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A Symmetric Oxyselenenylation of Simple Olefins Using Optically Active Selenobinaphthyls

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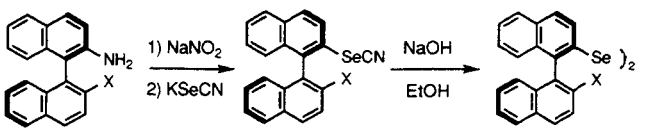
ABSTRACT

Asymmetric trans-addition reactions of simple olefins have been performed by using optically active 2-selenobinaphthyls **1**,**2a–g**. *Introduction of an amide group at the 2'-position in the binaphthyl skeleton enhances considerably the diastereomeric excess (de) of the asymmetric methoxyselenenylation. In the case of trans-olefins, introduction of another chiral center in the amide group further enhances the de due to double stereodifferentiation between the (R)-binaphthyl skeleton and the chiral amide group introduced at the 2'-position in the binaphthyl skeleton. The use of chiral nucleophiles is also effective to enhance the de for symmetrical cis-olefins.*

INTRODUCTION

In spite of the importance of organoselenium reagents is selective organic synthesis [1], little attention has been paid to their application to asymmetric synthesis [2]. In 1988, we first reported asymmetric ring-opening of prochiral cyclohexene oxide [3] and asymmetric *trans*-addition reactions across simple olefins using optically active selenobinaphthyls [4], which showed a moderate degree of asymmetric recognition. Since these reports, several attempts to develop practical asymmetric reactions using selenobinaphthyls or other organoselenium compounds as a chiral selenium source have been made by us [5] and others [6]. In this article, we wish to summarize asymmetric oxyselenenylation reactions using optically active selenium-containing binaphthyl derivatives. In order to enhance the diastereomeric excess (de) of the oxyselenenylation products, the double stereodifferentiation between the binaphthyl skeleton and a chiral amide group introduced at the 2'-position was tested for *trans*-olefins. Moreover, a chiral nucleophile was employed specifically for *cis*-olefins.



SCHEME 1

RESULTS AND DISCUSSION

Optically active selenobinaphthyls **1** [3] and **2a** [5] were synthesized in an enantiomerically pure form by the method outlined in Scheme 1. Although the

Dedicated to Professor Shigeru Oae on the occasion of his seventy-fifth birthday.

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stereoconfiguration of these selenobinaphthyls is identical with one another, chirality of **2a** is represented by (*R*), whereas that of **1** is represented by (*S*), according to the rules of IUPAC nomenclature.

We carried out the asymmetric *trans*-addition reaction, methoxyselenenylation, of various simple olefins according to Scheme 2 using **1** and **2a** as chiral selenium reagents. Methoxyselenenylation products **8a–j** were obtained in moderate yields as the only products, the de of each of which was determined by integration of ^{1}H-NMR absorptions due to the methoxy group. The results are listed in Table 1.

The optical yields for simple olefins, whether they are *cis* or *trans*, were uniformly low when selenobinaphthyl **1** was employed (3–24% de) [4]. But *trans*-olefins gave slightly higher de than *cis*-olefins, probably because the de-determining step for *cis*- and *trans*-olefins is not the same. For *trans*-olefins (Scheme 3), if one assumes the mechanism of methoxyselenenylation to involve the generally accepted three-membered seleniranium cation **9** [7], two diastereomeric intermediates **9a** and **9b** could exist, which would be derived from enantiofacial stereoselection for the *trans*-olefins. Thus, the de-determining step for *trans*-olefins is the first step. The second step, the capture of a nucleophile (MeOH) by **9**, may not be responsible for determining the de if the latter step is rapid enough to prevent the equilibrium between **9a** and **9b**. When 1 was employed as an optically active selenium reagent, the induced de's were not high (24% de for *trans*-β-methylstyrene, 20% de for *trans*-2-butene). On the other hand, **2a** gave an improved de for each of these *trans*-olefins, probably due to the acetamide group introduced. Thus, the de for *trans*-olefins, which may be determined in the first step, was slightly enhanced by the substituent at the 2′-position of the binaphthyl skeleton. The methoxyselenenylation product of *trans*-β-methylstyrene gave the highest de (54% de) when **2a** was used. We therefore decided to use **2a** in the following attempt to improve the de. It should be noted that *trans*-β-methylstyrene exclusively gave one regioisomer, an α-methoxy-β-selenenylation product, under the reaction conditions employed.

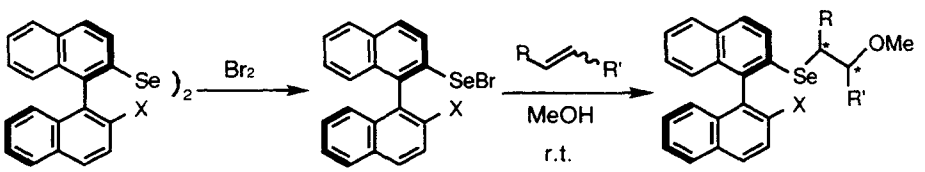
In order to improve the de of asymmetric methoxyselenenylation for *trans*-olefins, the effect of another chiral center on the 2′-amide group of **2a** was examined. Various 2′-amide derivatives of (*R*)-2-seleno-1,1′-binaphthyl **2b–g** were synthesized in an enantiomerically pure form by the method outlined in Scheme 4. Table 2 shows the results of asymmetric methoxyselenenylation of *trans*-β-methylstyrene using selenobinaphthyls **2a–g** (Scheme 5) [5]. When chiral menthol was introduced (**2b** and **2c**), the de's were significantly reduced, contrary to our expectation. The chiral reagent **2d**, which possesses an (*S*)-proline skeleton as another chiral center, gave a much better de than **2e**, which possesses an (*R*)-proline skeleton, probably due to the matched double stereodifferentiation between the (*S*)-proline skeleton and the (*R*)-binaphthyl skeleton. We then examined the effects of *N*-substituents in the proline ring having the (*S*)-configuration (**2f** and **2g**). Among these, **2g**, which has a 2,4-dinitrophenyl group on the proline nitrogen, gave the best de (79% de).

The NMR signals due to the methoxy group of the major diastereomer of products **11a–g**, which are described in the experimental section, were in all cases shifted to lower field relative to those of the minor ones. It was therefore assumed that the stereochemistry of the major isomer remained unchanged for all the substituents on the 2′-position of the selenobinaphthyl skeleton examined here.

These methoxyselenenylation products **11** could readily be converted into allyl methyl ethers by oxidation with an excess amount of hydrogen peroxide (Scheme 6). For example, **11a** or **11g**, when allowed to react with hydrogen peroxide in dichloromethane at room temperature, provided the corresponding selenoxide elimination product **12** in nearly quantitative yields [5]. The absolute configuration of the major enantiomer of **12** has been determined as (*R*) in these cases by the method described in the literature [5].

Whereas the de-determining step for *trans*-olefins is the first step, the corresponding step for *cis*-olefins is the one involving capture of the nucleophile (Scheme 7) because the same three-membered seleniranium cation **13** should be produced whether the selenenyl cation attacks from either face of symmetrical *cis*-olefins. It should therefore be difficult to enhance the de for *cis*-olefins be-

SCHEME 2



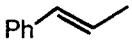
X=H **1**
X=NHAc **2a**

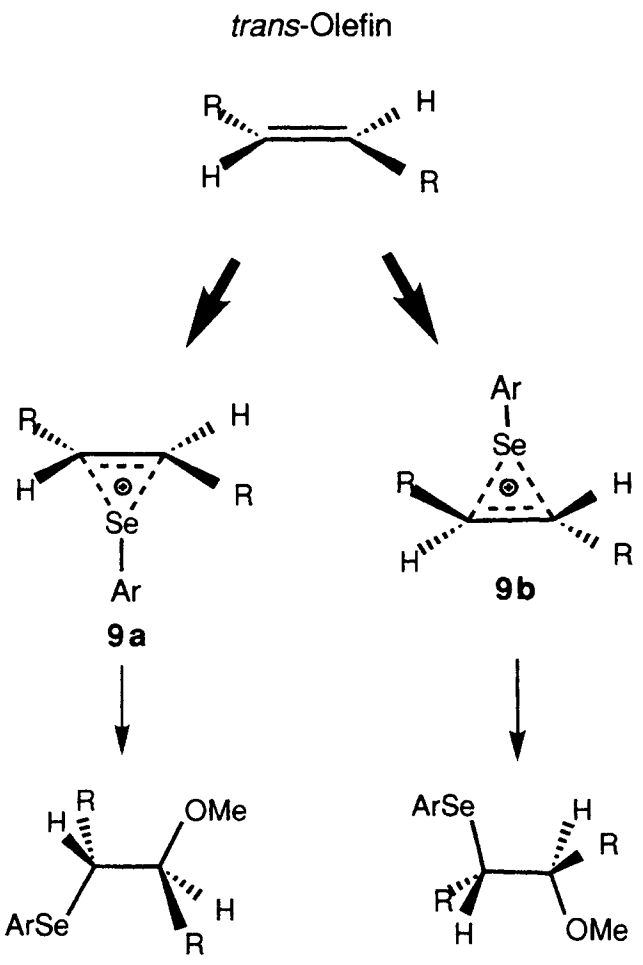
7

8a-j

(R and R' indicated in TABLE 1)

TABLE 1 Asymmetric Methoxyselenenylation of Olefins Using Selenobinaphthyl Compounds **1** or **2a** According to Scheme 2

Entry	Olefin	Product	**1** (*X* = *H*) Yield of **8**%	de%	Product	**2a** (*X* = *NHAc*) Yield of **8**%	de%
1		**8a**	49	24	**8f**	63	54
2		**8b**	48	20	**8g**	59	39
3		**8c**	59	13	**8h**	100	14
4		**8d**	80	3	**8i**	100	15
5		**8e**	61	17	**8j**	77	17



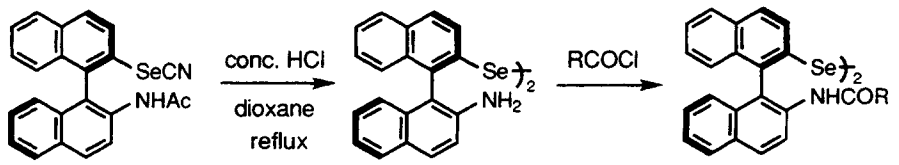
SCHEME 3

cause the attack of a nucleophile takes place from the opposite side of the optically modified electrophile (selenenyl cation in this case), far distant from the chiral moiety, which may cause significant reduction in optical induction. In fact by use of selenobinaphthyl **1**, *cis*-olefins gave lower de values than *trans*-olefins, and **2a** did not enhance the de values of methoxyselenenylation for *cis*-olefins (Table 1) because the de-determining step for *cis*-olefins is the step involving capture of the nucleophile by the seleniranium cation. We therefore examined the use of an optically active nucleophile.

We first examined the asymmetric oxyselenenylation of cyclooctene using achiral benzeneselenenyl bromide and *d*-menthol as a chiral nucleophile. But the oxyselenenylation product was obtained only in low yields with low de (5% de). In order to improve the de, we subsequently examined the double stereodifferentiation between the (*R*)-binaphthyl skeleton and optically active nucleophiles. Table 3 shows the results of asymmetric oxyselenenylation using **2a** and optically active nucleophiles such as menthol [5] and chiral silver carboxylates, according to Scheme 8.

Although the yields of **15** using menthol were not high, presumably due to the low nucleophilicity of bulky menthol, it should be mentioned that **15** was obtained as a major product and that **2a** was recovered in all cases as the reduction product of **14**. In the case of cyclooctene and cyclohexene, the des were significantly enhanced by using *d*-menthol as a nucleophile (59 and 69% de, respectively, Table 3, entries 1 and 4), while *l*-menthol gave low de as in the case using methanol as a nucleophile. This may be caused by the double stereodifferentiation between the binaphthyl skeleton and menthol. The enhancement of de by using *d*-

SCHEME 4



6 10 2b-g

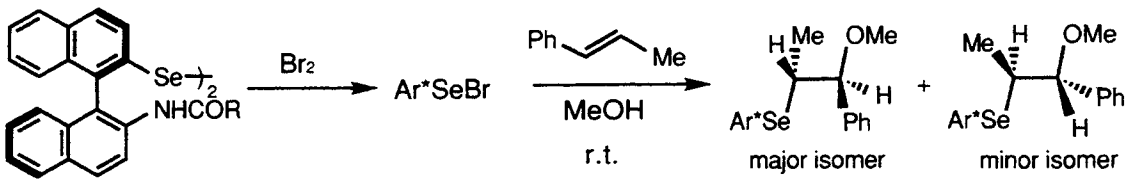
(Structures of R listed in TABLE 2)

TABLE 2 Asymmetric Methoxyselenenylation of *trans*-β-Methylstyrene Using 2'-Amido Derivatives of (*R*)-2-Seleno-1,1'-Binaphthyl **2a–g** According to Scheme 5

2a–g	*R*	*Yield of* **11a–g**%	*de*%
a	Me	63	54
b	*l*- CH_2O	98	12
c	*d*- CH_2O	87	8
d	$CO_2{}^tBu$	90	59
e	$CO_2{}^tBu$	77	36
f	$COCF_3$	100	67
g	NO_2, NO_2	87	79

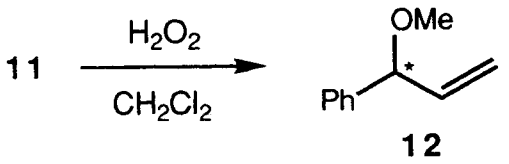
menthol indicates that the use of a chiral nucleophile is an effective strategy in the asymmetric *trans*-addition reaction of symmetrical *cis*-olefins. When similar reaction conditions were applied to *trans*-olefins, *trans*-β-methylstyrene, for example, the enhancement of de was also observed by using *d*-menthol (80% de, entry 9). The result seems interesting because the de-determining step for *trans*-olefins should be the first process to form seleniranium intermediates. In this case, however, since the nucleophilic attack of menthol on the seleniranium intermediates is expected to be relatively slow, the de of the products may be effectively controlled by the double stereodifferentiation between the binaphthyl skeleton and the nucleophile, even in the case of *trans*-olefin.

In order to obtain the corresponding carboxyselenenylation product, which should readily provide chiral allyl alcohols by hydrolysis, followed by selenoxide elimination, we have examined double stereodifferentiation using optically active silver carboxylates as a chiral nucleophile. Unlike the case of menthol, the reaction proceeded rapidly, and chemical yields of carboxyselenenylation products were high, presumably due to the higher nucleophilicity of silver carboxylates. In the case of cyclohexene, the de was enhanced by using silver (*S*)-*O*-acetylmandelate (39% de, entry 6) due to double stereodifferentiation between the (*R*)-binaphthyl skeleton and the chiral nucleophile. However, the enhancement of de was low compared with the case using *d*-menthol as a chiral nucleophile. This may be because the optically modified spot of the chiral silver carboxylate is more distant from the reaction site than that of menthol. When similar reaction conditions were applied to *trans*-β-methylstyrene, the de was not significantly changed from that of methoxyselenenylation because the de-determining step in this case is the step involving the formation of the seleniranium cation. The oxyselenenylation product **15i**, of *trans*-β-methylstyrene using silver (*S*)-*O*-acetylmandelate was hydro-



(=Ar*Se) 2a-g 11a-g

SCHEME 5

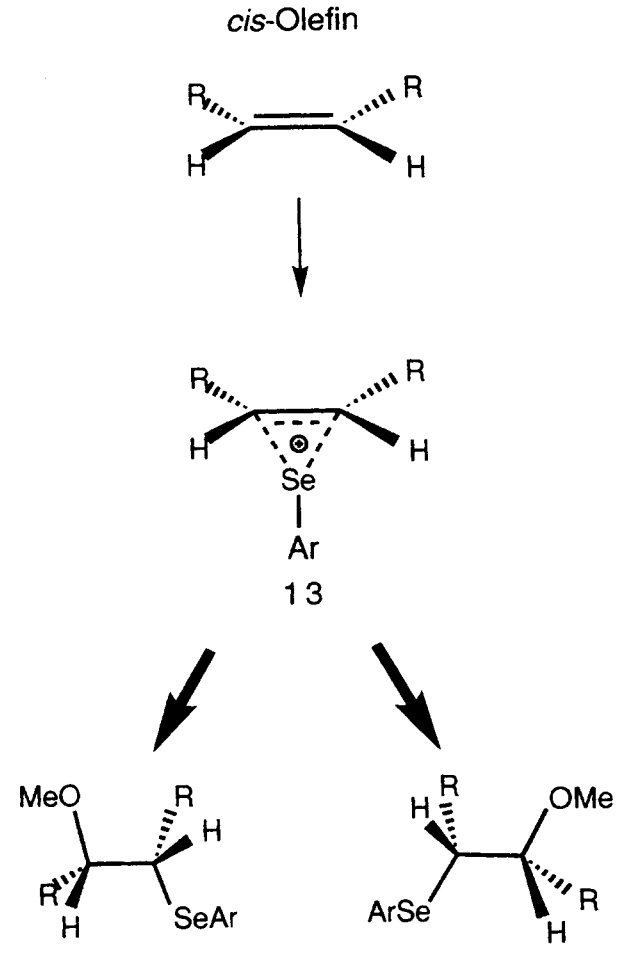


SCHEME 6

lyzed with sodium hydroxide-methanol solution to give the corresponding hydroxyselenide in good yield without racemization.

CONCLUSION

Introduction of an amide group at the 2'-position in the binaphthyl skeleton enhances considerably the de of the asymmetric methoxyselenenylation of *trans*-olefins. Introduction of a chiral amide group also enhances de due to double stereodifferentiation between the (*R*)-binaphthyl skeleton and the chiral amide group introduced. The highest optical yield (79% de) has been achieved in the case of the (*S*)-prolyl derivative containing a 2,4-dinitrophenyl substituent. The use of a chiral nucleophile such as menthol and chiral silver carboxylates is suggested to be an effective approach to the asymmetric oxyselenenylation, especially for *cis*-olefins.



SCHEME 7

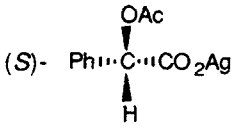
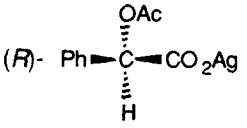
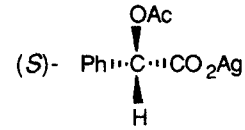
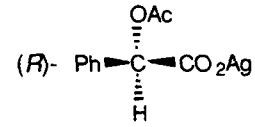
EXPERIMENTAL

General. IR spectra were recorded on a Shimazu IR-435 spectrometer. 90 MHz ^{1}H NMR, 270 MHz ^{1}H NMR, and 500 MHz ^{1}H NMR were measured on a Varian EM390, JEOL JMNGX-270 and a Bruker AM-500 instrument, respectively, in chloroform-d_1 containing tetramethylsilane (TMS) as internal standard. ^{13}C NMR and ^{77}Se NMR were measured on a JEOL FX90Q instrument in chloroform-d_1. Chemical shifts represent the lower field shift from TMS as internal standard and from dimethylselenide as external standard for ^{13}C NMR and ^{77}Se NMR, respectively. Optical rotations were measured on a Jasco DIP-370 digital polarimeter. Low-resolution mass spectra were recorded on a Shimazu GCMS-QP1000 mass spectrometer operating at 70 eV. High-resolution mass spectra were recorded on a HITACHI M-80B mass spectrometer operating at 70 eV. All melting points are uncorrected. Reactions were monitored by thin-layer chromatography (TLC) using precoated silica-gel plates (Merck Kieselgel 60 F-254 Art.5715). Column chromatography was carried out with silica gel (Wakogel C-300). High-performance liquid chromatography (HPLC) was done with TOSOH HLC-803D and Jasco 880-PU, JAI LC-908 instruments using ODS-120T or JAIGEL-1H, 2H. Methanol and dichloromethane were distilled from calcium hydride and stored over molecular sieves **3A** or **4A**. All of the oxyselenenylation reactions were carried out under a nitrogen atmosphere.

(S)-2-Selenocyanato-1,1'-binaphthyl (**4**). **4** was synthesized from **3** [8] according to our previous literature [5] (33% yield): pale yellow crystal; mp 149–151°C; $[\alpha]_D^{25}$: −61° (c 0.033, MeCN); IR (KBr) 2158, 1575, 1498, 810, 800, 780, 770, 743 cm^{-1}; ^{1}H-NMR (90 MHz): δ 8.2–7.2 (m, 13H); ^{13}C NMR: δ 137.4, 134.9, 133.9, 133.5, 132.9, 131.6, 130.3, 129.9, 128.6, 128.4, 128.3, 127.5, 127.2, 126.8, 126.7, 126.3, 126.0, 125.5, 125.3, 123.6, 102.3; ^{77}Se NMR: δ 310.4; LRMS: (*m/z*) 359 (M^+), 253 (base); anal. calcd for $C_{21}H_{13}NSe$: C, 70.40; H, 3.66; N, 3.91%. Found: C, 70.38; H, 3.72; N, 3.88%.

Bis[(S)-(1,1'-binaphthalene)-2-yl] Diselenide (**1**). **1** was synthesized from **4** according to our previous literature [5] (yield 100%): yellow crystal; mp 156–158°C; $[\alpha]_D^{25}$: −80° (c 0.075, MeCN); IR (KBr) 3070, 1580, 1505, 1370, 907, 802, 780, 773, 732 cm^{-1}; ^{1}H-NMR (90 MHz): δ 8.0–7.1 (m, 26H); ^{13}C, NMR: δ 136.6, 136.4, 133.8, 133.2, 132.4, 132.2, 129.6, 128.9, 128.8, 128.7, 128.4, 127.9, 127.4, 126.6, 126.4, 126.2,

TABLE 3 Asymmetric Oxyselenenylation of Olefins Using Bis[(*R*)-(2′-Acetylamino-1,1′-binaphthalene)-2-yl] Diselenide **2a** According to Scheme 8

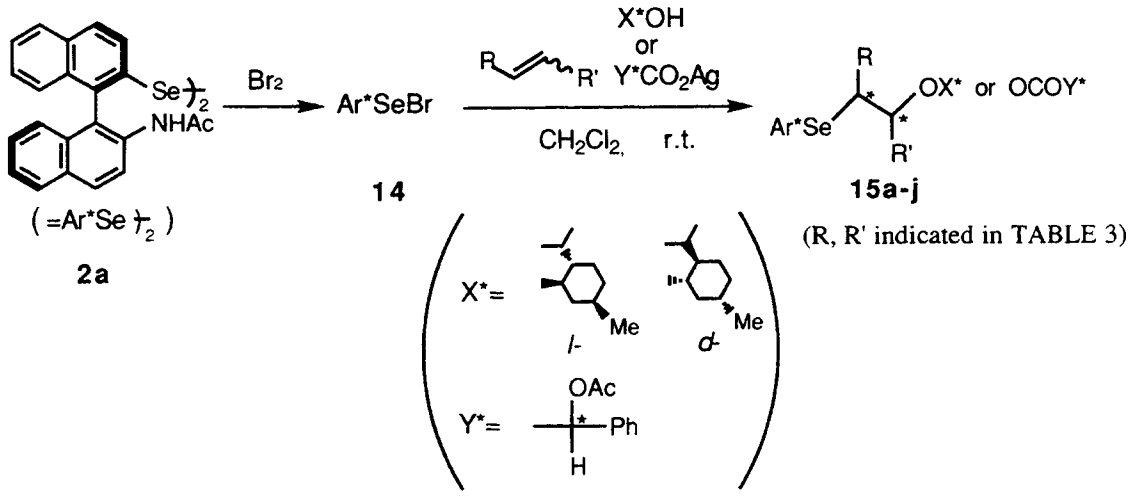
Entry	R, R′	Nucleophiles (*X*OH* or *Y*CO₂Ag*)	Product	Yield of **15**%	*de*%
1		*d*-menthol	**15a**	15	59[a]
2		*l*-menthol	**15b**	14	22[a]
3		MeOH	**8j**	77	17
4		*d*-menthol	**15c**	38	69[a]
5		*l*-menthol	**15d**	43	18[b]
6		(*S*)- 	**15e**	85	39[c]
7		(*R*)- 	**15f**	83	9[c]
8		MeOH	**8i**	100	15
9		*d*-menthol	**15g**	26	80[ad]
10		*l*-menthol	**15h**	17	12[bd]
11		(*S*)- 	**15i**	52	53[cd]
12		(*R*)- 	**15j**	55	59[cd]
13		MeOH	**8f**	63	54

[a]Determined by integration of ^{1}H NMR absorption due to OC*H* of the menthyl group.
[b]Determined by integration of the absorption due to $-CH_3$ of the menthyl group.
[c]Determined by integration of the absorption due to acetoxy group.
[d]It is assumed that the configuration of the major isomer is similar to that of entry 13.

126.0, 125.9, 125.6, 125.5: ^{77}Se NMR: δ 410.2; LRMS: (*m/z*) 666 (M^+), 252 (base); HRMS found: (*m/z*) 666.0315. Calcd for $C_{40}H_{26}Se_2$: M, 666.0363.

(*R*)-*2′-Acetylamino-2-selenocyanato-1,1′-binaphthyl* (**6**). The preparation of **6** was described in our previous literature [5]: (54% yield) pale yellow powder; mp 98.5–101.0°C; $[\alpha]_D^{25}$: 58.5° (c 1.14, $CHCl_3$); IR (KBr) 3280, 2140, 1668, 1497, 1273 cm^{-1}; ^{1}H NMR (90 MHz): δ 8.41 (d, J = 8.5 Hz, 1H), 8.21–6.38 (m, 12H), 1.83 (s, 3H); ^{13}C NMR: δ 168.6, 101.7, 24.1; ^{77}Se NMR: δ 321.2; LRMS: (*m/z*) 416 (M^+), 268 (base); anal. calcd for $C_{23}H_{16}N_2OSe$: C, 66.51; H, 3.88; N, 6.74%. Found: C, 66.42; H, 4.14; N, 6.38%.

Bis[(*R*)-(*2′-acetylamino-1,1′-binaphthalene*)-*2-yl*] *Diselenide* (**2a**). The preparation of **2a** was de-



SCHEME 8

scribed in our previous literature [5]: (92% yield) yellow crystal; mp 194.4–196.0°C; $[\alpha]_D^{25}$: 30.0° (c 0.301, CH_2Cl_2); IR (KBr) 3040, 1670, 1490, 1271 cm^{-1}; ^1H NMR (90 MHz): δ 8.42 (d, J = 8.1 Hz, 1H), 8.02–6.50 (m, 24H), 1.55 (s, 6H); ^{13}C NMR: δ 168.4, 24.2; ^{77}Se NMR: δ 415.3; LRMS: (m/z) 780 (M^+), 267 (base); anal. calcd for $C_{44}H_{32}N_2O_2Se_2$: C, 67.87; H, 4.14; N, 3.60%. Found: C, 67.76; H, 4.29; N, 3.55%.

Asymmetric Methoxyselenenylation

General Procedure [5]. To a dichloromethane solution (2 mL) of **2a** (33.4 mg, 0.0428 mmol), a 0.1 M tetrachloromethane solution of bromine (1.5 mL) was added dropwise at room temperature under a nitrogen atmosphere. After removal of the solvent and the excess amount of bromine, residual selenenyl bromide was dissolved in MeOH and to the solution was added *trans*-β-methylstyrene (60.8 mg, 0.514 mmol) under a nitrogen atmosphere. After having been stirred for several hours, triethylamine (8.6 mg, 0.086 mmol) was added to the mixture, which was then extracted with dichloromethane. The combined organic layer was dried over sodium sulfate, and the solvent evaporated under reduced pressure. After purification by column chromatography (benzene-ethyl acetate as eluent), methoxyselenenylation product **8f** (29.2 mg, 63%) was obtained as a colorless oil.

Erythro-2-{(S)-(1,1'-binaphthalene)-2-ylseleno}-1-methoxy-1-phenylpropane (**8a**). IR (neat) 3070, 2990, 2940, 1506, 1453, 1080, 802, 780, 702 cm^{-1}; ^1H NMR (90 MHz): δ 8.0–7.1 (m, 18H), 4.22 (d, J = 5 Hz, 0.62 × 1H), 4.11 (d, J = 5 Hz, 0.38 × 1H), 3.5–3.3 (m, 1H), 3.15 (s, 0.62 × 3H), 3.05 (s, 0.38 × 3H), 1.27 (d, J = 5 Hz, 0.62 × 3H), 1.19 (d, J = 6 Hz, 0.38 × 3H); LRMS: (m/z) 482 (M^+), 280 (base); HRMS found: m/z 482.1157. Calcd for $C_{30}H_{26}OSe$: M, 482.1148.

Erythro-2-{(S)-(1,1'-binaphthalene)-2-ylseleno}-3-methoxybutane (**8b**). IR (neat) 3070, 2990, 2940, 1580, 1505, 1090, 802, 780, 745 cm^{-1}; ^1H NMR (90 MHz): δ 8.0–7.1 (m, 13H), 3.4–3.2 (m, 2H), 3.23 (s, 0.60 × 3H), 3.10 (s, 0.40 × 3H), 1.33 (d, J = 6 Hz, 0.60 × 3H), 1.23 (d, J = 6 Hz, 0.40 × 3H), 1.05 (d, J = 5 Hz, 0.60 × 3H), 0.99 (d, J = 6 Hz, 0.40 × 3H); LRMS: (m/z) 420 (M^+), 87 (base); HRMS found: m/z 420.0975. Calcd for $C_{25}H_{24}OSe$: M, 420.0991.

Threo-2-{(S)-(1,1'-binaphthalene)-2-ylseleno}-3-methoxybutane (**8c**). IR (neat) 3060, 2980, 2940, 1580, 1506, 1092, 802, 780, 745 cm^{-1}; ^1H-NMR (90 MHz): δ 8.0–7.1 (m, 13H), 3.5–3.1 (m, 2H), 3.25 (s, 0.43 × 3H), 3.18 (s, 0.57 × 3H), 1.29 (d, J = 5 Hz, 0.57 × 3H), 1.21 (d, J = 6 Hz, 0.43 × 3H), 1.05 (d, J = 6 Hz, 0.43 × 3H), 0.85 (d, J = 6 Hz, 0.57 × 3H); LRMS: (m/z) 420 (M^+), 87 (base); HRMS found: m/z 420.0994. Calcd for $C_{25}H_{24}OSe$: M, 420.0991.

Threo-1-{(S)-(1,1'-binaphthalene)-2-ylseleno}-2-methoxycyclohexane (**8d**). IR (neat) 3060, 2940, 2860, 1580, 1505, 1090, 802, 780, 743 cm^{-1}; ^1H NMR (90 MHz): δ 8.0–7.1 (m, 13H), 3.4–3.0 (m, 2H), 3.24 (s, 0.51 × 3H). 3.16 (s, 0.49 × 3H), 1.9–1.0 (m, 8H); LRMS: (m/z) 446 (M^+), 114 (base); HRMS found: m/z 446.1125. Calcd for $C_{27}H_{26}OSe$: M, 446.1148.

Threo-1-{(S)-(1,1'-binaphthalene)-2-ylseleno}-2-methoxycyclooctane (**8e**). IR (neat) 3070, 2930, 2860, 1580, 1505, 1095, 800, 780, 743 cm^{-1}; ^1H NMR (90 MHz): δ 8.0–7.1 (m, 13H), 3.7–3.5 (m, 1H), 3.3–3.1 (m, 1H), 3.20 (s, 0.42 × 3H), 3.11 (s, 0.58 × 3H), 1.8–1.3 (m 12H); LRMS: (m/z) 474 (M^+), 109 (base) (**8e**); HRMS. found: m/z 482.1157. Calcd for $C_{30}H_{26}OSe$: M, 482.1148.

Erythro-2-{(R)-(2'-acetylamino-1,1'-binaphthalene)-2-ylseleno}-1-methoxy-1-phenylpropane (**8f**). IR (neat) 1695, 1600, 1500, 1428, 1277 cm^{-1}; ^1H NMR (270 MHz): δ 8.57 (d, J = 9.9 Hz, 1H), 8.06–6.79 (m, 17H), 4.31 (d, J = 4.6 Hz, 0.77 × 1H), 4.16 (d, J = 4.4 Hz, 0.23 × 1H), 3.65–3.56 (m, 1H), 3.17 (s, 0.77 × 3H), 3.05 (s, 0.23 × 3H), 1.82 (s, 0.23 × 3H), 1.78 (s, 0.77 × 3H), 1.31 (d, J = 7.3 Hz, 0.23 × 3H), 1.21 (d, J = 7.3 Hz, 0.77 × 3H); LRMS: (m/z) 539 (M^+), 280 (base); HRMS found: m/z 539.1362. Calcd for $C_{32}H_{29}O_2NSe$: M, 539.1362.

Erythro-2-{(R)-(2'-acetylamino-1,1'-binaphthalene)-2-ylseleno}-3-methoxybutane (**8g**).

IR (neat) 1692, 1507, 1278, 1085 cm^{-1}; ^1H NMR (270 MHz): δ 8.57 (d, J = 9.0 Hz, 1H), 8.33 (d, J = 9.0 Hz, 1H), 8.02–6.77 (m, 12H), 3.99–3.84 (m, 1H), 3.50–3.19 (m, 1H), 3.13 (s, 0.31 × 3H), 3.01 (s, 0.69 × 3H), 1.81 (s, 0.31 × 3H), 1.77 (s, 0.69 × 3H), 1.40 (d, J = 7 Hz, 0.31 × 3H), 1.24 (d, J = 7 Hz, 0.69 × 3H), 1.02 (d, J = 7 Hz, 0.69 × 3H), 1.06 (d, J = 7 Hz, 0.31 × 3H); LRMS: (m/z) 477 (M^+), 332 (base); HRMS found: m/z 477.1121. Calcd for $C_{27}H_{27}NO_2Se$: M, 477.1206.

Threo-2-{(R)-(2'-acetylamino-1,1'-binaphthalene)-2-ylseleno}-3-methoxybutane (**8h**). IR (neat) 2960, 1915, 1688, 1593, 1502, 1274 cm^{-1}; ^1H NMR (500 MHz): δ 8.59–8.53 (m, 1H), 8.04–6.82 (m, 12H), 3.61–3.48 (m, 1H), 3.36 (dd, J = 6.1, 4.5 Hz, 0.43 × 1H), 3.27 (dd, J = 6.1, 4.5 Hz, 0.57 × 1H), 3.23 (s, 0.43 × 3H), 3.15 (s, 0.57 × 3H), 1.80 (s, 3H), 1.32 (d, J = 8 Hz, 0.43 × 3H), 1.26 (d, J = 8 Hz, 0.57 × 3H), 1.12 (d, J = 7 Hz, 3H); LRMS: (m/z) 477 (M^+), 332 (base); HRMS found: m/z 477.1167. Calcd for $C_{27}H_{27}NO_2Se$: M, 477.1206.

Threo-1-{(R)-(2'-acetylamino-1,1'-binaphthalene)-2-ylseleno}-2-methoxycyclohexane (**8i**). IR (neat) 2925, 1690, 1593, 1503, 1498, 1275 cm^{-1}; ^1H NMR (500 MHz): δ 8.56–8.47 (m, 1H), 8.02–6.91 (m, 12H), 3.46–3.39 (m, 0.43 × 1H), 3.33–3.27 (m, 0.57 × 1H), 3.19 (s, 0.43 × 3H), 3.11 (s, 0.57 × 3H), 3.11–3.05 (m, 1H), 1.78 (s, 0.43 × 3H), 1.76 (s, 0.57 × 3H), 1.64–1.10 (m, 8H); LRMS: (m/z) 503 (M^+), 332 (base); HRMS found: m/z 503.1341. Calcd for $C_{29}H_{29}NO_2Se$: M, 503.1362.

Threo-1-{(R)-(2'-acetylamino-1,1'-binaphthalene)-2-ylseleno}-2-methoxycyclooctane (**8j**). IR (neat) 3405, 2905, 1688, 1592, 1501, 1274 cm^{-1}; ^1H NMR (500 MHz): δ 8.49 (d, J = 9 Hz, 0.42 × 1H), 8.37 (d, J = 9 Hz, 0.58 × 1H), 8.03–6.93 (m, 12H), 3.66–3.60 (m, 0.42 × 1H), 3.51–3.46 (m, 0.58 × 1H), 3.41–3.36 (m, 0.58 × 1H), 3.26–3.21 (m, 0.42 × 1H), 3.16 (s, 0.58 × 3H), 2.93 (s, 0.42 × 3H), 1.79 (s, 0.42 × 3H), 1.72 (s, 0.58 × 3H), 1.77–1.06 (m, 12H); LRMS: (m/z) 531 (M^+), 332 (base); HRMS found: m/z 531.1649. Calcd for $C_{31}H_{33}NO_2Se$: M, 531.1675.

Bis[(R)-(2'-amino-1,1'-binaphthalene)-2-yl] Diselenide (**10**). **6** (589 mg, 1.42 mmol) was dissolved in a 1:1 (v/v) mixture (12 mL) of concentrated hydrochloric acid and dioxane, and the solution was refluxed for 1.5 hours. An aqueous solution of sodium hydroxide was then added to the cooled reaction mixture until it was neutralized. The mixture was extracted with dichloromethane, and the organic layer was dried over sodium sulfate. After purification of the crude products by column chromatography (benzene-hexane as eluent), pure **10** (368 mg, 0.530 mmol) was obtained as yellow crystals (yield 74.6%). Mp 202.7–204.4°C; $[\alpha]_D^{25}$: −88.3° (c 0.463, $CHCl_3$); IR (KBr) 3400, 3365, 1625, 1508, 818, 747 cm^{-1}; ^1H NMR (90 MHz): δ 8.00–6.71 (m, 24H), 3.32 (s, 4H); ^{13}C NMR: δ 142.4, 133.5, 132.9, 132.7, 132.3, 130.9, 130.1, 129.1, 128.1, 127.4, 127.1, 126.9, 125.9, 125.2, 123.7, 122.5, 118.2, 114.7; ^{77}Se NMR: δ 409.9; LRMS: (m/z) 696 (M^+), 348 (base); anal. calcd for $C_{40}H_{28}N_2Se_2$: C, 69.17; H, 4.06; N, 4.03%. Found: C, 69.12; H, 4.16; N, 4.07%.

Bis[(R)-{2'-(1-menthoxyacetylamino)-1,1'-binaphthalene}-2-yl] Diselenide (**2b**). **10** (37.5 mg, 0.0540 mmol) was dissolved in anhydrous ether (4 mL) under a nitrogen atmosphere, and triethylamine (10.9 mg, 0.108 mmol) and *l*-menthoxyacetyl chloride [9] (126 mg, 0.54 mmol) were successively added to the solution at 0°C. White precipitates were immediately generated. The reaction mixture was stirred overnight. After an aqueous solution of sodium hydroxide had been added in order to neutralize the excess acid chloride, the mixture was extracted with ether. The organic layer was then washed with ammonium chloride and dried over sodium sulfate. Obtained crude products were purified by column chromatography (benzene-ethyl acetate as eluent), and pure **2b** (66.2 mg, 0.0609 mmol) was obtained as yellow powder (100% yield). Mp 176.6–178.5°C; $[\alpha]_D^{25}$: −62.6° (c 1.14 × 10^{-1}, $CHCl_3$); IR (KBr) 3360, 2980, 2930, 1703, 1598, 1510 cm^{-1}; ^1H NMR (90 MHz): δ 8.67 (d, J = 8.7 Hz, 2H), 8.18–6.76 (m, 24H), 3.40 (d, J = 15.5 Hz, 2H), 3.32 (d, J = 15.5 Hz, 2H), 2.62 (td, J = 9.9, 3.6 Hz, 2H), 1.62–0.30 (m, 36H); ^{13}C NMR: δ 168.8, 79.6, 67.4, 47.2, 39.1, 34.2, 31.2, 25.3, 23.0, 22.0, 20.6, 15.9; ^{77}Se NMR: δ 399.9; HRMS. Found: m/z 544.1771. Calcd for $C_{32}H_{34}NO_2Se$: M/2, 544.1753.

2c–2g were prepared according to the previously mentioned procedure. In the case of **2d**, **2e**, **2f**, and **2g**, acid chlorides were synthesized in situ from the corresponding *N*-substituted proline by the reaction with oxalyl chloride [10].

Bis[(R)-{2'-(d-menthoxyacetylamino)-1,1'-binaphthalene}-2-yl] Diselenide (**2c**). Yellow powder (100% yield); mp 243.2–243.7°C; $[\alpha]_D^{25}$: −99.9° (c 1.16, $CHCl_3$); IR (KBr) 3340, 2950, 2925, 1700, 1593, 1501, 1108 cm^{-1}; ^1H NMR (90 MHz): δ 8.77 (d, J = 8.7

Hz, 2H), 8.40–6.85 (m, 24H), 3.77 (d, J = 15.4 Hz, 2H), 3.70 (d, J = 15.4 Hz, 2H), 2.68 (td, J = 10.1, 3.6 Hz, 2H), 1.85–0.20 (m, 36H); ^{13}C NMR: δ 168.8, 79.6, 67.5, 47.1, 38.6, 34.0, 30.9, 25.4, 23.0, 21.9, 20.6, 16.1; ^{77}Se NMR: δ 407.5; anal. Calcd for $C_{64}H_{68}O_4N_2Se_2$: C, 70.71; H, 6.30; N, 2.58%. Found: C, 70.58; H, 6.32; N, 2.63%.

Bis[(*R*)-{2'-(*N*-(*tert-butoxycarbonyl*)-(*S*)-*prolylamino*)-*1,1'-binaphthalene*}-*2-yl*] *Diselenide* (**2d**). Yellow powder (100% yield); mp 144.7–146.3°C; $[\alpha]_D^{33}$: −91.9° (c 6.67 × 10^{-2}, CH_2Cl_2); IR (KBr) 1700, 1508, 1365, 1160 cm^{-1}; ^{1}H NMR (90 MHz): δ 8.68 (d, J = 9 Hz, 2H), 8.11–6.93 (m, 24H), 4.12–3.79 (m, 2H), 3.02–2.57 (m, 4H), 2.07–1.65 (m, 8H), 1.03 (s, 18H); ^{13}C NMR: δ 171.0, 80.1, 61.9, 46.6, 27.9, 22.6, 14.1; ^{77}Se NMR: δ 402.5; anal. calcd for $C_{60}H_{58}O_6N_4Se_2$: C, 66.02; H, 5.60; N, 5.36%. Found: C, 66.17; H, 5.37; N, 5.14%.

Bis[(*R*)-{2'-(*N*-(*tert-butoxycarbonyl*)-(*R*)-*prolylamino*)-*1,1'-binaphthalene*}-*2-yl*] *Diselenide* (**2e**). Yellow powder (yield 50%); mp 141.5–144.4 °C; $[\alpha]_D^{25}$: −39.8° (c 0.45, $CHCl_3$); IR (KBr) 1698, 1597, 1508, 1369, 1160 cm^{-1}; ^{1}H NMR (90 MHz): δ 8.63 (d, J = 9 Hz, 2H), 8.20–6.77 (m, 24H), 4.15–3.87 (m, 2H), 3.01–2.77 (m, 4H), 2.25–1.72 (m, 8H), 1.12 (s, 18H); ^{13}C NMR: δ 170.9, 80.4, 61.6, 46.4, 28.2, 23.2, 17.4; ^{77}Se NMR: δ 398.3.

Bis[(*R*)-{2'-(*N*-(*trifluoroacetyl*)-(*S*)-*prolylamino*)-*1,1'-binaphthalene*}-*2-yl*] *Diselenide* (**2f**). Yellow powder (82% yield); mp 155.5–157.4°C; $[\alpha]_D^{25}$: −19.9° (c 1.14, $CHCl_3$); IR (KBr) 3410, 1739, 1512, 1268, 1160 cm^{-1}; ^{1}H NMR (90 MHz): δ 8.55 (d, J = 9 Hz, 2H), 8.20–6.83 (m, 24H), 4.15–3.87 (m, 2H), 3.01–2.77 (m, 4H), 2.25–1.72 (m, 8H); ^{13}C NMR: δ 167.8, 80.4, 62.2, 46.9, 21.1, 14.1 ^{77}Se NMR: δ 410.4; anal. calcd for $C_{54}H_{40}O_4N_4F_6Se_2$: C, 60.01; H, 3.73; N, 5.18%. Found: C, 60.06; H, 4.00; N, 4.90%.

Bis[(*R*)-{2'-(*N*-(*2,4-dinitrophenyl*)-(*S*)-*prolylamino*)-*1,1'-binaphthalene*}-*2-yl*] *Diselenide* (**2g**). Yellow powder (99.8% yield); mp 199.5–202.0°C; $[\alpha]_D^{33}$: −168° (c 8.25 × 10^{-2}, CH_2Cl_2); IR (KBr) 1693, 1609, 1509, 1330 cm^{-1}; ^{1}H NMR (90 MHz): δ 8.37 (d, J = 9 Hz, 2H), 8.20–6.55 (m, 28H), 6.08 (d, J = 10 Hz, 2H), 4.06 (t, J = 7.0 Hz, 2H), 3.20–2.77 (m, 4H), 2.66–2.27 (m, 4H), 2.27–1.43 (m, 4H); ^{13}C NMR: δ 169.0, 65.5, 53.1, 25.2, 22.7; ^{77}Se NMR: δ 411.6.

Erythro-2-[(*R*)-{2'-(*1-menthoxyacetylamino*)-*1,1'-binaphthalene*}-*2-ylseleno*]-*1-methoxy-1-phenylpropane* (**11b**). IR (neat) 2930, 1700, 1599, 1510, 1110 cm^{-1}; ^{1}H NMR (90 MHz): δ 8.75 (d, J = 8.4 Hz, 1H), 8.33–6.70 (m, 12H), 4.24 (d, J = 4 Hz, 0.56 × 1H), 4.12 (d, J = 4 Hz, 0.44 × 1H), 3.90–3.60 (m, 2H), 3.55–3.30 (m, 1H), 3.13 (s, 0.56 × 3H), 3.05 (s, 0.44 × 3H), 2.96–2.50 (m, 1H), 1.37–1.10 (m, 3H), 0.94–0.26 (m, 18H); HRMS found: m/z 693.2685. Calcd for $C_{42}H_{47}NO_3Se$: M, 693.2718.

Erythro-2-[(*R*)-{2'-(*d-menthoxyacetylamino*)-*1,1'-binaphthalene*}-*2-ylseleno*]-*1-methoxy-1-phenylpropane* (**11c**). IR (neat) 2940, 1700, 1600, 1510, 1110 cm^{-1}; ^{1}H NMR (500 MHz): δ 8.40–8.32 (m, 1H), 8.35–6.98 (m, 12H), 4.31 (d, J = 4 Hz, 0.54 × 1H), 4.18 (d, J = 4 Hz, 0.46 × 1H), 3.51–3.42 (m, 1H), 3.44–3.12 (m, 2H), 3.14 (s, 0.54 × 3H), 3.08 (s, 0.46 × 3H), 2.79–2.64 (m, 1H), 1.38–1.10 (m, 3H), 1.07–0.30 (m, 18H); HRMS found: m/z 693.2648. Calcd for $C_{42}H_{47}NO_3Se$: M, 693.2718.

Erythro-2-[(*R*)-{2'-(*N*-(*tert-butoxycarbonyl*)-(*S*)-*prolylamino*)-*1,1'- binaphthalene*}-*2-ylseleno*]-*1-methoxy-1-phenylpropane* (**11d**). IR (neat) 1700, 1508, 1368, 1160 cm^{-1}; ^{1}H NMR (500 MHz): δ 8.69 (d, J = 8 Hz, 0.2 × 1H), 8.64 (d, J = 8 Hz, 0.8 × 1H), 8.09–6.90 (m, 17H), 4.23 (d, J = 5.0 Hz, 0.8 × 1H), 4.11 (d, J = 4.9 Hz, 0.2 × 1H), 4.09–4.00 (br, 1H), 3.51–3.40 (br, 2H), 3.27–3.06 (m, 1H), 3.16 (s, 0.8 × 3H), 2.99 (s, 0.2 × 3H), 2.78–2.61 (br, 2H), 2.08–1.80 (br, 2H), 1.25 (d, J = 7 Hz, 0.2 × 3H), 1.17 (d, J = 7 Hz, 0.8 × 3H), 1.09 (br, 0.2 × 9H), 1.02 (br, 0.8 × 9H); HRMS found: m/z 694.2324. Calcd for $C_{40}H_{42}N_2O_4Se$: M, 694.2307.

Erythro-2-[(*R*)-{2'-(*N*-(*tert-butoxycarbonyl*)-(*R*)-*prolylamino*)-*1,1'- binaphthalene*}-*2-ylseleno*]-*1-methoxy-1-phenylpropane* (**11e**). IR (neat) 3000, 1696, 1598, 1509, 1370 cm^{-1}; ^{1}H NMR (500 MHz): δ 8.70–8.50 (m, 1H), 8.09–6.85 (m, 17H), 4.44–4.29 (m, 1H), 4.17–3.98 (m, 1H), 3.58–3.40 (m, 2H), 3.14 (s, 0.68 × 3H), 3.02 (s, 0.32 × 3H), 3.00–2.80 (m, 1H), 2.18–2.06 (m, 2H), 1.86–1.66 (m, 2H), 1.46–1.30 (m, 3H), 1.26 (s, 0.68 × 9H), 1.20 (s, 0.32 × 9H); HRMS found: m/z 694.2328. Calcd for $C_{40}H_{42}N_2O_4Se$: M, 694.2307.

Erythro-2-[(*R*)-{2'(*N*-(*trifluoroacetyl*)-(*S*)-*prolylamino*)-*1,1'-binaphthalene*}-*2-ylseleno*]-*1-methoxy-1-phenylpropane* (**11f**). IR (neat) 1694, 1508, 1142, 816 cm^{-1}; ^{1}H NMR (500 MHz): δ 8.55 (d, J = 10 Hz, 0.17 × 1H), 8.44 (d, J = 10 Hz, 0.83 × 1H), 8.07–6.92 (m, 17H), 4.35–4.26 (m, 1H), 4.26 (d, J = 3.6 Hz, 0.83 × 1H), 4.10 (d, J = 4.0 Hz, 0.17 × 1H), 3.64–3.42 (m, 2H), 3.41–3.30 (m, 1H), 3.15 (s, 0.83 × 3H), 3.01 (s, 0.17 × 3H), 2.05–1.50 (m, 4H), 1.33–1.14 (m, 3H).

Erythro-2-[(*R*)-{2'-(*N*-(*2,4-dinitrophenyl*)-(*S*)-*prolylamino*)-*1,1'-binaphthalene*)-*2-ylseleno*]-*1-methoxy-1-phenylpropane* (**11g**). IR (neat) 1689, 1607, 1505, 1330 cm^{-1}; ^{1}H NMR (500 MHz): δ 8.46 (d, J = 9.1 Hz, 0.1 × 1H), 8.39 (d, J = 2.6 Hz, 0.9 × 1H), 8.35 (d, J = 9.1 Hz, 0.9 × 1H), 8.32 (d, J = 2.7 Hz, 0.1 × 1H), 8.06–6.66 (m, 18H), 6.21 (d, J = 9.5 Hz, 0.1 × 1H), 6.16 (d, J = 9.5 Hz, 0.9 × 1H), 4.50 (d, J = 4.3 Hz, 0.9 × 1H), 4.46 (d, J = 3 Hz, 0.1 × 1H), 4.26–4.20 (m, 0.1 × 1H), 4.19–4.11 (m, 0.9 × 1H),

3.52–3.37 (m, 1H), 3.21 (s, 0.9 × 3H), 3.05 (s, 0.1 × 3H), 2.77–2.60 (m, 2H), 2.24–2.06 (m, 2H), 1.86–1.76 (m, 2H), 1.18 (d, J = 7.1 Hz, 0.9 × 3H), 1.13 (d, J = 7.2 Hz, 0.1 × 3H).

Asymmetric Oxyselenenylation Using Menthol

General Procedure [5]. To a dichloromethane solution (2 mL) of **2a** (27 mg, 0.035 mmol), a 0.1 M tetrachloromethane solution of bromine (1.5 mL) was added dropwise at room temperature under a nitrogen atmosphere. After removal of the solvent and the excess amount of bromine, the residual selenenyl bromide **14** was dissolved in dichloromethane (2 mL), and, to the solution, was added an excess amount of *d*-menthol (218 mg, 1.40 mmol) and cyclohexene (57 mg, 0.70 mmol) and pyridine (11 mg, 0.14 mmol) successively under a nitrogen atmosphere. The mixture was stirred for 2 days at room temperature and extracted with dichloromethane. The organic layer was dried over sodium sulfate and evaporated at reduced pressure. After purification by HPLC (acetonitrile as eluent), oxyselenenylation product **15c** (16.6 mg, yield 38.1%) was obtained as a colorless oil.

Threo-1-{(R)-(2'-acetylamino-1,1'-binaphthalene)-2-ylseleno}-2-(d-menthoxy)-cyclooctane (**15a**). IR (neat) 2935, 1700, 1502, 1277 cm^{-1}; ^1H NMR (500 MHz): δ 8.60 (d, J = 8.6 Hz, 0.2 × 1H), 8.52 (d, J = 8.6 Hz, 0.8 × 1H), 8.00–6.87 (m, 12H), 3.76 (td, J = 7.5, 1.6 Hz, 0.2 × 1H), 3.55 (td, J = 7.5, 2.0 Hz, 0.8 × 1H), 3.50–3.38 (m, 1H), 3.02–2.92 (m, 1H), 1.81 (s, 0.8 × 3H), 1.79 (s, 0.2 × 3H), 1.76–1.10 (m, 21H), 0.85 (d, J = 7.0 Hz, 3H), 0.81 (d, J = 6.5 Hz, 3H), 0.69 (d, J = 6.9 Hz, 0.8 × 3H), 0.47 (d, J = 7 Hz, 0.2 × 3H); HRMS found: m/z 655.2931. Calcd for $C_{40}H_{49}NO_2Se$: M, 655.2926.

Threo-1-{(R)-(2'-acetylamino-1,1'-binaphthalene)-2-ylseleno}-2-(1-menthoxy)-cyclooctane (**15b**). IR (neat) 2935, 1700, 1508, 1503 cm^{-1}; ^1H NMR (500 MHz): δ 8.57 (d, J = 10 Hz, 1H), 8.05–6.72 (m, 12H), 3.79–3.73 (m, 0.39 × 1H), 3.67–3.59 (m, 0.61 × 1H), 3.57–3.44 (m, 0.61 × 1H), 3.43–3.35 (m, 0.39 × 1H), 3.06 (td, J = 7.5, 4.5 Hz, 0.39 × 1H), 2.96 (td, J = 7.0, 3.9 Hz, 0.61 × 1H), 1.79 (s, 0.61 × 3H), 1.68 (s, 0.39 × 3H), 1.64–0.75 (m, 21H), 0.72 (d, J = 6 Hz, 3H), 0.68 (d, J = 6 Hz, 3H), 0.66–0.46 (m, 3H); HRMS found: m/z 655.2894. Calcd for $C_{40}H_{49}NO_2Se$: M, 655.2926.

Threo-1-{(R)-(2'-acetylamino-1,1'-binaphthalene)-2-ylseleno}-2-(d-menthoxy)-cyclohexane (**15c**). IR (neat) 2940, 1700, 1600, 1510, 1505, 1280 cm^{-1}; ^1H NMR (500 MHz): δ 8.60 (d, J = 11 Hz, 0.15 × 1H), 8.55 (d, J = 11 Hz, 0.85 × 1H), 8.10–6.73 (m, 12H), 3.59–3.28 (m, 2H), 3.05 (td, J = 10.4, 3.9 Hz, 0.85 × 1H), 2.99 (td, J = 10.4, 4.3 Hz, 0.15 × 1H), 1.92 (s, 0.15 × 3H), 1.80 (s, 0.85 × 3H), 1.70–0.73 (m, 23H), 0.70 (d, J = Hz, 0.85 × 3H), 0.53 (d, J = 8 Hz, 0.15 × 3H); HRMS found: m/z 627.2596. Calcd for $C_{38}H_{45}NO_2Se$: M, 627.2612.

Threo-1-{(R)-(2'-acetylamino-1,1'-binaphthalene)-2-ylseleno}-2-(1-menthoxy)-cyclohexane (**15d**). IR (neat) 2900, 1680, 1593, 1490, 1270 cm^{-1}; ^1H NMR (500 MHz): δ 8.59 (d, J = 9.0 Hz, 1H), 8.01–6.75 (m, 12H), 3.61–3.56 (m, 0.59 × 1H), 3.46–3.38 (m, 0.41 × 1H), 3.38–3.29 (m, 1H), 3.04 (td, J = 10.3, 4.0 Hz, 1H), 2.35–0.72 (m, 26H), 0.71 (d, J = 6.9 Hz, 0.59 × 3H), 0.68 (d, J = 6.9 Hz, 0.41 × 3H); HRMS found: m/z 627.2523. Calcd for $C_{38}H_{45}NO_2Se$: M, 627.2613.

Erythro-2-{(R)-(2'-acetylamino-1,1'-binaphthalene)-2-ylseleno}-1-(d-menthoxy)-1-phenylpropane (**15g**). IR (neat) 2960, 2930, 1700, 1500, 1275 cm^{-1}; ^1H NMR (500 MHz): δ 8.61 (d, J = 9.5 Hz, 1H), 8.02–6.75 (m, 17H), 4.48 (d, J = 6.3 Hz, 0.1 × 1H), 4.36 (d, J = 6.3 Hz, 0.9 × 1H), 3.62–3.52 (m, 1H), 3.04 (td, J = 10.3, 3.8 Hz, 0.1 × 1H), 2.80 (td, J = 10.5, 4.0 Hz, 0.9 × 1H), 1.82 (s, 0.9 × 3H), 1.76 (s, 0.1 × 3H), 1.73–0.61 (m, 18H), 0.37 (d, J = 6 Hz, 0.1 × 3H), 0.28 (d, J = 6 Hz, 0.9 × 3H); HRMS found: m/z 663.2584. Calcd for $C_{41}H_{45}NO_2Se$: M, 663.2613.

Erythro-2-{(R)-(2'-acetylamino-1,1'-binaphthalene)-2-ylseleno}-1-(1-menthoxy)-1-phenylpropane (**15h**). IR (neat) 2900, 1720, 1492, 1270 cm^{-1}; ^1H NMR (500 MHz): δ 8.62 (d, J = 9.1 Hz, 0.44 × 1H), 8.55 (d, J = 9.0 Hz, 0.56 × 1H), 8.00–6.64 (m, 17H), 4.37 (d, J = 6.5 Hz, 0.44 × 1H), 4.31 (d, J = 6.5 Hz, 0.56 × 1H), 4.23 (td, J = 11.0, 5.7 Hz, 0.44 × 1H), 4.21 (td, J = 10.8, 6.0 Hz, 0.56 × 1H), 3.59–3.54 (m, 0.56 × 1H), 3.54–3.47 (m, 0.44 × 1H), 1.82 (s, 0.44 × 3H), 1.74 (s, 0.56 × 3H), 1.73–0.61 (m, 18H), 0.29 (d, J = 6.9 Hz, 0.44 × 3H), 0.25 (d, J = 6.8 Hz, 0.56 × 3H); HRMS found: m/z 663.2591. Calcd for $C_{41}H_{45}NO_2Se$: M, 663.2613.

Asymmetric Oxyselenenylation Using Silver O-acetylmandelate

General Procedure. To a dichloromethane solution (2 mL) of **2a** (14.1 mg, 0.0180 mmol), a 0.1 M tetrachloromethane solution of bromine (1.5 mL) was added dropwise at room temperature under a nitrogen atmosphere. After removal of the solvent and the excess amount of bromine, the residual selenenyl bromide **14** was dissolved in dichloromethane (1 mL), and, to the solution, was added a dichloromethane solution (2 mL) of silver (*S*)-*O*-acetylmandelate (10.9 mg, 0.0361 mmol), which was synthesized from the corresponding acid according to the literature [11]. The mixture was stirred in the dark for 1 hour at room temperature and was treated with cyclohexene (23.7 mg, 0.289 mmol). After the mixture had been stirred overnight, the silver bromide produced was filtered off

by short column chromatography (dichloromethane as eluent). The filtrate was evaporated under reduced pressure and then purified by HPLC (chloroform as eluent). Oxyselenenylation product **15e** (20.4 mg, yield 85.1%) was obtained as a colorless oil.

Threo-1-[2-{(R)-(2'-acetylamino-1,1'-binaphthalene)-2-ylseleno}-cyclohexyl]-(S)-2-acetoxy-phenylpropionate (**15e**). IR (neat) 2915, 1736, 1490, 1270, 1227 cm^{-1}; ^1H NMR (500 MHz): δ 8.57 (d, J = 12 Hz, 1H), 8.04–6.70 (m, 17H), 5.89 (s, 0.70 × 1H), 5.86 (s, 0.30 × 1H), 4.92–4.86 (m, 0.70 × 1H), 4.86–4.81 (m, 0.30 × 1H), 4.27–4.18 (m, 1H), 2.16 (s, 0.30 × 3H), 2.15 (s, 0.70 × 3H), 1.75 (s, 3H), 1.71–0.80 (m, 8H); HRMS found: m/z 665.1616. Calcd for $C_{38}H_{35}NO_5Se$: M, 665.1678.

Threo-1-[2-{(R)-(2'-acetylamino-1,1'-binaphthalene) -2-ylseleno} -cyclohexyl]- (R)-2-acetoxy-phenylpropionate (**15f**). IR (neat) 2915, 1737, 1491, 1270, 1224 cm^{-1}; ^1H NMR (500 MHz): δ 8.58–8.48 (m, 1H), 8.03–6.65 (m, 17H), 5.87 (s, 0.45 × 1H), 5.79 (s, 0.55 × 1H), 4.90–4.80 (m, 1H), 4.26–4.18 (m, 1H), 2.16 (s, 0.55 × 3H), 1.98 (s, 0.45 × 3H), 1.87 (s, 0.55 × 3H), 1.78 (s, 0.45 × 3H), 1.82–0.82 (m, 8H); HRMS found: m/z 665.1548. Calcd for $C_{38}H_{35}NO_5Se$: M, 665.1678.

Erythro-1- [2{(R)- (2'-acetylamino-1,1'-binaphthalene)-2-ylseleno} -1-phenylpropyl]- (S)-2-acetoxy-phenylpropionate (**15i**). IR (neat) 1740, 1684, 1492, 1268, 1223 cm^{-1}; ^1H NMR (500 MHz): δ 8.60 (d, J = 8.9 Hz, 0.23 × 1H), 8.37 (d, J = 8.9 Hz, 0.77 × 1H), 8.04–6.66 (m, 22H), 6.05 (s, 0.77 × 1H), 6.00 (d, J = 2.8 Hz, 0.77 × 1H), 5.92 (s, 0.23 × 1H), 5.76 (d, J = 2.8 Hz, 0.23 × 1H), 3.72–3.61 (m, 0.77 × 1H), 3.58–3.50 (m, 0.23 × 1H), 2.17 (s, 0.77 × 3H), 2.09 (s, 0.23 × 3H), 1.77 (s, 3H), 1.07 (d, J = 7.2 Hz, 0.77 × 3H), 1.06 (d, J = 7.2 Hz, 0.23 × 1H); HRMS found: m/z 701.1745. Calcd for $C_{41}H_{35}NO_5Se$: M, 701.1678.

Erythro-1- [2-{(R)- (2'-acetylamino-1,1'-binaphthalene)-2-ylseleno}-1-phenylpropyl]-(R)-2-acetoxyphenylpropionate (**15j**). IR (neat) 1740, 1683, 1490, 1224 cm^{-1}; ^1H NMR (500 MHz): δ 8.58 (d, J = 9.0 Hz, 0.20 × 1H), 8.46 (d, J = 9.0 Hz, 0.80 × 1H), 8.10–6.66 (m, 22H), 6.18 (d, J = 2.0 Hz, 0.80 × 1H), 6.03 (s, 0.80 × 1H), 5.91 (s, 0.20 × 1H), 5.71 (d, J = 5.0 Hz, 0.20 × 1H), 3.74–3.67 (m, 0.80 × 1H), 3.67–3.60 (m, 0.20 × 1H), 2.14 (s, 0.20 × 3H), 2.11 (s, 0.80 × 3H), 1.85 (s, 0.80 × 3H), 1.79 (s, 0.20 × 3H), 0.80 (d, J = 7.1 Hz, 3H); LRMS: (m/z) 701 (M^+), 107 (base); HRMS found: m/z 701.1803. Calcd for $C_{41}H_{35}NO_5Se$: M, 701.1678.

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