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First Synthesis of Optically Pure Selenuranes and Stereoselective Alkaline Hydrolysis. Their Application to Asymmetric [2,3] Sigmatropic Rearrangement of Allylic Selenoxides

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Abstract : The first synthesis of optically pure selenuranes **1** has been accomplished by utilizing 2-*exo*-hydroxy-10-bornyl group as a chiral ligand. Complete retention of the configuration has been observed in alkaline hydrolysis of **1** to give selenoxides **2**. The structure of **1** and **2** has been fully established by X-ray crystallography. [2,3] Sigmatropic rearrangement of allylic selenoxides **2** gave the corresponding allylic alcohols **3** with up to 88% enantiomeric excess (ee). The [2,3] sigmatropic rearrangement of allylic selenoxides **2** progresses predominantly *via* an *endo* transition state.

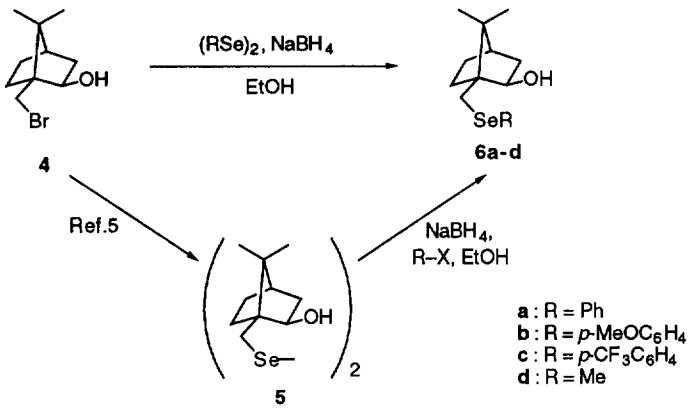
INTRODUCTION

Although the synthesis, structural features of hypervalent organoselenium species (selenurane) have been fairly well reported,[1] the stereochemistry of the optically active selenuranes is little known.[1d,e] In particular, the stereochemical aspects of the nucleophilic substitution reactions of selenuranes have not been reported. We report here the first synthesis of the optically pure selenuranes **1** using 2-*exo*-hydroxy-10-bornyl group as a chiral ligand, and established the new method for the synthesis of optically pure selenoxides **2** by diastereoselective alkaline hydrolysis of the haloselenuranes **1**.[2] We also report their application to asymmetric [2,3] sigmatropic rearrangement of allylic selenoxides, leading to chiral allylic alcohols **3**.

RESULTS AND DISCUSSION

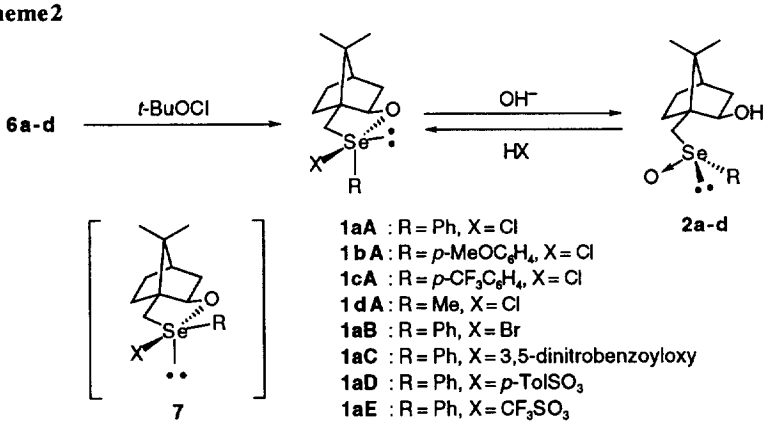
Synthesis, Structure and Reaction of Selenuranes. Selenides **6** were prepared by two routes shown in Scheme 1. One is a reaction of (1*S*)-10-bromo-2-*exo*-borneol[3] with sodium aryl or methylselenolate,[4] and the other is a reaction of alkyl halides with sodium bornylselenolate prepared from diselenide **5**[5] and sodium borohydride. Both routes readily afforded selenides **6** in good yield.

Scheme 1



Oxidation of selenides **6a-d** with *t*-BuOCl was complete within 10 min at 0 ℃ to give chloroselenuranes **1a-dA** (X = Cl) as a single diastereomer (89-100% yield) (Scheme 2). Addition of aqueous $NaHCO_3$ to a CH_2Cl_2 solution of **1a-dA** at 0 ℃ instantaneously resulted in complete hydrolysis, leading to the selenoxide **2a-d** as a sole product (90-100% yield). Treatment of the selenoxide **2a** with HCl gave chloroselenurane **1aA** as a single diastereomer (100% yield). In a similar manner, bromoselenurane **1aB** was obtained by treatment of **2a** with HBr (96% yield). The selenuranes **1aC-E** were also prepared by the reaction of the selenoxide **2a** with 3,5-dinitrobenzoic acid, *p*-toluenesulfonic acid and trifluoromethanesulfonic acid in the presence of $MgSO_4$ (88-91% yield). No selenuranes **7**, epimeric at selenium, were detected in all of these reactions. Formation of the selenuranes **7** might be unfavorable because of steric repulsion between the 7-methyl group of the bornyl moiety and the aryl or methyl group.

Scheme2



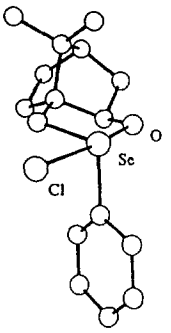


Figure 1 The crystal structure of **1aA**.

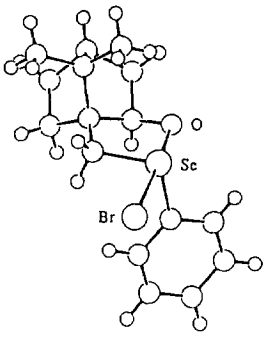
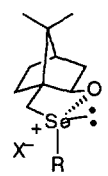


Figure 2 The crystal structure of **1aB**.

The structures of the chloroselenurane **1aA** and bromoselenurane **1aB** were determined by X-ray analysis as a trigonal-bipyramidal (TBP) structure (*R* configuration[6] at the selenium center) (Figs. 1 and 2, respectively). The apical-bond distances of Se–O [1.838(5) Å and 1.835(6) Å, respectively] are shorter than the sum of van der Waals radii (3.40 Å), indicating transannular bond formation between Se and O. The Se–Cl bond length [2.587(2) Å] and the Se–Br bond length [2.703(2) Å] are shorter than the sums of van der Waals radii (3.80 and 3.90 Å, respectively), and little longer than that of diphenyl selenium dichloride (2.30 Å) and that of diphenyl selenium dibromide (2.42 Å), respectively.[1c] The ^{77}Se NMR chemical shift (δ 901 and δ 909, respectively) of **1aA** and **1aB** is characteristic for the selenuranes.[1f-k] The formation of the other chloroselenuranes **1b-dA** is evidenced by the ^{77}Se NMR spectra (δ 858–906). The ^{77}Se NMR chemical shift (δ 922) of **1aC** is characteristic for the selenuranes and a carbonyl absorption of **1aC** showed 1623 cm^{-1} in the FT-IR spectrum, which is lower than that of an acyloxyselenurane reported previously.[1g] The ^{77}Se NMR chemical shifts (δ 1015 and 1058) of **1aD** and **1aE** are shifted to the lower field compared to that of **1aA**, suggesting that those selenuranes have a tendency to show ionic character represented by the structure **8** (Fig. 3).



8

Figure 3

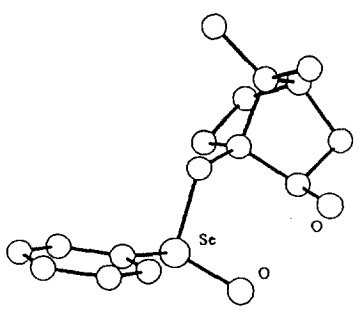
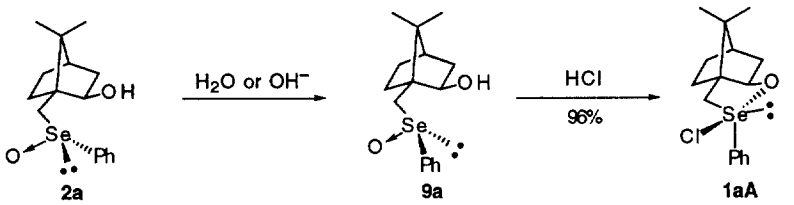


Figure 4 The crystal structure of **2a**.

The absolute configuration of the selenium atom in **2a** is unequivocally established to be *R* by X-ray crystallography (Fig. 4). Selenoxide **2** is stable at room temperature in the solid state or in aprotic solvents. The configurational stability of **2** could be attributed to the stabilization by a bulkiness of the bornyl group

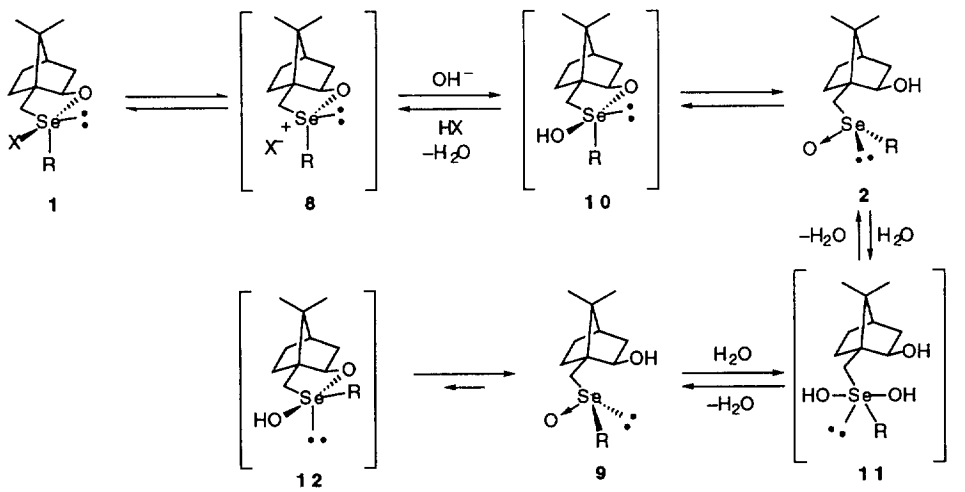
as well as an intramolecular hydrogen bond between the seleninyl oxygen and the secondary hydroxyl group. The presence of the intramolecular hydrogen bond is supported by a 3299 cm^{-1} absorption in the FT-IR spectrum of a highly dilute (0.005M) CCl_4 solution of **2a**. No epimerization of selenoxide **2a** in aqueous solution was observed at room temperature for 10 min, but the treatment of **2a** with MeOH-H_2O (4 : 1) or 1N aqueous NaOH in MeOH for a longer time (24 h) gave an equilibrium mixture of **2a** and **9a**, approximately in a ratio of 2 : 1 (Scheme 3). Interestingly, treatment of the mixture of **2a** and **9a** (2 : 1) with 1N aqueous HCl in MeOH yielded **1aA** as an exclusive product (96% yield).

Scheme 3



Stereochemistry of Interconversion Reaction between the Selenuranes and the Selenoxides. Alkaline hydrolysis of the selenurane **1** proceeds with retention of configuration to afford the selenoxide **2** as a sole product. Treatment of **2** with aqueous or alkaline solution for a long time afforded an equilibrium mixture of **2** and **9**.

Scheme 4

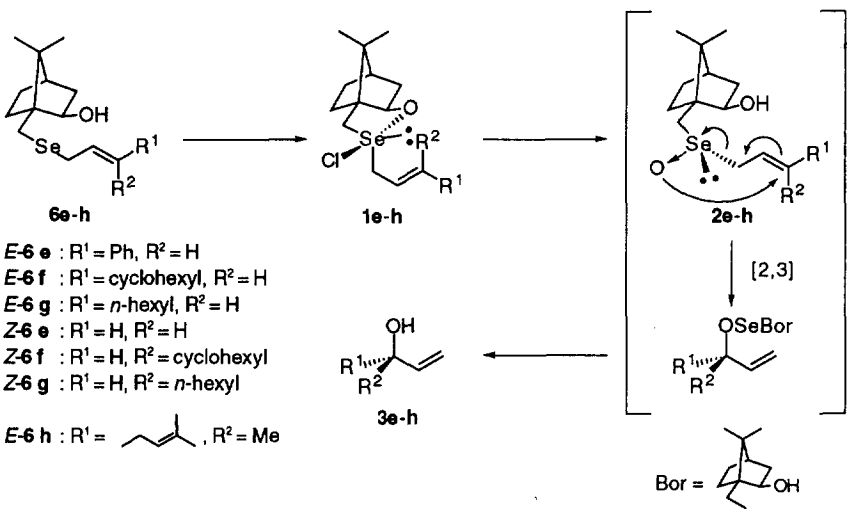


Treatment of a mixture of **2** and **9** with HX gave **1** as a single diastereomer. These results can be reasonably explained by assuming the alkoxyselenonium ion **8**, hydroxyselenuranes **10** and **12** and dihydroxyselenurane **11** as shown in Scheme 4.

In the hydrolysis of selenurane **1**, the selenurane **1** gives the alkoxyselenonium ion **8** by dissociation of the Se–X bond, followed by stereoselective association with OH^-, leading to **10**. Hydroxyselenurane **10** decomposes to give selenoxide **2** by cleavage of the oxaselenurane ring. Treatment of **2** with aqueous or alkaline solution generates dihydroxyselenurane **11** to give an equilibrium mixture of the selenoxides **2** and **9**. Formation of selenuranes **1** from selenoxide **2** can be explained by the reverse pathway involving the generation of **10** by protonation of seleninyl oxygen, followed by intramolecular attack of secondary hydoxy group. In the presence of X^-, **10** is converted to the corresponding **1** by dissociation of the Se–OH bond, followed by stereoselective association of the resulting ion **8** with X^-. Formation of **12** is so unfavorable that selenoxide **9** epimerizes to afford **2** *via* dihydroxyselenurane **11**.

Asymmetric [2,3] Sigmatropic Rearrangement of Chiral Allylic Selenoxides. Asymmetric [2,3] sigmatropic rearrangement of chiral allylic selenoxides have been reported by Reich,[7] Davis,[8] and Uemura.[9] The key steps of those [2,3] sigmatropic rearrangements are enantio- or diastereoselective oxidation of the allylic selenides and transfer of the chirality of the selenium atom to C-3 of the resulting allylic alcohols. In those papers, the stereochemical aspects for the [2,3] sigmatropic rearrangement of the allylic selenoxides have not been fully elucidated.

Scheme 5



E-**6 e** : R^1 = Ph, R^2 = H
E-**6 f** : R^1 = cyclohexyl, R^2 = H
E-**6 g** : R^1 = *n*-hexyl, R^2 = H
Z-**6 e** : R^1 = H, R^2 = H
Z-**6 f** : R^1 = H, R^2 = cyclohexyl
Z-**6 g** : R^1 = H, R^2 = *n*-hexyl
E-**6 h** : R^1 = , R^2 = Me

We intended to utilize the above mentioned diastereoselective hydrolysis of chloroselenuranes **1** for the *in situ* formation of optically active allylic selenoxides **2e-h**, whose [2,3] sigamtropic rearrangement should afford chiral allylic alcohols **3e-h**.

Allylic selenides **6e-h** were prepared in 67–98% yield from diselenide **5** and corrsponding allyl halides.[5] Treatment of these selenides **6e-h** with *t*-BuOCl afforded the corresponding chloroselenuranes **1e-h**. The chloroselenurane were used without purification. Treatment of (*E*)-**1e-g** with aqueous $NaHCO_3$ at 0 ℃ gave the corresponding allylic alcohols **3e-g** in low ee (Table 1, entries 1-3). (*Z*)-**1e-g** gave the corresponding allylic alcohols **3e-g** in modest to high ee (entries 4-6). When geranylselenurane **1h** was used for this reaction, we obtained (*S*)-linalool[12] **3h** with 88% ee (entry 7).

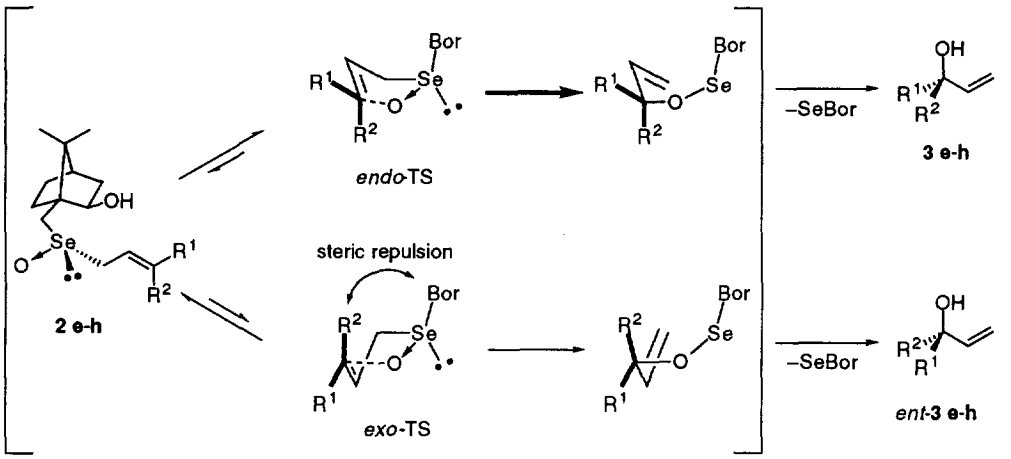
Table 1 Asymmetric [2,3] Sigmatropic Rearrangement of Chiral Allylic Selenoxides **2e-h**.

entry	*E* : *Z*[a]	product	yield (%)	ee (%)	*config*[e]
1	99:<1	**3e**	68	32[b]	*R*
2	95: 5	**3f**	74	26[c]	*R*
3	89:11	**3g**	72	42[c]	*S*
4	10:90	**3e**	57	51[b]	*S*
5	16:84	**3f**	77	80[c]	*S*
6	6 :94	**3g**	72	76[c]	*R*
7	99:<1	**3h**	48	88[d]	*S*[f]

[a] Determined by ^{1}H NMR spectra. [b] Determined by HPLC. [c] Determined by ^{1}H NMR spectra using $Eu(hfc)_3$. [d] Determined by ^{1}H NMR spectrum using $Eu(dcm)_3$. [e] Determined by comparison of the sign of optical rotation with the reported one.[8,10,11] [f] Determined by comparison with the authentic sample by ^{1}H NMR spectrum using $Eu(dcm)_3$.[13]

Stereochemical course of the [2,3] sigmatropic rearrangement of the allylic selenoxides can be reasonably explained by assuming five-membered transition states, the *endo* and *exo* transition states (Scheme 6).[7,8,9] The absolute configuration of the resulting allylic alcohols **3** suggested that the [2,3] sigmatropic rearrangement of the allylic selenoxides **2** progresses predominantly *via* the *endo* transition state. In the case of (*E*)-allylic selenoxides **2e-g** (entries 1-3), the low transfer of chirality reveals that the energy difference between the *exo*- and *endo* transition states is small. In contrast, (*Z*)-allylic selenoxides **2f-h** showed high stereoselectivity in the rearrangement to afford **3f-h**, which reveals the *exo* transition state is strongly destabilized by the steric repulsion between R^2 substituent and bornyl moiety (entries 5-7). The results of [2,3] sigmatropic rearrangement of allylic selenoxides **2** is similar to those of [2,3] sigmatropic rearrangement of allylic sulfoxides reported by Hoffmann.[14]

Scheme 6



In conclusion, we accomplished the first synthesis of optically pure selenuranes **1** by utilizing the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand. Alkaline hydrolysis of selenuranes **1** proceeds with complete retention of the configuration to give selenoxides **2**. Treatment of selenoxides **2** and **9** with HX proceeds stereoselectively to afford **1**. We achieved the [2,3] sigmatropic rearrangement of the allylic selenoxides **2** to give the corresponding allylic alcohols **3** with up to 88% enantiomeric excess (ee). The [2,3] sigmatropic rearrangement of allylic selenoxides **2** progresses predominantly *via* an *endo* transition state.

EXPERIMENTAL SECTION

General. Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. Microanalyses were performed by Microanalysis Center of Toyama Medical & Pharmaceutical University. Spectroscopic measurements were carried out with the following instruments: optical rotations, JASCO DIP-1000 digital polarimeter; circular dichroism spectra (CD), JASCO J-500 C spectrometer; IR, Perkin-Elmer 1600 Series FT-IR; mass (MS) and high resolution mass spectra (HRMS), JEOL JMS AX-505H; ^{1}H NMR, Varian Gemini 300 (300 MHz) for solutions in $CDCl_3$ with Me_4Si as an internal standard; ^{13}C NMR, Varian Gemini 300 (75 MHz) for solutions in $CDCl_3$. The chemical shifts from Me_4Si were calculated based on $CDCl_3$; ^{77}Se NMR, Varian XL-200 (38 MHz) and Varian Unity 500 (95 MHz) for solutions in $CDCl_3$ with $(MeSe)_2$ as an external standard. The chemical shifts from Me_2Se were calculated based on $(MeSe)_2$. Column chromatography, flash column chromatography, and preparative TLC (PLC) were performed on Kieselgel 60 (Merck, Art. 7734, Art. 9385, and Art. 7748, respectively). Medium-pressure liquid chromatography (MPLC) was performed with a Tosoh CCPS pump, and a Tosoh UV-8020 UV detector, a Tosoh RI-8020 RI detector, and a Kusano CIG Pre-Packed Column: ID-22 (22 x 300 mm, 10 μm SiO_2). High-pressure liquid chromatography (HPLC) was performed with a Tosoh CCPM-II pump and a Tosoh UV-8020 UV detector.

$Eu(hfc)_3$ was purchased from Aldrich Chemical Co., Inc. $Eu(dcm)_3$ was purchased from Fluka Chemie.

General Procedure for Preparation of Selenides 6a-d from (1*S*)-10-Bromo-2-*exo*-borneol 4. To a solution of (1*S*)-10-bromo-2-*exo*-borneol[3] **4** (1.00 g, 4.29 mmol) in EtOH (45 mL) were added diaryl- or dimethyl diselenide (2.07 g, 6.44 mmol) and $NaBH_4$ (489 mg, 12.9 mmol) at room temperature. The whole mixture was refluxed under an Ar atmosphere for 6 h and cooled to room temperature. 1N HCl (150 mL) was added slowly to the mixture and stirred for 0.5 h. After the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (100 mL x 3). The combined organic layer was dried over $MgSO_4$ and the solvent was evaporated. The residue was subjected to column chromatography (hexane / AcOEt = 10) to give the selenides **6a-d**.

(1*S*)-10-(Phenylselenenyl)-2-*exo*-borneol 6a: 100% yield; pale yellow oil; $[\alpha]^{24}_D$ –19.0 °(*c* 2.67, $CHCl_3$); IR (neat) 3463, 2951, 1578, 1477, 1072 cm^{-1}; ^1H NMR δ: 0.86 (s, 3H), 1.0-1.15 (m, 1H), 1.06 (s, 3H), 1.15-1.3 (m, 1H), 1.45-1.6 (m, 1H), 1.6-1.85 (m, 4H), 1.9-2.2 (brs, 1H), 3.00 (d, *J* = 11.0 Hz, 1H), 3.18 (d, *J* = 10.4 Hz, 1H), 3.88-3.92 (m, 1H), 7.2-7.35 (m, 3H), 7.5-7.6 (m, 2H); ^{13}C NMR δ: 19.9, 20.6, 27.1, 29.0, 31.7, 39.3, 45.3, 48.1, 52.7, 77.3, 126.9, 129.1, 130.7, 132.6; MS *m/z*: 310 (M^+) (^{80}Se); HRMS Calcd for $C_{16}H_{22}O^{80}Se$: 310.0834. Found: 310.0821.

(1*S*)-10-(*p*-Methoxyphenylselenenyl)-2-*exo*-borneol 6b: 96% yield; pale yellow oil; $[\alpha]^{26}_D$ –6.1 °(*c* 2.06, $CHCl_3$); IR (neat) 3474, 2951, 1591, 1491, 1285, 1246, 1071, 1031, 824 cm^{-1}; ^1H NMR δ: 0.83 (s, 3H), 1.04 (s, 3H), 0.9-1.0 (m, 1H), 1.1-1.3 (m, 1H), 1.49 (dt, *J* = 3.8, 12.1 Hz, 1H), 0.7-0.8 (m, 4H), 2.12 (brs, 1H), 2.92 and 3.11 (ABq, *J* = 11.0 Hz, 2H), 3.78 (s, 3H), 3.88 (m, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR δ: 20.2, 20.9, 27.3, 30.5, 31.9, 39.4, 45.5, 48.2, 53.1, 55.4, 77.4, 115.0, 120.4, 135.5, 159.2; MS *m/z*: 340(M^+) (^{80}Se), 338(M^+) (^{78}Se); HRMS Calcd for $C_{17}H_{24}O_2{}^{80}Se$: 340.0940. Found: 340.0916.

(1*S*)-10-(*p*-Trifluorophenylselenenyl)-2-*exo*-borneol 6c: 68% yield; pale yellow oil; $[\alpha]^{27}_D$ – 26.3 °(*c* 1.94, $CHCl_3$); IR (neat) 3474, 2954, 2880, 1603, 1327, 1125, 1072 cm^{-1}; ^1H NMR δ: 0.89 (s, 3H), 1.09 (s, 3H), 1.0-1.85 (m, 7H), 3.05 and 3.25 (ABq, *J* = 10.4 Hz, 2H), 3.89 (brs, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR δ: 20.2, 20.8, 27.3, 28.7, 31.9, 45.5, 48.4, 52.8, 77.4, 124.3 (q, *J* = 272.5 Hz), 125.9 (q, *J* = 3.5 Hz), 128.9 (q *J* = 33 Hz), 131.7, 136.8; MS *m/z*: 378 (M^+) (^{80}Se), 376 (M^+) (^{78}Se); HRMS Calcd for $C_{17}H_{21}F_3O^{80}Se$: 378.0708. Found: 378.0716.

(1*S*)-10-(Methylselenenyl)-2-*exo*-borneol 6d: 84% yield; colorless oil; $[\alpha]^{24}_D$ –44.0 ° (*c* 0.92, $CHCl_3$); IR (neat) 3463, 2951, 1453, 1388, 1023 cm^{-1}; ^1H NMR δ: 0.84 (s, 3H), 1.06 (s, 3H), 0.9-1.85 (m, 7H), 2.04 (s, 3H), 2.40 (brs, 1H), 2.71 (ABq, *J* = 10.5 Hz, 2H), 3.86 (dd, *J* = 3.4, 7.8 Hz, 1H); ^{13}C NMR δ: 5.5, 20.1, 20.8, 26.4, 27.3, 32.0, 39.4, 45.4, 52.9, 77.7; MS *m/z*: 248 (M^+) (^{80}Se); HRMS Calcd for $C_{11}H_{20}O^{80}Se$: 248.0678 Found: 248.0705.

General Procedure for Preparation of Chloroselenuranes 1a-dA from Selenides 6a-d with *t*-BuOCl. To a solution of selenide **6a-d** (0.15 mmol) in dry CH_2Cl_2 (1.5 mL) was added *t*-BuOCl (20 μL, 0.17 mmol) under an Ar atmosphere at 0 ℃. The whole mixture was stirred at room temperature for 10 min and

the solvent was evaporated. The residue was recrystallized from hexane to give the chloroselenuranes **1a-dA**.

(1*S*,R_{Se})-5-Chloro-10,10-dimethyl-5-phenyl-5λ⁴-selena-4-oxatricyclo[5.2.1.0^{3,7}]decane 1aA. 100% yield; colorless prisms, mp 134-135 ℃; $[\alpha]^{26}_{D}$ +211.9 °(*c* 1.00, $CHCl_3$); CD (MeCN) 242 nm ([θ] +4.27 x 10^4); IR (KBr) 2956, 1440, 1044, 994, 869, 745, 684 cm^{-1}; ^1H NMR δ: 0.93 (s, 3H), 1.0-1.2 (m, 2H), 1.18 (s, 3H), 1.65-2.07 (m, 5H), 3.97 (dd, *J* = 3.2, 7.6 Hz), 4.15 and 4.32 (ABq, *J* = 13.5 Hz, 2H), 7.53-7.55 (m, 3H), 8.03-8.06 (m, 2H); ^{13}C NMR δ: 20.2, 26.4, 29.4, 39.4, 45.8, 46.7, 57.1, 58.4, 96.3, 128.6, 129.7, 131.5, 138.5; ^{77}Se NMR δ: 901; MS *m/z*: 344 (M^+) (^{80}Se); Anal. Calcd for $C_{16}H_{21}ClOSe$: C, 55.91; H, 6.16. Found: C, 56.05; H, 6.05.

X-Ray Analysis of Chloroselenurane 1aA. A colorless prismatic crystal of $C_{16}H_{21}OClSe$ having approximate dimensions of 0.50 X 0.15 X 0.10 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated CuKα radiation and a 12KW rotating anode generator. Crystal data for **1aA**: $C_{16}H_{21}OClSe$, orthorhombic, space group $P2_12_12_1$, with a = 9.573(2) Å, b = 20.975(4) Å, c = 7.796(3) Å, *V* = 1561.2(6) $Å^3$, and *Z* = 4 (d_{calcd} = 1.462 g cm^{-3}), μ (CuKα) = 48.55 cm^{-1} absorption corrected by ω scans; 1552 unique reflections; 1379 with $I > 3.00\sigma(I)$ were used in refinement; R = 3.8%, R_w = 6.6%. The crystal data have been deposited at the Cambridge Crystallographic Data Centre.

(1*S*,R_{Se})-5-Chloro-10,10-dimethyl-5-(*p*-methoxyphenyl)-5λ⁴-selena-4-oxatricyclo-[5.2.1.0^{3,7}]decane 1bA: 100% yield; colorless needles, mp 121-123 ℃; $[\alpha]^{25}_{D}$ +196.3 °(*c* 1.02, $CHCl_3$); IR (KBr) 2956, 2881, 1587, 1496, 1456, 1300, 1255, 1178, 1026 cm^{-1}; ^1H NMR δ: 1.0-1.2 (m, 2H), 0.92 and 1.17 (s, each 3H), 1.6-2.1 (m, 5H), 3.86 (s, 3H), 4.01 (dd, *J* = 3.0, 7.4 Hz, 1H), 4.08 and 4.30 (ABq, *J* = 13.4 Hz, 2H), 7.02 (d, *J* = 9.3 Hz, 2H), 7.94 (d, *J* = 9.3 Hz, 2H); ^{13}C NMR δ: 20.2, 20.3, 26.6, 29.5, 39.5, 45.9, 46.7, 55.7, 57.3, 58.7, 96.4, 115.2, 128.8, 130.4, 162.0; ^{77}Se NMR δ: 906; MS *m/z*: 376, 374, 372, 370; Anal. Calcd for $C_{17}H_{23}ClO_2Se$: C, 54.63; H, 6.20. Found: C, 54.25; H, 6.16.

(1*S*,R_{Se})-5-Chloro-10,10-dimethyl-5-(*p*-trifluoromethylphenyl)-5λ⁴-selena-4-oxatricyclo[5.2.1.0^{3,7}]decane 1cA: 95% yield; colorless needles, mp 118-121 ℃; $[\alpha]^{25}_{D}$ +177.6 °(*c* 1.24, $CHCl_3$); IR (KBr) 2956, 2883, 1603, 1400, 1325, 1169, 1127, 1075, 1056, 1011 cm^{-1}; ^1H NMR δ: 1.0-1.2 (m, 2H), 0.94 and 1.19 (s, each 3H), 1.6-2.1 (m, 5H), 3.93 (dd, *J* = 3.3, 7.7 Hz, 1H), 4.14 and 4.37 (ABq, *J* = 13.7 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H), 8.25 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR δ: 20.2, 20.3, 26.5, 29.5, 39.6, 45.8, 46.9, 57.2, 58.7, 96.6, 123.3 (q, *J* = 273.7 Hz), 126.7 (q, *J* = 3.4 Hz), 129.7, 133.6 (q, *J* = 33.2 Hz), 142.9; ^{77}Se NMR δ: 888; MS *m/z*: 414, 412, 410, 408; Anal. Calcd for $C_{17}H_{20}ClF_3O_2Se$: C, 49.59; H, 4.90. Found: C, 49.59; H, 4.80.

(1*S*,R_{Se})-5-Chloro-10,10-dimethyl-5-methyl-5λ⁴-selena-4-oxatricyclo[5.2.1.0^{3,7}]decane 1dA: 89% yield; colorless needles, mp 166-170 ℃; $[\alpha]^{25}_{D}$ +143.0 °(*c* 1.04, $CHCl_3$); IR (KBr) 2957, 2878, 1386, 1046, 996, 869 cm^{-1}; ^1H NMR δ: 1.15-1.35 (m, 2H), 0.92, 1.09 and 3.39 (s, each 3H), 1.7-2.2 (m, 5H), 3.84 and 4.23 (ABq, *J* = 13.5 Hz, 2H), 4.49 (dd, *J* = 3.3, 7.1 Hz, 1H); ^{13}C NMR δ: 20.0, 20.2, 26.6, 29.7, 38.9, 39.6, 45.8, 46.6, 57.5, 57.8, 96.8; ^{77}Se NMR δ: 858; MS *m/z*: 284, 282, 280, 247, 245; Anal. Calcd for $C_{11}H_{19}ClO_2Se$: C, 46.90; H, 6.80. Found: C, 46.97; H, 6.66.

General Procedure for Alkaline Hydrolysis of Chloroselenuranes 1a-dA. A solution of **1a-dA** (0.099 mmol) in AcOEt (10 mL) and saturated $NaHCO_3$ (2 mL) was placed in a separatory funnel. The two-phase solution was shaken vigorously and separated. The organic layer was washed with water, dried over $MgSO_4$ and concentrated to give the selenoxides **2a-d**.

(1*S*)-10-(Phenylseleninyl)-2-*exo*-borneol 2a: 100% yield; colorless prisms, mp 133-135 ℃; $[\alpha]^{25}_D$ +134.0 ° (*c* 1.03, $CHCl_3$); CD ($CHCl_3$) 251 nm ([θ] +5.90 x 10^4); IR (KBr) 3204, 2952, 1443, 1078 cm^{-1}; ^1H NMR δ: 0.81 (s, 3H), 1.04 (s, 3H), 1.15-1.3 (m, 1H), 1.5-1.95 (m, 6H), 2.67 (d, *J* = 12 Hz, 1H), 3.37 (d, *J* = 12 Hz, 1H), 4.16 (m, 1H), 5.33 (d, *J* = 3.4 Hz, 1H), 7.5-7.65 (m, 3H), 7.7-7.8 (m, 2H); ^{13}C NMR δ: 19.9, 20.4, 27.2, 31.8, 38.4, 45.3, 48.5, 52.2, 56.8, 77.3, 125.7, 129.8, 131.4, 140.3; ^{77}Se NMR δ: 852; MS *m/z*: 325 (M^+-1) (^{80}Se); Anal. Calcd for $C_{16}H_{22}O_2Se$: C, 59.08; H, 6.82. Found: C, 59.30; H, 6.96.

X-Ray Analysis of Selenoxide 2a. A colorless prismatic crystal of $C_{16}H_{22}O_2Se$ having approximate dimensions of 0.30 X 0.30 X 0.30 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated CuKα radiation and a 12KW rotating anode generator. Crystal data for **2a**: $C_{16}H_{21}O_2Se$, orthorhombic, space group $P2_12_12_1$, with a = 11.455(3) Å, b = 13.535(3) Å, c = 9.879(3) Å, *V* = 1531.7(5) $Å^3$, and *Z* = 4 (d_{calcd} = 1.411 g cm^{-3}), μ (CuKα) = 33.46 cm^{-1} absorption corrected by ω scans; 1336 unique reflections; 1224 with $I > 3.00\sigma(I)$ were used in refinement; *R* = 3.3%, R_w = 4.4%. The crystal data have been deposited at the Cambridge Crystallographic Data Centre.

(1*S*,R_{Se})-10-(*p*-Methoxyphenylseleninyl)-2-*exo*-borneol 2b: 99% yield; colorless prisms, mp 129-130 ℃; $[\alpha]^{28}_D$ +103.5 ° (*c* 1.1, $CHCl_3$); IR (KBr) 3135, 2938, 1591, 1493, 1077, 1028 cm^{-1}; ^1H NMR δ: 0.80 (s, 3H), 1.07 (s, 3H), 1.2-1.3 (m, 1H), 1.5-1.9 (m, 6H), 2.62 and 3.35 (ABq, *J* = 11.8 Hz, 2H), 3.87 (s, 3H), 4.14 (ddd, *J* = 3.8, 3.8, 8.2 Hz, 1H), 5.39 (d, *J* = 3.3 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR δ: 20.0, 20.6, 27.3, 31.9, 38.5, 45.4, 48.6, 52.2, 55.7, 56.9, 77.3, 115.3, 127.4, 130.7, 162.1; ^{77}Se NMR δ: 851; MS *m/z*: M^+ none, 338; Anal. Calcd for $C_{17}H_{24}O_3Se$: C,57.47; H, 6.80. Found: C, 57.44; H, 6.71.

(1*S*,R_{Se})-10-(*p*-Trifluoromethylphenylseleninyl)-2-*exo*-borneol 2c: 95% yield; colorless needles, mp 127-129 ℃; $[\alpha]^{25}_D$ +107.0 ° (*c* 1.04, $CHCl_3$); IR (KBr) 3266, 2955, 2878, 1598, 1397, 1166, 1130, 1056 cm^{-1}; ^1H NMR δ: 0.82 (s, 3H), 1.06 (s, 3H), 1.2-1.3 (m, 1H), 1.5-1.95 (m, 6H), 2.70 and 3.37 (ABq, *J* = 12.1 Hz, 2H), 4.15 (ddd, *J* = 3.8, 3.8, 8.2 Hz, 1H), 5.11 (d, *J* = 3.3 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR δ: 20.0, 20.6, 27.4, 32.0, 38.7, 45.6, 49.0, 52.4, 57.5, 77.5, 123.6 (q, *J* = 272.5 Hz), 126.5, 126.9 (q, *J* = 3.4 Hz), 133.8 (q, *J* = 33.2 Hz), 144.9; ^{77}Se NMR δ: 856; MS *m/z*: M^+ none, 378, 376; Anal. Calcd for $C_{17}H_{21}F_3O_2Se$: C, 51.91; H, 5.38. Found: C, 51.99; H, 5.40.

(1*S*,S_{Se})-10-(Methylseleninyl)-2-*exo*-borneol 2d: 90% yield; colorless needles, mp 110 ℃; $[\alpha]^{25}_D$ +31.4 ° (*c* 1.30, $CHCl_3$); IR (KBr) 2950, 2719, 1455, 1418, 1074, 766 cm^{-1}; ^1H NMR δ: 0.86 (s, 3H), 1.14 (s, 3H), 1.15-1.3 (m, 1H), 1.4-1.65 (m, 2H), 1.7-1.9 (m, 5H), 2.60 (s, 3H), 2.71 and 3.42 (ABq, *J* = 11.5 Hz, 2H), 4.04 (ddd, *J* = 3.9, 3.9, 8.2 Hz, 1H); ^{13}C NMR δ: 20.2, 20.7, 27.3, 31.9, 32.9, 38.6, 45.5, 48.5, 52.0, 52.3, 77.3; ^{77}Se NMR δ: 831; MS *m/z*: M^+ none, 153, 135, 112, 109; Anal. Calcd for $C_{11}H_{20}O_2Se$:

C, 50.19; H, 7.66. Found: C, 50.32; H, 7.79.

Preparation of Chloroselenuranes 1aA from Selenoxides 2a. To a solution of **2a** (300 mg, 0.92 mmol) in MeOH (2 mL) was added 3 drops of conc. HCl at room temperature. After being stirred for 2 h, the mixture was concentrated under reduced pressure. The residue was recrystallized from hexane to give 317 mg (100%) of the chloroselenurane **1aA** as colorless prisms.

(1*S*, R_{Se})-5-Bromo-10,10-dimethyl-5-phenyl-5λ⁴-selena-4-oxatricyclo[5.2.1.0^{3,7}]decane 1aB was prepared from **2a** (101 mg, 0.310 mmol) and 2 drops of aqueous 48% HBr in MeOH (3 mL). Reaction time: 2h. After evaporation of the solvent, the residue was treated with hexane (5 mL) and cyclopentene (0.5 mL) at room temperature for 10 h. The crystals formed were collected. The filtrate was concentrated to give further crystals. Total yield of **1aB** was 114 mg (95%): colorless prisms. mp 125-126 ℃; $[\alpha]^{26}_{D}$ +200.6 ° (*c* 1.58, $CHCl_3$); IR (KBr) 2946, 2857, 1440, 1368, 1342, 1074, 1043, 995, 866, 751, 687 cm^{-1}; ^{1}H NMR δ: 0.94 (s, 3H), 1.08 (m, 2H), 1.20 (s, 3H), 1.63-1.78 (m, 2H), 1.88-2.07 (m, 3H), 4.00 (dd, *J* = 7.6, 3.2 Hz, 1H), 4.26 and 4.40 (ABq, *J* = 13.5 Hz, 2H), 7.48-7.6 (m, 3H), 8.0-8.1 (m, 2H); ^{13}C NMR δ: 20.1, 26.3, 29.3, 39.5, 45.7, 46.7, 57.2, 58.8, 97.1, 128.8, 129.7, 131.5, 137.4; ^{77}Se NMR δ: 909; MS *m/z*: 388 (M^+) (^{80}Se); Anal. Calcd for $C_{16}H_{21}BrOSe$: C, 49.50; H, 5.45. Found: C, 49.27; H, 5.46.

X-Ray Analysis of Bromoselenurane 1aB. A colorless prismatic crystal of $C_{16}H_{21}OSeBr$ having approximate dimensions of 0.30 X 0.20 X 0.10 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Cu-Kα radiation and a 12kW rotating anode generator. Crystal data for **1aB**: $C_{16}H_{21}OSeBr$, monoclinic, space group *C*2, with a = 20.807(5) Å, b = 6.916(6) Å, c = 13.117(7) Å, β=123.75(2) °, *V* = 1574(1) Å^3, and *Z* = 4 (d_{calcd} = 1.638 g cm^{-3}), μ (CuKα) = 61.13 cm^{-1} absorption corrected by ω scans; 1348 unique reflections; 1232 with $I > 3.00\sigma(I)$ were used in refinement; *R* = 3.8%, R_w = 5.7%. The crystal data have been deposited at the Cambridge Crystallographic Data Centre.

(1*S*, R_{Se})-10,10-Dimethyl-5-(3,5-dinitrobenzoyloxy)-5-phenyl-5λ⁴-selena-4-oxatricyclo[5.2.1.0^{3,7}]decane 1aC was prepared from **2a** (325 mg, 1.0 mmol), 3,5-dinitrobenzoic acid (212 mg, 1.0 mmol) and $MgSO_4$ (500 mg) in dry CH_2Cl_2 (10 mL). Reaction time: 1 h. After $MgSO_4$ was filtered off, the filtrate was concentrated under reduced pressure. The residue was recrystallized from MeOH-hexane to give **1aC** (465 mg, 88%) as colorless needles. mp 152-152.5 ℃; $[\alpha]^{25}_{D}$ +4.7 °(*c* 1.15, $CHCl_3$); CD (MeCN) 250 nm ([θ] +3.05 x 10^4); IR (KBr) 3107, 2958, 2879, 1623, 1542, 1455, 1442, 1344, 721 cm^{-1}; ^{1}H NMR δ: 0.99 (s, 3H), 1.27 (s, 3H), 0.95-1.19 (m, 2H), 1.69-2.13 (m, 5H), 3.95 and 4.39 (ABq, *J* = 12.8 Hz, 2H), 3.97 (dd, *J* = 6.7, 3.8 Hz, 1H), 7.57-7.60 (m, 3H), 7.64-7.98 (m, 2H), 9.06 (s, 3H); ^{13}C NMR δ: 20.2, 20.3, 26.6, 29.4, 39.2, 45.7, 46.7, 52.7, 56.5, 95.2, 120.3, 128.5, 129.2, 129.9, 131.5, 138.1, 140.0, 148.2, 167.2; ^{77}Se NMR δ: 922; MS *m/z*: 520 (M^+) (^{80}Se); Anal. Calcd for $C_{23}H_{24}N_2O_7Se$: C, 53.18; H, 4.66; N, 5.39. Found: C, 53.25; H, 4.48; N, 5.24.

(1*S*, R_{Se})-10,10-Dimethyl-5-phenyl-5-(*p*-toluenesulfonyloxy)-5λ⁴-selena-4-oxatricyclo[5.2.1.0^{3,7}]decane 1aD was prepared from **2a** (260 mg, 0.80 mmol), *p*-TsOH•H_2O (152 mg, 0.80 mmol)

and $MgSO_4$ (500 mg) in dry CH_2Cl_2 (16 mL). Reaction time: 1.5 h. After $MgSO_4$ was filtered off, the filtrate was concentrated under reduced pressure. The residue was recrystallized from CH_2Cl_2-ether to give **1aD** (350mg, 91%) as colorless prisms. mp 138-139 ℃; $[\alpha]^{25}_D$ +31.4 ° (*c* 1.02, $CHCl_3$); CD (MeCN) 234 ([θ] +4.87 x 10^4), 213 nm ([θ] –4.04 x 10^4); IR (KBr) 3017, 2970, 2917, 1442, 1258, 1247, 1152, 1110, 986 cm^{-1}; ^1H NMR δ: 0.95 (s, 3H), 1.18 (s, 3H), 2.34 (s, 3H), 1.03-1.18 (m, 2H), 1.71-2.19 (m, 5H), 4.09 and 4.64 (ABq, *J* = 13.2 Hz, 2H), 4.19 (dd, *J* = 7.5, 2.8 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.23-7.55 (m, 3H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.86-7.89 (m, 2H); ^{13}C NMR δ: 19.9, 21.3, 26.2, 28.8, 38.9, 46.1, 46.8, 54.8, 58.6, 99.3, 125.9, 128.5, 128.7, 130.1, 132.1, 135.8, 140.2, 141.6; ^{77}Se NMR δ: 1016; MS *m/z*: 308 (M^+-$TolSO_3$) (^{80}Se); Anal. Calcd for $C_{23}H_{28}O_4SSe$: C, 57.61; H, 5.89. Found: C, 57.50; H, 5.78.

(1*S*,R_{Se})-10,10-Dimethyl-5-phenyl-5-(trifluoromethanesulfonyloxy)-5λ⁴-selena-4-oxatricyclo[5.2.1.0^{3,7}]decane 15aE was prepared from **2a** (33 mg, 0.10 mmol), CF_3SO_3H (9 μl, 0.10 mmol) and $MgSO_4$ (100 mg) in dry CH_2Cl_2 (3 mL). Reaction time: 10 min. After $MgSO_4$ was filtered off, the filtrate was concentrated under reduced pressure. The residue was recrystallized from CH_2Cl_2-ether to give **1aE** (41mg, 89%) as colorless prisms. mp 95-96 ℃; $[\alpha]^{25}_D$ +56.3° (c 1.17, $CHCl_3$). IR (KBr) 2966, 2906, 1480, 1445, 1291, 1233, 1218, 1170, 1024, 746 cm^{-1}; ^1H NMR δ: 1.1-2.3 (m, 7H), 0.99 and 1.20 (s, each 3H), 4.09 and 4.60 (ABq, *J* = 13.2 Hz, 2H), 4.43 (dd, *J* = 2.7, 7.7 Hz, 1H); ^{13}C-NMR δ: 19.96, 19.99, 26.2, 28.6, 39.0, 46.6, 47.1, 54.2, 60.3, 101.9, 128.4, 130.8, 133.4, 134.3; ^{77}Se-NMR δ:1058; MS m/z: M^+ none, 314, 292, 290; Anal. Calcd for $C_{17}H_{21}F_3O_4SSe$: C, 44.64; H, 4.63. Found: C, 44.44; H, 4.58.

General Procedure for Preparation of Allylic Selenides 6e-h.[5] To a solution of diselenide **5** (500 mg, 1.08 mmol) in EtOH (20 mL) was added $NaBH_4$ (150 mg, 3.95 mmol) at 0 ℃. After 10 min, an allyl halide (2.7 mmol) was added to the solution at 0 ℃. The resulting mixture was stirred for 30 min at 0 ℃ and concentrated to a half of its original volume. The residual mixture was poured into saturated aqueous NH_4Cl and extracted with CH_2Cl_2 (15 mL x 3). The extracts were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash column chromatography (hexane/AcOEt = 20) to give **6e-h**.

(1*S*,*E*)-3'-Phenyl-2'-propenyl 2-*exo*-Hydroxy-10-bornyl Selenide (*E*)-6e: 100% yield (*E* : *Z* = 99 : <1); pale yellow oil; $[\alpha]^{25}_D$ –51.3 °(*c* 1.00, $CHCl_3$); IR (neat) 3462, 3024, 2952, 2878, 1071, 751 cm^{-1}; ^1H NMR δ: 0.81 (s, 3H), 1.03 (s, 3H), 0.95-1.8 (m, 7H), 2.33 (brs, 1H), 2.63 and 2.78 (ABq, *J* = 10.6 Hz, 2H), 3.38 (d, *J* = 7.4 Hz, 2H), 3.84 (dd, *J* = 3.2, 7.8 Hz, 1H), 6.28 (dt, *J* = 7.6, 15.4 Hz, 1H), 6.41 (d, *J* = 15.7 Hz, 1H), 7.15-7.4 (m, 5H); ^{13}C NMR δ: 20.1, 20.8, 24.1, 26.7, 27.2, 32.0, 39.4, 45.4, 48.0, 52.6, 77.6, 126.4, 126.7, 127.6, 128.7, 131.8, 136.9; MS *m/z*: 350 (M^+) (^{80}Se), 348 (M^+) (^{78}Se); HRMS Calcd for $C_{19}H_{26}O^{80}Se$: 350.1147. Found: 350.1141.

Z-**6e** was converted into the corresponding chloroselenurane **1e** without purification. (*Z*)-**6e** isomerized to *E*-**6e** at room temperature.

(1*S*,*E*)-3'-Cyclohexyl-2'-propenyl 2-*exo*-Hydroxy-10-bornyl Selenide (*E*)-6f: 98% yield (*E* : *Z* = 95 : 5); pale yellow oil; IR (neat) 3462, 2942, 2850, 1449 cm^{-1}; ^1H NMR δ: 0.82 (s, 3H), 1.03 (s, 3H),

1.0-2.0 (m, 19H), 2.30 (brs, 1H), 2.54 and 2.63 (ABq, J = 10.7 Hz, 2H), 3.05-3.2 (m, 2H), 3.82 (brd, J = 6.6 Hz, 1H), 5.3-5.5 (m, 2H); ^{13}C NMR δ: 20.1, 20.8, 23.4, 26.1, 26.3, 26.4, 27.3, 32.1, 33.3, 39.2, 40.7, 45.2, 48.0, 52.6, 77.6, 124.0, 139.8; MS *m/z*: 356 (M^+) (^{80}Se), 354 (M^+) (^{78}Se); HRMS Calcd for $C_{19}H_{32}O^{80}Se$: 356.1616. Found: 356.1631.

(1*S*,*Z*)-3'-Cyclohexyl-2'-propenyl 2-*exo*-Hydroxy-10-bornyl Selenide (*Z*)--6f: 91% yield (E : Z = 16 : 84); pale yellow oil; IR (neat) 3462, 2924, 2850, 1448, 1071, 963, 751 cm^{-1}; ^{1}H NMR δ: 0.83 (s, 3H), 1.05 (s, 3H), 1.0-1.7 (m, 17H), 2.15-2.35 (m, 1H), 2.37 (d, J = 3.3 Hz, 1H), 2.64 and 2.72 (ABq, J = 10.4 Hz, 2H), 3.22 (dd, J = 8.2, 12.1 Hz, 1H), 3.28 (dd, J = 9.3, 12.1 Hz, 1H), 3.84 (ddd, J = 3.6, 3.6, 8.6 Hz, 1H), 5.32 (dd J = 10.2, 10.2 Hz, 1H), 5.45 (dt, J = 8.5, 10.4 Hz, 1H); ^{13}C NMR δ: 20.1, 20.8, 20.9, 24.0, 26.0, 27.3, 31.9, 33.46, 33.51, 36.3, 39.2, 45.4, 47.9, 52.5, 77.5, 124.1, 138.5, 138.5; MS *m/z*: 350 (M^+) (^{80}Se), 348 (M^+) (^{78}Se); HRMS Calcd for $C_{19}H_{32}O^{80}Se$: 356.1616. Found: 356.1631.

(1*S*,*E*)-2'-Nonenyl 2-*exo*-Hydroxy-10-bornyl Selenide (*E*)--6g: 94% yield (E : Z = 89 : 11); pale yellow oil; IR (neat) 3474, 2953, 2926, 2876, 2855, 1458, 1072, 962 cm^{-1}; ^{1}H NMR δ: 0.82 (s, 3H), 0.87 (t, J = 6.6 Hz, 3H), 1.04 (s, 3H), 0.8-2.0 (m, 17H), 2.29 (d, J = 3.3 Hz, 2H), 2.57 and 2.65 (ABq, J = 10.4 Hz, 2H) , 3.1-3.2 (m, 2H), 3.82 (ddd, J = 3.8, 3.8, 8.2 Hz, 1H), 5.4-5.6 (m, 2H); ^{13}C NMR δ: 14.3, 20.1, 20.77, 22.78, 23.6, 26.3, 27.3, 29.0, 29.7, 31.9, 32.1, 32.5, 39.2, 45.4, 48.0, 52.6, 77.6, 126.6, 133.9; MS *m/z*: 358 (M^+) (^{80}Se), 356 (M^+) (^{78}Se); HRMS Calcd for $C_{19}H_{34}O^{80}Se$: 358.1773. Found: 358.1760.

(1*S*,*Z*)-2'-Nonenyl 2-*exo*-Hydroxy-10-bornyl Selenide (*Z*)--6g: 94% yield (E : Z = 6 : 94); pale yellow oil; IR (neat) 3448, 2953, 2926, 1071 cm^{-1}; ^{1}H NMR δ: 0.83 (s, 3H), 0.89 (t, J = 6.9 Hz, 3H), 1.05 (s, 3H), 1.0-1.8 (m, 15H), 2.08 (dt, J = 6.4, 6.4 Hz, 2H), 2.35 (d, J = 3.3 Hz, 1H), 2.64 and 2.72 (ABq, J = 10.4 Hz, 2H), 3.21 (dd, J = 7.4, 11.8 Hz, 1H), 3.29 (dd, J = 8.0, 11.8 Hz, 1H), 3.84 (ddd, J = 3.6, 3.6, 7.7 Hz, 1H), 5.4-5.65 (m, 2H); ^{13}C NMR δ: 14.3, 20.1, 20.6, 20.8, 22.8, 23.8, 27.3, 29.2, 29.8, 31.9, 39.2, 45.3, 48.0, 52.5, 77.5, 126.0, 132.7; MS *m/z*: 358 (M^+) (^{80}Se), 356 (M^+) (^{78}Se); HRMS Calcd for $C_{19}H_{34}O^{80}Se$: 358.1773. Found: 358.1786.

(1*S*,*E*)-3',7'-Dimethylocta-2',6'-dienyl 2-*exo*-Hydroxy-10-bornyl Selenide (*E*)--6h: 61% yield (E : Z = 99 : <1); pale yellow oil; $[\alpha]^{26}_D$ –33.3 °(c 1.43, $CHCl_3$); IR (neat) 3447, 2951, 2930, 2879 cm^{-1}; ^{1}H NMR δ: 0.83 (s, 3H), 0.95-1.2 (m, 2H), 1.04 (s, 3H), 1.45-1.85 (m, 5H), 2.0-2.15 (m, 4H), 1.60 (s, 3H), 1.68 (s, 6H), 2.39 (brs, 1H), 2.62 and 2.71 (ABq, J = 10.4 Hz, 2H), 3.21 and 3.28 (ABqd, J = 8.2, 12.2 Hz, 2H), 3.83 (m, 1H), 5.09 (m, 1H), 5.38 (brt, J = 8.2 Hz, 1H); ^{13}C NMR δ: 16.2, 17.9, 20.1, 20.8, 21.8, 23.5, 25.9, 26.8, 27.3, 31.9, 39.1, 39.8, 45.3, 47.9, 52.6, 77.5, 121.1, 124.1, 131.8, 138.9; MS *m/z*: 370 (M^+) (^{80}Se), 368 (M^+) (^{78}Se); HRMS Calcd for $C_{20}H_{34}O^{80}Se$: 370.1773. Found: 370.1771.

General Procedure for Asymmetric [2,3] Sigmatropic Rearrangement of (*E*)- and (*Z*)-Allylic Selenoxides 2e-h. To a solution of allylic selenides **6e-h** (0.50-0.83 mmol) in CH_2Cl_2 (10-16 mL) was added *t*-BuOCl (1 equiv, 0.50-0.83 mmol) at 0 ℃. After 10 min, saturated aqueous $NaHCO_3$ (5-8 mL) was added to the solution at 0 ℃. After being stirred at 0 ℃ for 10 min, the mixture was extracted with CH_2Cl_2 (5 mL x 2). The combined extracts were dried over $MgSO_4$ and the solvent was evaporated. The crude mixture

was purified by MPLC or PLC (hexane/AcOEt or hexane/ether). The product yield and enantiomeric excess are listed in Table 1.

(*R*)-1-Phenyl-2-propen-1-ol 3e: $[\alpha]^{26}_{D}$ +2.7 °(*c* 4.97, benzene) from (*E*)-**6e**, {lit.[8] $[\alpha]^{20}_{D}$ –8.4 °(*c* 5.0, benzene)(*S*-form)}, ^{1}H NMR δ: 1.97 (brs, 1H), 5.205 (d, *J* = 11.0 Hz, 1H), 5.215 (d, *J* = 5.5 Hz, 1H), 5.36 (d, *J* = 17.0 Hz, 1H), 6.06 (ddd, *J* = 6.6, 10.7, 16.8 Hz, 1H), 7.2-7.4 (m, 5H). The ee value of **3e** was determined by HPLC on a Daicel Chiralcel OJ column (hexane/*i*-PrOH = 9).

(*R*)-1-Cyclohexyl-2-propen-1-ol 3f: $[\alpha]^{26}_{D}$ +5.2 °(*c* 1.12, 95% EtOH) from (*E*)-**6f**, $[\alpha]^{26}_{D}$ = –19.0 °(*c* 1.02, 95% EtOH) from (*Z*)-**6f**, {lit.[10] $[\alpha]^{20}_{D}$ +26 °(*c* 1.142, 95% EtOH)(*R*-form)}, ^{1}H NMR δ: 0.9-1.9 (m, 12H), 3.85 (dd, *J* = 6.3, 10.7 Hz, 1H), 5.14 (ddd, *J* = 1.4, 1.4, 10.4 Hz, 1H), 5.20 (ddd, *J* = 1.4, 1.4, 17.6 Hz, 1H), 5.86 (ddd, *J* = 6.6, 10.4, 17.0 Hz, 1H). The ee value of **3f** was determined by ^{1}H NMR spectra using Eu(hfc)$_3$ {**3f** (5 mg) and Eu(hfc)$_3$ (30 mg) in $CDCl_3$ (0.6 mL)}.

(*S*)-2-Nonen-1-ol 3g: $[\alpha]^{26}_{D}$ +3,7 °(*c* 1.07, $CHCl_3$) from (*E*)-**6g**; $[\alpha]^{26}_{D}$ = –6.4 °(*c* 1.28, $CHCl_3$), $[\alpha]^{25}_{D}$ = –14.3 °(*c* 1.15, EtOH) from (*Z*)-**6g**, {lit.[11] $[\alpha]^{20}_{D}$ –17.0 °(*c* 0.96, EtOH)(*R*-form)}; ^{1}H NMR δ: 0.88 (t, *J* = 6.7 Hz, 3H), 1.2-1.6 (m, 11H), 4.09 (dd, *J* = 6.3, 12.7 Hz, 1H), 5.10 (ddd, *J* = 1.4, 1.4, 10.4 Hz, 1H), 5.21 (ddd, *J* = 1.4, 1.4, 17.6 Hz, 1H), 5.87 (ddd, *J* = 6.6, 10.4, 17.0 Hz, 1H). The ee value of **3g** was determined by ^{1}H NMR spectra using Eu(hfc)$_3$ {**3g** (5 mg) and Eu(hfc)$_3$ (70 mg) in $CDCl_3$ (0.6 mL)}.

(*S*)-Linalool 3h: ^{1}H NMR δ: 1.27 (s, 3H), 1.60 (s, 3H), 1.68 (s, 3H), 1.5-1.7 (m, 3H), 2.02 (m, 2H), 5.06 (dd, *J* = 1.1, 9.9 Hz, 1H), 5.12 (m, 1H), 5.21 (dd, *J* = 1.1, 17.0 Hz, 1H), 5.91 (dd, *J* = 10.7, 17.3 Hz, 1H). The ee value of **3h** was determined by ^{1}H NMR spectra using Eu(dcm)$_3$ {**3h** (5 mg) and Eu(dcm)$_3$ (30 mg) in $CDCl_3$ (0.6 mL)}. The configuration of **3h** was determined by comparison with the commercial linalool (*R*- form, ca. 30% ee) by ^{1}H NMR spectrum using Eu(dcm)$_3$.[13]

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