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Asymmetric imidation of organic selenides into selenimides

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Abstract

Treatment of aryl benzyl selenides with [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane [TsN=IPh] in the absence or presence of copper(I) salt in toluene or acetonitrile affords the corresponding *N*-tosylselenimides in 31–46% yield. When the reaction is carried out in the presence of optically active 4,4′-disubstituted bis(oxazoline) as a ligand together with molecular sieves, enantioselective imidation occurs to give optically active *N*-tosylselenimides and the best result is obtained from benzyl 2-naphthyl selenide (64% yield and 36% ee). Similar treatment of allylic selenides gives the corresponding optically active allylic amides (up to 71% yield and 30% ee). In the case of diastereoselective imidation, the reaction of diaryl selenides bearing a chiral oxazolinyl moiety with TsN=IPh or Chloramine–T trihydrate [TsN(Cl)Na·3H_2O] has been successfully carried out to give the corresponding optically active *N*-tosylselenimides in good yields (up to 97% isolated yield and 76% de). The absolute configuration around the selenium atom of (4*S*)-*Se*-[2-(4-isopropyloxazolin-2-yl)phenyl]-*Se*-phenyl-*N*-(*p*-toluenesulfonyl)selenimide [(4*S*)-**13**], obtained by diastereoselective imidation of the corresponding selenide with Chloramine–T trihydrate, has been determined to be *S* by X-ray crystallographic analysis, from the result of which an ionic reaction pathway involving a chloroselenonium ion intermediate is proposed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Asymmetric imidation; Organic selenides; Organic selenimides; Chloramine–T trihydrate; [*N*-(Tosyl)imino]phenyliodinane

1. Introduction

The chemistry of chiral sulfoxides, sulfonium ylides, and sulfimides has been investigated with a good deal of success [1]. In this field, we also succeeded in the synthesis of optically active organosulfur compounds [2]. In contrast, the asymmetric synthesis of analogous organoselenium compounds has been limited [3]. We have already demonstrated the asymmetric induction to several organoselenium compounds to afford chiral organic selenoxides which lead to optically active compounds by the successive selenoxide elimination and [2,3] sigmatropic rearrangement [4]. Compared to the chemistry of chiral organic selenoxides, that of organic selenimides, *N*-analogous to the selenoxides, has been much less studied. In 1981, Krasnov et al. reported the first synthesis of the optically active organic selenimides starting from dialkyl- and diaryl-selenium dichloride, but the scope of this reaction has not been fully developed, probably because of low yields of the products as well as their quite low optical activity [5]. Koizumi et al. attempted the transformation of optically pure alkoxychloroselenuranes, prepared by chlorination of optically active selenides having the 2-exo-hydroxy-10-bornyl group as a chiral auxiliary with *tert*-butyl hypochlorite, to the corresponding *N*-tosylselenimides by treatment with *N*-tosylamine chloride, but they could not isolate the expected selenimide [6]. Very recently, Kamigata and co-workers have shown examples of (i) the conversion of an optically active selenoxide, obtained by optical resolution of a diastereomeric mixture, into the corresponding enantiomerically pure organic selenimide and (ii) the conversion of racemic organic selenimides into the corresponding enantiomerically pure organic selenimides by optical resolution, and ascertained the detailed stereochemistry of these compounds [7]. We have already demonstrated the diastereoselective imidation of chiral cinnamyl 2-(1-dimethylaminoethyl)ferrocenyl selenide using TsN=IPh or

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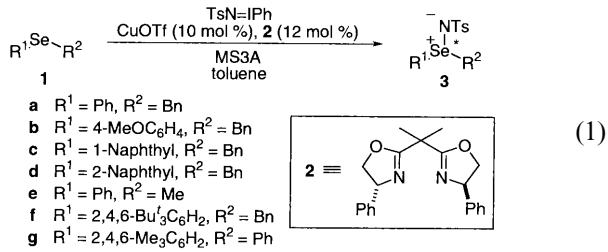
Chloramine–T [TsN(Cl)Na] as imidation reagents to produce the optically active allylic amine derivatives [8]. However, the direct synthesis of chiral organic selenimides from the corresponding selenides has not yet been reported. We report here the results of the direct enantioselective and diastereoselective imidation of various organic selenides into the corresponding chiral organic selenimides in detail [9] and also propose the reaction pathway of diastereoselective imidation by considering the absolute configuration of the obtained diaryl selenimide.

2. Results and discussion

2.1. Catalytic enantioselective imidation of prochiral organic selenides

First, we describe the first example of the direct catalytic enantioselective imidation of prochiral organic selenides into the corresponding optically active *N*-tosylselenimides (Eq. (1)). We have already reported that the direct catalytic imidation of prochiral organic sulfides to the corresponding optically active *N*-tosylsulfimides proceeded with TsN=IPh in the presence of CuOTf and bis(oxazoline) in various solvents [2c–f]. Since the combination of Cu(I) salt and bis(oxazoline) was necessary for asymmetric imidation, we first looked for the solvent in which the imidation of prochiral selenides **1** with TsN=IPh did not proceed in the absence of CuOTf. Treatment of benzyl phenyl selenide (**1a**) with TsN=IPh in MeCN and CH_2Cl_2 at 25°C for 24 h afforded benzyl phenyl *N*-tosylselenimide (**3a**) in 46% yield and in a trace amount, respectively, but in toluene no reaction occurred (Table 1, entries 2 and 3 versus 4).



(1)

Therefore, we chose toluene as solvent [10] and carried out imidation of **1a** with TsN=IPh in the presence of CuOTf (10 mol%) and the optically active bis(oxazoline) **2** (12 mol%) at 25°C for 24 h under N_2 [11]. The *N*-tosylselenimide **3a** was formed in 40% yield, but the expected asymmetric induction did not occur. However, further studies revealed that the reaction proceeded enantioselectively when molecular sieves were added to a reaction mixture (Eq. (1); compare entry 1 with entry 2 in Table 2). This is probably due to the interference of the rapid selenimide–selenoxide equilibrium (Scheme 1) by removal of water present in the reaction mixture [12]. Rapid racemization of the selenoxide is well known (Scheme 2, (a) and (b)) [13]. The rearrangement of selenurane intermediate into a stable selenurane [14] by means of pseudorotation has also been reported (Scheme 2, (c)) [12,15].

At a lower temperature the reaction was slower (entry 3). The reaction also proceeded with several other aryl benzyl selenides. In the case of methyl phenyl selenide (**1e**) the reaction proceeded, but the corresponding *N*-tosylselenimide **3e**, the formation of which was determined by ^{1}H-NMR spectral analysis of the crude product, could not be isolated because of decomposition to the corresponding selenoxide. Selenides hav-

Table 1
Effect of solvent on imidation of benzyl phenyl selenide **1a** [a]

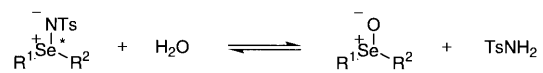
Entry	Solvent	Time (h)	**3a** yield (%)
1	CH_3CN	2	7
2	CH_3CN	24	46
3	CH_2Cl_2	24	trace
4	Toluene	24	0
5 [b]	Toluene	24	31

[a] All reactions were performed in solvent (0.02 M) at 25°C using selenide (**1a**) (0.2 mmol) and TsN=IPh (0.1 mmol).
[b] CuOTf (0.01 mmol, 10 mol%) was added.

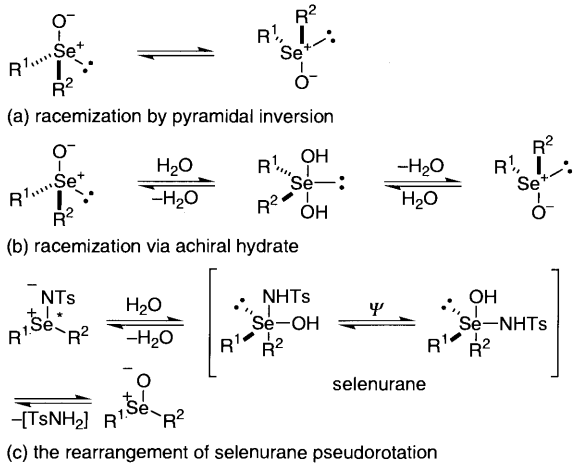
Table 2
Catalytic enantioselective imidation of selenides **1** [a]

Entry	Substrate	Product	Yield (%) [b]	ee (%) [c]
1 [d]	**1a**	**3a**	40	0
2	**1a**	**3a**	53	32
3 [e]	**1a**	**3a**	18	33
4	**1b**	**3b**	37	20
5	**1c**	**3c**	23	29
6 [f]	**1d**	**3d**	64	36
7	**1e**	**3e**	Not isolated	
8	**1f**	**3f**	No reaction	
9	**1g**	**3g**	No reaction	

[a] All reactions were performed in toluene (0.02 M) at 25°C in the presence of 12 mol% chiral ligand **2**, 10 mol% CuOTf and MS 3A for 24 h unless otherwise noted.
[b] Isolated yield.
[c] Enantiomeric excesses were determined by HPLC using suitable chiral columns.
[d] Without MS3A.
[e] At 0°C.
[f] MS4A was added, for 48 h.



Scheme 1.



Scheme 2.

ing bulky substituents on an aryl ring such as benzyl 2,4,6-tri-*tert*-butylphenyl selenide (**1f**) did not react at all. To make clear the absolute configuration of the produced selenimides, we tried to synthesize the selenimide **3g**, the absolute configuration of which is known [7b], but the diaryl selenide **1g** did not react at all under the present reaction conditions. Typical results are shown in Table 2.

When this reaction was applied to various allyl aryl selenides **4**, the expected chiral allylic *N*-tosylamides **6a** and **6b** (up to 30% ee) were obtained in moderate to good yields via [2,3] sigmatropic rearrangement of the initially produced chiral allylic *N*-tosylselenimide **5** (Eq. (2), Table 3). This result clearly shows that the chirality transfer occurred at the rearrangement step.

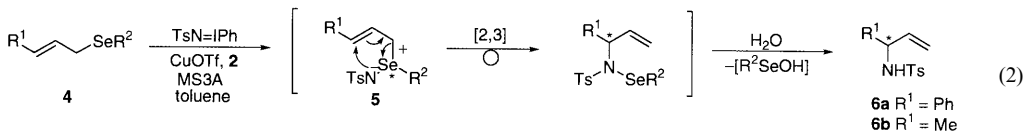
2.2. Diastereoselective imidation of chiral diaryl selenides

We have already reported that the diastereoselective sulfimidation of various diaryl sulfides having a chiral auxiliary to the corresponding *N*-tosylsulfimides proceeded with NTs sources in the presence of copper salts [16]. We describe here the selenium version of this reaction, namely, the direct diastereoselective imidation of diaryl selenides having a chiral auxiliary into the corresponding optically active *N*-tosylselenimides (Eqs. (3) and (4)).

The optically active chiral organic selenides **7**–**10** were prepared by methods similar to those reported by Williams et al. as shown in Schemes 3 and 4 [17]. After (1*S*,2*S*)-(+)-2-amino-1-phenyl-1,3-propanediol-derived oxazoline was protected as its silyl ether, it was *ortho*-lithiated and then quenched with the corresponding diaryl diselenides to produce diaryl selenides (4*S*,5*S*)-**7a**–**7d**. Subsequently, the silyl protecting group was removed to give (4*S*,5*S*)-**8** and then it was converted to diaryl selenide (4*S*,5*S*)-**9** by methylation of a hydroxyl group (Scheme 3). On the other hand, diaryl selenide (4*S*)-**10** bearing an L-valinol-derived oxazolinyl moiety was prepared by condensation of benzonitrile with L-valinol followed by lithiation of the benzene ring and quenching with diphenyl diselenide (Scheme 4).

On treatment of the selenide (4*S*,5*S*)-**7a** with TsN=IPh in acetonitrile or toluene, both the product yield and the asymmetric induction were improved using a copper salt (10 mol%) as catalyst and the corresponding optically active *N*-tosylselenimides (4*S*,5*S*)-**11a** were obtained in 77–92% yield with moderate diastereoselectivity (up to 41% de) as shown in Eq. (3), Table 4 (entries 1–6). Unfortunately, a lower

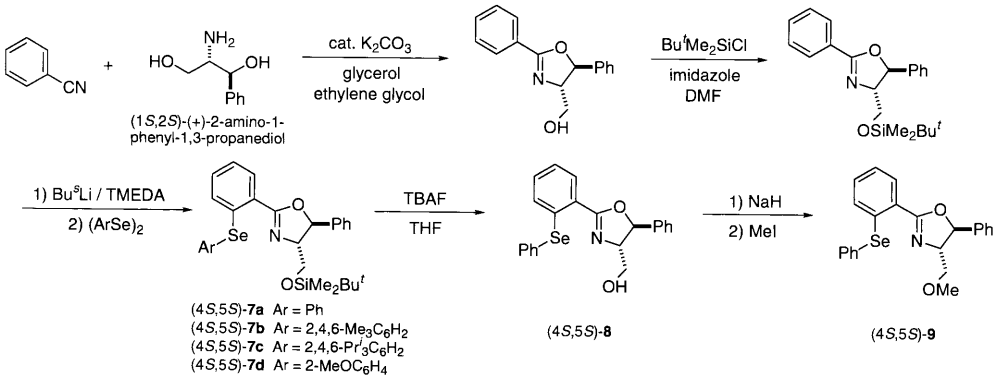
Table 3
Catalytic enantioselective imidation of allylic selenides **4** [a]



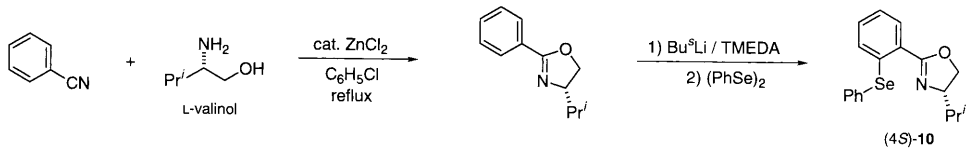
(2)

Entry	Substrate	R^1	R^2	Product	Yield (%) [b]	ee (%) [c]
1	**4a**	Ph	Ph	**6a**	63	20
2	**4b**	Ph	Ferrocenyl	**6a**	35	17
3	**4c**	Ph	1-Naphthyl	**6a**	71	28
4	**4d**	Ph	2-Naphthyl	**6a**	52	30
5	**4e**	Ph	2-$NO_2C_6H_4$	**6a**	Trace	–
6	**4f**	Me	Ph	**6b**	34	8 [d]
7	**4g**	Me	2-Naphthyl	**6b**	53	17 [d]

[a] All reactions were performed in toluene (0.02 M) in the presence of 12 mol% chiral ligand **2**, 10 mol% CuOTf and MS3A for 24 h.
[b] Isolated yield.
[c] Enantiomeric excesses were determined by HPLC using Daicel Chiralcel OD column unless otherwise noted.
[d] Enantiomeric excesses were determined by ^{1}H-NMR analysis in the precence of Eu(hfc)$_3$.

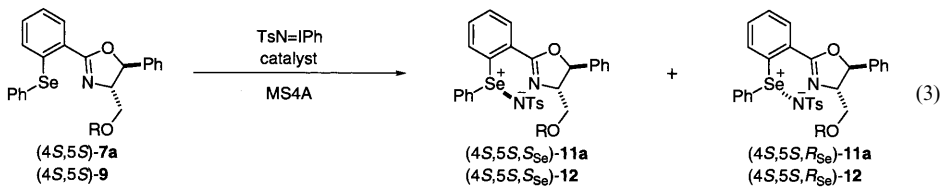


Scheme 3.



Scheme 4.

Table 4
Diastereoselective imidation of organic selenides using TsN=IPh [a]



Entry	(4*S*,5*S*)-Selenide	R	Catalyst	Solvent	Product	Yield (%) [b]	de (%) [c]
1	**7a**	$SiMe_2Bu^t$	None	CH_3CN	**11a**	42	17
2	**7a**	$SiMe_2Bu^t$	CuOTf	CH_3CN	**11a**	92	41
3	**7a**	$SiMe_2Bu^t$	$Cu(OTf)_2$	CH_3CN	**11a**	83	41
4	**7a**	$SiMe_2Bu^t$	None	Toluene	**11a**	42	13
5	**7a**	$SiMe_2Bu^t$	CuOTf	Toluene	**11a**	79	41
6	**7a**	$SiMe_2Bu^t$	$Cu(OTf)_2$	Toluene	**11a**	77	38
7	**9**	Me	CuOTf	CH_3CN	**12**	91	11

[a] All reactions were performed in solvent (0.20 M) at 25°C using selenide (0.20 mmol), TsN=IPh (0.24 mmol), catalyst (0.02 mmol), MS4A for 24 h.
[b] Isolated yield.
[c] The value was determined by ^{1}H-NMR spectroscopy.

stereoselectivity was obtained from the selenide (4*S*,5*S*)-**9**, the products being (4*S*,5*S*)-**12** (entry 7).

On the other hand, when commercially available Chloramine–T trihydrate [TsN(Cl)Na·$3H_2O$] was employed as an NTs source in toluene in the presence of copper salt, a better result in stereoselectivity was obtained (Eq. (4), Table 5 (entry 1)). Further studies revealed that a similar result was obtained even in the absence of a copper salt in a variety of solvents except acetonitrile (entries 2–6). Hoping to obtain better diastereoselectivity, we applied these reaction conditions to (4*S*,5*S*)-**7b**, **7c** and **7d**, in which the substituent was introduced to the *ortho*-position of the phenyl group of (4*S*,5*S*)-**7a** (entries 2, 7–9). In the case of (4*S*,5*S*)-**7b**, the reaction proceeded with better diastereoselectivity, the product being (4*S*,5*S*)-**11b**, whereas the use of (4*S*,5*S*)-**7c** gave only a trace amount of the corresponding selenimide (4*S*,5*S*)-**11c** (entries 7 and 8). On the contrary, a slightly lower diastereoselectivity (53–55% de) was observed on treatment of (4*S*,5*S*)-diaryl selenides such as **9** and **10** with TsN(Cl)Na·$3H_2O$ in toluene, where the substituent at

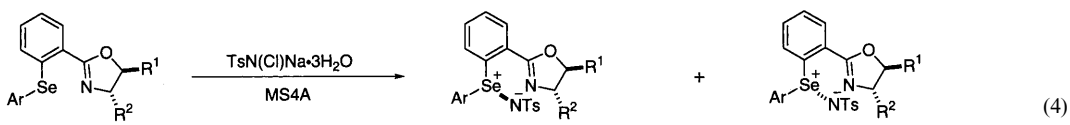
the 4-position of the oxazoline ring was a methoxymethyl group or an isopropyl group, the products being (4*S*,5*S*)-**12** and **13**, respectively (entries 10 and 11).

In order to determine the absolute configuration of the produced *N*-tosylselenimides, we tried to obtain a single crystal of a single diastereoisomer of (4*S*)-**13** from the diastereomeric mixture of 53% de by means of recrystallization from *n*-hexane–CH_2Cl_2. The molecular structure was clarified by X-ray analysis. As shown in an ORTEP drawing (Fig. 1), the major *N*-tosylselenimide of the present imidation was revealed to have an absolute configuration of $4S,S_{Se}$ ($[\alpha]_D^{25} = -161.8$; *c* 0.22 in $CHCl_3$). In analogy with ($4S,S_{Se}$)-**13**, the absolute configuration around the selenium atom of the major *N*-tosylselenimides **11a**, **11b**, **11d** and **12** might be assigned to *S*.

A plausible reaction pathway of the diastereoselective imidation of (4*S*)-**10** is shown in Scheme 5. This pathway is different from that proposed in the imidation of organic sulfides in which the presence of copper salt is necessary for the reaction and therefore the presence of an intermediate having a coordination between Cu, S and N was assumed [16]. First, the selenium of **10** attacks the chlorine atom of *N*-tosylamine chloride [H(Cl)NTs] produced by the hydrolysis of Chloramine–T [18] to afford chloroselenonium ion intermediates **14a** and **14b**. Then, the replacement of the dissociative chlorine atom on the selenium of **14b** with the *N*-tosylamine anion occurs retentively to give the product in which the configuration around selenium atom is *S* [6]. From the X-ray analysis, we recognized the distance (2.68 Å) between Se and N of the oxazoline ring, which was shorter than the sum of van der Waals radii of Se and N (3.45 Å) [19]. This result suggests the existence of Se···N interaction, as has been reported [20], which might affect the stereochemistry of the replacement [21].

We have revealed the effectiveness of optically active diaryl sulfides and sulfimides having a chiral oxazolinyl moiety (sulfur version of **9**, **11a** and **12**) as chiral ligands in the Pd-catalyzed allylic substitution [16]. In view of synthetic application of the produced selenides and *N*-tosylselenimides containing an oxazolinyl group, we have now attempted to use these compounds as chiral ligands in asymmetric reactions (Eqs. (5) and (6)). The results of the use of **7a**, **8**, **9** and **11a** as chiral ligands in the Pd-catalyzed allylic alkylation of 1,3-diphenyl-3-acetoxy-1-propene with dimethyl malonate are summarized in Table 6. A good enentioselectivity was obtained, but unfortunately the chemical yield was quite low. The application of these compounds as chiral ligands in Rh-catalyzed hydrosilylation of ketones with diphenyl silane [22] resulted in a very low stereoselectivity with moderate chemical yields (Eq. (6), Table 7).

Table 5
Diastereoselective imidation of organic selenides using $TsN(Cl)Na{\cdot}3H_2O$ [a]



(4*S*,5*S*)-**7a, 7b, 7c, 7d**
(4*S*,5*S*)-**9**
(4*S*)-**10**

($4S,5S,S_{Se}$)-**11a, 11b, 11c, 11d**
($4S,5S,S_{Se}$)-**12**
($4S,S_{Se}$)-**13**

+

($4S,5S,R_{Se}$)-**11a, 11b, 11c, 11d**
($4S,5S,R_{Se}$)-**12**
($4S,R_{Se}$)-**13**

(4)

Entry	(4*S*,5*S*)-Selenide	Ar	R^1	R^2	Solvent	Product	Yield (%) [b]	de (%) [c]
1 [d]	**7a**	Ph	Ph	$CH_2OSiMe_2Bu^t$	Toluene	**11a**	80	60
2	**7a**	Ph	Ph	$CH_2OSiMe_2Bu^t$	Toluene	**11a**	92	67
3	**7a**	Ph	Ph	$CH_2OSiMe_2Bu^t$	CH_3CN	**11a**	68	9
4	**7a**	Ph	Ph	$CH_2OSiMe_2Bu^t$	Cyclohexane	**11a**	40	60
5	**7a**	Ph	Ph	$CH_2OSiMe_2Bu^t$	Et_2O	**11a**	83	63
6	**7a**	Ph	Ph	$CH_2OSiMe_2Bu^t$	THF	**11a**	69	47
7	**7b**	2,4,6-$Me_3C_6H_2$	Ph	$CH_2OSiMe_2Bu^t$	Toluene	**11b**	64	76
8	**7c**	2,4,6-$Pr^i_3C_6H_2$	Ph	$CH_2OSiMe_2Bu^t$	Toluene	**11c**	Trace	–
9	**7d**	2-$MeOC_6H_4$	Ph	$CH_2OSiMe_2Bu^t$	Toluene	**11d**	75	30
10	**9**	Ph	Ph	CH_2OMe	Toluene	**12**	92	55
11	**10**	Ph	H	Pr^i	Toluene	**13**	97	53

[a] All reactions were performed in solvent (0.20 M) at 25°C using selenide (0.20 mmol), $TsN(Cl)Na{\cdot}3H_2O$ (0.24 mmol), catalyst (0.02 mmol), MS4A for 24 h.
[b] Isolated yield.
[c] The value was determined by ^{1}H-NMR spectroscopy.
[d] $Cu(OTf)_2$ (0.02 mmol, 10 mol%) was added.

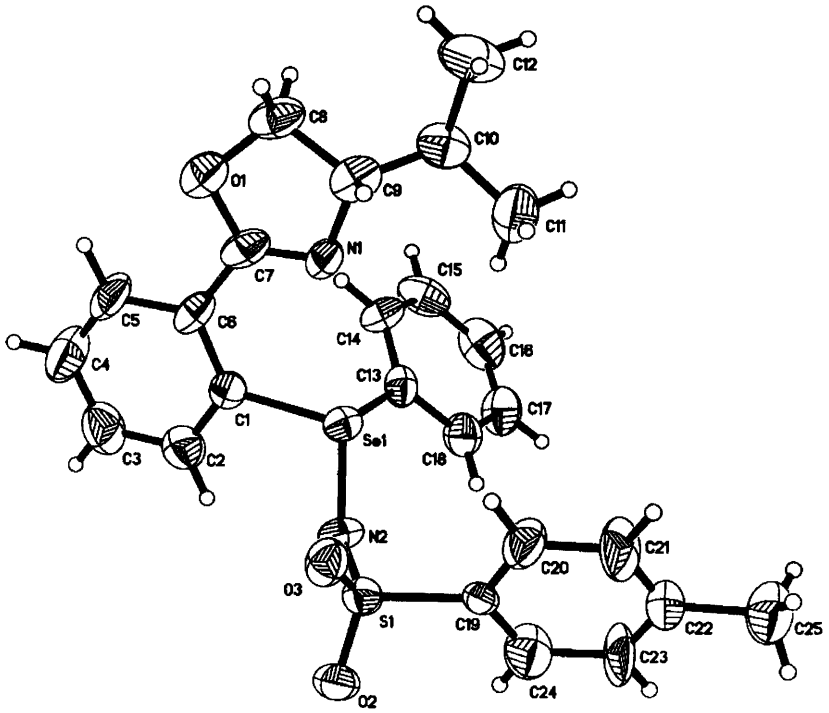
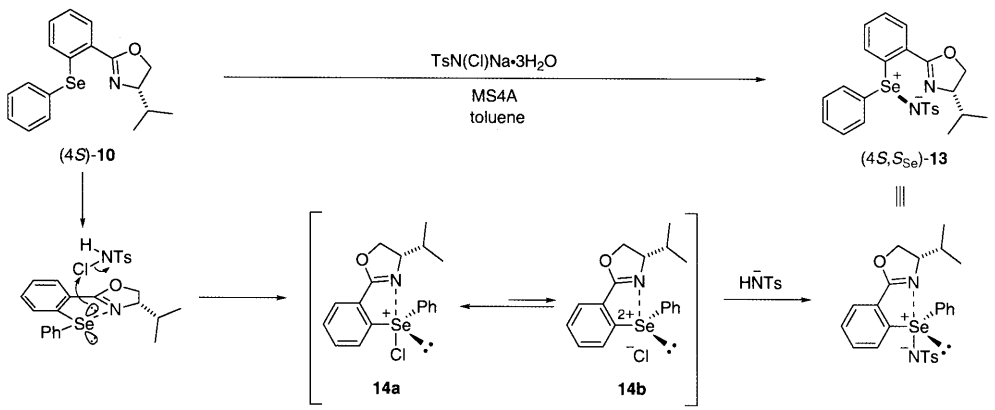


Fig. 1. Crystal structure of the *N*-tosylselenimide (4*S*,S_{Se})-**13**. Selected bond lengths (Å) and angles (°): Se(1)–N(2), 1.805(5); Se(1)–C(1), 1.969(7); Se(1)–C(13), 1.937(8); N(2)–Se(1)–C(1), 100.4(3); N(2)–Se(1)–C(13), 96.7(3); C(1)–Se(1)–C(13), 97.5(3).



Scheme 5.

3. Conclusion

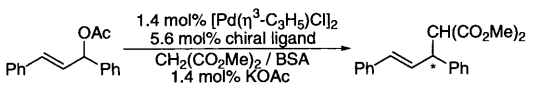
Although the enantioselectivity and diastereoselectivity obtained in the imidation of organic selenides are not yet satisfactory (up to 36% ee and 76% de) and are lower than for the corresponding sulfur case [2c–f], the findings presented here are (i) the first example of the direct catalytic enantioselective imidation of organic selenides into the corresponding optically active selenimides, and also (ii) the first example of the direct imidation of diaryl selenides having a chiral auxiliary into the corresponding optically active selenimides. The absolute configuration around the selenium atom of the isolated diastereomerically pure selenimide (4*S*)-**13**, obtained by imidation of the corresponding selenide with Chloramine–T trihydrate, was determined to be *S* by X-ray crystallographic analysis. In the diastereoselective imidation with Chloramine–T trihydrate, an ionic reaction scheme involving a chloroselenonium ion intermediate is proposed.

4. Experimental

^{1}H- and ^{13}C-NMR spectra were measured on JEOL EX-400, JEOL JNM-AL300 and JEOL JNM-GSX270 spectrometers for solutions in $CDCl_3$ with Me_4Si as an internal standard. The following abbreviations are

used: s singlet, d doublet, sep septet, m multiplet. IR spectra were recorded with a Nicolet Impact 400D FT-IR spectrometer. Analytical thin layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates. Column chromatography on silica gel was performed with Cica-Merck silica gel 60. Melting points are uncorrected. GLC analyses were carried out with a Shimadzu GC-14A instrument equipped with a 5% OV-17 on Chromosorb W column (glass column, 3 mm × 2 m) and a Shimadzu GC-14B instrument equipped with a Chiraldex G-TA column (TCI, fused silica capillary column, 0.25 mm × 30 m, 0.125 μm film thickness). GLC yields were determined using pentamethylbenzene as an internal standard. HPLC analyses were carried out on a D-7500 instrument (Hitachi) with an L-7400 detector at 40°C. Optical rotations were measured on a Jasco DIP-1000 instrument. High-resolution mass spectra (HRMS) were obtained with a JEOL JMS-SX102A spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl under argon. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride. Toluene, acetonitrile (CH_3CN) and cyclohexane were distilled from P_2O_5 just before use. Chloramine–T trihydrate, CuOTf, $Cu(OTf)_2$, (1*S*,2*S*)-(+)-2-amino-1-phenyl-1,3-propanediol, (*R*)-(+)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) (**2**) and $Eu(hfc)_3$ were commercial products. L-Valinol was prepared from L-valine according to the reported method [23]. 1,3-Diphenyl-3-acetoxy-1-propene was prepared by acetylation of 1,3-diphenyl-2-propen-1-ol. The isolated selenides **7a**–**7d**, **8**, **9** and **10** and *N*-tosylselenimides **3b**–**3d**, **11a**, **11b**, **11d**, **12** and **13** are new compounds.

Table 6
Enantioselective Pd-catalyzed allylic alkylation [a]

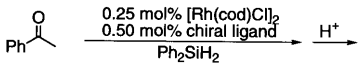


(5)

Entry	Ligand	Yield (%) [b]	ee (%) [c]	Configuration
1	(4*S*,5*S*)-**7a**	3	72	(*S*)
2	(4*S*,5*S*)-**8**	5	82	(*S*)
3	(4*S*,5*S*)-**9**	4	71	(*S*)
4	(4*S*,5*S*)-**11a**	No reaction	–	–

[a] Acetate (0.6 mmol), CH_2Cl_2 (2.0 ml), BSA (three equivalents), $CH_2(CO_2Me)_2$ (three equivalents), rt, 72 h.
[b] Isolated yield.
[c] The value was determined by HPLC using a suitable chiral column.

Table 7
Enantioselective Rh-catalyzed hydrosilylation [a]



(6)

Entry	Ligand	Yield (%) [b]	ee (%) [c]
1	(4*S*,5*S*)-**7a**	70	1
2	(4*S*,5*S*)-**9**	35	1
3	(4*S*,5*S*)-**11a**	43	6
4	(4*S*,5*S*)-**12**	40	1

[a] Acetophenone (1.0 mmol), catalyst (0.0025 mmol), ligand (0.0050 mmol), Ph_2SiH_2 (1.35 mmol), rt, 20 h.
[b] GLC yield.
[c] The value was determined by GLC.

4.1. Typical procedure for asymmetric catalytic imidation of aryl benzyl selenides

To a solution of MS3A (ca. 300 mg), CuOTf (2.5 mg, 0.010 mmol) and chiral bis(oxazoline) **2** (4.0 mg, 0.012 mmol) in 5.0 ml of toluene were added first TsN=IPh (37.3 mg, 0.10 mmol) and then the selenide (0.20 mmol), and the resulting mixture was stirred under nitrogen at 25°C for 24 h. Removal of the precipitates from the mixture through Celite and evaporation of the solvent gave a crude product. Purification by silica gel column chromatography gave a pure selenimide. Enantiomeric excesses were determined by HPLC using a suitable chiral column as shown below.

4.1.1. *Se*-Benzyl-*Se*-phenyl-*N*-(*p*-toluenesulfonyl)-selenimide (**3a**)

A white solid; 53% yield; 32% ee by Daicel Chiralcel OD column with 25% 2-propanol–hexane; eluent, AcOEt; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H, Me), 4.18 (d, $J = 11.3$ Hz, 1H, C*H*H), 4.54 (d, $J = 11.3$ Hz, 1H, CH*H*), 6.95–7.74 (m, 14H, Ar); ^{13}C-NMR

(100 MHz, $CDCl_3$) δ 21.3, 57.3, 126.0, 128.0, 128.9, 129.1, 129.2, 129.8, 130.3, 132.3, 141.1, 142.7.

4.1.2. *Se*-Benzyl-*Se*-(4-methoxyphenyl)-*N*-(*p*-toluenesulfonyl)selenimide (**3b**)

A white solid; 37% yield; 20% ee by Daicel Chiralpak AD column with 25% 2-propanol–hexane; eluent, AcOEt; m.p. 144.0–145.0°C; IR (KBr) 1587, 1493, 1255, 1126, 1082, 937, 828, 702, 662, 565 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.34 (s, 3H, Me), 3.83 (s, 3H, OMe), 4.14 (d, $J = 11.3$ Hz, 1H, C*H*H), 4.53 (d, $J = 11.3$ Hz, 1H, CH*H*), 6.95–7.74 (m, 14H, Ar); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 21.3, 55.6, 57.5, 115.3, 121.7, 126.0, 128.6, 128.9, 129.06, 129.13, 129.8, 130.4, 141.0, 142.7, 162.9; FAB LRMS m/z 448 $(M+1)^+$; FAB HRMS calc. for $C_{21}H_{21}NO_3SSe$ $(M+1)^+$: 448.0486; found: 448.0465. Anal. Calc. for $C_{21}H_{21}NO_3SSe$: C, 56.50; H, 4.74; N, 3.14. Found: C, 55.18; H, 4.72; N, 3.16% [24].

4.1.3. *Se*-Benzyl-*Se*-(1-naphthalenyl)-*N*-(*p*-toluenesulfonyl)selenimide (**3c**)

A white solid; 23% yield; 29% ee by Daicel Chiralpak AS column with 25% 2-propanol–hexane; eluent, AcOEt; m.p. 43.0–44.0°C; IR (KBr) 1494, 1268, 1159, 1133, 1085, 938, 800, 768, 697, 568, 549 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H, Me), 4.32 (d, $J = 11.7$ Hz, 1H, C*H*H), 4.50 (d, $J = 11.7$ Hz, 1H, CH*H*), 6.84–8.16 (m, 16H, Ar); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.3, 56.5, 121.9, 125.9, 126.0, 126.9, 127.5, 127.8, 128.5, 128.9, 129.0, 129.1, 130.2, 131.0, 132.3, 133.6, 141.0, 142.7; FAB LRMS m/z 468 $(M+1)^+$; FAB HRMS calc. for $C_{24}H_{22}NO_2SSe$ $(M+1)^+$: 468.0537; found: 468.0534. Anal. Calc. for $C_{24}H_{22}NO_2SSe$: C, 61.80; H, 4.54; N, 3.00. Found: C, 61.10; H, 4.47; N, 2.66% [24].

4.1.4. *Se*-Benzyl-*Se*-(2-naphthalenyl)-*N*-(*p*-toluenesulfonyl)selenimide (**3d**)

A white solid; 64% yield; 36% ee by Daicel Chiralcel OD column with 25% 2-propanol–hexane; eluent, AcOEt; m.p. 156.0–157.0°C; IR (KBr) 1264, 1161, 1132, 1084, 946, 937, 814, 697 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.27 (s, 3H, Me), 4.26 (d, $J = 11.3$ Hz, 1H, C*H*H), 4.58 (d, $J = 11.3$ Hz, 1H, CH*H*), 6.94–7.92 (m, 16H, Ar); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 21.2, 57.2, 122.7, 125.9, 127.5, 128.0, 128.3, 128.4, 128.5, 128.8, 129.1, 129.18, 129.24, 129.9, 130.4, 132.8, 134.6, 141.0, 142.7; FAB LRMS m/z 468 $(M+1)^+$; FAB HRMS calc. for $C_{24}H_{22}NO_2SSe$ $(M+1)^+$: 468.0537; found: 468.0535. Anal. Calc. for $C_{24}H_{22}NO_2SSe$: C, 61.80; H, 4.54; N, 3.00. Found: C, 60.06; H, 4.69; N, 3.33% [24].

4.2. Preparation of (4*S*,5*S*)-2-(4-*tert*-butyldimethylsilyloxymethyl-5-phenyloxazolin-2-yl)phenyl, phenyl selenide (4*S*,5*S*)-(**7a**)

sec-Butyllithium (23.0 ml of 1.06 M cyclohexane–hexane solution, 24.4 mmol) was added to a stirred solution of (4*S*,5*S*)-2-(4-*tert*-butyldimethylsilyloxymethyl-5-phenyloxazolin-2-yl)benzene [25] (7.78 g, 21.2 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (9.6 ml, 63.6 mmol) in THF (35 ml) at −78°C. The resulting red solution was stirred at −78°C for 15 min before the addition of a solution of the corresponding diphenyl diselenide (6.61 g, 21.2 mmol) in THF (35 ml). The reaction mixture was allowed to warm to room temperature and stirred for 24 h under nitrogen. The resulting yellow solution was extracted with Et_2O (50 ml × 3) and the combined organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Diaryl selenides (4*S*,5*S*)-**7b**–**d** were also prepared by this method.

Purification by silica gel column chlomatography afforded the title compound. A pale yellow oil; 42% yield; eluent, hexane–AcOEt = 40:1; $[\alpha]_D^{25}$ +21.0 (c 1.025, $CHCl_3$); IR (KBr) 3072, 2953, 2928, 1645 (C=N), 1470, 1256, 1135, 1083, 1030, 836, 778, 742, 731, 696 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.14 (s, 6H, $SiMe_2$), 0.94 (s, 9H, $SiBu^t$), 3.82 (dd, $J = 10.0$, 7.6 Hz, 1H, C*H*HOSi), 4.13 (dd, $J = 10.0$, 4.0 Hz, 1H, CH*H*OSi), 4.45 (ddd, $J = 7.6$, 6.1, 4.0 Hz, 1H, CHN), 5.61 (d, $J = 6.1$ Hz, 1H, CHO), 6.93–8.02 (m, 14H, Ar); ^{13}C-NMR (68 MHz, $CDCl_3$) δ −5.3, 18.2, 25.9, 65.3 (CH_2O), 77.3 (CHN), 83.3 (CHO), 124.7, 125.3, 125.6, 127.9, 128.6, 128.9, 129.0, 129.7, 130.1, 131.0, 137.3, 138.6, 141.3, 163.2 (C=N); FAB LRMS m/z 524 $(M+1)^+$; FAB HRMS calc. for $C_{28}H_{33}NO_2SeSi$ $(M+1)^+$: 524.1526; found: 524.1501. Anal. Calc. for $C_{28}H_{33}NO_2SeSi$: C, 64.35; H, 6.36; N, 2.68. Found: C, 63.57; H, 6.40; N, 2.61%.

4.2.1. (4*S*,5*S*)-2-(4-*tert*-butyldimethylsilyloxymethyl-5-phenyloxazolin-2-yl)phenyl, 2,4,6-trimethylphenyl selenide (4*S*,5*S*)-(**7b**)

A white solid; 45% yield; eluent, hexane–AcOEt = 40:1; m.p. 32.5–33.0°C; $[\alpha]_D^{25}$ +14.6 (c 1.29, $CHCl_3$); IR (KBr) 2952, 2926, 2854, 1645 (C=N), 1469, 1254, 1135, 1078, 1031, 1023, 835, 777, 730, 697 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 3H, Si*Me*Me), 0.15 (s, 3H, SiMe*Me*), 0.93 (s, 9H, $SiBu^t$), 2.36 (s, 3H, *p*-Me), 2.45 (s, 6H, *o*-Me), 3.89 (dd, $J = 10.3$, 6.8 Hz, 1H, C*H*HOSi), 4.11 (dd, $J = 10.3$, 3.9 Hz, 1H, CH*H*OSi), 4.47 (ddd, $J = 6.8$, 6.3, 3.9 Hz, 1H, CHN), 5.61 (d, $J = 6.3$ Hz, 1H, CHO), 6.72–8.02 (m, 12H, Ar); ^{13}C-NMR (100 MHz, $CDCl_3$) δ −5.3, 18.2, 21.1, 24.0, 25.9, 65.1 (CH_2O), 77.5 (CHN), 82.7 (CHO), 124.3, 125.6, 127.4, 127.9, 128.3, 128.6, 128.8, 130.3, 131.0, 137.7, 139.2, 141.5, 144.2, 163.2 (C=N); FAB LRMS

m/z 566 $(M+1)^+$; FAB HRMS calc. for $C_{31}H_{39}NO_2SeSi$ $(M+1)^+$: 566.1996; found: 566.2001. Anal. Calc. for $C_{31}H_{39}NO_2SeSi$: C, 65.94; H, 6.96; N, 2.48. Found: C, 66.04; H, 6.98; N, 2.45%.

4.2.2. (4S,5S)-2-(4-tert-butyldimethylsilyloxymethyl-5-phenyloxazolin-2-yl)phenyl, 2,4,6-triisopropylphenyl selenide (4S,5S)-(7c)

A pale yellow oil; 18% yield; eluent, hexane–AcOEt = 40:1; $[\alpha]_D^{25}$ +6.0 (c 1.33, $CHCl_3$); IR (KBr) 2959, 2928, 2860, 1645 (C=N), 1464, 1255, 1135, 1078, 1042, 1031, 836, 778, 731, 698 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.13 (s, 3H, Si*Me*Me), 0.14 (s, 3H, SiMe*Me*), 0.92 (s, 9H, SiBu^t), 1.15 (dd, $J = 6.8$, 6.8 Hz, 12H, *o*-CH*Me*$_2$), 1.32 (d, $J = 6.8$ Hz, 6H, *p*-CH*Me*$_2$), 2.96 (sep, $J = 6.8$ Hz, 1H, *p*-C*H*Me$_2$), 3.72 (sep, $J = 6.8$ Hz, 2H, *o*-C*H*Me$_2$), 3.92 (dd, $J = 10.3$, 6.4 Hz, 1H, C*H*HOSi), 4.08 (dd, $J = 10.3$, 3.9 Hz, 1H, CH*H*OSi), 4.46 (ddd, $J = 6.4$, 5.9, 3.9 Hz, 1H, CHN), 5.62 (d, $J = 5.9$ Hz, 1H, CHO), 6.73–8.00 (m, 12H, Ar); ^{13}C-NMR (100 MHz, $CDCl_3$) δ −5.3, 18.3, 23.9, 24.6, 25.9, 34.1, 34.3, 64.9 (CH_2O), 77.2 (CHN), 82.6 (CHO), 122.1, 124.2, 125.3, 125.6, 127.4, 128.0, 128.6, 128.8, 130.3, 130.8, 139.4, 141.4, 150.6, 153.9, 163.4 (C=N); FAB LRMS *m/z* 650 $(M+1)^+$; FAB HRMS calc. for $C_{37}H_{51}NO_2SeSi$ $(M+1)^+$: 650.2936; found: 650.2932. Anal. Calc. for $C_{37}H_{51}NO_2SeSi$: C, 68.49; H, 7.92; N, 2.16. Found: C, 68.49; H, 8.03; N, 1.86%.

4.2.3. (4S,5S)-2-(4-tert-butyldimethylsilyloxymethyl-5-phenyloxazolin-2-yl)phenyl, 2-methoxyphenyl selenide (4S,5S)-(7d)

A colorless oil; 5% yield; eluent, hexane–CH_2Cl_2 = 1:1; $[\alpha]_D^{25}$ +23.2 (c 0.50, $CHCl_3$); IR (KBr) 2953, 2928, 2855, 1645 (C=N), 1580, 1471, 1431, 1247, 1124, 1080, 1027, 974, 837, 777, 754, 732, 698 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 3H, Si*Me*Me), 0.17 (s, 3H, SiMe*Me*), 0.97 (s, 9H, SiBu^t), 3.83 (s, 3H, OMe), 3.84 (dd, $J = 9.5$, 9.1 Hz, 1H, C*H*HOSi), 4.18 (dd, $J = 9.5$, 4.1 Hz, 1H, CH*H*OSi), 4.48 (ddd, $J = 9.1$, 6.1, 4.1 Hz, 1H, CHN), 5.63 (d, $J = 6.1$ Hz, 1H, CHO), 6.93–8.04 (m, 13H, Ar); ^{13}C-NMR (75 MHz, $CDCl_3$) δ −5.34, 18.2, 25.8, 55.8, 65.4 (CH_2O), 77.2 (CHN), 83.3 (CHO), 111.1, 118.8, 121.6, 124.5, 125.4, 125.5, 127.8, 128.5, 128.8, 130.0, 130.7, 131.1, 137.6, 139.0, 141.3, 160.3, 163.2 (C=N); FAB LRMS *m/z* 554 $(M+1)^+$; FAB HRMS calc. for $C_{29}H_{35}NO_3SeSi$ $(M+1)^+$: 554.1632; found: 554.1633. Anal. Calc. for $C_{29}H_{35}NO_3SeSi$: C, 63.03; H, 6.38; N, 2.53. Found: C, 62.91; H, 6.35; N, 2.37%.

4.2.4. Preparation of (4S,5S)-2-(4-hydroxymethyl-5-phenyloxazolin-2-yl)phenyl, phenyl selenide (4S,5S)-(8)

Removal of the *tert*-butyldimethylsilyl protecting group of (4*S*,5*S*)-**7a** (1.05 g, 2.0 mmol) was effected by stirring with a solution of tetrabutylammonium fluoride (TBAF) (2.0 ml of 1.0 M THF solution, 2.0 mmol) in THF (15 ml) at room temperature. After extraction with Et_2O, the combined organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure.

Purification by silica gel column chlomatography afforded the title compound. A white solid; 92% yield; eluent, CH_2Cl_2; m.p. 33.5–34.5°C; $[\alpha]_D^{25}$ −4.7 (c 0.53, $CHCl_3$); IR (KBr) 3413 (OH), 1643 (C=N), 1468, 1436, 1333, 1275, 1257, 1136, 1035, 969, 742, 732, 695 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.22 (m, 1H, OH), 3.81 (m, 1H, C*H*HO), 4.10 (m, 1H, CH*H*O), 4.45 (m, 1H, CHN), 5.52 (d, $J = 7.3$ Hz, 1H, CHO), 6.94–7.94 (m, 14H, Ar); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 64.0 (CH_2OH), 77.1 (CHN), 82.6 (CHO), 124.9, 125.4, 125.8, 128.4, 128.9, 129.0, 129.2, 129.7, 129.8, 130.0, 131.2, 137.1, 138.4, 140.4, 164.1 (C=N); FAB LRMS *m/z* 410 $(M+1)^+$; FAB HRMS calc. for $C_{22}H_{19}NO_2Se$ $(M+1)^+$: 410.0660; found: 410.0657. Anal. Calc. for $C_{22}H_{19}NO_2Se$: C, 64.71; H, 4.69; N, 3.43. Found: C, 64.53; H, 4.73; N, 3.32%.

4.2.5. Preparation of (4S,5S)-2-(4-methoxymethyl-5-phenyloxazolin-2-yl)phenyl, phenyl selenide (4S,5S)-(9)

The selenide (4*S*,5*S*)-**8** (0.65 g, 1.59 mmol) in THF (5 ml) was added dropwise at 0°C to a stirred solution of abt. 60% sodium hydride (83.5 mg, 2.1 mmol; oil removed by washing with 5 ml of dry hexane) in THF (5 ml) under nitrogen. When the addition was complete, the pale yellow solution was stirred at room temperature for 30 min before the addition of methyl iodide (0.13 ml, 2.0 mmol) at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 4 h and slowly poured into 20 ml ice-water, then extracted with Et_2O. The combined extract was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure.

Purification by silica gel column chlomatography afforded the title compound. A pale yellow oil; 87% yield; eluent, hexane–AcOEt = 2:1; $[\alpha]_D^{25}$ +37.5 (c 1.13, $CHCl_3$); IR (KBr) 1643 (C=N), 1469, 1435, 1331, 1135, 1089, 1030, 742, 731, 696 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.49 (s, 3H, OMe), 3.68 (dd, $J = 9.5$, 8.5 Hz, 1H, C*H*HO), 3.88 (dd, $J = 9.5$, 4.2 Hz, 1H, CH*H*O), 4.52 (ddd, $J = 8.5$, 6.8, 4.2 Hz, 1H, CHN), 5.54 (d, $J = 6.8$ Hz, 1H, CHO), 6.94–7.99 (m, 14H, Ar); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 59.4 (OMe), 74.6 (CH_2O), 75.2 (CHN), 83.5 (CHO), 124.7, 125.2, 125.6, 128.1, 128.7, 128.9, 129.0, 129.7, 130.0, 131.1, 137.3, 138.6, 140.8, 163.4 (C=N); FAB LRMS *m/z* 424 $(M+1)^+$; FAB HRMS calc. for $C_{23}H_{21}NO_2Se$ $(M+1)^+$: 424.0817; found: 424.0815. Anal. Calc. for $C_{23}H_{21}NO_2Se$: C, 65.40; H, 5.01; N, 3.32. Found: C, 65.41; H, 4.82; N, 3.17%.

*4.2.6. (4S)-2-(4-Isopropyloxazolin-2-yl)phenyl, phenyl selenide (4S)-**(10)***

To a solution of (4*S*)-(4-isopropyloxazolin-2-yl)benzene [17,26] (4.54 g, 24.0 mmol) and TMEDA (10.8 ml, 71.6 mmol) in THF (50 ml) at −78°C was added slowly *sec*-butyllithium (26.0 ml of 1.00 M cyclohexane–hexane solution, 26.0 mmol). The resulting red solution was stirred at −78°C for 3 h before the addition of a solution of diphenyl diselenide (7.48 g, 24.0 mmol) in THF (50 ml). The reaction mixture was allowed to warm to room temperature and stirred for 24 h under nitrogen. The resulting yellow solution was extracted with Et_2O (50 ml × 3) and the combined organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by silica gel column chromatography gave the title compound. A pale yellow solid; 51% yield; eluent, hexane–AcOEt = 80:1; m.p. 44.0–45.0°C; $[\alpha]_D^{25}$ −28.6 (c 2.09, $CHCl_3$); IR (KBr) 2958, 2897, 1650 (C=N), 1467, 1436, 1357, 1250, 1135, 1082, 1047, 1029, 964, 742, 732, 695 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.02 (d, J = 6.4 Hz, 3H, CH*Me*Me), 1.14 (d, J = 6.8 Hz, 3H, CHMe*Me*), 1.86 (m, 1H, C*H*Me_2), 4.13 (m, 1H, C*H*HO), 4.21 (m, 1H, CHN), 4.44 (m, 1H, CH*H*O), 6.88–7.84 (m, 9H, Ar); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 18.8, 19.1, 33.4, 70.3 (CHN), 73.5 (CHO), 124.6, 125.4, 128.8, 129.6, 129.7, 130.3, 130.7, 137.3, 138.5, 162.5 (C=N); FAB LRMS m/z 346 $(M+1)^+$; FAB HRMS calc. for $C_{18}H_{19}NOSe$ $(M+1)^+$: 346.0711; found: 346.0705. Anal. Calc. for $C_{18}H_{19}NOSe$: C, 62.79; H, 5.56; N, 4.07. Found: C, 62.71; H, 5.50; N, 3.83%.

4.3. Typical procedure for diastereoselective imidation of diaryl selenide

To a solution of MS4A (ca. 80 mg) and Chloramine–T trihydrate (67.6 mg, 0.24 mmol) in 1 ml of toluene, the selenide (0.20 mmol) was added and the resulting mixture was stirred under nitrogen at 25°C for 24 h. Removal of the precipitate through Celite and evaporation of the solvent gave a crude product. Purification by silica gel column chromatography gave a pure selenimide. Diastereomeric excesses were determined by ^{1}H-NMR analysis.

*4.3.1. (4S,5S)-Se-[2-(4-tert-Butyldimethylsilyloxymethyl-5-phenyloxazolin-2-yl)phenyl]-Se-phenyl-N-(p-toluenesulfonyl)selenimide, (4S,5S)-**(11a)***

A white solid as a mixture of diastereomers; 92% yield; 67% de; eluent, hexane–AcOEt = 1:1; m.p. 58–59°C; IR (KBr) 1650 (C=N), 1261 (SO_2), 1131 (SO_2) cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) a major product δ −0.03 (s, 3H, Si*Me*Me), 0.02 (s, 3H, SiMe*Me*), 0.84 (s, 9H, SiBu^t), 2.36 (s, 3H, Me), 3.16 (dd, J = 10.3, 7.6 Hz, 1H, C*H*HOSi), 4.10 (dd, J = 10.3, 5.9 Hz, 1H, CH*H*OSi), 4.29 (ddd, J = 7.6, 6.4, 5.9 Hz, 1H, CHN), 5.49 (d, J = 6.4 Hz, 1H, CHO), 6.90–8.97 (m, 18H, Ar); a minor product δ 0.12 (s, 3H, Si*Me*Me), 0.13 (s, 3H, SiMe*Me*), 0.90 (s, 9H, SiBu^t), 2.35 (s, 3H, Me), 3.63 (dd, J = 10.1, 4.4 Hz, 1H, C*H*HOSi), 3.80 (dd, J = 10.1, 6.1 Hz, 1H, CH*H*OSi), 3.97 (ddd, J = 6.2, 6.1, 4.4 Hz, 1H, CHN), 5.48 (d, J = 6.2 Hz, 1H, CHO), 6.88–8.87 (m, 18H, Ar); ^{13}C-NMR (75 MHz, $CDCl_3$) a major product δ −5.6, 18.0, 21.2, 25.6, 64.1 (CH_2O), 76.2 (CHN), 84.6 (CHO), 125.4, 125.9, 126.4, 128.3, 128.7, 128.8, 128.9, 129.4, 130.9, 131.8, 133.1, 135.3, 138.6, 139.6, 140.6, 143.5, 161.8 (C=N); a minor product δ −5.5, 18.1, 21.2, 25.7, 64.5 (CH_2O), 75.9 (CHN), 84.2 (CHO), 125.3, 125.8, 126.3, 128.4, 128.6, 128.8, 129.1, 129.8, 130.9, 131.6, 133.0, 136.2, 139.1, 139.6, 140.5, 143.5, 161.9 (C=N); FAB LRMS m/z 693 $(M+1)^+$; FAB HRMS calc. for $C_{35}H_{40}N_2O_4SSeSi$ $(M+1)^+$: 693.1724; found: 693.1749. Anal. Calc. for $C_{35}H_{40}N_2O_4SSeSi$: C, 60.77; H, 5.83; N, 4.05. Found: C, 60.51; H, 5.82; N, 3.90%.

*4.3.2. (4S,5S)-Se-[2-(4-tert-Butyldimethylsilyloxymethyl-5-phenyloxazolin-2-yl)phenyl]-Se-2,4,6-trimethylphenyl-N-(p-toluenesulfonyl)selenimide, (4S,5S)-**(11b)***

A colorless oil as a mixture of diastereomers; 64% yield; 76% de; eluent, hexane–AcOEt = 1:1; IR (KBr) 1656 (C=N), 1270 (SO_2), 1129 (SO_2) cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) a major product δ −0.08 (s, 3H, Si*Me*Me), −0.01 (s, 3H, SiMe*Me*), 0.82 (s, 9H, SiBu^t), 2.11 (s, 6H, *o*-Me_2), 2.23 (s, 3H, Me), 2.35 (s, 3H, *p*-Me), 2.70 (dd, J = 9.7, 9.5 Hz, 1H, C*H*HOSi), 3.38 (dd, J = 9.7, 4.3 Hz, 1H, CH*H*OSi), 4.16 (ddd, J = 9.5, 5.1, 4.3 Hz, 1H, CHN), 5.48 (d, J = 5.1 Hz, 1H, CHO), 6.52–9.09 (m, 15H, Ar); a minor product δ 0.04 (s, 3H, Si*Me*Me), 0.07 (s, 3H, SiMe*Me*), 0.85 (s, 9H, SiBu^t), 2.11 (s, 6H, *o*-Me_2), 2.21 (s, 3H, Me), 2.35 (s, 3H, *p*-Me), 3.68–3.86 (m, 3H, CH_2OSi and CHN), 5.34 (d, J = 5.7 Hz, 1H, CHO), 6.52–8.95 (m, 15H, Ar); ^{13}C-NMR (75 MHz, $CDCl_3$) a mixture of diastereomers δ −5.7, −5.6, 20.6, 20.8, 20.9, 21.3, 25.6, 25.7, 63.9, 64.2, 75.6, 76.5, 84.0, 84.2, 125.0, 125.7, 126.0, 126.1, 126.4, 126.5, 128.2, 128.5, 128.6, 128.7, 128.8, 129.5, 129.8, 130.6, 131.0, 131.2, 131.5, 132.7, 132.8, 135.0, 135.4, 139.3, 139.7, 140.1, 140.4, 140.5, 141.0, 141.3, 143.7, 161.6, 161.8; FAB LRMS m/z 736 $(M+1)^+$; FAB HRMS calc. for $C_{38}H_{46}N_2O_4SSeSi$ $(M+1)^+$: 735.2194; found: 735.2182.

*4.3.3. (4S,5S)-Se-[2-(4-tert-Butyldimethylsilyloxymethyl-5-phenyloxazolin-2-yl)phenyl]-Se-2-methoxyphenyl-N-(p-toluenesulfonyl)selenimide, (4S,5S)-**(11d)***

A colorless oil as a mixture of diastereomers; 75% yield; 30% de; eluent, hexane–AcOEt = 1:3; IR (KBr)

1651 (C=N), 1338 (SO_2), 1275, 1128 (SO_2), 1084, 937 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) a major product δ −0.09 (s, 3H, Si*Me*Me), −0.05 (s, 3H, SiMe*Me*), 0.81 (s, 9H, SiBu^t), 2.37 (s, 3H, Me), 2.66 (dd, $J = 9.7$, 9.5 Hz, 1H, C*H*HO), 3.37 (dd, $J = 9.7$, 4.2 Hz, 1H, CH*H*O), 3.62 (s, 3H, OMe), 4.18 (ddd, $J = 9.5$, 6.1, 4.2 Hz, 1H, CHN), 5.43 (d, $J = 6.1$ Hz, 1H, CHO), 6.63–8.94 (m, 17H, Ar); a minor product δ 0.102 (s, 3H, Si*Me*Me), 0.104 (s, 3H, SiMe*Me*), 0.88 (s, 9H, SiBu^t), 2.36 (s, 3H, Me), 3.69 (s, 3H, OMe), 3.70–3.93 (m, 3H, CH_2O and CHN), 5.45 (d, $J = 6.4$ Hz, 1H, CHO), 6.63–8.11 (m, 17H, Ar); ^{13}C-NMR (75 MHz, $CDCl_3$) a mixture of diastereomers δ −5.6, −5.5, −5.4, 18.0, 18.1, 21.2, 25.66, 25.70, 55.86, 55.92, 63.9, 64.3, 75.8, 75.9, 84.6, 84.9, 111.2, 122.0, 122.1, 125.3, 125.4, 126.06, 126.13, 126.4, 126.7, 127.5, 127.8, 127.9, 128.25, 128.31, 128.58, 128.63, 128.7, 128.8, 129.7, 129.8, 130.4, 130.7, 131.5, 131.7, 132.5, 132.7, 132.8, 133.1, 133.8, 134.9, 139.9, 140.1, 140.2, 143.9, 156.7, 156.8, 161.7, 162.0; FAB LRMS m/z 723 $(M+1)^+$; FAB HRMS calc. for $C_{36}H_{42}N_2O_5SSeSi$ $(M+1)^+$: 723.1830; found: 723.1801.

4.3.4. (4S,5S)-Se-[2-(4-Methoxymethyl-5-phenyloxazolin-2-yl)phenyl]-Se-phenyl-N-(p-toluenesulfonyl)selenimide, (4S,5S)-(12)

A white solid as a mixture of diastereomers; 92% yield; 55% de; eluent, hexane–AcOEt = 1:3; m.p. 100.0–102.0°C; IR (KBr) 1651 (C=N), 1341 (SO_2), 1269, 1129 (SO_2), 1082, 933 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) a major product δ 2.34 (s, 3H, Me), 3.19 (s, 3H, OMe), 3.24 (dd, $J = 9.7$, 5.3 Hz, 1H, C*H*HO), 3.39 (dd, $J = 9.7$, 4.4 Hz, 1H, CH*H*O), 4.33 (ddd, $J = 7.5$, 5.3, 4.4 Hz, 1H, CHN), 5.44 (d, $J = 7.5$ Hz, 1H, CHO), 7.13–8.80 (m, 18H, Ar); a minor product δ 2.35 (s, 3H, Me), 3.46 (s, 3H, OMe), 3.61 (dd, $J = 9.7$, 6.1 Hz, 1H, C*H*HO), 3.72 (dd, $J = 9.7$, 4.2 Hz, 1H, CH*H*O), 4.14 (ddd, $J = 6.1$, 4.6, 4.2 Hz, 1H, CHN), 5.47 (d, $J = 4.6$ Hz, 1H, CHO), 6.90–8.83 (m, 18H, Ar); ^{13}C-NMR (75 MHz, $CDCl_3$) a major product δ 21.3, 59.0 (CH_2O), 72.9 (OMe), 74.5 (CHN), 84.2 (CHO), 125.7, 126.0, 126.3, 128.5, 128.8, 128.95, 128.96, 129.01, 129.4, 130.0, 130.9, 131.7, 133.2, 135.9, 138.6, 139.2, 140.6, 143.6, 161.9 (C=N); a minor product δ 21.3, 59.5 (CH_2O), 73.8 (OMe), 74.1 (CHN), 84.5 (CHO), 125.4, 125.9, 126.2, 128.5, 128.7, 128.9, 129.0, 129.5, 129.9, 130.9, 131.6, 133.1, 136.6, 139.2, 139.5, 140.6, 143.5, 162.1 (C=N); FAB LRMS m/z 593 $(M+1)^+$; FAB HRMS calc. for $C_{30}H_{28}N_2O_4SSe$ $(M+1)^+$: 593.1015; found: 593.1022. Anal. Calc. for $C_{30}H_{28}N_2O_4SSe$: C, 60.91; H, 4.77; N, 4.74. Found: C, 60.10; H, 4.75; N, 4.63%.

4.3.5. (4S)-Se-[2-(4-Isopropyloxazolin-2-yl)phenyl]-Se-phenyl-N-(p-toluenesulfonyl)selenimide, (4S)-(13)

A pale yellow solid as a mixture of diastereomers; 92% yield; 55% de; eluent, hexane–AcOEt = 1:1; IR (KBr) 1650 (C=N), 1269 (SO_2), 1128 (SO_2), 1082 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) a major product δ 0.48 (d, $J = 6.9$ Hz, 3H, CH*Me*Me), 0.63 (d, $J = 6.9$ Hz, 3H, CHMe*Me*), 1.59 (m, 1H, C*H*Me$_2$), 2.35 (s, 3H, Me), 3.85–4.45 (m, 3H, CH_2O and CHN), 7.13–8.67 (m, 13H, Ar); a minor product δ 0.98 (d, $J = 6.6$ Hz, 3H, CH*Me*Me), 1.08 (d, $J = 6.6$ Hz, 3H, CHMe*Me*), 1.80 (m, 1H, C*H*Me$_2$), 2.33 (s, 3H, Me), 3.90–4.45 (m, 3H, CH_2O and CHN), 7.11–8.80 (m, 13H, Ar); ^{13}C-NMR (68 MHz, $CDCl_3$) a major product δ 17.3 (CH*Me*Me), 18.4 (CHMe*Me*), 21.3, 31.9 (*C*HMe$_2$), 70.5 (CHN), 72.6 (CHO), 125.9, 127.0, 128.2, 128.9, 129.2, 129.5, 130.9, 131.7, 132.9, 134.9, 138.5, 140.6, 143.6, 161.5 (C=N); a minor product δ 19.0 (CH*Me*Me), 19.1 (CHMe*Me*), 21.3, 33.1 (*C*HMe$_2$), 71.5 (CHN), 72.7 (CHO), 126.2, 128.3, 128.4, 128.8, 128.9, 129.4, 131.5, 136.2, 138.7, 140.5, 161.4 (C=N); FAB LRMS m/z 515 $(M+1)^+$; FAB HRMS calc. for $C_{25}H_{26}N_2O_3SSe$ $(M+1)^+$: 515.0909; found: 515.0920. Anal. Calc. for $C_{25}H_{26}N_2O_3SSe$: C, 58.47; H, 5.10; N, 5.46. Found: C, 58.37; H, 4.95; N, 5.39%.

4.3.6. (4S,S_{Se})-Se-[2-(4-Isopropyloxazolin-2-yl)phenyl]-Se-phenyl-N-(p-toluenesulfonyl)selenimide, (4S,S_{Se})-(13)

Purification by recrystallization from *n*-hexane–CH_2Cl_2 afforded the title compound. A colorless crystal; 99% de; m.p. 185.0–185.5°C; $[\alpha]_D^{25}$ −161.8 (c 0.22, $CHCl_3$); IR (KBr) 1650 (C=N), 1269 (SO_2), 1128 (SO_2), 1082 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.49 (d, $J = 6.9$ Hz, 3H, CH*Me*Me), 0.64 (d, $J = 6.9$ Hz, 3H, CHMe*Me*), 1.60 (m, 1H, C*H*Me$_2$), 2.35 (s, 3H, Me), 4.06–4.20 (m, 2H, C*H*HO and CHN), 4.43 (dd, $J = 8.5$, 7.1 Hz, 1H, CH*H*O), 7.13–8.68 (m, 13H, Ar); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 17.3 (CH*Me*Me), 18.4 (CHMe*Me*), 21.3, 31.8 (*C*HMe$_2$), 70.5 (CHN), 72.6 (CHO), 125.9, 127.0, 128.1, 128.9, 129.2, 129.5, 130.8, 131.7, 132.8, 134.8, 138.4, 140.6, 143.6, 161.5 (C=N); FAB LRMS m/z 515 $(M+1)^+$; FAB HRMS calc. for $C_{25}H_{26}N_2O_3SSe$ $(M+1)^+$: 515.0909; found: 515.0908. Anal. Calc. for $C_{25}H_{26}N_2O_3SSe$: C, 58.47; H, 5.10; N, 5.46. Found: C, 58.40; H, 5.01; N, 5.43%.

4.4. X-ray structural analysis of (4S,S_{Se})-13

The measurement was carried out on a Bruker SMART CCD detector system using graphite-monochromated Mo–K_α ($\lambda = 0.71073$ Å) radiation from a sealed-tube X-ray source at 299 K. The SMART software package [27] was used for data collection as well as frame integration. Structure solution and refinement were carried out using the SHELXTL software package [28]. The structure was solved by direct methods. Full-matrix least-squares refinement was carried out against F^2. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were geometrically

fixed and allowed to ride on the attached atoms. The crystallographic data are listed in Table 8.

4.5. Typical procedure of enantioselective allylic alkylation

To a stirring solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.9 mg, 0.008 mmol) in CH_2Cl_2 (1 ml) was added the chiral selenide ligand (4*S*,5*S*)-**7a** (17.2 mg, 0.033 mmol) under a nitrogen atmosphere. After 15 min, racemic 1,3-diphenyl-3-acetoxy-1-propene (150 mg, 0.60 mmol) was added. The solution was then allowed to be stirred for 30 min. *N*,*O*-Bis(trimethylsilyl)acetamide (0.44 ml, 1.8 mmol), dimethyl malonate (0.21 ml, 1.8 mmol) and potassium acetate (3.0 mg, 0.03 mmol) were added in this order. After the solvent was evaporated under reduced pressure, silica gel column chromatography of the residue yielded the pure dimethyl (1,3-diphenyl-2-propen-1-yl)propanedioate. The optical purity was determined by HPLC using Daicel Chiralpak AD column.

4.6. Typical procedure of enantioselective hydrosilylation

To a stirring solution of $[Rh(cod)Cl]_2$ (1.3 mg, 0.003 mmol) in THF (3 ml) was added the chiral selenide ligand (4*S*,5*S*)-**7a** (3.3 mg, 0.006 mmol) under a nitrogen atmosphere. After 30 min, acetophenone (0.12 ml, 1.00 mmol) was added. The solution was then allowed to be stirred for 1 h. After addition of diphenylsilane (0.25 ml, 1.35 mmol), the solution was stirred for 20 h. To quench the reaction, MeOH (3 ml) and 1 N HCl (1 ml) were added. The resulting solution was extracted with Et_2O (10 ml × 3) and the combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by distillation afforded the pure *sec*-phenethyl alcohol. The optical purity was determined by GLC analysis using TCI Chiraldex G-TA column.

Table 8
Crystal data and structure refinement for (4*S*,S_{Se})-**13**

Empirical formula	$C_{25}H_{26}N_2O_3SSe$
Formula weight	513.50
Temperature (K)	299
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*P*2(1)2(1)2(1)
Unit cell dimensions	
a (Å)	9.5674(5)
b (Å)	9.8667(6)
c (Å)	26.1167(14)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	2465.4(2)
Z	4
Density (calculated) (Mg m^{-3})	1.383
Absorption coefficient (mm^{-1})	1.636
Crystal size (mm)	0.05 × 0.10 × 0.19
θ range for data collection (°)	1.56–24.70
Index ranges	$-11 \le h \le 11$, $-11 \le k \le 10$, $-30 \le l \le 28$
Reflections collected	13835
Independent reflections	4211 ($R_{int} = 0.1103$)
Independent reflections	2888 [$I > 2\sigma(I)$]
Absorption correction	Empirical (SADABS [29])
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4211/0/292
Goodness-of-fit on F^2	0.948
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0663$, $wR_2 = 0.0955$
Max shift/esd	0.024
Largest difference peak and hole (e Å^{-3})	0.729 and −0.486

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 141693 for (4*S*,S_{Se})-**13**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] See for example: P. Metzner, A. Thuillier, Sulfur Reagents in Organic Synthesis, Academic Press, London, 1994.
[2] (a) N. Komatsu, M. Hashizume, T. Sugita, S. Uemura, J. Org. Chem. 58 (1993) 4529. (b) N. Komatsu, M. Hashizume, T. Sugita, S. Uemura, J. Org. Chem. 58 (1993) 7624. (c) H. Takada, Y. Nishibayashi, K. Ohe, S. Uemura, Chem. Commun. (1996) 931. (d) H. Takada, Y. Nishibayashi, K. Ohe, S. Uemura, C.P. Baird, T.J. Sparey, P.C. Taylor, J. Org. Chem. 62 (1997) 6512. (e) H. Takada, Y. Nishibayashi, K. Ohe, S. Uemura, Phosphorus Sulfur Silicon Relat. Elements 120–121 (1997) 363. (f) Y. Miyake, H. Takada, K. Ohe, S. Uemura, J. Chem. Soc. Perkin Trans. 1 (1998) 2373.
[3] (a) T. Shimizu, N. Kamigata, Org. Prep. Proced. Int. 29 (1997) 603. (b) F.A. Davis, R.T. Reddy, J. Org. Chem. 57 (1992) 2599.

[4] (a) N. Komatsu, T. Murakami, Y. Nishibayashi, T. Sugita, S. Uemura, J. Org. Chem. 58 (1993) 3697. (b) N. Komatsu, S. Matsunaga, T. Sugita, S. Uemura, J. Am. Chem. Soc. 115 (1993) 5847. (c) Y. Nishibayashi, J.D. Singh, S. Fukuzawa, S. Uemura, J. Org. Chem. 60 (1995) 4114.
[5] (a) V.P. Krasnov, V.I. Naddaka, V.I. Minkin, Zh. Org. Khim. 17 (1981) 445. (b) V.P. Krasnov, V.I. Naddaka, V.I. Minkin, Chem. Abstr. 95 (1981) 42551x.
[6] J. Zhang, N. Kurose, S. Saito, T. Takahashi, T. Koizumi, J. Synth. Org. Chem. Jpn. 57 (1999) 587.
[7] (a) T. Shimizu, N. Seki, H. Taka, N. Kamigata, J. Org. Chem. 61 (1996) 6013. (b) H. Taka, T. Shimizu, F. Iwasaki, M. Yasui, N. Kamigata, J. Org. Chem. 64 (1999) 7433.
[8] Y. Nishibayashi, T. Chiba, K. Ohe, S. Uemura, J. Chem. Soc. Chem. Commun. (1995) 1243.
[9] Preliminary communication of enantioselective imidation: H. Takada, M. Oda, Y. Miyake, K. Ohe, S. Uemura, Chem. Commun. (1998) 1557.
[10] Toluene has already been revealed to be the solvent of choice for asymmetric sulfimidation of organic sulfides, refs. [2c–f].
[11] The excess selenide was employed (2.0 equivalents) and TsN=IPh served as the limiting reagent.
[12] S. Tamagaki, S. Oae, K. Sasaki, Tetrahedron Lett. (1975) 649.
[13] (a) F.A. Davis, R.T. Reddy, Tetrahedron 41 (1985) 4747. (b) K.B. Sharpless, M.W. Young, R.F. Lauer, Tetrahedron Lett. (1973) 1979. (c) M. Oki, H. Iwamura, Tetrahedron Lett. (1966) 2917. (d) W.J. Burlant, E.S. Gould, J. Am. Chem. Soc. 76 (1954) 5775. (e) T.W. Cambell, H.G. Walker, G.M. Coppinger, Chem. Rev. 50 (1952) 279. (f) R. Gaithwaite, W.J. Kenyon, H. Phillips, J. Chem. Soc. (1928) 2280.
[14] In general, selenurane is more stable when an electron-withdrawing group lies at the apical position.
[15] R.S. Berry, J. Chem. Phys. 32 (1960) 933.
[16] (a) H. Takada, K. Ohe, S. Uemura, Angew. Chem. Int. Ed. Engl. 38 (1999) 1288. (b) H. Takada, M. Oda, A. Oyamada, K. Ohe, S. Uemura, Chirality 12 (2000) 299.
[17] (a) J.F. Bower, C.J. Martin, D.J. Rawson, A.M.Z. Slawin, J.M.J. Williams, J. Chem. Soc. Perkin Trans 1. (1996) 333. (b) J.F. Bower, J.M.J. Williams, Tetrahedron Lett. 35 (1994) 7111.
[18] K. Tsujihara, N. Furukawa, K. Oae, S. Oae, Bull. Chem. Soc. Jpn. 42 (1969) 2631.
[19] A. Bondi, J. Phys. Chem. 68 (1964) 441.
[20] (a) M. Iwaoka, S. Tomoda, Phosphorus Sulfur Silicon Relat. Elements 67 (1992) 125. (b) M. Iwaoka, S. Tomoda, J. Org. Chem. 60 (1995) 5299. (c) M. Iwaoka, S. Tomoda, J. Am. Chem. Soc. 118 (1996) 8077. (d) G. Mugesh, H.B. Singh, R.J. Butcher, Tetrahedron: Asymmetry 10 (1999) 237.
[21] Some recent examples of stereocontrolled reaction using organoselenium compounds including the Se···N or Se···O interactions: (a) K. Fujita, K. Murata, M. Iwaoka, S. Tomoda, Tetrahedron 53 (1997) 2029. (b) S. Fukuzawa, K. Takahashi, H. Kato, H. Yamazaki, J. Org. Chem. 62 (1997) 7711. (c) T. Wirth, G. Fragale, M. Spichty, J. Am. Chem. Soc. 120 (1998) 3376 and refs. cited therein.
[22] (a) Y. Nishibayashi, J.D. Singh, K. Segawa, S. Fukuzawa, S. Uemura, J. Chem. Soc. Chem. Commun. (1994) 1375. (b) Y. Nishibayashi, K. Segawa, J.D. Singh, S. Fukuzawa, K. Ohe, S. Uemura, Organometallics 15 (1996) 370.
[23] M.J. McKennon, A.I. Meyers, J. Org. Chem. 58 (1993) 3568.
[24] Although the reason is not yet clear, combustion analysis of the selenimides **3b**, **3c** and **3d** does not give the expected values even after many attempts.
[25] D.P. Schumacker, J.E. Clark, B.L. Murphy, P.A. Fischer, J. Org. Chem. 55 (1990) 5291.
[26] C. Bolm, K. Weickhardt, M. Zehnder, T. Ranff, Chem. Ber. 124 (1991) 1173.
[27] SMART and SAINT, Area Detector Control and Integration Software, Bruker Analytical X-ray Systems, Madison, WI, 1998.
[28] G.M. Sheldrick, SHELXTL, Program for the Solution and Refinement of Crystal Structures, Bruker Analytical X-ray Systems, Madison, WI, 1998.
[29] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1996.