-phenyl group. To avoid this undesired formylation, the lithium anion generated from **9** was treated with methyl iodide

Abstract in Japanese:

ハロゲン置換基の導入により耐久性を向上させた新規ルテニウムサレン錯体触媒がアジド化合物を用いるオレフィンの不斉アジリジン化で高エナンチオ選択性を示すことを見出した。新触媒を用いると、2-（トリメチルシリル）エタンスルホニルアジドのように反応性は低いものの温和な条件下で除去できる*N*-置換基をもつアジド化合物をナイトレン前駆体として用いるアジリジン化が、室温で高エナンチオ選択的（>90% *ee*）に進行する。この反応の基質は末端オレフィンと一部のシス－二置換オレフィンに限られているが、反応性の低いα,β-不飽和エステルなども収率良くアジリジン化される。本法は、原子利用率が高く環境への負荷が小さなアジリジン化であるばかりでなく、キラルな無保護アミン類の合成に新たな方法論を提供するものである。

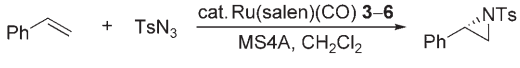


Scheme 2. Reagents and conditions: a) *n*BuLi, THF, −78 °C; $ClP(O)(OEt)_2$, Li/naphthalene, I_2, 45 %; b) $[Pd(PPh_3)_4]$ (5 mol %), 3,5-difluorobenzeneboronic acid, CsF, DMF, 115 °C, 98 %; c) *n*BuLi, THF, −78 °C, then CH_3I, 93 %; d) *n*BuLi, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), −78 °C, then DMF, 97 %; e) HCl/*i*PrOH (20 % *w*/*w*), 99 %; f) $[Pd(PPh_3)_4]$ (5 mol %), 3,5-dichlorobenzeneboronic acid, toluene, 1 M Na_2CO_3, 100 °C, 92 %; g) *n*BuLi, TMEDA, THF, −78 °C, then CH_3I, 100 %; h) *n*BuLi, TMEDA, −78 °C, then DMF, 28 %, **13** was recovered in 35 % yield; i) *sec*-BuLi, THF, −78 °C, then $(CH_3)_3SiCl$, 65 %; j) *n*BuLi, TMEDA, −78 °C, then DMF, 84 %; k) HCl/*i*PrOH (20 % *w*/*w*), THF, 99 %.

to give *p*-methylated **10**, which was treated again with *n*-butyllithium followed by *N*,*N*-dimethylformamide (DMF). Hydrolysis of the product gave the desired *o*-hydroxy aldehyde **11**. Subsequently, the synthesis of the corresponding chlorinated aldehyde from **12** was attempted in the same way; however, the lithiation of the *p*-methylated **13** occurred not at the *o*-position of the MOMO group but at the *p*-methyl group, and the subsequent formylation gave the undesired **14**. Accordingly, the lithium anion derived from **12** was treated with chlorotrimethylsilane, and then the trimethylsilylated **15** was subjected to *o*-lithiation, formylation, and hydrolysis to give the desired *o*-hydroxy aldehyde **16**. The condensation of aldehydes **11** or **16** with (1*R*,2*R*)-1,2-cyclohexanediamine sulfate in the presence of potassium carbonate gave the desired salen ligands, treatment of which with triruthenium dodecacarbonyl ($[Ru_3(CO)_{12}]$) in EtOH furnished **5** and **6**, respectively.

With complexes **3**–**6** in hand, we examined the asymmetric aziridination of styrene with TsN_3 (Table 1). Aziridination in the presence of MS4A and 0.1 mol % of **3** or **4** in CH_2Cl_2 at room temperature for 24 h furnished 2-phenyl-1-(*p*-toluenesulfonyl)aziridine in 41 % and 23 % yields, respectively (Table 1, entries 1 and 2). As expected, the TONs of catalysts **3** and **4** increased to 410 and 230, respectively.[21] Furthermore, **3** and **4** showed identical enantioselectivity (87 % *ee*) with **1**. Further enhancement of TON was observed when **5** and **6** were used. The TON of **5** was 867 and that of **6** was 982, albeit with slightly reduced enantioselectivity (85 % and 86 % *ee*, respectively) (Table 1, entries 3 and 4). However, the reaction with **6** at 0 °C improved the enantioselectivity to 90 % *ee* without significant decrease of the TON (Table 1, entry 5). Further lowering of the temperature did not improve the selectivity much, but significantly

Table 1. Asymmetric aziridination of styrene with Ru(salen)(CO) complexes **3**–**6** and TsN_3.



Entry	Catalyst [mol %]	*T* [°C]	*t* [h]	Yield[a] [%]	*ee*[b] [%]	TON[a]
1	**3** (0.1)	RT	24	41	87 (*S*)	410
2	**4** (0.1)	RT	24	23	87	230
3	**5** (0.09)	RT	24	78	85	867
4	**6** (0.1)	RT	12	93[c]	86	982
5	**6** (0.1)	0	12	92	90	920
6	**6** (0.1)	−15	12	30	91	–
7	**6** (0.1)	−30	12	19	92	–

[a] Calculated according to ^1H NMR spectroscopic analysis. [b] Determined by HPLC analysis. [c] Yield of isolated product after silica-gel column chromatography.

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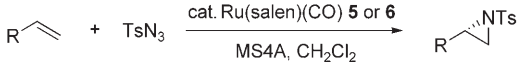
slowed the reaction (Table 1, entries 6 and 7). The TON of **6** was decreased to 628 at −30 °C even with an extended reaction time (72 h).

Based on these results, we next examined the aziridination of *p*-bromostyrene in the presence of **5** or **6**, and the results are summarized in Table 2. Although **5** and **6** showed identical enantioselectivity (90 % *ee*), a better TON was again observed with **6** (Table 2, entries 1 and 2). The reaction with **6** at 0 °C improved the enantioselectivity to 93 % *ee* with almost similar TON (Table 2, entry 3). Thus, we examined the aziridination of other conjugated olefins with **6** at 0 °C. Aziridination of terminal conjugated olefins such as 4-bromostyrene, 2-vinylnaphthalene, and but-3-en-1-ynylbenzene also proceeded with high enantioselectivity along with high TONs (Table 2, entries 3–6). On the other hand, the aziridination of 1-octene was slow, but high selectivity as well as moderate yield was obtained, when 2 mol % of the catalyst was used (Table 2, entry 7).[22] Although **5** showed better enantioselectivity, the reaction was slow even at room temperature (Table 2, entry 8). The reaction of indene proceeded with excellent enantioselectivity of >99 % *ee* even at room temperature, but the reaction was slow (Table 2, entry 9). In all the reactions, no product other than the corresponding aziridine was detected by ^{1}H NMR spectroscopic analysis.

Table 2. Asymmetric aziridination of various olefins with TsN_3 in the presence of Ru(salen)(CO) complex **5** or **6**.



Entry	R or substrate	Catalyst [mol %]	*T* [°C]	*t* [h]	Yield[a] [%]	*ee*[b] [%]	TON[a]
1	4-BrC_6H_4	**5** (0.09)	RT	24	79	90	878
2	4-BrC_6H_4	**6** (0.1)	RT	12	91	90	910
3	4-BrC_6H_4	**6** (0.1)	0	12	90	93	900
4	2-$C_{10}H_7$	**6** (0.1)	RT	12	99	82	990
5	2-$C_{10}H_7$	**6** (0.1)	0	12	69	91	960
6	PhC≡C	**6** (0.1)	0	12	76	98	760
7	*n*-C_6H_{13}	**6** (2.0)	0	38	64	84	32
8	*n*-C_6H_{13}	**5** (2.0)	RT	24	20	86	10
9	indene	**6** (2.0)	RT	38	48	>99	24

[a] Calculated according to ^{1}H NMR analysis. [b] Determined by HPLC analysis. [c] Yield of isolated product after silica-gel column chromatography.

With these results, we turned to aziridination with azide compounds that carry an easily removable N-substituent in the presence of **5** or **6** as catalyst. We first examined the aziridination of styrene with *p*- or *o*-NsN_3 as the nitrene precursor (Table 3). These azides were less reactive than TsN_3; for example, the TON of **1** in the reaction with *p*-NsN_3 was only 5 (Table 3, entry 1). The TON of the catalyst was not very much improved (up to 34) even with **5** (Table 3, entry 2). However, it was remarkably improved to 746 when **6** was used, but the enantioselectivity was reduced to 81 % *ee* (Table 3, entry 3). *o*-NsN_3 was also examined as the precursor, but it was even less reactive, and its use further reduced the enantioselectivity (Table 3, entry 4).

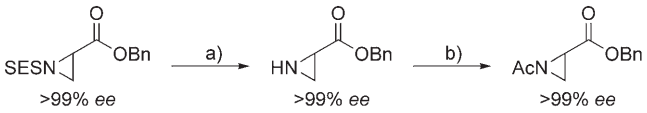
Complexes **3**–**6** consist of many aromatic subunits, and it is likely that the salen ligand of the active species interacts with the substituent on the nitrene unit through weak bonding interaction(s) such as CH–π interaction and/or π–π stacking. Thus, it is likely that the nature of the N-substituent affects the enantioselectivity of the aziridination, and we were intrigued by the aziridination with *N*-alkylsulfonyl azide. Komatsu and co-workers reported that chiral *N*-SES-protected aziridines can be converted into the corresponding unprotected aziridines without diminishing enantiomeric excess.[4d] $SESN_3$ can be prepared by the treatment of 2-trimethylsilylethanesulfonyl chloride[4d] with sodium azide. Taking into consideration the removability of the SES group and the availability of $SESN_3$, we examined aziridination with it as the precursor.[23] Though the reactivity of $SESN_3$ was as low as that of *p*-NsN_3, to our delight, the aziridination of styrene with the former in the presence of **5** or **6** was found to be more enantioselective than that with *p*-NsN_3 (compare Table 3, entries 2 and 3 with entries 5 and 6, respectively). Complex **6** showed better enantioselectivity and higher TON than **5** (Table 3, entries 5–7). The reactions of *p*-bromostyrene and but-3-en-1-ynylbenzene with $SESN_3$ and **6** also proceeded with enantioselectivity of greater than

Table 3. Asymmetric aziridination of various olefins with *p*-NsN_3, *o*-NsN_3, or $SESN_3$ catalyzed by Ru(salen)(CO) complex **5** or **6**.

Entry	Azide	Catalyst [mol %]	Substrate	*T* [°C]	*t* [h]	Yield[a] [%]	*ee*[b] [%]	TON[c]
1	*p*-NsN_3	**1** (4.0)	styrene	RT	24	22	84	5
2	*p*-NsN_3	**5** (1.0)	styrene	RT	24	34	84	34
3	*p*-NsN_3	**6** (0.1)	styrene	RT	38	70	81	746
4	*o*-NsN_3	**6** (0.1)	styrene	RT	12	62	73	660
5	$SESN_3$	**5** (1.0)	styrene	RT	12	67	88 (*S*)	67
6	$SESN_3$	**6** (0.1)	styrene	RT	12	26	91 (*S*)	260
7	$SESN_3$	**6** (1.0)	styrene	0	12	99	92 (*S*)	99
8	$SESN_3$	**6** (1.0)	4-BrC_6H_4-CH=CH_2	0	12	76	92	98
9	$SESN_3$	**6** (1.0)	PhC≡C-CH=CH_2	0	12	50	>99	51
10	$SESN_3$	**6** (5.0)	1-octene	reflux	38	28[c]	77[d]	6
11	$SESN_3$	**6** (5.0)	indene	reflux	38	65	98	13
12	$SESN_3$	**6** (2.0)	CH_2=$CHCO_2$Bn	RT	24	81	>99 (*R*)	41
13	$SESN_3$	**6** (2.0)	CH_2=CHCON(OMe)Bn	RT	24	85	>99	43

[a] Yield of isolated product after silica-gel chromatography, unless otherwise noted. [b] Determined by HPLC analysis. [c] Calculated according to ^{1}H NMR analysis. [d] Determined by chiral HLPC analysis after conversion into the 2-naphthylsulfide derivative.[24]

90% *ee* (Table 3, entries 8 and 9). The reaction of 1-octene was slow even at elevated temperature, but no product other than the corresponding aziridine was detected. The TON of the catalyst was only modest, though good enantioselectivity of 77% *ee* was still observed (Table 3, entry 10).[24] The reaction of indene proceeded with excellent selectivity, albeit with moderate TON (Table 3, entry 11). The reaction at room temperature gave no product other than the corresponding aziridine, whereas in the reaction at reflux, formation of trace amounts of unidentified products was detected by ^{1}H NMR analysis. Notably, the aziridination of less-reactive olefins such as benzyl acrylate and *N*-methoxy-*N*-benzyl-2-propenamide (a Weinreb amide)[25,26] with $SESN_3$ proceeded in a highly enantioselective manner (>99% *ee*) in good chemical yields, thus expanding the scope of the present aziridination (Table 3, entries 12 and 13). The absolute configuration of the aziridine derived from benzyl acrylate was confirmed by chemical transformation to the known acetylated aziridine (Scheme 3); by following the procedure of Komatsu and co-



Scheme 3. Reagents and conditions: a) tris(dimethylamino)sulfonium difluorotrimethylsilicate, DMF, room temperature, 70%; b) Ac_2O, pyridine, dichloromethane, 0°C, 81%.

workers,[4d] the SES group was removed by treatment with tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF), and the resulting unprotected aziridine was acetylated. The absolute configuration was determined to be *R* by comparison of the specific rotation.[27] No racemization was observed in the deprotection step,[28] thus proving that the present procedure provides a useful tool for asymmetric synthesis of not only protected but also unprotected aziridines.

It was reported that metal-mediated aziridination proceeds through an imino metal species (RN=M).[9c] Although the structures of **5** and **6** are unclear at present, the sense of asymmetric induction in the aziridination by these complexes is identical to that by **1**. The structures of the former are considered to be similar to that of **1**, which has been unambiguously determined by X-ray analysis. Based on the stereochemistry of the present aziridination and the structure of **1**, we propose the mechanism of asymmetric induction by **5** and **6** as follows (Figure 1): The olefin approaches the imino species along the Ru–N bond (shown in red) adjacent to the downward naphthalene ring of the basal salen ligand.[29] The 2′′-aryl substituent on the left rear (purple) is located close to the imino group. Therefore, the *N*-sulfonyl group (yellow circle) is inevitably directed to the front, and the bulkiest substituent of the incoming olefin is placed at the back to minimize steric repulsion with the *N*-sulfonyl group. Thus, aziridination of styrene preferentially gives the corresponding *S* product.

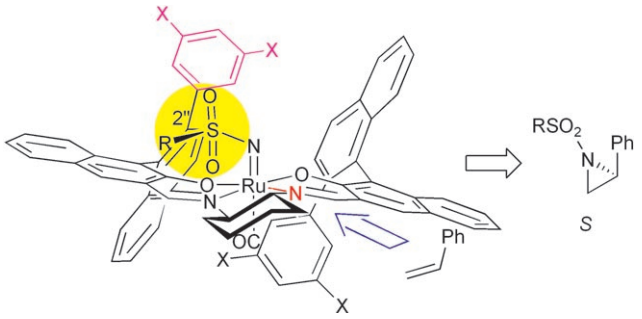


Figure 1. Schematic explanation of the proposed mechanism of asymmetric induction by Ru(salen)(CO) complexes.

It is unclear how the *m*-chloro substituents enhance the durability of the catalyst. However, X-ray analysis of **1** demonstrates that both the *m*- and *o*-carbon atoms of the phenyl moiety are close to the apical ligand (3.71 and 3.84 Å, respectively),[18] and it seems possible that the *o*-carbon atom might be aminated when the *m*-carbon atoms are protected by a fluoro substituent. We speculate that the chloro substituent at the *m*-carbon atoms also blocks the vicinal *o*-C–H bond somewhat more efficiently than the less-bulky fluoro substituent.

Conclusions

We have constructed durable Ru(salen)(CO) complex **6** by introducing chloro and trimethylsilyl substituents at the *m*- and *p*-carbon atoms of the 2-phenyl group of the parent Ru(salen)(CO) complex **1** and achieved enantioselective aziridination by using 2-(trimethylsilyl)ethanesulfonyl azide as the nitrene precursor. High enantioselectivity and high TON of the catalyst were realized in the aziridination of terminal conjugated olefins. Notably, aziridination of less-reactive α,β-unsaturated esters and amides also proceeded with excellent enantioselectivity in acceptable yields. The present study opens a new way to ecologically benign, atom-efficient, and highly enantioselective syntheses of both protected and unprotected aziridines.

Experimental Section

General

All oxygen or moisture-sensitive reactions were carried out under nitrogen or argon atmosphere in glassware, which were preliminarily dried by heating under reduced pressure. Sensitive liquids and solutions were transferred by syringe or cannula and introduced through rubber septa. Freshly distilled olefins were employed in the present aziridination. Dichloromethane and THF were distilled over calcium hydride and sodium/benzophenone, respectively, before use. Unless otherwise noted, all other commercial reagents and solvents were used without additional purification. Reactions were monitored with analytical thin-layer chromatography (TLC) on silica gel 60 F_{254} precoated plates available from Merck Ltd. Visualization on TLC was achieved by UV light (254 nm) or treatment with 5% phosphomolybdic acid in ethanol followed by heating. Column chromatography was conducted on silica gel 60N (spherical, neu-

tral), 63–210 μm, available from Kanto Chemical Co., Inc. ^{1}H NMR spectra were recorded at 400 MHz on a JEOL JNM-AL-400 instrument at room temperature. Chemical shifts of ^{1}H NMR spectra, reported in ppm, were determined relative to tetramethylsilane ($\delta = 0.00$ ppm) as an internal standard. The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet. Coupling constants (J) are reported in Hertz (Hz). Optical rotations were measured with a JASCO P-1020 polarimeter. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8400 spectrometer with KBr pellets or sodium chloride cells when neat. Frequencies are given in reciprocal centimeters (cm^{-1}). High-resolution mass spectra were recorded on a JEOL JMS-SX 102 A mass spectrometer by using EI or FAB methods. Elemental analysis data were recorded on a Yanaco CHN Corder MT-5 instrument. All known compounds were identified by comparison of their spectroscopic data.

Syntheses

8: Compound **7** (4.0 g, 12.1 mmol) prepared according to the reported procedure[19] was dissolved in THF (60 mL) under N_2 at −78 °C. *n*BuLi (1.58 M in hexane, 8.4 mL, 13.2 mmol) was added to the solution, which was stirred for 1 h. Diethyl chlorophosphate (2.1 mL, 13.2 mmol) was added to the solution at that temperature, which was then warmed to room temperature, stirred for 1 h, and cooled to −78 °C. The mixture was added to a solution of lithium/naphthalene (39.6 mmol, 3.3 equiv) in THF (60 mL) and stirred for 1.5 h at the temperature. The mixture was treated with iodine (16.7 g, 65.8 mmol, 5.5 equiv), stirred for another 2 h, warmed to room temperature, and concentrated in vacuo. The residue was passed through a short silica-gel column (hexane/toluene = 1:0–0:1) to obtain a roughly 1:1 mixture of **8** and (*S*)-2-methoxymethoxy-1,1′-binaphthyl. Crystallization of the mixture from CH_2Cl_2/hexane gave pure **8** as a solid (2.4 g, 45 % yield). $[\alpha]_D^{25} = +32$ ($c = 0.32$, $CHCl_3$); IR (KBr): $\tilde{\nu}$ = 3055, 2991, 2961, 2935, 2905, 2849, 2827, 1624, 1593, 1580, 1508, 1472, 1352, 1335, 1300, 1259, 1242, 1198, 1150, 1107, 1084, 1059, 1034, 1015, 949, 920, 903, 826, 812, 783, 773, 754, 692, 671, 621, 548 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.01$ (d, $J = 8.5$ Hz, 1H), 7.95 (d, $J = 9.3$ Hz, 1H), 7.83 (t, $J = 8.5$ Hz, 2H), 7.59 (d, $J = 8.8$ Hz, 1H), 7.56 (d, $J = 9.3$ Hz, 1H), 7.38–7.42 (m, 1H), 7.31 (t, $J = 7.4$ Hz, 1H), 7.15–7.22 (m, 3H), 6.99 (d, $J = 8.5$ Hz, 1H), 5.05 (ABq, $J = 6.8$ Hz, 2H), 3.17 ppm (s, 3H); elemental analysis: calcd (%) for $C_{22}H_{17}IO_2$: C 60.02, H 3.89; found: C 60.23, H 3.89.

9: Iodobinaphthyl **8** (1.0 g, 2.27 mmol), $[Pd(PPh_3)_4]$ (131 mg, 0.11 mmol, 5 mol %), cesium fluoride (1.03 g, 6.81 mmol, 3.0 equiv), and 3,5-difluorophenylboronic acid (860 mg, 5.5 mmol, 2.4 equiv) were added to DMF (8 mL). The mixture was stirred at 115 °C for 24 h and then cooled to room temperature. The mixture was partitioned between diethyl ether and aqueous ammonium chloride, and the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was subjected to chromatography on silica gel (hexane/ethyl acetate = 19:1) to give **9** as a white solid (0.95 g, 98 % yield). $[\alpha]_D^{25} = +39$ ($c = 0.82$, $CHCl_3$); IR (KBr): $\tilde{\nu}$ = 3422, 3057, 2999, 2957, 2931, 2900, 2826, 1634, 1593, 1578, 1560, 1506, 1472, 1458, 1431, 1412, 1358, 1339, 1308, 1259, 1242, 1198, 1150, 1082, 1061, 1034, 1015, 922, 905, 862, 818, 777, 750, 731, 650, 617, 552 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.01$ (d, $J = 8.5$ Hz, 1H), 7.94 (d, $J = 8.3$ Hz, 1H), 7.85 (d, $J = 9.0$ Hz, 1H), 7.78 (d, $J = 8.3$ Hz, 1H), 7.60 (d, $J = 8.5$ Hz, 1H), 7.45–7.49 (m, 2H), 7.17–7.30 (m, 4H), 7.01–7.03 (m, 1H), 6.67–6.73 (m, 2H), 6.44–6.50 (m, 1H), 4.98 (ABq, $J = 7.0$ Hz, 2H), 3.13 ppm (s, 3H); HRMS (FAB): m/z calcd for $C_{28}H_{20}F_2O_2$: 426.1445 $[M]^+$; found: 426.1431.

10: Coupling product **9** (938.0 mg, 2.2 mmol) was dissolved in THF (5.6 mL) at −78 °C under N_2. *n*BuLi (1.58 M in hexane, 1.4 mL, 2.2 mmol, 1.0 equiv) was added to the solution, which was stirred for 1 h. At that temperature, iodomethane (415 μL, 6.7 mmol, 3.0 equiv) was added to the solution, which was stirred for 1 h and warmed to room temperature. The reaction was quenched with aqueous ammonium chloride, and the mixture was extracted with diethyl ether. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was subjected to chromatography on silica gel (hexane/ethyl acetate = 8:2) to give **10** as a solid (901.0 mg, 93 % yield). $[\alpha]_D^{25} = +51$ ($c = 0.67$, $CHCl_3$); IR (KBr): $\tilde{\nu}$ = 3057, 2997, 2955, 2930, 2903, 2851, 2826, 1728, 1634, 1593, 1580, 1501, 1472, 1462, 1431, 1412, 1356, 1340, 1306, 1259, 1242, 1198, 1150, 1082, 1061, 1034, 1015, 966, 935, 921, 903, 862, 818, 777, 750, 729, 706, 692, 677, 617, 552, 538 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.98$ (d, $J = 8.5$ Hz, 1H), 7.91 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 9.0$ Hz, 1H), 7.76 (d, $J = 8.1$ Hz, 1H), 7.57 (d, $J = 8.3$ Hz, 1H), 7.48 (d, $J = 9.0$ Hz, 1H), 7.45 (ddd, $J = 8.2$, 6.1, 2.1 Hz, 1H), 7.15–7.28 (m, 4H), 7.01–7.03 (m, 1H), 6.68 (d, $J = 8.3$ Hz, 2H), 4.97 (ABq, $J = 7.0$ Hz, 2H), 3.12 (s, 3H), 2.03 ppm (s, 3H); elemental analysis: calcd (%) for $C_{29}H_{22}F_2O_2$: C 79.08, H 5.03; found: C 79.11, H 5.17.

11: Compound **10** (90.2 mg, 0.2 mmol) was dissolved in THF (1.0 mL) at −78 °C under N_2. *n*BuLi (1.60 M in hexane, 140.8 μL, 0.23 mmol, 1.1 equiv) and TMEDA (34.0 μL, 0.23 mmol, 1.1 equiv) were added to the solution, which was stirred for 1 h at that temperature. At the same temperature, DMF (76.1 μL, 0.98 mmol, 4.8 equiv) was added, and the solution was stirred for 1 h and warmed to room temperature. The reaction was quenched with water, and the mixture was extracted with diethyl ether. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was subjected to chromatography on silica gel (hexane/ethyl acetate = 8:2) to give (*R*)-2′-(3,5-difluoro-4-methylphenyl)-3-formyl-2-methoxymethoxy-1,1′-binaphthyl (93.3 mg, 97 % yield). Subsequently, this compound (81.3 mg, 1.0 mmol) was dissolved in hydrogen chloride/2-propanol (20 % *w*/*w*, 2 mL), and the mixture was stirred overnight at room temperature. The mixture was neutralized with aqueous $NaHCO_3$ and extracted with diethyl ether. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was subjected to chromatography on silica gel (hexane/ethyl acetate = 15:1) to give **11** as a yellow solid (63.3 mg, 88 % yield). $[\alpha]_D^{25} = -38$ ($c = 0.08$, $CHCl_3$); IR (KBr): $\tilde{\nu}$ = 3408, 3202, 3059, 2928, 2851, 1659, 1632, 1580, 1501, 1462, 1441, 1431, 1414, 1387, 1340, 1306, 1292, 1256, 1219, 1182, 1151, 1115, 1082, 1049, 1024, 959, 935, 889, 858, 820, 795, 777, 752, 729, 704, 652, 556 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.48$ (s, 1H), 10.13 (s, 1H), 8.22 (s, 1H), 8.04 (d, $J = 8.3$ Hz, 1H), 7.96 (d, $J = 8.3$ Hz, 1H), 7.88–7.91 (m, 1H), 7.58 (d, $J = 8.5$ Hz, 1H), 7.47–7.51 (m, 1H), 7.29–7.37 (m, 3H), 7.22 (d, $J = 8.8$ Hz, 1H), 7.03–7.06 (m, 1H), 6.71 (d, $J = 8.1$ Hz, 2H), 2.00 ppm (s, 3H); elemental analysis: calcd (%) for $C_{28}H_{18}F_2O_2$: C 79.23, H 4.27; found: C 79.10, H 4.53.

Salen ligand for the synthesis of **5**: (1*R*,2*R*)-1,2-diaminocyclohexane sulfate (20.2 mg, 0.10 mmol) and K_2CO_3 (13.1 mg, 0.09 mmol) were added to a solution of **11** (80.5 mg, 0.19 mmol) in EtOH (1.5 mL), and the mixture was stirred overnight at room temperature. The resulting light-yellow precipitate was filtered, washed with water and EtOH, and dried in vacuo to give the salen ligand (63.4 mg, 72 % yield). This compound was used for the following reaction without further purification. $[\alpha]_D^{26} = -185$ ($c = 0.3$, $CHCl_3$); IR (KBr): $\tilde{\nu}$ = 3441, 3055, 3013, 2932, 2860, 1659, 1632, 1580, 1501, 1464, 1443, 1431, 1414, 1383, 1350, 1340, 1321, 1306, 1286, 1258, 1219, 1148, 1119, 1084, 1047, 1024, 939, 887, 860, 818, 791, 775, 748, 729, 704, 654, 619, 563, 540 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 13.18$ (s, 2H), 8.41 (s, 2H), 8.00 (d, $J = 8.3$ Hz, 2H), 7.92 (d, $J = 8.3$ Hz, 2H), 7.63–7.66 (m, 4H), 7.57 (d, $J = 8.5$ Hz, 2H), 7.34–7.38 (m, 2H), 7.16–7.23 (m, 4H), 7.06 (d, $J = 8.3$ Hz, 2H), 6.89 (d, $J = 7.6$ Hz, 2H), 6.75–6.81 (m, 6H), 3.27–3.34 (m, 2H), 1.95–2.02 (m, 8H), 1.86–1.89 (m, 2H), 1.67–1.76 (m, 2H), 1.42–1.47 ppm (m, 2H); HRMS (FAB): m/z calcd for $C_{62}H_{46}F_4N_2O_2$: 926.3495 $[M]^+$; found: 926.3495.

5: A solution of the above salen ligand (63.4 mg, 0.07 mmol) and triruthenium dodecacarbonyl (57.0 mg, 0.09 mmol) in dehydrated ethanol (2.0 mL) was heated at reflux under nitrogen atmosphere for 2 days. The resulting mixture was evaporated and subjected to chromatography on silica gel (CH_2Cl_2 then CH_2Cl_2/ethanol = 20:1) to give **5** as a reddish-brown solid (32.2 mg, 45 % yield). IR (KBr): $\tilde{\nu}$ = 3053, 2934, 2860, 2044, 1936, 1732, 1717, 1701, 1634, 1612, 1578, 1545, 1499, 1487, 1448, 1425, 1385, 1339, 1323, 1308, 1288, 1258, 1244, 1229, 1188, 1167, 1144, 1123, 1080, 1045, 1024, 939, 862, 816, 795, 777, 748, 727, 704, 696, 667, 625, 600, 571, 557, 538 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.38$ (br s, 1H), 8.29 (br s, 1H), 8.08 (d, $J = 8.3$ Hz, 1H), 7.97 (dd, $J = 7.3$, 7.1 Hz, 2H), 7.92 (d, $J = 8.1$ Hz, 1H), 7.77–7.85 (m, 2H), 7.62–7.70 (m, 2H), 7.38–7.44 (m, 5H), 7.31 (dd, $J = 7.3$ Hz, 1H), 7.24–7.27 (m, 1H), 7.14–7.21 (m, 3H), 7.03–7.11 (m, 2H), 6.92–6.99 (m, 1H), 6.73–6.75 (m, 1H), 6.09 (d, $J =$

7.6 Hz, 2H), 5.88 (d, J=8.1 Hz, 2H), 3.23–3.34 (m, 1H), 3.07–3.18 (m, 1H), 2.64–2.76 (m, 2H), 1.99–2.09 (m, 2H), 1.78 (s, 6H), 1.51–1.66 (m, 2H), 1.31–1.43 ppm (m, 2H); elemental analysis: calcd (%) for $C_{63}H_{44}F_4N_2O_3Ru{\cdot}1.5H_2O{\cdot}1.5CH_2Cl_2$: C 64.10, H 4.17, N 2.32; found: C 64.09, H 4.27, N 2.32.

12: A mixture of **8** and (*S*)-2-methoxymethoxy-1,1′-binaphthyl (1.00:0.94, 3.38 mmol of **8**) obtained in the course of the preparation of **8** was used without separation as the starting material for this synthesis. This mixture, [Pd(PPh$_3$)$_4$] (273.7 mg, 0.24 mmol, 5 mol%), and 3,5-dichlorophenylboronic acid (1207.2 mg, 6.33 mmol, 1.9 equiv) were added to toluene (12 mL) and aqueous Na_2CO_3 (1 M, 12 mL). The reaction mixture was stirred at 100 °C for 24 h and then cooled to room temperature. The mixture was partitioned between ethyl acetate and brine, and the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was subjected to chromatography on silica gel (hexane/ethyl acetate = 30:1–15:1) to give **12** as a solid (1426.5 mg, 92% yield). $[\alpha]_D^{25}=+79$ (c=0.5, $CHCl_3$); IR (KBr): $\tilde{\nu}$=3059, 3001, 2957, 2930, 2899, 2826, 1622, 1587, 1556, 1506, 1474, 1431, 1408, 1354, 1333, 1242, 1198, 1150, 1084, 1063, 1034, 1013, 922, 903, 860, 820, 802, 752, 677 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.02 (d, J=8.5 Hz, 1H), 7.95 (d, J=8.1 Hz, 1H), 7.86 (d, J=9.0 Hz, 1H), 7.80 (d, J=8.1 Hz, 1H), 7.58 (d, J=8.5 Hz, 2H), 7.46–7.51 (m, 2H), 7.18–7.32 (m, 4H), 7.06 (d, J=2.0 Hz, 2H), 6.99–7.06 (m, 2H), 5.00 (ABq, J=6.8 Hz, 2H), 3.18 ppm (s, 3H); HRMS (FAB): m/z calcd for $C_{28}H_{20}Cl_2O_2$: 458.0840 $[M]^+$; found: 458.0881.

15: Coupling product **12** (335.1 mg, 0.73 mmol) was dissolved in THF (5.0 mL) at −78 °C under N_2. *sec*-BuLi (1.58 M in cyclohexane and hexane, 1.5 mL, 1.52 mmol, 2.1 equiv) was added to the solution, which was stirred for 2 h. At that temperature, chlorotrimethylsilane (93.0 μL, 0.73 mmol, 1.0 equiv) was added, and the solution was stirred for 1 h. The mixture was warmed to room temperature, stirred for another 6 h, quenched with brine, and extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo after filtration. The residue was subjected to chromatography on silica gel (hexane/ethyl acetate = 40:1–15:0) to give **15** as a solid (246.4 mg, 64% yield). $[\alpha]_D^{25}=+102$ (c=0.6, $CHCl_3$); IR (KBr): $\tilde{\nu}$=3057, 2988, 2955, 2932, 2897, 2847, 2826, 2789, 1622, 1589, 1566, 1510, 1475, 1464, 1427, 1404, 1363, 1348, 1331, 1306, 1261, 1250, 1242, 1196, 1175, 1150, 1084, 1063, 1034, 1014, 957, 922, 903, 851, 820, 775, 748, 710, 689, 640, 615, 554 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.02 (d, J=8.5 Hz, 1H), 7.95 (d, J=8.1 Hz, 1H), 7.89 (d, J=9.0 Hz, 1H), 7.82 (d, J=8.1 Hz, 1H), 7.59 (d, J=8.5 Hz, 1H), 7.52 (d, J=9.3 Hz, 1H), 7.45–7.49 (m, 1H), 7.19–7.32 (m, 4H), 7.06–7.07 (m, 2H), 7.00 (d, J=8.3 Hz, 1H), 5.04 (d, J=7.1 Hz, 1H), 4.94 (d, J=7.1 Hz, 1H), 3.16 (s, 3H), 0.38 ppm (s, 9H); HRMS (FAB): m/z calcd for $C_{31}H_{28}Cl_2O_2Si$: 530.1236 $[M]^+$; found: 530.1235.

16: Compound **15** (168.2 mg, 0.32 mmol) was dissolved in THF (2.8 mL) at −78 °C under N_2. *n*BuLi (1.60 M, 218.0 μL, 0.35 mmol, 1.1 equiv) and TMEDA (53.0 μL, 0.35 mmol, 1.1 equiv) were added to the solution, which was stirred for 3 h. At that temperature, DMF (27.0 μL, 0.35 mmol, 1.1 equiv) was added, and the solution was stirred for 1 h and warmed to room temperature. After the mixture was stirred for 6 h, the reaction was quenched with brine, and the mixture was extracted with diethyl ether. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was subjected to chromatography on silica gel (hexane/ethyl acetate = 15:1) to give the formylated intermediate (148.3 mg, 84% yield). Subsequently, this compound (146.5 mg, 0.26 mmol) was dissolved in THF (1.3 mL) and hydrogen chloride/2-propanol (20% *w*/*w*, 0.30 mL), and the mixture was stirred overnight at room temperature. The mixture was neutralized with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was subjected to chromatography on silica gel (hexane/ethyl acetate = 10:1) to give **16** as a yellow solid (134.5 mg, 100% yield). $[\alpha]_D^{27}=-108$ (c=0.6, $CHCl_3$); IR (KBr): $\tilde{\nu}$=3445, 3209, 3059, 2986, 2955, 2899, 2851, 1659, 1630, 1587, 1506, 1460, 1441, 1427, 1412, 1387, 1358, 1340, 1308, 1290, 1250, 1178, 1150, 1117, 1039, 1024, 943, 918, 891, 851, 822, 793, 775, 750, 710, 689, 640, 625, 598, 581 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 10.52 (s, 1H), 10.13 (s, 1H), 8.23 (s, 1H), 8.04 (d, J=8.3 Hz, 1H), 7.96 (d, J=8.1 Hz, 1H), 7.90 (dd, J=7.6, 1.7 Hz, 1H), 7.58 (d, J=8.5 Hz, 1H), 7.50 (dd, J=7.8, 6.8 Hz, 1H), 7.38–7.30 (m, 3H), 7.23–7.27 (m, 1H), 7.16–7.18 (m, 1H), 7.11 (s, 2H), 7.02 (d, J=9.3 Hz, 1H), 0.37 ppm (s, 9H); HRMS (FAB): m/z calcd for $C_{30}H_{24}Cl_2O_2Si$: 514.0923 $[M]^+$; found: 530.0928.

Salen ligand for the synthesis of **6**: (1*R*,2*R*)-1,2-diaminocyclohexane sulfate (32.8 mg, 0.15 mmol) and K_2CO_3 (23.5 mg, 0.17 mmol) were added to a solution of **16** (159.1 mg, 0.31 mmol) in ethanol (4.0 mL), and the mixture was stirred for 9.5 h at room temperature. The resulting light-yellow precipitate was filtered, washed with water and ethanol, and then dried in vacuo at 50 °C for 2 h to give a diimine (163.4 mg, 95% yield), which was used for the synthesis of **6** without further purification. $[\alpha]_D^{26}=-313$ (c=0.3, $CHCl_3$). IR (KBr): $\tilde{\nu}$=3055, 2934, 2897, 2860, 1690, 1676, 1659, 1632, 1587, 1551, 1512, 1502, 1467, 1443, 1429, 1402, 1381, 1344, 1317, 1288, 1250, 1173, 1148, 1096, 1040, 1024, 945, 851, 820, 775, 746, 710, 640 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=13.33 (s, 2H), 8.45 (s, 2H), 8.02 (d, J=8.5 Hz, 2H), 7.95 (d, J=8.1 Hz, 2H), 7.66–7.68 (m, 4H), 7.58 (d, J=8.3 Hz, 2H), 7.40–7.44 (m, 2H), 7.15–7.24 (m, 10H), 6.97 (ddd, J=7.1, 6.8, 1.3 Hz, 2H), 6.85 (d, J=7.6 Hz, 2H), 3.71–3.73 (m, 1H), 3.32–3.35 (m, 1H), 1.86–1.96 (m, 4H), 1.70–1.72 (m, 2H), 1.42–1.47 (m, 2H), 0.35 ppm (s, 18H); HRMS (FAB): m/z calcd for $C_{66}H_{58}Cl_4N_2O_2Si_2$: 1106.2791 $[M]^+$; found: 1106.2798.

6: A solution of the above salen ligand (91.8 mg, 0.08 mmol) and triruthenium dodecacarbonyl (68.8 mg, 0.11 mmol) in dehydrated ethanol (7.0 mL) was heated at reflux under argon atmosphere for 40 h. The resulting mixture was evaporated and subjected to chromatography on silica gel (hexane/ethyl acetate = 5:1–3:1) to give **6** as a reddish-brown solid (63.7 mg, 62% yield). IR (KBr): $\tilde{\nu}$=3053, 2984, 2939, 2899, 2860, 1940, 1732, 1717, 1699, 1683, 1612, 1580, 1545, 1510, 1487, 1448, 1425, 1387, 1342, 1327, 1290, 1250, 1229, 1177, 1146, 1124, 1040, 1024, 953, 922, 851, 818, 795, 777, 746, 710, 692, 637, 581, 559, 548, 536 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.37 (s, 1H), 8.30 (d, J=1.6 Hz, 1H), 8.13 (d, J= 8.3 Hz, 1H), 8.01 (dd, J=9.3, 8.8 Hz, 2H), 7.93 (d, J=8.1 Hz, 1H), 7.80 (d, J=3.7 Hz, 2H), 7.69 (d, J=8.3 Hz, 1H), 7.63 (d, J=8.1 Hz, 1H), 7.46–7.50 (m, 1H), 7.37–7.43 (m, 3H), 7.30 (t, J=8.1 Hz, 1H), 6.98–7.22 (m, 8H), 6.79 (d, J=8.5 Hz, 1H), 6.44 (s, 2H), 6.33 (s, 2H), 3.23–3.28 (m, 1H), 3.11–3.14 (m, 1H), 2.67–2.72 (m, 2H), 1.99–2.09 (m, 2H), 1.53–1.63 (m, 2H), 1.35–1.43 ppm (m, 2H); HRMS (FAB): m/z calcd for $C_{66}H_{56}Cl_4N_2O_2RuSi_2$: 1206.1678 $[M-CO]^+$; found: 1206.1670; elemental analysis: calcd (%) for $C_{67}H_{56}Cl_4N_2O_3RuSi_2{\cdot}1.5H_2O$: C 63.70, H 4.71, N 2.22; found: C 63.80, H 4.87, N 2.10.

N-2-(trimethylsilyl)ethanesulfonyl azide: Sodium azide (1.26 mg, 19.4 mmol) was added to a solution of 2-trimethylsilylethanesulfonyl chloride (2.54 mg, 12.7 mmol) in acetone (2.0 mL), and the mixture was stirred at room temperature for 12 h. After filtration and concentration in vacuo at room temperature, 2-(trimethylsilyl)ethanesulfonyl azide was obtained (2.39 mg, 91% yield) as an oil that was spectroscopically pure but gradually decomposed in a freezer (−20 °C). When the compound was faintly colorized, it was subjected to kugelrohr distillation under reduced pressure behind a safety shield in a hood before use (91 °C, 0.1 mmHg). IR (neat): $\tilde{\nu}$=2955, 2359, 2133, 1420, 1364, 1252, 1202, 1175, 1155, 1115, 1022, 897, 862, 843, 793, 756, 696, 625, 584, 565 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=3.20–3.25 (m, 2H), 1.11–1.15 (m, 2H), 0.07 ppm (s, 9H); elemental analysis: calcd (%) for $C_5H_{13}N_3O_2SSi$: C 28.97, H 6.32, N 20.27; found: C 29.08, H 6.27, N 20.25.

Typical experimental procedure for enantioselective aziridination (aziridination of styrene with *N*-2-(trimethylsilyl)ethanesulfonyl azide): Ru(salen)(CO) complex **6** (0.6 mg, 0.5 μmol) was dried twice by azeotropic concentration of its solution in toluene (0.25 mL) in vacuo under nitrogen atmosphere. Then, MS4A (10 mg), styrene (5.7 μL, 0.05 mmol), 2-bromonaphthalene (2.0 mg, as the internal standard), and dichloromethane (0.25 mL) were added to the dried **6**. After the mixture was stirred for 0.5 h at room temperature, SES azide (9.6 μL, 0.05 mmol) was added to the suspension at 0 °C, which was stirred for another 12 h at that temperature. The reaction mixture was filtrated through a celite pad and evaporated. The TON of **6** was determined by ^{1}H NMR (400 MHz) analysis of the filtrate. Then, the filtrate was subjected to chromatography on silica gel (hexane/ethyl acetate = 10:1–5:1) to give *N*-1-[2-(trimethylsilyl)ethanesulfonyl]-2-phenylaziridine in 99% yield (92% *ee*). The enantiomeric

excess was determined by HPLC analysis with DAICEL CHIRALCEL OJ-H (hexane/*i*PrOH = 97:3, 1.0 mL min^{-1}, t_S = 17.8 min, t_R = 28.0 min). $[\alpha]_D^{25}$ = +115 (c = 1.3, $CHCl_3$) (reference [4d]: $[\alpha]_D^{30}$ = −59.8 (40% *ee*, c = 0.704, $CHCl_3$)). Absolute configuration was determined to be *S* by comparison of the specific rotation.

2-(*p*-Bromophenyl)-1-[2-(trimethylsilyl)ethanesulfonyl]aziridine: A yellow oil. The enantiomeric excess was determined by HPLC analysis with DAICEL CHIRALCEL OJ-H (hexane/*i*PrOH = 90:10, 0.5 mL min^{-1}, t_{major} = 25.7 min, t_{minor} = 31.8 min). $[\alpha]_D^{24}$ = +107 (c = 0.9, $CHCl_3$) (92% *ee*); IR (neat): $\tilde{\nu}$ = 2953, 2930, 2899, 2856, 1736, 1595, 1491, 1456, 1412, 1375, 1325, 1250, 1173, 1148, 1109, 1072, 1011, 984, 912, 833, 750, 725, 706, 673, 631, 619, 573, 552, 532 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.46 (d, J = 8.5 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 3.64 (dd, J = 7.1, 4.4 Hz, 1H), 3.07–3.12 (m, 2H), 2.94 (d, J = 7.1 Hz, 1H), 2.35 (d, J = 4.4 Hz, 1H), 1.07–1.12 (m, 2H), 0.02 ppm (s, 9H); HRMS (EI): m/z calcd for $C_{13}H_{20}BrNO_2SSi$: 362.0246 $[M]^+$; found: 362.0243.

2-Phenylethynyl-1-[2-(trimethylsilyl)ethanesulfonyl]aziridine: A yellow oil. The enantiomeric excess was determined by HPLC analysis with DAICEL CHIRALCEL OJ-H (hexane/*i*PrOH = 90:10, 1.0 mL min^{-1}, t_{minor} = 18.3 min, t_{major} = 26.5 min). $[\alpha]_D^{24}$ = +199 (c = 1.3, $CHCl_3$) (>99% *ee*); IR (neat): $\tilde{\nu}$ = 3082, 3057, 3034, 3020, 3001, 2953, 2899, 2858, 2818, 2243, 1730, 1599, 1574, 1491, 1443, 1420, 1375, 1329, 1285, 1252, 1205, 1173, 1148, 1113, 1070, 1038, 1020, 999, 941, 897, 858, 806, 758, 721, 692, 673, 613, 575, 567, 552, 536, 521 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.43–7.46 (m, 2H), 7.29–7.35 (m, 3H), 3.39 (dd, J = 7.1, 4.4 Hz, 1H), 3.15–3.20 (m, 2H), 2.84 (d, J = 7.1 Hz, 1H), 2.54 (d, J = 4.4 Hz, 1H), 1.17–1.22 (m, 2H), 0.09 ppm (s, 9H); HRMS (EI): m/z calcd for $C_{15}H_{21}NO_2SSi$: 307.1062 $[M]^+$; found: 307.1057.

N-[2-(trimethylsilyl)ethanesulfonyl]indeno[1,2-β]aziridine: A yellow oil. The enantiomeric excess was determined by HPLC analysis with DAICEL CHIRALCEL OJ-H (hexane/*i*PrOH = 90:10, 0.5 mL min^{-1}, t_{minor} = 16.7 min, t_{major} = 18.2 min). $[\alpha]_D^{24}$ = +52 (c = 0.7, $CHCl_3$) (98% *ee*); IR (neat): $\tilde{\nu}$ = 3047, 3026, 2953, 2901, 2826, 1735, 1618, 1597, 1474, 1421, 1358, 1323, 1250, 1213, 1171, 1140, 1109, 1020, 999, 974, 936, 835, 772, 746, 725, 692, 671, 623, 571, 557, 549 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.49 (d, J = 7.3 Hz, 1H), 7.22–7.31 (m, 3H), 4.23 (d, J = 5.1 Hz, 1H), 3.89–3.92 (m, 1H), 3.24 (br s, 2H), 3.07–3.12 (m, 2H), 1.09–1.14 (m, 2H), 0.04 ppm (s, 9H); HRMS (EI): m/z calcd for $C_{14}H_{21}NO_2SSi$: 296.1141 $[M+H]^+$; found: 296.1139.

2-(*n*-Hexyl)-1-[2-(trimethylsilyl)ethanesulfonyl]aziridine: A yellow oil. $[\alpha]_D^{24}$ = +21 (c = 1.4, $CHCl_3$) (77% *ee*); IR (neat): $\tilde{\nu}$ = 2955, 2930, 2856, 1458, 1421, 1408, 1325, 1286, 1251, 1171, 1146, 1109, 1069, 1020, 935, 895, 860, 842, 802, 758, 713, 698, 669, 551, 524 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.04–3.09 (m, 2H), 2.69–2.73 (m, 1H), 2.60 (d, J = 6.8 Hz, 1H), 2.08 (d, J = 4.6 Hz, 1H), 1.22–1.62 (m, 10H), 1.12–1.17 (m, 2H), 0.89 (t, J = 6.8 Hz, 1H), 0.07 ppm (s, 9H); HRMS (EI): m/z calcd for $C_{13}H_{29}NO_2SSi$: 291.1688 $[M]^+$; found: 291.1693.

2-Phenylethynyl-1-(*p*-toluenesulfonyl)aziridine: A yellow oil. The enantiomeric excess was determined by HPLC analysis with DAICEL CHIRALCEL OJ-H (hexane/*i*PrOH = 95:5, 1.15 mL min^{-1}, t_{minor} = 67.2 min, t_{major} = 74.6 min). $[\alpha]_D^{24}$ = +136 (c = 0.9, $CHCl_3$) (98% *ee*); IR (neat): $\tilde{\nu}$ = 3082, 3063, 3034, 3022, 2999, 2982, 2957, 2924, 2870, 2243, 1734, 1597, 1574, 1493, 1443, 1373, 1329, 1306, 1292, 1267, 1244, 1204, 1186, 1163, 1117, 1096, 1070, 1042, 1018, 999, 941, 862, 816, 802, 758, 719, 692, 669, 660, 635, 575, 556, 538 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.88 (d, J = 8.3 Hz, 2H), 7.36–7.41 (m, 4H), 7.28–7.32 (m, 3H), 3.48 (dd, J = 7.1, 4.4 Hz, 1H), 2.84 (d, J = 7.1 Hz, 1H), 2.50 (d, J = 4.4 Hz, 1H), 2.46 ppm (s, 3H); HRMS (EI): m/z calcd for $C_{17}H_{15}NO_2S$: 297.0823 $[M]^+$; found: 297.0836.

1-(*p*-Nitrobenzenesulfonyl)-2-phenylethynylaziridine: A yellow oil. The enantiomeric excess was determined by HPLC analysis with DAICEL CHIRALCEL OD-H (hexane/*i*PrOH = 66:34, 0.5 mL min^{-1}, t_{minor} = 35.5 min, t_{major} = 44.0 min). $[\alpha]_D^{24}$ = +104 (c = 0.7, $CHCl_3$) (98% *ee*); IR (neat): $\tilde{\nu}$ = 3105, 3036, 2928, 2869, 2243, 1732, 1684, 1607, 1533, 1491, 1445, 1400, 1346, 1312, 1204, 1167, 1092, 1038, 1015, 939, 860, 756, 694, 629, 567, 536 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 9.0 Hz, 1H), 8.22 (d, J = 9.0 Hz, 1H), 7.38–7.41 (m, 2H), 7.27–7.37 (m, 3H), 3.59 (dd, J = 7.1, 4.5 Hz, 1H), 2.99 (d, J = 7.1 Hz, 1H), 2.63 ppm (d, J = 4.5 Hz, 1H); HRMS (EI): m/z calcd for $C_{16}H_{12}N_2O_4S$: 328.0518 $[M]^+$; found: 328.0511.

1-(*o*-Nitrobenzenesulfonyl)-2-phenylethynylaziridine: A yellow oil. The enantiomeric excess was determined by HPLC analysis with DAICEL CHIRALPAK AD-H (hexane/*i*PrOH = 90:10, 1.0 mL min^{-1}, t_{major} = 21.7 min, t_{minor} = 23.9 min). $[\alpha]_D^{24}$ = +96 (c = 0.6, $CHCl_3$) (87% *ee*); IR (neat): $\tilde{\nu}$ = 3096, 3024, 2957, 2924, 2854, 2237, 1593, 1545, 1491, 1467, 1443, 1367, 1342, 1304, 1269, 1205, 1167, 1124, 1061, 1038, 997, 941, 862, 781, 756, 713, 691, 654, 621, 602, 536 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.28–8.31 (m, 1H), 7.76–7.82 (m, 3H), 7.42–7.45 (m, 2H), 7.27–7.36 (m, 3H), 3.73 (dd, J = 7.1, 4.7 Hz, 1H), 3.16 (d, J = 7.1 Hz, 1H), 2.77 ppm (d, J = 4.7 Hz, 1H); HRMS (EI): m/z calcd for $C_{16}H_{12}N_2O_4S$: 328.0518 $[M]^+$; found: 328.0527.

Benzyl 1-[2-(trimethylsilyl)ethanesulfonyl]aziridine-2-carboxylate: A yellow oil. The enantiomeric excess was determined by HPLC analysis with DAICEL CHIRALCEL OJ-H (hexane/*i*PrOH = 90:10, 0.5 mL min^{-1}, 210 nm, t_{major} = 43.0 min, t_{minor} = 39.0 min). $[\alpha]_D^{26}$ = +52 (c = 0.28, $CHCl_3$) (>99% *ee*); IR (neat): $\tilde{\nu}$ = 2955, 2918, 2851, 1751, 1456, 1408, 1364, 1331, 1281, 1252, 1225, 1190, 1177, 1151, 1113, 1084, 1022, 901, 860, 843, 800, 779, 750, 700, 654, 600, 550 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.35–7.38 (m, 5H), 5.22 (s, 2H), 3.33 (dd, J = 7.1, 4.2 Hz, 1H), 3.13–3.17 (m, 2H), 2.76 (d, 7.1 Hz, 1H), 2.61 (d, J = 3.9 Hz), 1.10–1.14 ppm (m, 2H); HRMS (EI): m/z calcd for $C_{15}H_{23}NO_4SSi$: 341.1117 $[M]^+$; found: 341.1067.

N-benzyl-1-[2-(trimethylsilyl)ethanesulfonyl]-*N*-methoxyaziridine-2-carboxamide: A yellow oil. The enantiomeric excess was determined by HPLC analysis with DAICEL CHIRALCEL OJ-H (hexane/*i*PrOH = 90:10, 0.5 mL min^{-1}, 210 nm, t_{major} = 36.6 min, t_{minor} = 42.4 min). $[\alpha]_D^{26}$ = +31 (c = 0.19, $CHCl_3$) (>99% *ee*); IR (neat): $\tilde{\nu}$ = 2953, 2918, 2849, 1670, 1466, 1454, 1439, 1427, 1319, 1250, 1175, 1150, 1130, 1115, 989, 881, 864, 835, 748, 700, 623, 550 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.30–7.36 (m, 5H), 4.83 (ABq, J = 15.6 Hz, 2H), 3.81–3.84 (m, 1H), 3.77 (s, 3H), 3.13–3.18 (m, 2H), 2.75 (d, J = 3.9 Hz, 1H), 2.74 (d, J = 6.8 Hz, 1H), 1.10–1.15 ppm (m, 2H); HRMS (EI): m/z calcd for $C_{16}H_{26}N_2O_4SSi$: 370.1383 $[M]^+$; found: 370.1373.

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