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Design of Optically Active Selenium Reagents Having a Chiral *Tertiary* Amino Group and Their Application to Asymmetric Inter- and Intramolecular Oxyselenenylations

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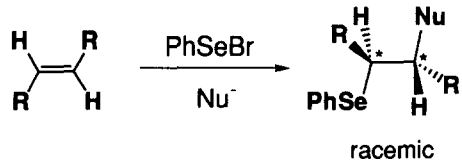
Abstract: A new class of chiral selenium reagents **4-7** was synthesized on the basis of the concept that the strong intramolecular interaction between an electrophilic selenium and an optically modified *tertiary* amine (Se···N interaction) would induce asymmetric induction in the reaction between the selenium reagent and olefins. When **7**, which showed the most powerful asymmetric induction, was applied to asymmetric methoxyselenenylation of (*E*)-phenylpropene under optimum reaction conditions, the highest diastereomeric excess (d.e.) of the *trans*-addition product was obtained (97 % d.e.). The same reaction conditions were employed in asymmetric methoxyselenenylation of various olefins (up to 97 % d.e.) and also in asymmetric intramolecular oxyselenenylation of terminal olefins (up to 59 % d.e.) and internal olefins (up to 98 % d.e.). The results show that this class of selenium reagents with a strong Se···N interaction is useful for asymmetric organic synthesis.

INTRODUCTION

Organic selenium compounds are frequently used as convenient reagents for introducing various functional groups into the carbon-carbon double bond[1] and for constructing a heterocyclic skeleton *via* an intramolecular ring-closure process.[2] Selenium reagents have some advantages for these purposes, because they are highly reactive enough to carry out the reaction under mild conditions at low temperature. Such unique properties of selenium reagents usually allows extremely high stereoselectivity.

Benzeneselenenyl bromide (PhSeBr) is one of the useful selenium reagents.[3] This reagent readily reacts with a carbon-carbon double bond in the presence of various nucleophiles, such as methanol and acetic acid,[4] to produce exclusively a *trans*-addition product which generally has two asymmetric carbon atoms (Scheme 1). The reaction, however, in principle provides only a racemic mixture of two possible enantiomers if there is no chiral source in the substrate. The focus of this paper is to modify this reaction for selective synthesis of one of the stereoisomers preferentially. The reaction is nothing more than asymmetric *trans*-addition, which will be of

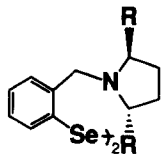


Scheme 1

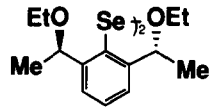
significant utility of the selenium methodology in general organic synthesis.

There are two possible ways for asymmetric modification of the reaction shown in Scheme 1 . One is to use an optically active selenium reagent and the other is to use an optically active nucleophile. Preliminary results showed that the former strategy[5,6] is much more effective than the latter.[7] This is quite reasonable because in ordinary cases the stereochemistry of the reaction product is determined by initial facial-selective addition process of the selenium reagent to the olefin, not by the subsequent regioselective quenching of the highly reactive cationic intermediate (a seleniranium cation) by a nucleophile.[6]

In our early attempts to obtain one of the stereoisomers preferentially,[5-10] a binaphthyl skeleton, which is well-known as a powerful inducer of asymmetric reactions,[11] was employed. We synthesized optically active selenobinaphthyl compounds and first applied them to asymmetric methoxyselenenylation of simple olefins. As a result, moderate diastereomeric excess (d.e.) was obtained (54 % d.e.).[8,9] Moreover, the d.e. was improved up to about 80 % d.e. by introducing another chiral source either in the selenobinaphthyl skeleton[6,8] or in the nucleophile.[7] A similar approach was recently reported by Fukuzawa et al.[12] They utilized an optically active ferrocenyl group having another chiral center on the side chain. By using this reagent, high diastereoselectivity (~ 98 % d.e.) was achieved though the chemical yield was low. Thus simple modifications of arylselenenyl bromide with powerful chiral sources such as binaphthyl and ferrocenyl skeletons have already met some extent of success in the literature. However, there still remain technical problems, such as difficulty in the synthesis, to be solved for practical use.



1



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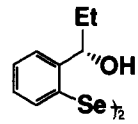


3

Recently it has been found by us[13] and other groups[14,15] that another class of optically active selenium compounds **1-3** show good asymmetric induction in similar reactions. These compounds have a heteroatom (nitrogen or oxygen) at the position segregated by four bonds from the selenium atom. For compound **1**, it was unambiguously demonstrated that there should be a strong Se···N intramolecular interaction when **1** is converted to the selenenyl bromide.[16] The strong interaction may allow chiral sources on the nitrogen atom to come close to the reaction center in the transition state of the reaction. Accordingly, distinct asymmetric induction is expected. For compounds **2**[14] and **3**,[15] there is no strong evidence for the existence of such an interaction. However, it is reasonable to assume that a similar intramolecular Se···O interaction plays some role in the

asymmetric induction because the Se···O interaction has been characterized for some other selenium derivatives.[17]

In this paper, we wish to describe briefly the fundamental concept of molecular design of chiral selenium reagent **1** having an intramolecular Se···N interaction. Applications of the new selenium reagents **4-7** to asymmetric methoxyselenenylation and intramolecular oxyselenenylation of olefins will be presented in some detail.

RESULTS AND DISCUSSION

1. Design of chiral selenium reagents.

Recently, we reported experimental characterization and evaluation of the intramolecular Se···N interaction of 2-selenobenzylamine derivatives.[16] It was found by NMR and X-ray analyses that the strength of the Se···N interaction depends on the electrophilicity of the selenium atom[18,19] and that, in the case of selenenyl bromide (Figure 1), the interaction is quite strong (>18.8 kcal), which means that the interaction is too strong to be cleaved at room temperature, and the molecular structure is approximately planar.[16] The mechanism of the interaction is revealed to be the electron donation of the amino nitrogen to the selenium from the backside of the Se-Br bond.

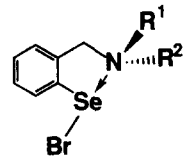


Figure 1

These properties of 2-selenobenzylamine derivatives are very useful for the design of chiral selenium reagents. The strong Se···N interaction should allow the chiral source located on R^1 and / or R^2 to come close to the reaction center during the reaction process. This will result in decent asymmetric induction. It is also expected that the strong Se···N interaction should dictate the molecular structure of the active selenium reagent so that the reaction proceeds through a relatively confined transition-state. This is a generally important point for the design of asymmetric reactions.

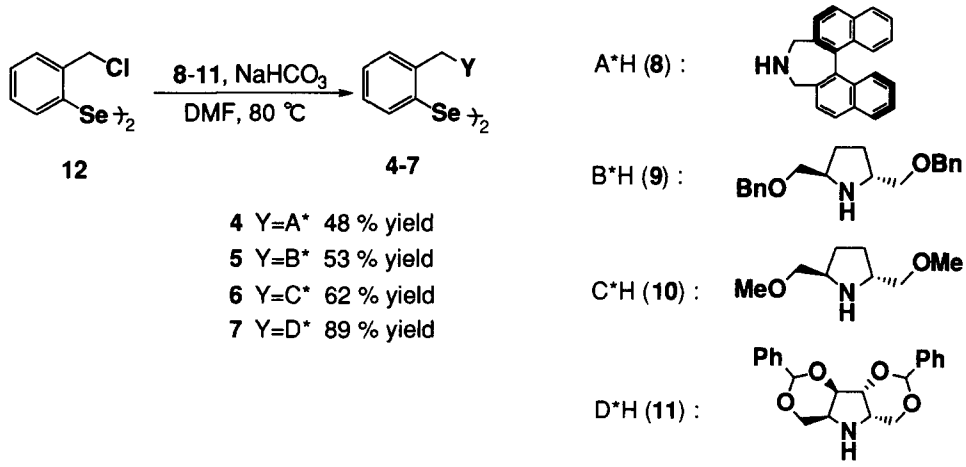
In applying the 2-selenobenzylamine skeleton to the syntheses of chiral selenium reagents, however, there is one problem concerning a nitrogen inversion. If substituent R^1 and R^2 on the nitrogen atom are different from each other, there are two possible conformations of the selenium reagent, which will significantly reduce the asymmetric induction of the reagent. To avoid this, we chose C_2-symmetrical cyclic amines, *i.e. trans*-2,5-disubstituted pyrrolidines as R^1 and R^2. Based on the idea using a 2-selenobenzylamine derivative and C_2-symmetrical cyclic amines, we designed four chiral selenium reagents **4-7**.

2. Syntheses of 4-7.

Four types of *secondary* amines with C_2-symmetry **8-11** were employed as chiral sources. Amine **8** has a binaphthyl skeleton as a part of the ring structure. Amines **9** and **10** have two flexible arms with an ethereal

oxygen atom. In the case of amine **11**, which is easily synthesized from a natural sugar (D-mannitol),[20] the arms are fixed by the dioxane rings.

Optically active diselenides **4-7** were synthesized in moderate yields as shown in Scheme 2 from 2,2'-diselenobis(benzyl chloride) **12**, which was prepared from methyl anthranilate *via* three steps,[18] and chiral cyclic amine **8-11**.



Scheme 2

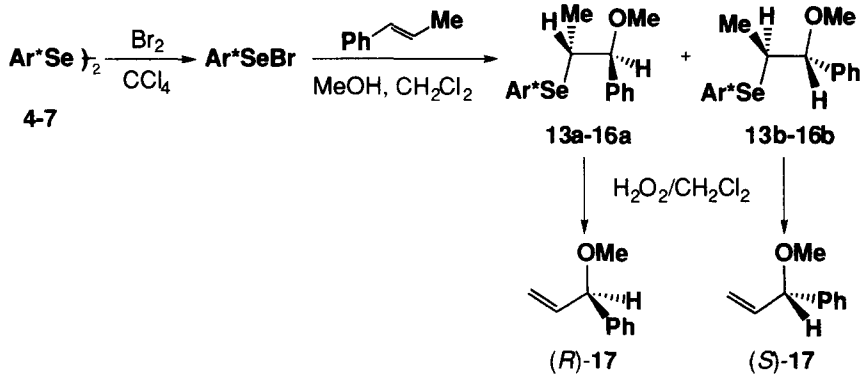
Among these four chiral selenium reagents, diselenide **7** has a synthetic advantage since the chiral source of the cyclic amine **11** is derived from D-mannitol and the yield of the final coupling reaction with **12** is high (89 %). After examining the conditions of the coupling reaction, the yield was increased up to 99 % by addition of an excess amount of potassium iodide. Accordingly, we could obtain **7** in grame scale very easily from an inexpensive chiral source. As mentioned below, it was revealed that **7** was the most powerful for asymmetric inducer among the four chiral selenium reagents we synthesized.

3. Asymmetric methoxyselenenylation of (*E*)-phenylpropene.

The utility of diselenides **4-7** as chiral inducers was demonstrated by asymmetric methoxyselenenylation of (*E*)-phenylpropene as shown in Scheme 3. Each diselenide was first converted to the reactive selenenyl bromide by addition of bromine, and then an olefin was allowed to react with the selenenyl bromide in the presence of methanol at controlled temperature. It should be noted that (*E*)-phenylpropene exclusively gave one regioisomer, α-methoxy-β-selenenylation product, under the reaction conditions employed. The d.e.'s of methoxyselenenylation product **13-16** determined by the integration of ^{1}H NMR absorptions are listed in Table 1. To determine the absolute stereochemistry of the major stereoisomer, **13-16** were oxidized with hydrogen peroxide to yield **17** at room temperature (Scheme 3), stereochemistry of which was then determined according to the literature method.[9]

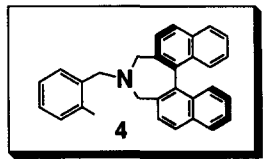
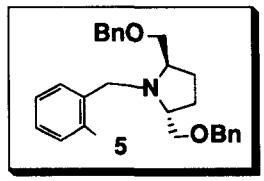
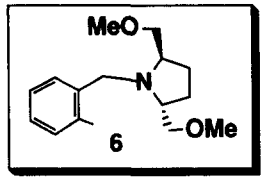
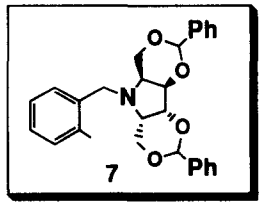
In all cases, the reaction temperature was raised because the reactions did not proceed at −78 ℃. The reaction was monitored by thin layer chromatography (TLC). In cases of Entries 2 and 4 (using **4** and **5**), the reactions proceeded near room temperature due to the low reactivity of the corresponding selenenyl bromides.

Therefore, each d.e. was nearly the same as the ones proceeded at room temperature (Entries 1 and 3). This is probably because the reactivity of the selenium reagents was suppressed by steric hindrance of the binaphthyl skeleton and the benzyl group. On the other hand, when **6** and **7** were employed, reactions proceeded at about



Scheme 3

Table 1 Asymmetric Methoxyselenenylation of (*E*)-Phenylpropene Using **4-7**

Entry	Ar*	Product **13-16**	Temp.	Yield (%)	**a** : **b**[1)]	d.e.(%)
1		**13**	r. t.	42	39 : 61	21
2			−78 ℃→r. t.	63	37 : 63	25
3		**14**	r. t.	90	54 : 46	8
4			−78 ℃→r. t.	79	46 : 54	7
5		**15**	r. t.	65	47 : 53	5
6			−78 ℃→r. t.	62	56 : 44	12
7		**16**	r. t.	84	64 : 36	28
8			−78 ℃→r. t.	85	76 : 24	52

[1)] The ratio was determined by the integration of ^{1}H NMR absorption at 500 MHz.

−40 ℃ and the diastereoselectivity of the reactions (Entries 6 and 8) was better than that obtained at room temperature (Entries 5 and 7) (5 to 12 % d.e. for **6**; 28 to 52 % d.e. for **7**). The d.e.'s are comparable with those attained by the use of optically active selenobinaphthyl derivatives.[6]

The asymmetric induction arises from the optically active cyclic amine introduced at the *ortho*-benzylic position of the arylseleno group. In the case of the reaction with (*E*)-olefins, the stereochemistry of the reaction product is determined by the step of the facial-selective addition of the selenium reagent to the olefin.[6] This process generates two diastereomeric seleniranium cations, which may generally equilibrate at low temperature before the nucloephilic attack of methanol takes place (Figure 2, a). Therefore, the equilibrium would probably decrease the stereoselectivity. On the other hand, in the case of a selenium reagent which possesses an intramolecular *tertiary* amino nitrogen such as **6** or **7**, the retro-reaction of the formation of seleniranium cations is suppressed because the seleniranium cations are stabilized by the coordination of the nitrogen to the electrophilic selenium (Figure 2, b). Therefore, it is expected that the stereoselectivity is enhanced at lower temperature because the transition state may be confined and the equilibrium between the two seleniranium cations may not take place. Thus the stereoselectivity is expected to increase by introducing a *tertiary* nitrogen. This is another reason for the use of a *tertiary* amino group as a chiral source in our molecular design.

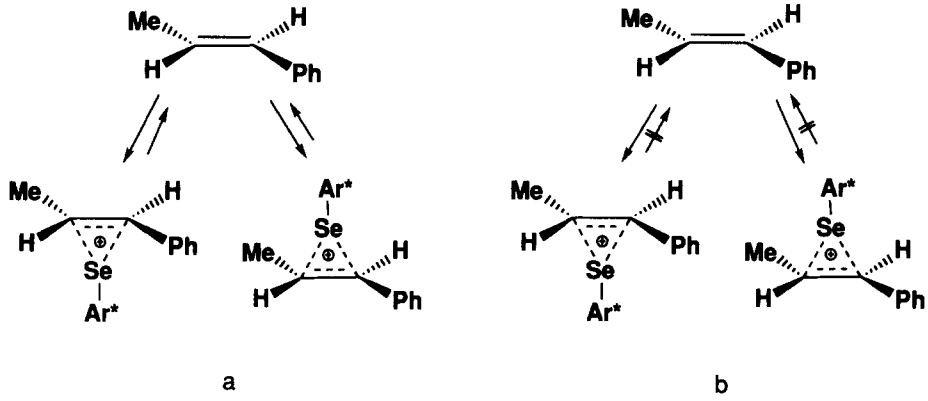


Figure 2

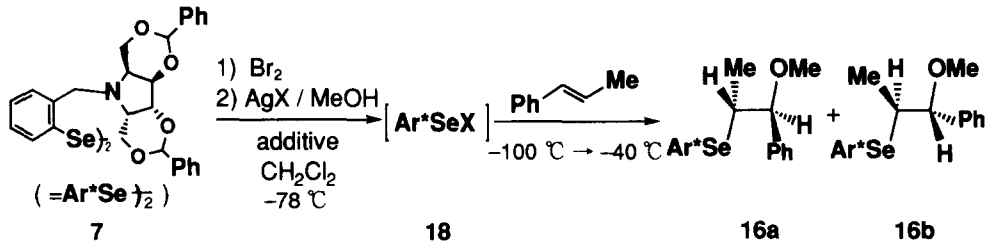
The relationship between the chiral selenium reagents and their asymmetric yields shows that diselenide **7** possessing a rigid three-ring skeleton gives a better d.e. than **5** and **6** possessing a *trans*-2,5-disubstituted pyrrolidine ring (7 % d.e. for **5** (Entry 4); 12 % d.e. for **6** (Entry 6); 52 % d.e. for **7** (Entry 8)). This is probably because diselenide **7** with the rigid skeleton affords more effective asymmetric environment than **5** and **6** with two flexible arms on the ring. In the following attempts to find optimum reaction conditions and to apply them to asymmetric reactions with various olefins, we used **7** as a chiral selenium reagent.

4. Optimizing reaction conditions.

In order to increase the d.e. of the asymmetric reaction, it is necessary to carry out the reaction at the temperature as low as possible. However, lowering the reaction temperature usually causes a reduction in reactivity of chiral selenium reagents. In the case of selenium reagent **7**, this effect is obvious: a lower limit of the reaction temperature was about −40 ℃. We therefore attempted to optimize the reaction conditions to

maximize the reactivity of the active selenium species so that the asymmetric reaction proceeds at lower temperature.[21]

Various selenoesters **18**, which were prepared *in situ* by the treatment of the selenenyl bromide with the corresponding silver salt, were utilized for asymmetric methoxyselenenylation of (*E*)-phenylpropene at the temperatures from −100 ℃ to −40 ℃ (Scheme 4, Table 2). Since these selenoesters **18** were much more reactive than the corresponding selenenyl bromide, the reactions were carried out at lower temperature than that employed for the selenenyl bromide. The selenoperchlorate (Entry 2) showed significant enhancement in the d.e. of the methoxyselenenylation product **16** (80 % d.e.) compared to the corresponding selenenyl bromide (52 % d.e., Entry 1). This suggested that a decrease in the nucleophilicity of the counter anion, *i.e.* an increase in the electrophilicity of the selenium reagent, is effective to enhance the d.e. of the reaction. We therefore examined the effect of the counter anion (Entries 3-6). Among these, the selenohexafluorophosphate (Entry 6) gave the highest d.e. (95 % d.e.). Moreover, when the reaction was performed in the presence of molecular sieves (M.S.) 4A, **16** was obtained in better chemical and asymmetric yield (75 % yield, 97 % d.e., Entry 7). This may be understood by assuming possible activation of the methoxyselenenylation by M.S.4A due to its acidic property. Thus the optimum reaction conditions were obtained by employing the selenohexafluorophosphate as a selenoester and M.S.4A as an additive.



Scheme 4

Table 2 Asymmetric Methoxyselenenylation of (*E*)-Phenylpropene Using Various Selenoesters (**18**)

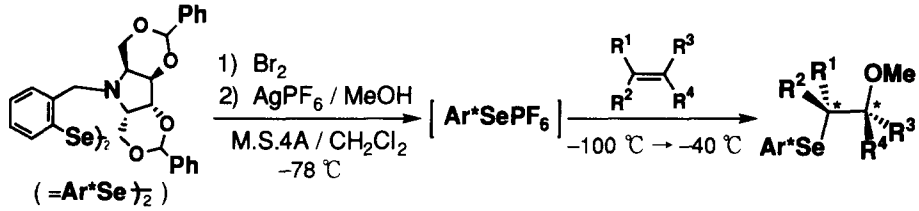
Entry	X of **18**	Additive	Yield (%)	**16a : 16b**[1)]	d.e. (%)
1[2)]	Br	none	85	3.2 : 1	52
2	ClO_4	none	47	9.0 : 1	80
3	OSO_2CF_3	none	68	17 : 1	89
4	BF_4	none	67	18 : 1	90
5	SbF_6	none	64	31 : 1	94
6	PF_6	none	58	37 : 1	95
7	PF_6	M.S.4A	75	64 : 1	97

[1)] The ratio was determined by the integration of ^1H NMR absorption at 500 MHz.
[2)] Taken from Table 1 Entry 8

5. Asymmetric methoxyselenenylation of various olefins.

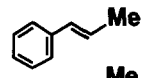
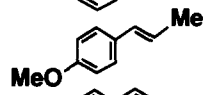
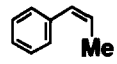
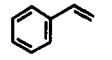
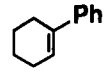
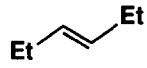
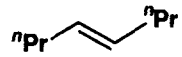
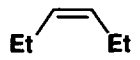
By using the optimum conditions described above, we subsequently performed asymmetric methoxyselenenylation of various olefins (Scheme 5). Table 3 lists the results of the reaction.

Styrene derivatives (Entries 1-5) exclusively gave one regioisomer, α-methoxy-β-selenenylation product, under the reaction conditions employed. The (*E*)-disubstituted styrenes (Entries 1 and 2) proceeded with high diastereoselectivity (97 % d.e. for **19a** and **19b**). On the other hand, symmetrical (*E*)-aliphatic olefins (Entries 6 and 7), the facial selectivity of which is difficult to control for various asymmetric reactions,[22] gave moderate d.e.'s (54 % d.e. for **19f** and 52 % d.e. for **19g**). Symmetrical (*Z*)-aliphatic olefins (Entries 8 and 9) gave slightly less d.e.'s (28 % d.e. for **19h**, 46 % d.e. for **19i**) than those for **19f** and **19g**. This is because the d.e. determining step for (*Z*)-olefins is not the facial stereoselection step of an optically modified selenenyl cation but the one involving capture of the nucleophile as previously described.[6]



Scheme 5

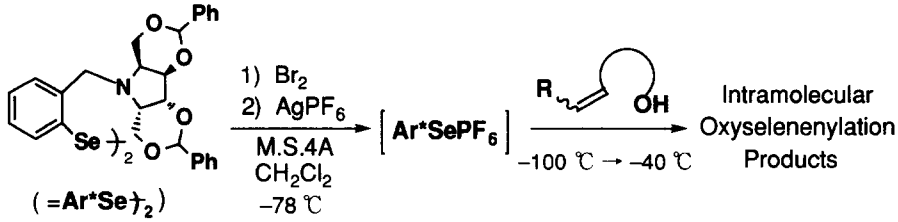
Table 3 Asymmetric Methoxyselenenylation of Various Olefins

Entry	Olefin	Product	Yield of **19** (%)	d.e. (%)[1)]
1		**19a**	75	97
2		**19b**	74	97
3		**19c**	30	57
4		**19d**	79	42
5		**19e**	82	35
6		**19f**	87	54
7		**19g**	80	52
8		**19h**	79	28
9		**19i**	84	46

[1)] The d.e. was determined by the integration of ^{1}H NMR absorption at 500 MHz.

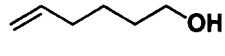
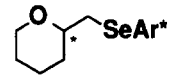
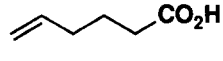
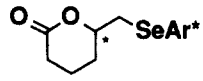
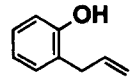
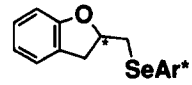
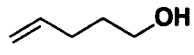
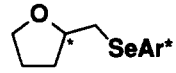
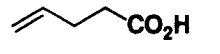
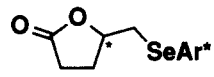
6. Asymmetric intramolecular oxyselenenylation of unsaturated alcohols and carboxylic acids.

If intramolecular oxyselenenylation proceeds with high diastereoselectivity, optically active cyclic ethers and lactones can be easily obtained. Therefore the method using **7** was applied to asymmetric selenoetherification of unsaturated alcohols and selenolactonization of unsaturated carboxylic acids (Scheme 6).[23]



Scheme 6

Table 4 Asymmetric Intramolecular Oxyselenenylation of *mono*-Substituted Olefins Containing Hydroxyl or Carboxyl Groups

Entry		Product **20**	Yield of **20** (%)	d.e. (%)[1]
1		 **20a**	80	59
2		 **20b**	90	39
3		 **20c**	83	13
4		 **20d**	100	22
5		 **20e**	81	57

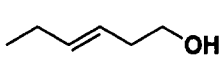
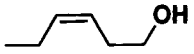
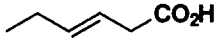
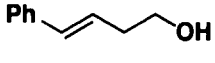
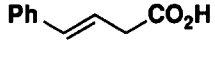
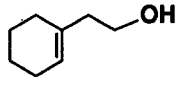
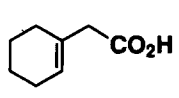
[1] The d.e. was determined by the integration of ^{1}H NMR absorption at 500 MHz.

We initially examined asymmetric reactions of various monosubstituted olefins (Table 4). All reactions proceeded immediately at −100 °C and the chemical yields were fairly good. In Entries 4 and 5, the corresponding five-membered product was exclusively obtained as a single product. In spite of difficulty in the diastereofacial selective control of the chiral selenium reagent toward monosubstituted olefins, moderate d.e.'s were obtained in Entries 1 and 5 (59 % d.e. for **20a** and 57 % d.e. for **20e**).

Encouraged by these results, we subsequently examined the diastereofacial selectivity of disubstituted olefins (Table 5, Entries 1-5). Asymmetric intramolecular selenoetherification of (*E*)-3-hexenol gave a much

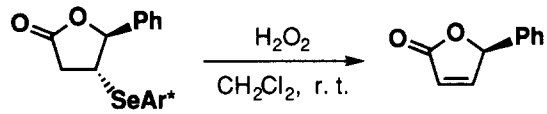
better d.e. than that of the corresponding (*Z*)-isomer (>98 % d.e. for **20f**, 56 % d.e. for **20g**). This tendency for facial selectivity is in accordance with that of the asymmetric methoxyselenenylation with (*E*)- and (*Z*)-phenylpropene (Table 3). When (*E*)-3-olefinic acids were employed as a disubstituted olefin, the intramolecular oxyselenenylations proceeded with high diastereoselectivity to provide the corresponding chiral selenolactones (>98 % d.e. for **20h**, 92 % d.e. for **20j**). We then examined the reaction of trisubstituted olefins containing cyclohexene ring (Table 5, Entries 6, 7). Both reactions proceeded in reasonable chemical yields and especially with cyclohexenyl acetic acid, the corresponding selenolactone **20l** was obtained in 93% d.e. (Table 5, Entry 7).

Table. 5 Asymmetric Intramolecular Oxyselenenylation of *di*-and *tri*-Substituted Olefins Containing Hydroxyl or Carboxyl Groups

Entry		Product **20**	Yield of **20** (%)	d.e. (%)[1]
1		**20f**[2]	86	>98
2		**20g**[3]	71	56
3		**20h**[2]	90	>98
4		**20i**[2]	88	94
5		**20j**	87	92
6		**20k**[2]	62	13
7		**20l**[2]	77	93[4]

[1] The d.e. was determined by the integration of ^{1}H NMR absorption at 500 MHz.
[2] The stereochemistry of the major isomer was assumed to be equal to **20j** (Entry 5).
[3] The stereochemistry of the major isomer was unknown.
[4] In our previous paper,[23] we indicated data in error because of decomposition of **20l** during purification procedure.

We have established only the absolute stereochemistry of the major isomer of **20j** so far by measuring the sign of optical rotation[24] of its oxidative deselenenylation product **21**, which is obtained by addition of hydrogen peroxide in dichloromethane at room temperature (Scheme 7). This tendency for facial selectivity of **7** toward a (*E*)-disubstituted olefin may hold in the asymmetric methoxyselenenylation with (*E*)-phenylpropene. Although the absolute stereochemistries of major isomers for other products have not been determined, they are assumed to be the same as that of **20j** for (*E*)-olefins (Table 5).



major isomer **20j** (+)-(*R*)-**21**

Scheme 7

CONCLUSIONS

Optically active diaryl diselenide **7**, which possesses a chiral pyrrolidine ring derived from D-mannitol at the *ortho*-benzylic position of the arylseleno group, shows high diastereoselectivities in both inter- and intramolecular asymmetric oxyselenenylations when **7** was converted to a highly reactive electrophilic selenium species by treating sequentially with bromine and silver hexafluorophosphate under the optimum conditions. In these asymmetric reactions, the strong Se···N interaction plays important role to keep the chiral source close to the reaction center and to fix the conformation of the reactive species. It is found that the molecular design of chiral selenium reagents according to this line is very useful.

EXPERIMENTAL SECTION

General. Infrared (IR) spectra were recorded on a Shimazu IR-435 spectrometer. 90 MHz ^{1}H-NMR, 200 MHz ^{1}H-NMR, 270 MHz ^{1}H-NMR and 500 MHz ^{1}H-NMR were measured on a Varian EM 390, Bruker AC-200, JEOL JMNGX-270 and Bruker AMX-500 instrument, respectively, in chloroform-*d*$_1$ containing tetramethylsilane (TMS) as an internal standard. ^{13}C-NMR and ^{77}Se-NMR were measured on a JEOL FX90Q instrument in chloroform-*d*$_1$. Chemical shifts are shown by the lower field shifts from TMS as an internal standard and from dimethylselenide as an 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. High-resolution FAB mass spectra were recorded on a JEOL HX110 mass spectrometer. All melting points are uncorrected. Reactions were monitored by thin-layer chromatography (TLC) using pre-coated silica-gel plates (Merck Kieselgel 60 F-254 Art.5715). Column chromatography was carried out with silica gel (Wakogel C-300, Wako) or alumina (activated alumina, 300 mesh, Wako). High performance liquid chromatography (HPLC) was done with JAI LC-908 instruments using JAIGEL-1H, 2H. Methanol and dichloromethane were distilled from calcium hydride and stored over molecular

sieves 3A and 4A, respectively. All oxyselenenylation reactions were carried out under a dry nitrogen atmosphere.

2,2'-Diselenobis(benzyl chloride) (12): The preparation of **12** was described in our previous literature.[18]

Chiral amines **8**[25], **9**[26], **11**[20] were prepared according to the literatures. The pyrrolidine **10** was purchased from JANSSEN CHIMICA.

***N,N'*-(Diselenodi-2,1-phenylenemethylene)bis[(*S*)-(+)-3,5-dihydro-4*H*-dinaphth[2,1-*c*:1',2'-*e*]azepine] (4)**: Amine **8** (49 mg, 0.17 mmol) and **12** (32 mg, 0.079 mmol) were dissolved in *N,N*-dimethylformamide (3 ml) and sodium hydrogen carbonate (17 mg, 0.20 mmol) was added to the solution. The reaction mixture was stirred for 12 hours at 80 ℃. An aqueous solution of sodium hydroxide (2 N) was then added to the cooled reaction solution. The mixture was extracted with dichloromethane. The organic layer was then washed with a saturated aqueous solution of sodium chloride, dried over sodium sulfate and evaporated under reduced pressure. After purification of the crude products by column chromatography on silica gel (hexane-ethyl acetate as eluent), pure **4** (35 mg, 0.039 mmol) was obtained as yellow powder (48 % yield). m.p. 173.0 - 173.5 ℃; $[\alpha]_D^{25}$ −24° (c 0.193, $CHCl_3$); IR (CH_2Cl_2): 3100, 1210, 750, 670 cm^{-1}; ^{1}H-NMR (200 MHz): δ (ppm) 8.08 - 7.06 (m, 32H), 3.76 (d, J = 9.3 Hz, 4H), 3.70 (d, J = 12.3 Hz, 4H), 3.23 (d, J = 12.3 Hz, 4H); ^{13}C-NMR: δ 60.0, 53.9 ppm; ^{77}Se-NMR: δ 438.1 ppm; HRMS Found: m/z 464.0878. Calcd for $C_{29}H_{22}NSe$: M/2, 464.0919.

5 and **6** were prepared according to the above procedure.

***N,N'*-(Diselenodi-2,1-phenylenemethylene)bis[(2*R*,5*R*)-bis(benzyloxymethyl)pyrrolidine] (5)**: pale yellow oil (53 % yield). $[\alpha]_D^{25}$ +30° (c 0.40, $CHCl_3$); IR (CH_2Cl_2): 2910, 2840, 1450, 1258, 1090, 730 cm^{-1}; ^{1}H-NMR (90 MHz): δ (ppm) 7.67 - 6.60 (m, 28H), 4.37 (s, 8H), 4.13 (d, J = 13 Hz, 2H), 3.93 (d, J = 13 Hz, 2H), 3.67 - 3.33 (m, 8H), 3.33 - 2.90 (m, 4H), 2.23 - 1.48 (m, 8H); ^{13}C-NMR: δ 73.2, 72.1, 61.2, 54.5, 27.5 ppm; ^{77}Se-NMR: δ 418.4 ppm; LRMS: m/z 480 (M^+/2); HRMS Found: m/z 480.1411; Calcd for $C_{27}H_{30}NO_2Se$: M/2, 480.1439.

***N,N'*-(Diselenodi-2,1-phenylenemethylene)bis[(2*R*,5*R*)-bis(methoxymethyl)pyrrolidine] (6)**: yellow oil (62 % yield). $[\alpha]_D^{25}$ +52.8° (c 0.711, $CHCl_3$); IR (neat): 2978, 2812, 1584, 1444, 1100, 752 cm^{-1}; ^{1}H-NMR (200 MNz): δ (ppm) 7.72 - 7.06 (m, 8H), 4.16 (d, J = 14 Hz, 2H), 4.03 (d, J = 14 Hz, 2H), 3.43 - 3.29 (m, 8H), 3.25 (s, 12H), 3.25 - 3.17 (m, 4H), 2.08 - 1.97 (m, 4H), 1.72 - 1.62 (m, 4H); ^{13}C-NMR: δ 139.5, 132.4, 130.4, 128.0, 127.6, 125.6, 74.8, 60.7, 58.8, 54.3, 27.5 ppm; ^{77}Se-NMR: δ 420.1 ppm; Anal Calcd for $C_{30}H_{44}O_4N_2Se_2$: C, 55.04; H, 6.77; N, 4.28 %. Found: C, 55.06; H, 7.05; N, 4.24 %.

In the case of preparation of **7**, addition of an excess amount of potassium iodide improved chemical yield significantly. This procedure is described below.

***N,N'*-(Diselenodi-2,1-phenylenemethylene)bis[1,3:4,6-di-*O*-benzylidene-2,5-dihydro-2,5-epimino-L-iditol] (7)**: Amine **11** (144 mg, 0.425 mmol) and **12** (81.8 mg, 0.200 mmol) were dissolved in *N,N*-dimethylformamide (5 ml) and sodium hydrogen carbonate (44.2 mg, 0.526 mmol) and potassium iodide (202 mg, 1.21 mmol) were added to the solution, which was stirred overnight at room temperature. An aqueous solution of sodium hydroxide (2 N) was then added to the reaction solution and the mixture was extracted with dichloromethane. The organic layer was then washed with a saturated aqueous solution of sodium chloride, dried over sodium sulfate and evaporated under reduced pressure. After purification

of the crude products by column chromatography on alumina (hexane-ethyl acetate as eluent), pure **7** (200 mg, 0.197 mmol) was obtained as yellow powder (98.7 % yield). m.p. 125 - 127 ℃; $[\alpha]_D^{25}$ +141° (c 0.714, $CHCl_3$); IR (KBr): 2900, 2850, 1385, 1115, 980, 750 cm^{-1}; ^{1}H-NMR (270 MHz): δ (ppm) 7.90 - 6.95 (m, 28H), 5.49 (s, 4H), 4.73 (d, J = 15 Hz, 2H), 4.37 (d, J = 2.0 Hz, 4H), 4.21 (d, J = 13 Hz, 4H), 4.06 (d, J = 15 Hz, 2H), 3.92 (d, J = 12 Hz, 4H), 3.50 (s, 4H); ^{13}C-NMR: δ 99.9, 79.5, 66.7, 59.1, 56.0 ppm; ^{77}Se-NMR: δ 414.5 ppm; LRMS: m/z 508 (M^+/2), 105 (base); Anal Calcd for $C_{54}H_{52}O_8N_2Se_2$: C, 63.93; H, 5.43; N, 2.77 % Found: C, 63.90; H, 5.16; N, 2.76 %.

General procedure for asymmetric methoxyselenenylation (Scheme 3). To a dichloromethane solution (2 ml) of **7** (23.7 mg, 0.0234 mmol) 0.2 M tetrachloromethane solution of bromine (0.13 ml) was added dropwise and stirred for 30 min at room temperature under nitrogen atmosphere. After removal of the solvent *in vacuo*, residual selenenyl bromide was dissolved in methanol (2 ml) and dichloromethane (1 ml) and to the solution was added dichloromethane solution (1 ml) of (*E*)-phenylpropene (44.1 mg, 0.374 mmol) at −78 ℃ under nitrogen atmosphere. The resulting mixture was stirred overnight from −78 ℃ to room temperature. A saturated aqueous solution of sodium hydrogen carbonate was added to the reaction mixture which was then extracted with dichloromethane. The combined organic layers were dried over sodium sulfate and the solvent was evaporated under reduced pressure. After purification by column chromatography on silica gel (hexane-ethyl acetate as eluent), methoxyselenenylation product **16** (26.0 mg, 0.0198 mmol) was obtained as a colorless oil (84.7 % yield).

***N*-[2-{((1*S*/*R*,2*R*/*S*)-2-Methoxy-1-methyl-2-phenylethyl)seleno}benzyl]-(*S*)-(+)-3,5-dihydro-4*H*-dinaphth[2,1-*c*:1',2'-*e*]azepine (13)**: IR (neat): 3056, 2930, 1454, 1267, 1125, 1083, 818, 739, 704 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.98 - 7.18 (m, 21H), 4.45 (d, J = 4.3 Hz, 0.62×1H), 4.40 (d, J = 4.3 Hz, 0.38×1H), 3.82 (d, J = 12.6 Hz, 0.38×1H), 3.77 (d, J = 12.6 Hz, 0.62×1H), 3.64 (d, J = 12.2 Hz, 0.38×2H), 3.63 (d, J = 12.2 Hz, 0.62×2H), 3.62 - 3.49 (m, 2H), 3.32 (s, 0.62×3H), 3.28 (s, 0.38×3H), 3.18 (d, J = 12.4 Hz, 0.38×2H), 3.16 (d, J = 12.4 Hz, 0.62×2H), 1.37 (d, J = 6.9 Hz, 0.38×3H), 1.34 (d, J = 6.9 Hz, 0.62×3H); HRMS Found: m/z 613.1868. Calcd for $C_{39}H_{35}NOSe$: M, 613.1882.

***N*-[2-{((1*S*/*R*,2*R*/*S*)-2-Methoxy-1-methyl-2-phenylethyl)seleno}benzyl]-(2*R*,5*R*)-bis(benzyloxymethyl)pyrrolidine (14)**: IR (neat): 2840, 1450, 1077, 740, 693 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.50 - 7.01 (m, 19H), 4.45 (s, 4H), 4.40 - 4.35 (m, 1H), 4.14 (d, J = 13.4 Hz, 1H), 3.96 (d, J = 13.7 Hz, 1H), 3.50 - 3.28 (m, 7H), 3.26 (s, 3H), 2.12 - 1.95 (m, 2H), 1.80 - 1.60 (m, 2H), 1.32 (d, J = 6.4 Hz, 3H); HRMS Found: m/z 629.2530. Calcd for $C_{37}H_{43}NO_3Se$: M, 629.2406.

***N*-[2-{((1*R*/*S*,2*S*/*R*)-2-Methoxy-1-methyl-2-phenylethyl)seleno}benzyl]-(2*R*,5*R*)-bis(methoxymethyl)pyrrolidine (15)**: IR (neat): 2786, 1458, 1197, 1110, 754, 704 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.49 - 7.10 (m, 9H), 4.43 - 4.40 (m, 1H), 4.14 (d, J = 14.3 Hz, 0.44×1H), 4.13 (d, J = 14.3 Hz, 0.56×1H), 3.93 (d, J = 14.3 Hz, 0.44×1H), 3.89 (d, J = 14.3 Hz, 0.56×1H), 3.43 - 3.38 (m, 1H), 3.31 - 3.15 (m, 6H), 3.30 (s, 3H), 3.26 (s, 0.44×3H), 3.24 (s, 0.56×3H), 2.01 - 1.93 (m, 2H), 1.70 - 1.64 (m, 2H), 1.36 (d, J = 6.8 Hz, 0.56×3H), 1.35 (d, J = 6.8 Hz, 0.44×3H); HRMS Found: m/z 477.1765. Calcd for $C_{25}H_{35}NO_3Se$: M, 477.1780.

***N*-[2-{((1*R*/*S*,2*S*/*R*)-2-Methoxy-1-methyl-2-phenylethyl)seleno}benzyl]-1,3:4,6-di-*O*-benzylidene-2,5-dihydro-2,5-epimino-L-iditol (16)**: IR (neat): 2900, 2840, 1448, 1385, 1120, 1080, 1018, 750 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.72 - 7.12 (m, 19H), 5.51 (s, 0.015×2H), 5.50 (s, 0.985×2H), 4.80 (d, J = 16 Hz, 0.015×1H), 4.75 (d, J = 16 Hz, 0.985×1H), 4.46 (d, J = 4.4 Hz, 0.015×1H),

4.41 (d, J = 2.3 Hz, 2H), 4.36 (d, J = 4.4 Hz, 0.985×1H), 4.13 (d, J = 13 Hz, 2H), 3.99 (d, J = 16 Hz, 0.015×1H), 3.94 (dd, J = 13, 2.3 Hz, 2H), 3.91 (d, J = 16 Hz, 0.985×1H), 3.52 (s, 2H), 3.52 - 3.48 (m, 1H), 3.28 (s, 0.015×3H), 3.26 (s, 0.985×3H), 1.37 (d, J = 7.1 Hz, 0.985×3H), 1.33 (d, J = 7.1 Hz, 0.015×3H); HRMS Found: m/z 657.1853. Calcd for $C_{37}H_{39}NO_5Se$: M, 657.1991.

General procedure for oxidative deselenenylation of 13-16 (Scheme 3). To a dichloromethane solution (1.5 ml) of **15** (13.5 mg, 0.0284 mmol), 30 % hydrogen peroxide (0.3 ml) was added dropwise. The resulting mixture was stirred overnight at room temperature and was then filtered through short column chromatography on silica gel (dichloromethane as eluent). The filtrate was evaporated under reduced pressure to provide crude **17** in 72 % yield, which was confirmed by integration of ^{1}H-NMR absorption due to - OCH_3 *versus* internal standard.

General procedure for asymmetric methoxyselenenylation by preparing the selenoester (Scheme 4). To a dichloromethane solution (2 ml) of **7** (20.2 mg, 0.0199 mmol) in the presence of M.S.4A (20 mg), a 0.1 M tetrachloromethane solution of bromine (0.20 ml) was added dropwise to afford selenenyl bromide at −78 °C under nitrogen atmosphere. After 20 min stirring, a 0.70 M methanol solution of silver hexafluorophosphate (65 μl, 0.046 mmol) was added. The resulting heterogeneous mixture of selenohexafluorophosphate was stirred at −78 ℃ for 20 min and cooled to −100 °C. Then a dichloromethane solution (1 ml) of (*E*)-phenylpropene (38 mg, 0.32 mmol) was added at −100 °C. The resulting mixture was stirred for several hours from −100 °C to −40 °C. It was then quenched with aqueous sodium hydrogen carbonate solution at −40 °C and filtered off by celite to remove M.S.4A. The filtrate was extracted with dichloromethane. The combined organic layers were dried over sodium sulfate and the solvent was evaporated under reduced pressure. After purification by column chromatography on silica gel (hexane-ethyl acetate as eluent), methoxyselenenylation product **16** (=**19a**) (19.6 mg, 0.0149 mmol) was obtained as a colorless oil (75.1 % yield).

***N*-[2-[{(1*R*/*S*,2*S*/*R*)-2-Methoxy-1-methyl-2-(4-methoxyphenyl)ethyl}seleno]benzyl]-1,3:4,6-di-*O*-benzylidene-2,5-dihydro-2,5-epimino-L-iditol (19b)**: IR (neat): 2908, 1512, 1456, 1247, 1125, 1029, 758, 698 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.71 - 6.79 (m, 18H), 5.49(s, 2H), 4.79 (d, J = 16.4 Hz, 0.015×1H), 4.74 (d, J = 16.4 Hz, 0.985×1H), 4.40 (d, J = 2.3 Hz, 2H), 4.29 (d, J = 5.1 Hz, 1H), 4.12 (d, J = 12.9 Hz, 2H), 3.94 (dd, J = 13.0, 2.2 Hz, 2H), 3.89 (d, J = 16.6 Hz, 1H), 3.77 (s, 0.015×3H), 3.76 (s, 0.985×3H), 3.53 (s, 2H), 3.51 - 3.47 (m, 1H), 3.24 (s, 0.015×3H), 3.23 (s, 0.985×3H), 1.38 (d, J = 7.0 Hz, 0.985×3H), 1.34 (d, J = 7.0 Hz, 0.015×3H); HRMS Found: m/z 687.2078. Calcd for $C_{38}H_{41}NO_6Se$: M, 687.2097.

***N*-[2-{((1*S*/*R*,2*S*/*R*)-2-Methoxy-1-methyl-2-phenylethyl)seleno}benzyl]-1,3:4,6-di-*O*-benzylidene-2,5-dihydro-2,5-epimino-L-iditol (19c)**: IR (neat): 2924, 2856, 1456, 1392, 1125, 1089, 1025, 992, 756, 700 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.76 - 7.08 (m, 19H), 5.50 (s, 0.79×2H), 5.49 (s, 0.21×2H), 4.79 (d, J = 16.8 Hz, 0.79×1H), 4.78 (d, J = 16.8 Hz, 0.21×1H), 4.41 (d, J = 2.1 Hz, 2H), 4.20 (d, J = 7.0 Hz, 0.79×1H), 4.17 (d, J = 7.0 Hz, 0.21×1H), 4.11 (d, J = 12.9 Hz, 0.79×2H), 4.09 (d, J = 12.9 Hz, 0.21×2H), 3.93 (dd, J = 13.0, 2.1 Hz, 2H), 3.84 (d, J = 16.9 Hz, 1H), 3.62 - 3.56 (m, 1H), 3.53 (s, 0.21×2H), 3.51 (s, 0.79×2H), 3.22 (s, 0.79×3H), 3.19 (s, 0.21×3H), 1.19 (d, J = 7.0 Hz, 0.79×3H), 1.12 (d, J = 7.0 Hz, 0.21×3H); HRMS Found: m/z 657.1819. Calcd for $C_{37}H_{39}NO_5Se$: M, 657.1991.

***N*-[2-{2-(1-Methoxy-1-phenylethyl)seleno}benzyl]-1,3:4,6-di-*O*-benzylidene-2,5-dihydro-2,5-epimino-L-iditol (19d)**: IR (neat): 2906, 2856, 1456, 1392, 1125, 1025, 992, 758, 700 cm^{-1};

^{1}H-NMR (500 MHz): δ (ppm) 7.66 - 7.10 (m, 19H), 5.49 (s, 2H), 4.71 (d, J = 16.0 Hz, 0.29×1H), 4.70 (d, J = 16.0 Hz, 0.71×1H), 4.40 (d, J = 2.3 Hz, 0.71×2H), 4.39 (d, J = 2.3 Hz, 0.29×2H), 4.36 (dd, J = 8.4, 5.4 Hz, 0.29×1H), 4.34 (dd, J = 8.4, 5.4 Hz, 0.71×1H), 4.13 (d, J = 12.9 Hz, 0.71×2H), 4.12 (d, J = 12.9 Hz, 0.29×2H), 3.95 (d, J = 2.4 Hz, 0.71×2H), 3.94 (d, J = 2.4 Hz, 0.29×2H), 3.92 - 3.85 (m, 1H), 3.34 (dd, J = 12.1, 8.2 Hz, 0.29×1H), 3.29 (dd, J = 12.1, 8.2 Hz, 0.71×1H), 3.21 (s, 0.71×3H), 3.20 (s, 0.29×3H), 3.10 (dd, J = 12.2, 5.1 Hz, 0.71×1H), 3.04 (dd, J = 12.2, 5.1 Hz, 0.29×1H); HRMS Found: m/z 643.1848. Calcd for $C_{36}H_{37}NO_5Se$: M, 643.1835.

(1*R*/*S*,2*S*/*R*)-2-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-Diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)]-1-methoxy-1-phenylcyclohexane (19e): IR (neat): 2936, 2858, 1450, 1390, 1156, 1125, 1067, 1027 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.60 - 6.90 (m, 19H), 5.49 (s, 0.32×2H), 5.46 (s, 0.68×2H), 4.56 (d, J = 16.3 Hz, 0.32×1H), 4.38 (d, J = 16.3 Hz, 0.68×1H), 4.38 (d, J = 2.2 Hz, 0.32×2H), 4.36 (d, J = 2.2 Hz, 0.68×2H), 4.05 (d, J = 12.9 Hz, 0.32×2H), 3.97 (d, J = 12.9 Hz, 0.68×2H), 3.89 (dd, J = 8.3, 2.1 Hz, 0.68×2H), 3.87 (dd, J = 8.3, 2.1 Hz, 0.32×2H), 3.68 (brs, 0.32×1H), 3.64 (brs, 0.68×1H), 3.52 (d, J = 16.4 Hz, 1H), 3.45 (s, 0.32×2H), 3.42 (s, 0.68×2H), 2.89 (s, 0.32×3H), 2.88 (s, 0.68×3H), 2.00 - 1.50 (m, 8H); HRMS Found: m/z 697.2327. Calcd for $C_{40}H_{43}NO_5Se$: M, 697.2304.

(3*R*/*S*,4*S*/*R*)-3-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-Diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)]-4-methoxyhexane (19f): IR (neat): 2968, 2914, 2856, 1456, 1392, 1127, 1025, 994 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.74 - 7.08 (m, 14H), 5.50 (s, 2H), 4.82 (d, J = 16.5 Hz, 0.23×1H), 4.80 (d, J = 16.5 Hz, 0.77×1H), 4.41 (d, J = 2.2 Hz, 2H), 4.14 (d, J = 13.0 Hz, 2H), 3.99 (d, J = 16.6 Hz, 1H), 3.94 (dd, J = 12.9, 2.2 Hz, 2H), 3.55 (s, 2H), 3.36 - 3.28 (m, 2H), 3.32 (s, 3H), 1.83 - 1.55 (m, 4H), 1.05 (t, J = 7.3 Hz, 0.77×3H), 1.03 (t, J = 7.3 Hz, 0.23×3H), 0.90 (t, J = 7.4 Hz, 0.77×3H), 0.87 (t, J = 7.4 Hz, 0.23×3H); HRMS Found: m/z 623.2078. Calcd for $C_{34}H_{41}NO_5Se$: M, 623.2148.

(4*R*/*S*,5*S*/*R*)-4-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-Diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)]-5-methoxyoctane (19g): IR (neat): 2960, 2912, 2872, 1456, 1392, 1125, 1025, 992, 756, 698 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.76 - 7.11 (m, 14H), 5.50 (s, 2H), 4.81 (d, J = 16.5 Hz, 0.24×1H), 4.78 (d, J = 16.5 Hz, 0.76×1H), 4.41 (d, J = 2.1 Hz, 2H), 4.15 (d, J = 12.9 Hz, 0.24×2H), 4.14 (d, J = 12.9 Hz, 0.76×2H), 3.99 (d, J = 16.6 Hz, 0.76×1H), 3.98 (d, J = 16.6 Hz, 0.24×1H), 3.94 (dd, J = 13.0, 2.1 Hz, 2H), 3.55 (s, 2H), 3.41 - 3.32 (m, 2H), 3.31 (s, 3H), 1.76 - 1.24 (m, 8H), 0.87 (t, J = 7.4 Hz, 3H), 0.85 (t, J = 7.3 Hz, 3H); HRMS Found: m/z 651.2475. Calcd for $C_{36}H_{45}NO_5Se$: M, 651.2460.

(3*R*/*S*,4*R*/*S*)-3-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-Diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)]-4-methoxyhexane (19h): IR (neat): 2966, 2928, 2856, 1458, 1390, 1125, 1089, 1027, 992 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.74 - 7.12 (m, 14H), 5.50 (s, 2H), 4.78 (d, J = 16.6 Hz, 0.64×1H), 4.77 (d, J = 16.6 Hz, 0.36×1H), 4.41 (d, J = 2.2 Hz, 2H), 4.14 (d, J = 12.9 Hz, 0.36×2H), 4.13 (d, J = 12.9 Hz, 0.64×2H), 3.98 (d, J = 16.8 Hz, 0.64×1H), 3.96 (d, J = 16.8 Hz, 0.36×1H), 3.94 (dd, J = 12.9, 2.0 Hz, 2H), 3.55 (s, 2H), 3.36 - 3.29 (m, 1H), 3.34 (s, 0.64×3H), 3.32 (s, 0.36×3H), 3.27 - 3.22 (m, 0.64×1H), 3.21 - 3.17 (m, 0.36×1H), 1.96 - 1.52 (m, 4H), 1.05 (t, J = 7.3 Hz, 0.36×3H), 1.04 (t, J = 7.3 Hz, 0.64×3H), 0.92 (t, J = 7.4 Hz, 0.36×3H), 0.88 (t, J = 7.4 Hz, 0.64×3H); HRMS Found: m/z 623.2147. Calcd for $C_{34}H_{41}NO_5Se$: M, 623.2148.

(1*R*/*S*,2*R*/*S*)-1-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-Diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)]-2-methoxycyclopentane (19i): IR (neat): 2964, 2908, 2858, 1456, 1392, 1125, 1089, 1025, 992 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.73 - 7.14 (m, 14H), 5.50 (s, 2H), 4.74 (d, J = 16.1 Hz, 0.27×1H), 4.71 (d, J = 16.1 Hz, 0.73×1H), 4.40 (d, J = 2.2 Hz, 2H), 4.15 (d, J = 12.9 Hz, 2H), 3.95 (d, J = 13.0 Hz, 1H), 3.94 (dd, J = 13.0, 1.6 Hz, 2H), 3.78 - 3.75 (m, 1H), 3.71 - 3.64 (m, 1H), 3.53 (s, 2H), 3.21 (s, 0.73×3H), 3.18 (s, 0.27×3H), 2.27 - 2.18 (m, 1H), 2.04 - 1.97 (m, 1H), 1.81 - 1.60 (m, 4H); HRMS Found: m/z 607.1773. Calcd for $C_{33}H_{37}NO_5Se$: M, 607.1835.

General procedure for asymmetric intramolecular oxyselenenylation (Scheme 6). To a dichloromethane solution (2 ml) of **7** (21.4 mg, 0.0211 mmol) in the presence of M.S.4A (20 mg) a 0.1 M tetrachloromethane solution of bromine (0.21 ml) was added dropwise to afford selenenyl bromide at −78 °C under nitrogen atmosphere. After 20 min stirring, a 0.32 M dichloromethane solution of silver hexafluorophosphate (150 μl, 0.048 mmol) was added. The resulting heterogeneous mixture of selenohexafluorophosphate was stirred at −78 ℃ for 20 min and cooled to −100 °C. Then a dichloromethane solution (1 ml) of 4-pentenoic acid (34 mg, 0.34 mmol) was added at −100 °C. The resulting mixture was stirred for several hours from −100 °C to −40 °C. It was then quenched with aqueous sodium hydrogen carbonate solution at −40 °C and filtered off by celite to remove M.S.4A. The filtrate was extracted with dichloromethane. The combined organic layers were dried over sodium sulfate and the solvent was evaporated under reduced pressure. After purification by HPLC (chloroform as eluent), the corresponding selenolactone **20e** (20.8 mg, 0.0171 mmol) was obtained as a colorless oil (81.1 % yield).

2-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-Diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)methyl]oxane (20a): IR (neat): 2934, 2852, 1456, 1392, 1125, 1089, 1025, 992 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.71 - 7.12 (m, 14H), 5.49 (s, 2H), 4.73 (d, J = 16.1 Hz, 1H), 4.40 (d, J = 2.3 Hz, 2H), 4.15 (d, J = 12.9 Hz, 0.20×2H), 4.14 (d, J = 12.9 Hz, 0.80×2H), 4.01 - 3.91 (m, 4H), 3.53 (s, 2H), 3.49 - 3.37 (m, 2H), 3.07 (dd, J = 12.2, 6.6 Hz, 0.20×1H), 3.04 (dd, J = 12.2, 6.6 Hz, 0.80×1H), 2.92 (dd, J = 12.1, 6.0 Hz, 0.80×1H), 2.88 (dd, J = 12.1, 6.0 Hz, 0.20×1H), 1.82 - 1.24 (m, 6H); HRMS Found: m/z 607.1891. Calcd for $C_{33}H_{37}NO_5Se$: M, 607.1835.

δ-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-Diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)methyl]-δ-valerolactone (20b): IR (neat): 2910, 2858, 1734, 1241, 1125, 1027 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.63 - 7.16 (m, 14H), 5.50 (s, 2H), 4.76 (d, J = 15.7 Hz, 0.70×1H), 4.72 (d, J = 15.7 Hz, 0.30×1H), 4.49 - 4.32 (m, 1H), 4.40 (d, J = 2.3 Hz, 2H), 4.12 (d, J = 12.8 Hz, 2H), 3.96 (dd, J = 13.0, 2.2 Hz, 2H), 4.02 - 3.90 (m, 1H), 3.51 (s, 2H), 3.31 (dd, J = 12.7, 4.8 Hz, 0.30×1H), 3.21 (dd, J = 12.7, 4.8 Hz, 0.70×1H), 3.04 (dd, J = 12.8, 8.2 Hz, 0.70×1H), 2.95 (dd, J = 12.8, 8.2 Hz, 0.30×1H), 2.52 - 2.31 (m, 2H), 1.90 - 1.42 (m, 4H); HRMS Found: m/z 621.1572. Calcd for $C_{33}H_{35}NO_6Se$: M, 621.1628.

2-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-Diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)methyl]-2,3-dihydrobenzofuran (20c): IR (neat): 2908, 2856, 1481, 1456, 1230, 1125, 1019, 992 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.65 - 6.70 (m, 18H), 5.49 (s, 2H), 4.99 - 4.89 (m, 1H), 4.75 (d, J = 13.8 Hz, 0.43×1H), 4.72 (d, J = 13.8 Hz, 0.57×1H), 4.40 (d, J = 2.3 Hz, 0.57×2H), 4.39 (d, J = 2.3 Hz, 0.43×2H), 4.13 (d, J = 6.3 Hz, 0.43×2H), 4.11 (d, J = 6.3 Hz, 0.57×2H), 3.98 - 3.91 (m, 3H), 3.51 (s, 2H), 3.37 (dd, J = 12.3, 5.2 Hz, 0.43×1H), 3.30 (dd, J = 12.3, 5.2

Hz, 0.57×1H), 3.33 - 3.26 (m, 1H), 3.11 (dd, J = 12.4, 7.9 Hz, 0.57×1H), 3.05 (dd, J = 12.4, 7.9 Hz, 0.43×1H), 3.03 (dd, J = 15.8, 6.8 Hz, 0.43×1H), 2.97 (dd, J = 15.8, 6.8 Hz, 0.57×1H); HRMS Found: m/z 641.1651. Calcd for $C_{36}H_{35}NO_5Se$: M, 641.1678.

2-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-Diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)methyl]oxolane (20d): IR (neat): 2974, 2908, 2860, 1456, 1392, 1125, 1029, 992 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.67 - 7.12 (m, 14H), 5.49 (s, 2H), 4.73 (d, J = 16 Hz, 0.61×1H), 4.71 (d, J = 16 Hz, 0.39×1H), 4.40 (d, J = 2.0 Hz, 2H), 4.15 (d, J = 13 Hz, 2H), 4.12 - 4.06 (m, 1H), 3.96 (d, J = 16 Hz, 1H), 3.94 (dd, J = 13, 2.2 Hz, 2H), 3.92 - 3.86 (m, 1H), 3.77 - 3.71 (m, 1H), 3.53 (s, 2H), 3.14 (dd, J = 12, 5.6 Hz, 0.39×1H), 3.11 (dd, J = 12, 5.6 Hz, 0.61×1H), 2.97 (dd, J = 12, 7.1 Hz, 0.61×1H), 2.93 (dd, J = 12, 7.1 Hz, 0.39×1H), 2.08 - 2.00 (m, 1H), 1.95 - 1.77 (m, 2H), 1.68 - 1.61 (m, 1H); HRMS Found: m/z 593.1693. Calcd for $C_{32}H_{35}NO_5Se$: M, 593.1678.

δ-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-Diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)]-γ-valerolactone (20e): IR (neat): 2916, 2858, 1773, 1458, 1394, 1170, 1125, 760, 700 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.61 - 7.18 (m, 14H), 5.50 (s, 2H), 4.76 (d, J = 16 Hz, 0.79×1H), 4.73 (d, J = 16 Hz, 0.21×1H), 4.70 - 4.64 (m, 0.21×1H), 4.62 - 4.57 (m, 0.79×1H), 4.40 (d, J = 2.3 Hz, 2H), 4.11 (d, J = 13 Hz, 2H), 3.96 (dd, J = 13, 2.4 Hz, 2H), 3.98 - 3.94 (m, 1H), 3.51 (s, 2H), 3.36 (dd, J = 13, 4.9 Hz, 0.21×1H), 3.25 (dd, J = 13, 4.9 Hz, 0.79×1H), 3.01 (dd, J = 13, 8.3 Hz, 0.79×1H), 2.92 (dd, J = 13, 8.3 Hz, 0.21×1H), 2.52 - 2.28 (m, 3H), 1.99 - 1.80 (m, 1H); HRMS Found: m/z 607.1456. Calcd for $C_{32}H_{33}NO_6Se$: M, 607.1471.

(2*S*/*R*,3*R*/*S*)-2-Ethyl-3-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)]oxolane(20f) : IR (neat): 2968, 2918, 2856, 1456, 1392, 1125, 1025, 992 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.71 - 7.13 (m, 14H), 5.50 (s, 2H), 4.76 (d, J = 16.2 Hz, 1H), 4.41 (d, J = 2.3 Hz, 2H), 4.13 (d, J = 12.9 Hz, 2H), 3.96 (d, J = 16.3 Hz, 1H), 3.95 (dd, J = 12.9, 2.2 Hz, 2H), 3.89 - 3.81 (m, 2H), 3.77 - 3.72 (m, 1H), 3.53 (s, 2H), 3.39 - 3.34 (m, 1H), 2.41 (dq, J = 13.0, 7.6 Hz, 1H), 2.05 - 1.97 (m, 1H), 1.66 - 1.56 (m, 1H), 1.52 - 1.43 (m, 1H), 0.93 (t, J = 7.4 Hz, 3H); HRMS Found: m/z 607.1838. Calcd for $C_{33}H_{37}NO_5Se$: M, 607.1835.

(2*S*/*R*,3*S*/*R*)-2-Ethyl-3-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)]oxolane(20g): IR (neat): 2966, 2912, 2860, 1456, 1392, 1125, 1089, 1023, 992 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.75 - 7.13 (m, 14H), 5.51 (s, 2H), 5.49 - 5.39 (m, 1H), 5.31 - 5.23 (m, 1H), 4.81 (d, J = 16.3 Hz, 0.23×1H), 4.78 (d, J = 16.3 Hz, 0.77×1H), 4.42 (d, J = 2.2 Hz, 0.23×2H), 4.41 (d, J = 2.2 Hz, 0.77×2H), 4.03 - 3.91 (m, 1H), 3.96 (dd, J = 12.9, 2.2 Hz, 2H), 3.66 - 3.59 (m, 1H), 3.55 (s, 0.77×2H), 3.54 (s, 0.23×2H), 3.35 - 3.21 (m, 1H), 2.28 - 2.18 (m, 1H), 2.11 - 1.92 (m, 2H), 1.92 - 1.77 (m, 1H), 1.13 (t, J = 7.3 Hz, 0.77×3H), 1.08 (t, J = 7.3 Hz, 0.23×3H); HRMS Found: m/z 607.1871. Calcd for $C_{33}H_{37}NO_5Se$: M, 607.1835.

(3*R*/*S*,4*S*/*R*)-γ-Ethyl-β-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)]-γ-butyrolactone (20h): IR (neat): 2974, 2910, 2856, 1779, 1392, 1158, 1125, 1087, 1021, 990 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.63 - 7.17 (m, 14H), 5.50 (s, 2H), 4.74 (d, J = 15.5 Hz, 1H), 4.40 (d, J = 2.2 Hz, 2H), 4.39 - 4.36 (m, 1H), 4.09 (d, J = 12.9 Hz, 2H), 3.97 (d, J = 15.5 Hz, 1H), 3.96 (dd, J = 13.0, 2.3 Hz, 2H), 3.65 (td, J = 8.2, 6.6 Hz, 1H), 3.50 (s, 2H), 2.99 (dd, J = 18.2, 8.6 Hz, 1H), 2.61 (dd, J = 13.0, 7.9 Hz, 1H), 1.74 - 1.64 (m, 1H), 1.61 - 1.51 (m, 1H), 0.93 (t, J = 7.4 Hz, 3H); HRMS Found: m/z 621.1587. Calcd for

$C_{33}H_{35}NO_6Se$: M, 621.1628.

(2*S*/*R*,3*R*/*S*)-2-Phenyl-3-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)]oxolane (20i): IR (neat): 2906, 2858, 1456, 1392, 1125, 1027, 992 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.65 - 7.02 (m, 19H), 5.49 (s, 0.97×2H), 5.47 (s, 0.03×2H), 4.85 (d, J = 6.3 Hz, 1H), 4.74 (d, J = 16.2 Hz, 0.03×1H), 4.70 (d, J = 16.2 Hz, 0.97×1H), 4.39 (d, J = 2.3 Hz, 0.97×2H), 4.35 (d, J = 2.3 Hz, 0.03×2H), 4.15 - 4.10 (m, 1H), 4.09 - 4.03 (m, 1H), 4.06 (d, J = 12.7 Hz, 2H), 3.91 (dd, J = 13.0, 2.2 Hz, 2H), 3.86 (d, J = 16.2 Hz, 1H), 3.58 (dt, J = 7.8, 6.1 Hz, 1H), 3.48 (s, 0.97×2H), 3.37 (s, 0.03×2H), 2.55 - 2.47 (m, 1H), 2.17 - 2.08 (m, 1H); HRMS Found: m/z 655.1839. Calcd for $C_{37}H_{37}NO_5Se$: M, 655.1835.

(3*R*/*S*,4*S*/*R*)-γ-Phenyl-β-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)]-γ-butyrolactone (20j): IR (neat): 2918, 2856, 1785, 1125, 990, 758, 698 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.58 - 7.06 (m, 19H), 5.49 (s, 0.96×2H), 5.46 (s, 0.04×2H), 5.41 (d, J = 6.4 Hz, 0.96×1H), 5.37 (d, J = 6.4 Hz, 0.04×1H), 4.72 (d, J = 15.5 Hz, 0.04×1H), 4.68 (d, J = 15.5 Hz, 0.96×1H), 4.39 (d, J = 2.2 Hz, 0.96×2H), 4.31 (d, J = 2.2 Hz, 0.04×2H), 4.03 (d, J = 13.0 Hz, 2H), 3.92 (dd, J = 13.0, 2.1 Hz, 2H), 3.88 (d, J = 15.7 Hz, 1H), 3.82 (dt, J = 8.0, 6.5 Hz, 1H), 3.46 (s, 2H), 3.10 (dd, J = 18.1, 8.4 Hz, 0.96×1H), 3.04 (dd, J = 18.1, 8.4 Hz, 0.04×1H), 2.76 (dd, J = 18.1, 7.8 Hz, 0.04×1H), 2.71 (dd, J = 18.1, 7.8 Hz, 0.96×1H); HRMS (FAB) Found: m/z 669.1720. Calcd for $C_{37}H_{35}NO_6Se$: M, 669.1628.

(3a*S*/*R*,7a*S*/*R*)-3a-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-Diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)]octahydrobenzofuran (20k): IR (neat): 2930, 2860, 1456, 1390, 1125, 1023, 988 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.88 - 7.12 (m, 14H), 5.50 (s, 2H), 4.90 (d, J = 16.0 Hz, 0.43×1H), 4.86 (d, J = 16.0 Hz, 0.57×1H), 4.42 (d, J = 2.2 Hz, 0.57×2H), 4.41 (d, J = 2.2 Hz, 0.43×2H), 4.16 - 4.09 (m, 2H), 4.06 (d, J = 17.0 Hz, 0.57×1H), 4.05 (d, J = 17.0 Hz, 0.43×1H), 3.96 (d, J = 12.9 Hz, 2H), 3.90 - 3.82 (m, 1H), 3.82 - 3.73 (m, 2H), 3.56 (s, 0.57×2H), 3.53 (s, 0.43×2H), 2.28 - 1.39 (m, 10H); HRMS Found: m/z 633.1923. Calcd for $C_{35}H_{39}NO_5Se$: M, 633.1991.

(3a*S*/*R*,7a*S*/*R*)-3a-[2-{(2*R*,4a*S*,5a*S*,8*R*,9a*R*,9b*R*)-2,8-Diphenyl(hexahydro-5*H*-bis[1,3]dioxino[4,5-*b*:4',5'-*d*]pyrrol-5-yl)}methyl(phenylseleno)]-2(3*H*)-hexahydrobenzofuranone (20l): IR (neat): 2938, 2862, 1783, 1456, 1394, 1243, 1205, 1158, 1125, 1089, 1023, 992 cm^{-1}; ^{1}H-NMR (500 MHz): δ (ppm) 7.59 - 7.18 (m, 14H), 5.63 (s, 0.11×2H), 5.51 (s, 0.89×2H), 4.82 (d, J = 16.8 Hz, 0.89×1H), 4.74 (d, J = 16.8 Hz, 0.11×1H), 4.43 (d, J = 2.2 Hz, 0.89×2H), 4.41 (d, J = 2.2 Hz, 0.11×2H), 4.14 - 4.08 (m, 1H), 4.06 (d, J = 12.9 Hz, 2H), 4.02 (d, J = 17.1 Hz, 1H), 3.97 (dd, J = 13.0, 2.0 Hz, 2H), 3.58 (s, 0.11×2H), 3.55 (s, 0.89×2H), 2.69 (d, J = 16.7 Hz, 0.89×1H), 2.63 (d, J = 16.7 Hz, 0.11×1H), 2.53 (d, J = 16.7 Hz, 1H), 2.02 - 1.83 (m, 3H), 1.75 - 1.40 (m, 5H); HRMS (FAB) Found: m/z 647.1797. Calcd for $C_{35}H_{37}NO_6Se$: M, 647.1784.

Oxidative deselenenylation of 20j (Scheme 7). To a dichloromethane solution (2 ml) of **20j** (71.6 mg, 0.107 mmol), 30 % hydrogen peroxide (0.5 ml) was added dropwise. The resulting mixture was stirred overnight at room temperature. It was quenched with aqueous sodium hydrogen carbonate solution and was extracted with dichloromethane. The organic layer was then washed with aqueous saturated ammonium chloride, dried over sodium sulfate and the solvent was evaporated under reduced pressure. After purification by HPLC (chloroform as eluent), the corresponding unsaturated lactone **21** (7.2 mg, 0.045 mmol) was obtained as

a colorless oil (42 % yield).

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