

Optical Resolution of Selenonium Imides Stabilized by an 8-Dimethylamino-1-naphthyl Group

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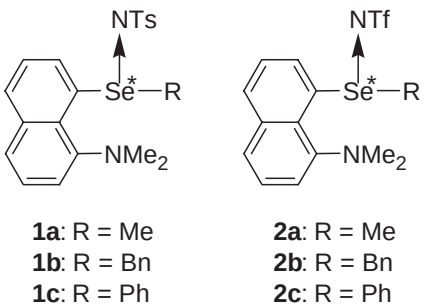
Selenonium imides **1** and **2**, stabilized by intramolecular coordination of the amino group of 8-dimethylamino-1-naphthyl substituent to the selenium atom, were synthesized. Optically active selenonium imides were obtained by chromatographic resolution on optically active columns and were found to be stable toward racemization both in the solid state and in solution. Absolute configurations of the optically active selenonium imides were assigned on the basis of specific rotations and circular dichroism spectra.

Chiral tricoordinate organosulfur compounds have been widely studied and are used for asymmetric synthesis, because optically active sulfur compounds can be obtained by various methods.[1] Optically active tricoordinate selenium and tellurium compounds have been isolated, and their properties and applicability to asymmetric reactions have been examined.[2–15] Some optically active selenonium imides have also been prepared[16–18] and used as important intermediates in asymmetric synthesis.[19] The first synthesis of an optically active selenonium imide was accomplished by Krasnov et al. in 1981.[16] However, the specific rotation was very low, and the absolute configuration was not determined. Optically pure diastereomeric and enantiomeric diaryl selenonium imides have also been prepared,[17,18] but no optically active alkyl aryl selenonium imides have been isolated so far, because they are sensitive to trace amounts of water in the solvent and/or atmospheric moisture, even though the aryl group possesses bulky substituents, and is rapidly hydrolyzed to the corresponding selenoxide and amine.[17]

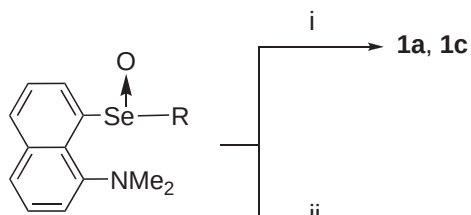
Nakanishi and co-workers have previously reported intramolecular coordination between selenium and halogen atoms at 1,8-positions of naphthalene skeletons.[20] Recently, we designed and synthesized stable alkyl aryl and diaryl selenonium imides possessing an 8-dimethylamino-1-naphthyl group that facilitates intramolecular coordination of the amino group to the selenium atom due to the rigid structure, and succeeded in resolving into their enantiomers. Here, we report the synthesis and optical resolution of selenonium imides **1** and **2** (Chart 1). Their chiroptical properties and absolute configurations are also reported.



1a: R = Me
1b: R = Bn
1c: R = Ph

2a: R = Me
2b: R = Bn
2c: R = Ph

Chart 1.



3a: R = Me
3b: R = Bn
3c: R = Ph

Scheme 1. i: $TsNH_2$, MS3A, toluene, reflux, 80 h; ii: $TfNH_2$, Na_2SO_4, CH_2Cl_2, rt, 17 h.

Results and Discussion

Preparation of Racemic Selenonium Imides. Selenonium imides **1a** and **1c** were prepared in 50% and 53% yields, respectively, by reacting the corresponding selenoxides[5m,5n] **3a** and **3c** with *p*-toluenesulfonamide in refluxing toluene,[21] whereas selenonium imide **1b** could not be obtained by the similar reaction (Scheme 1). On the other hand, selenonium imides **2a–2c** were synthesized in 53%, 19%, and 51% yields, respectively, by reacting the corresponding selenoxides **3a–3c** with trifluoromethanesulfonamide in the presence of sodium sulfate. These selenonium imides were stable in the solid state and in chloroform solution. In all of the selenonium imides obtained, two singlets assignable to protons of the two methyl groups of the amino group were observed on the ^1H NMR spectrum due to coordination of the nitrogen atom to the chiral selenium atom. These results mean that the selenonium imides are thermodynamically stable toward hydrolysis due to intramolecular coordination of the amino group to the selenium atom.

Optical Resolution of Selenonium Imides. Selenonium imide **1a** was subjected to an optically active column

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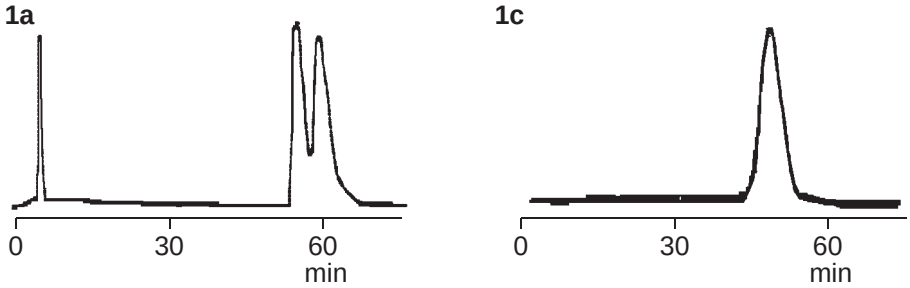


Fig. 1. Optical resolution of racemic selenonium imides **1** on an optically active column packed with cellulose carbamate derivative/silica gel (Daicel Chiralcel OD, $4.6 \times 250\,mm^2$) by means of HPLC on an analytical scale (hexane/ethanol = 95/5).

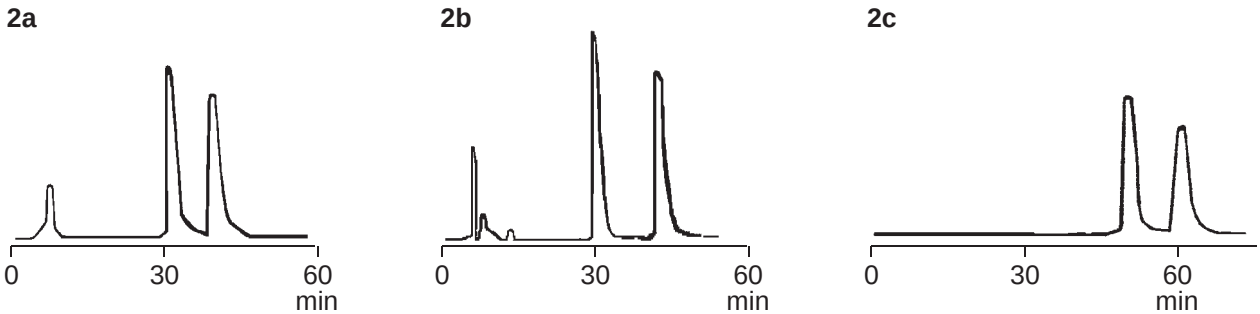


Fig. 2. Optical resolution of racemic selenonium imides **2** on an optically active column packed with amylose derivative/silica gel (Daicel Chiralpak AS-H, $4.6 \times 250\,mm^2$) by means of HPLC on an analytical scale (hexane/ethanol = 90/10).

Table 1. Optical Resolution and Specific Rotation of Selenonium Imides **1a** and **2a**–**2c**

		First-eluted enantiomer		Second-eluted enantiomer	
Compound	Ethanol/%[c]	$[\alpha]_D$ (c)[d]	ee/%	$[\alpha]_D$ (c)[d]	ee/%
1a[a]	5	+73.0 (0.05)	100	−46.0 (0.04)	60
2a[b]	10	+334.0 (0.19)	100	−336.0 (0.22)	100
2b[b]	10	+119.0 (0.89)	100	−118.0 (0.73)	100
2c[b]	10	−145.4 (0.89)	100	+147.6 (0.44)	100

a) Optical resolution was carried out by HPLC on an optically active column packed with cellulose carbamate derivative/silica gel (Daicel Chiralcel OD; $4.6 \times 250\,mm^2$) at 25 °C. b) Optical resolution was carried out by HPLC on an optically active column packed with amylose derivative/silica gel (Daicel Chiralpak AS-H; $4.6 \times 250\,mm^2$) at 25 °C. c) Volume percentage of ethanol in hexane as an eluent. d) Specific rotations were measured in chloroform at 28 °C.

($4.6 \times 250\,mm^2$) packed with cellulose carbamate derivative/silica gel (Daicel Chiralcel OD) using HPLC (hexane/ethanol = 95/5). Two peaks corresponding to each enantiomer of **1a** were observed on the chromatogram, as shown in Fig. 1. However, selenonium imide **1c** could not be resolved on optically active columns, such as Daicel Chiralcel OD and Chiralpak AS-H. Repeated resolution of the first fraction of **1a** on a preparative scale gave an optically pure selenonium imide. The second-eluted enantiomer could not be obtained in an optically pure form in spite of repeated resolution, perhaps due to tailing of the first-eluted enantiomer. The optical purities were determined by HPLC using a chiral column. The first-eluted enantiomer of **1a** showed positive specific rotation {(+)-**1a**: ee 100%; $[\alpha]_D$ +73.0 (c 0.05, $CHCl_3$)}, and the second-eluted enantiomer showed a negative one {(−)-**1a**: ee 60%; $[\alpha]_D$ −46.0 (c 0.04, $CHCl_3$)}.

Selenonium imide **2a** was well resolved into two peaks that correspond to the enantiomers on a column packed with amylose derivative/silica gel (Daicel Chiralpak AS-H) using HPLC (hexane/ethanol = 90/10) on an analytical scale, as shown in Fig. 2. In the case of **2a**, the first- and second-eluted enantiomers were obtained in optically pure forms by repeated resolution, in contrast to selenonium imide **1a**. The first-eluted enantiomer of **2a** showed positive specific rotation {(+)-**2a**: ee 100%; $[\alpha]_D$ +334.0 (c 0.19, $CHCl_3$)}, and the second-eluted enantiomer showed a negative one {(−)-**2a**: ee 100%; $[\alpha]_D$ −336.0 (c 0.22, $CHCl_3$)}. Selenonium imides **2b** and **2c** were also resolved into their corresponding optically pure enantiomers under the same conditions. The first-eluted enantiomer of **2b** also showed positive specific rotation. However, in the case of **2c**, the first-eluted enantiomer showed negative specific rotation. The specific rotations and optical purities of **1a** and **2a**–**2c** are summarized in Table 1.

Circular Dichroism Spectra, Absolute Configuration,

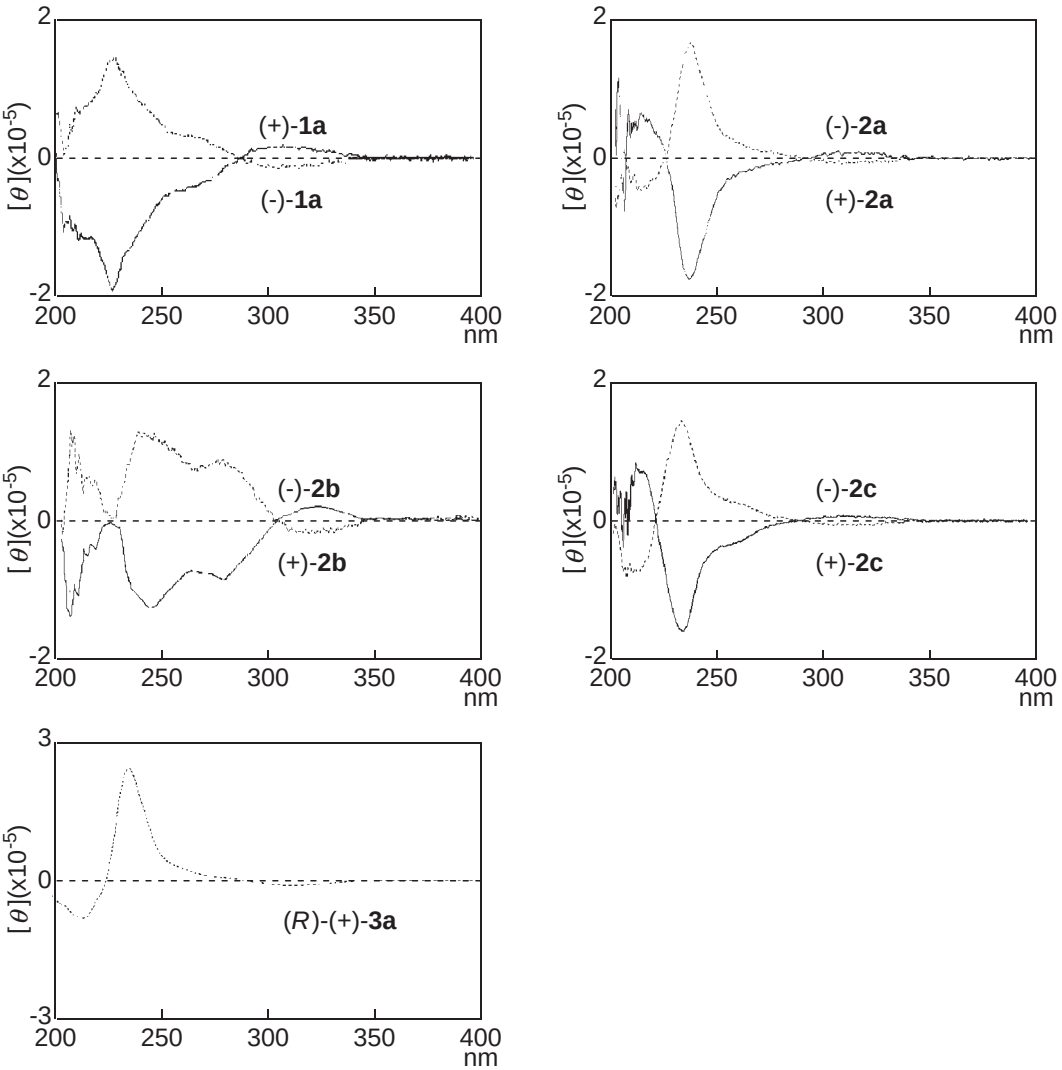
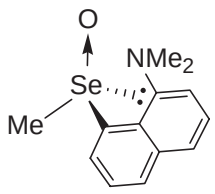


Fig. 3. Circular dichroism spectra of optically active selenonium imides **1a**, **2a**–**2c**, and selenoxide (*R*)-(+)-**3a** in cyclohexane.



(*R*)-(+)-**3a**

Chart 2.

and Stability of Optically Active Selenonium Imides. The absolute configuration of optically active selenonium imides **1a** and **2a**–**2c** could not be determined by X-ray analysis, because no suitable crystal for X-ray analysis could be obtained. Therefore, the absolute configurations of selenonium imides **1a** and **2a**–**2c** were assigned by comparing specific rotations and circular dichroism spectra with those of optically active selenoxide (*R*)-(+)-**3a** (Chart 2) having known absolute configuration.[5m,5n] Optically active selenonium imide (+)-**1a** showed a positive first Cotton effect at 318 nm on the circular dichroism spectrum in cyclohexane, whereas selenonium imide (−)-**1a** showed a negative first Cotton effect in the corresponding region, as shown in Fig. 3. On the other hand, optically active selenonium imides (+)-**2a**–**2c** showed negative first Cotton effects at 313, 316, and 315 nm, respectively. Selenoxide (*R*)-(+)-**3a** showed a negative Cotton effect at 318 nm.[5m,5n] Therefore, the absolute configuration of selenonium imides (+)-**2a**–**2c** was assigned to be *R*-form and that of (−)-**2a**–**2c** was *S*, whereas the absolute configuration of selenonium imides (+)-**1a** and (−)-**1a** could not be assigned.

The stabilities of optically active selenonium imides toward racemization were examined. Optically active selenonium imides (+)-**1** and (*R*)-(+)-**2a**–**2c** did not racemize in the solid state and were stable in chloroform and methanol solutions without racemization for 5 days. These results show that coordination of the intramolecular amino group to the selenium atom effectively prevents racemization, since the naphthyl group facilitates intramolecular coordination due to its rigid structure.

Conclusion

Thermodynamically stable asymmetric selenonium imides possessing the 8-dimethylamino-1-naphthyl group **1a**, **1c**, and

2a–2c were synthesized. Selenonium imides **1a** and **2a–2c** were optically resolved by using HPLC with optically active columns. The absolute configuration of selenonium imides (+)-**2a–2c** was assigned to be *R*-form and that of (−)-**2a–2c** was *S*. Optically active selenonium imides (+)-**1a** and (*R*)-(+)-**2a–2c** were found to be stable toward racemization both in the solid state and in solution.

Experimental

Toluene was distilled from sodium diphenylketyl before use. Cyclohexane, dichloromethane, and hexane were distilled from calcium hydride before use. Ethanol was distilled from sodium ethoxide before use. Methanol was distilled from sodium methoxide before use. Gel permeation chromatography (GPC) was performed using a JAI LC-908 liquid chromatograph with two JAIGEL-1H columns (20 mm × 600 mm), and the products were eluted with chloroform. All reactions were carried out under nitrogen. ^{1}H, ^{13}C, and ^{77}Se NMR spectra were measured on a JEOL JNM-LA-500 with Me_4Si, Me_4Si, and MeSeMe as internal or external standard, respectively. Elemental analysis was performed by using a Perkin-Elmer 240-C. Melting points were determined on a Yamato MP-21 melting point apparatus. UV–vis spectra were measured on a UV-3100PC UV–vis–NIR scanning spectrometer. IR spectra were measured on a Perkin-Elmer Spectrum GX FT-IR system. Mass spectra (MS) were determined on a JEOL JMS-GCmate System. Circular dichroism spectra were measured on a JASCO J-725 Spectropolarimeter. Specific rotations were measured on a JASCO DIP-140 Digital polarimeter.

Synthesis of Selenonium Imides 1a and 1c. A toluene solution (20 mL) of selenoxide[5m,5n] (1.0 mmol) and *p*-toluenesulfonamide (1.0 mmol) was refluxed for 80 h on a Dean-Stark condenser equipped with 3A molecular sieves.[21] The solution was concentrated under reduced pressure, and purification by gel permeation chromatography gave selenonium imide (**1a**: 50%, **1c**: 53%).

8-Dimethylamino-1-naphthylmethylselenonium *p*-Toluenesulfonimide (1a): White solid; mp 154–156 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.36 (3H, s), 2.64 (3H, s), 2.66 (3H, s), 2.90 (3H, s), 7.20 (1H, d, J = 8.0 Hz), 7.51 (2H, d, J = 8.5 Hz), 7.57 (1H, t, J = 8.0 Hz), 7.64 (1H, t, J = 8.0 Hz), 7.82 (1H, d, J = 8.0 Hz), 7.89 (2H, d, J = 8.5 Hz), 7.99 (1H, d, J = 8.0 Hz), 8.74 (1H, d, J = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 35.3, 43.3, 49.3, 119.9, 125.9, 126.7, 126.7, 126.9, 126.9, 128.1, 129.1, 129.8, 131.9, 135.8, 140.6, 144.0, 148.0; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 892; MS (EI, 30 eV) m/z 434 (^{80}Se, M^+), 432 (^{78}Se, M^+), 264, 262, 250, 248, 235, 233, 168, 155, 125, 91; IR (KBr) 3054, 2920, 1565, 1456, 1362, 1255, 1129, 1085, 959, 897, 828, 667, 570, 549 cm^{-1}; UV (cyclohexane) λ_{max} 221 (1.5×10^4), 290 (3.6×10^3) nm; UV (chloroform) λ_{max} 225 (1.2×10^4), 293 (1.1×10^4) nm; Anal. Calcd for $C_{20}H_{22}N_2O_2SSe$: C, 55.42; H, 5.12; N, 6.48%. Found: C, 55.11; H, 5.32; N, 6.21%.

8-Dimethylamino-1-naphthylphenylselenonium *p*-Toluenesulfonimide (1c): White solid; mp 171–173 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (3H, s), 2.33 (3H, s), 2.66 (3H, s), 6.97 (2H, d, J = 7.5 Hz), 7.14 (2H, d, J = 7.5 Hz), 7.19 (2H, t, J = 7.5 Hz), 7.28 (1H, d, J = 7.5 Hz), 7.36 (1H, t, J = 7.5 Hz), 7.52 (1H, t, J = 7.5 Hz), 7.75 (1H, d, J = 7.5 Hz), 7.81–7.83 (3H, m), 8.08 (1H, d, J = 7.5 Hz), 9.01 (1H, d, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 43.8, 49.1, 120.5, 126.0, 126.1, 126.9, 127.0, 127.1, 127.5, 128.1, 129.0, 129.7, 130.4, 130.8, 132.7, 135.6, 139.2, 140.4, 144.3, 148.4; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 829; MS (EI, 30 eV) m/z 496 (^{80}Se, M^+), 494 (^{78}Se, M^+), 327, 325, 311, 309, 297, 295, 250, 248, 170, 157; IR (KBr) 3064, 2956, 1562, 1441, 1366, 1179, 1055, 978, 817, 808, 655, 571, 567 cm^{-1}; UV (cyclohexane) λ_{max} 218 (1.5×10^4), 287 (3.6×10^3) nm; UV (chloroform) λ_{max} 225 (1.2×10^4), 286 (1.1×10^4) nm; Anal. Calcd for $C_{25}H_{24}N_2O_2SSe$: C, 60.60; H, 4.88; N, 5.65%. Found: C, 60.80; H, 5.12; N, 5.41%.

Synthesis of Selenonium Imides 2a–2c. A dichloromethane solution (100 mL) of selenoxide[5m,5n] (1.0 mmol) and trifluoromethanesulfonamide (1.0 mmol) was stirred for 17 h in the presence of sodium sulfate. The sodium sulfate was filtered off, and the filtrate was concentrated under reduced pressure. Purification by gel permeation chromatography gave selenonium imide (**2a**: 53%, **2b**: 19%, **2c**: 51%).

8-Dimethylamino-1-naphthylmethylselenonium Trifluoromethanesulfonimide (2a): White solid; mp 187–188 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.71 (3H, s), 2.83 (3H, s), 2.97 (3H, s), 7.60 (1H, d, J = 7.5 Hz), 7.65 (1H, t, J = 8.0 Hz), 7.77 (1H, t, J = 7.5 Hz), 7.89 (1H, d, J = 8.0 Hz), 8.10 (1H, d, J = 8.0 Hz), 8.82 (1H, d, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 36.8, 43.4, 49.3, 120.4, 126.5, 127.1, 127.3, 127.4, 127.9, 128.1, 132.6, 135.8, 147.3 ($\underline{C}F_3$ was not observed); ^{77}Se NMR (95 MHz, $CDCl_3$) δ 892; MS (EI, 30 eV) m/z 412 (^{80}Se, M^+), 410 (^{78}Se, M^+), 264, 262, 250, 248, 235, 233, 168, 155, 125, 91; IR (KBr) 3032, 2920, 1564, 1542, 1362, 1200, 1119, 1064, 941, 880, 866, 645, 571, 561 cm^{-1}; UV (cyclohexane) λ_{max} 217 (1.3×10^4), 278 (3.5×10^3) nm; UV (chloroform) λ_{max} 224 (1.3×10^4), 276 (1.0×10^4) nm; Anal. Calcd for $C_{14}H_{15}F_3N_2O_2SSe$: C, 40.88; H, 3.68; N, 6.81%. Found: C, 41.11; H, 4.01; N, 6.21%.

Benzyl-8-dimethylamino-1-naphthylselenonium Trifluoromethanesulfonimide (2b): White solid; mp 179–180 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.71 (3H, s), 3.09 (3H, s), 4.10 (1H, d, J = 11.0 Hz), 4.35 (1H, d, J = 11.0 Hz), 6.91 (2H, d, J = 7.5 Hz), 7.12 (2H, t, J = 7.5 Hz), 7.22 (1H, t, J = 7.5 Hz), 7.56 (1H, t, J = 7.5 Hz), 7.64 (1H, d, J = 7.5 Hz), 7.65 (1H, d, J = 7.5 Hz), 7.86 (1H, t, J = 7.5 Hz), 8.03 (1H, d, J = 7.5 Hz), 8.44 (1H, d, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 43.7, 49.3, 57.1, 119.7, 120.0, 122.3, 126.3, 126.8, 127.1, 127.3, 128.3, 128.5, 129.0, 129.3, 130.6, 132.5, 135.5 ($\underline{C}F_3$ was not observed); ^{77}Se NMR (95 MHz, $CDCl_3$) δ 842; MS (EI, 30 eV) m/z 488 (^{80}Se, M^+), 486 (^{78}Se, M^+), 341, 339, 264, 262, 250, 248, 235, 233, 168, 155, 91; IR (KBr) 3048, 2933, 1551, 1446, 1425, 1245, 1121, 1083, 950, 822, 678, 571 cm^{-1}; UV (cyclohexane) λ_{max} 228 (1.7×10^4), 291 (3.6×10^3) nm; UV (chloroform) λ_{max} 224 (1.4×10^4), 284 (1.0×10^4) nm; Anal. Calcd for $C_{20}H_{19}F_3N_2O_2SSe$: C, 49.29; H, 3.93; N, 5.75%. Found: C, 49.68; H, 4.23; N, 5.53%.

8-Dimethylamino-1-naphthylphenylselenonium Trifluoromethanesulfonimide (2c): White solid; mp 164–166 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.24 (3H, s), 2.64 (3H, s), 7.14–7.17 (5H, m), 7.25 (1H, d, J = 7.5 Hz), 7.39 (1H, t, J = 7.5 Hz), 7.70 (1H, d, J = 7.5 Hz), 7.71 (1H, t, J = 7.5 Hz), 7.95 (1H, d, J = 7.5 Hz), 8.76 (1H, d, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 43.6, 49.1, 119.8, 126.3, 126.7, 126.8, 127.1, 128.2, 129.3, 130.1, 130.3, 131.7, 134.0, 135.3, 145.6, 149.2 ($\underline{C}F_3$ was not observed); ^{77}Se NMR (95 MHz, $CDCl_3$) δ 884; MS (EI, 30 eV) m/z 474 (^{80}Se, M^+), 472 (^{78}Se, M^+), 327, 325, 311, 309, 297, 295, 250, 248, 170, 157; IR (KBr) 3070, 2980, 1575, 1476, 1367, 1255, 1159, 1061, 959, 867, 848, 560, 541 cm^{-1}; UV (cyclohexane) λ_{max} 219 (1.7×10^4), 285 (3.2×10^3) nm; UV (chloroform) λ_{max} 221 (1.3×10^4), 287 (1.1×10^4) nm; Anal. Calcd for $C_{19}H_{17}F_3N_2O_2SSe$: C, 48.21; H, 3.62; N, 5.92%. Found: C, 48.56; H, 3.94; N, 5.71%.

Optical Resolution of Racemic Selenonium Imides by Means of High-Performance Liquid Chromatography Using Optically Active Columns. Optical resolution of racemic selenonium imide **1a** was performed by HPLC using an optically active column packed with cellulose carbamate derivative/silica gel (Daicel Chiralcel OD, $4.6 \times 250\,mm^2$) with hexane/ethanol (95/5) as an eluent. Optical resolution of racemic selenonium imides **2a–2c** was performed by using an optically active column packed with amylose derivative/silica gel (Daicel Chiralpak AS-H, $4.6 \times 250\,mm^2$) with hexane/ethanol (90/10) as an eluent. Typically, 2 mg of selenonium imide was charged to the column. A 0.7-mg sample of the first-eluted selenonium imide was collected, and a 0.7-mg sample of the second-eluted selenonium imide was collected. This process was repeated at 10–15 times. Each of the collected components was subjected to the column again. Finally, ca. 5 mg of optically pure selenonium imides were obtained, except for (−)-**1a**.

(+)-8-Dimethylamino-1-naphthylmethylselenonium *p*-Toluenesulfonimide {(+)-1a}: White solid; mp 158–159 °C; 100% ee; $[\alpha]_D$ +73.0 (*c* 0.05, $CHCl_3$), $[\alpha]_{435}$ +110.6 (*c* 0.05, $CHCl_3$); CD (cyclohexane) λ_{max} 318 ($[\theta]$ 1.4×10^4), 228 ($[\theta]$ -2.0×10^5) nm; ^{1}H NMR, ^{13}C NMR, IR, MS, and UV spectra were almost the same as those of the racemic one.

(−)-8-Dimethylamino-1-naphthylmethylselenonium *p*-Toluenesulfonimide {(−)-1a}: White solid; mp 155–160 °C (55% ee); 60% ee; $[\alpha]_D$ −46.0 (*c* 0.04, $CHCl_3$), $[\alpha]_{435}$ −65.7 (*c* 0.04, $CHCl_3$); CD (cyclohexane) λ_{max} 318 ($[\theta]$ -8.8×10^3), 228 ($[\theta]$ 1.4×10^5) nm; ^{1}H NMR, ^{13}C NMR, IR, MS, and UV spectra were almost the same as those of the racemic one.

(*R*)-(+)-8-Dimethylamino-1-naphthylmethylselenonium Trifluoromethanesulfonimide {(*R*)-(+)-2a}: White solid; mp 160–161 °C; 100% ee; $[\alpha]_D$ +334.0 (*c* 0.19, $CHCl_3$), $[\alpha]_{435}$ +709.1 (*c* 0.19, $CHCl_3$); CD (cyclohexane) λ_{max} 313 ($[\theta]$ -1.2×10^4), 232 ($[\theta]$ 1.8×10^5) nm; ^{1}H NMR, ^{13}C NMR, IR, MS, and UV spectra were almost the same as those of the racemic one.

(*S*)-(−)-8-Dimethylamino-1-naphthylmethylselenonium Trifluoromethanesulfonimide {(*S*)-(−)-2a}: White solid; mp 161–162 °C; 100% ee; $[\alpha]_D$ −336.0 (*c* 0.22, $CHCl_3$), $[\alpha]_{435}$ −707.4 (*c* 0.22, $CHCl_3$); CD (cyclohexane) λ_{max} 312 ($[\theta]$ 1.3×10^4), 233 ($[\theta]$ -1.9×10^5) nm; ^{1}H NMR, ^{13}C NMR, IR, MS, and UV spectra were almost the same as those of the racemic one.

(*R*)-(+)-Benzyl-8-dimethylamino-1-naphthylselenonium Trifluoromethanesulfonimide {(*R*)-(+)-2b}: White solid; mp 164–165 °C; 100% ee; $[\alpha]_D$ +119.0 (*c* 0.89, $CHCl_3$), $[\alpha]_{435}$ +258.6 (*c* 0.89, $CHCl_3$); CD (cyclohexane) λ_{max} 316 ($[\theta]$ -2.2×10^4), 273 ($[\theta]$ 1.1×10^5), 230 ($[\theta]$ 1.3×10^5) nm; ^{1}H NMR, ^{13}C NMR, IR, MS, and UV spectra were almost the same as those of the racemic one.

(*S*)-(−)-Benzyl-8-dimethylamino-1-naphthylselenonium Trifluoromethanesulfonimide {(*S*)-(−)-2b}: White solid; mp 164–165 °C; 100% ee; $[\alpha]_D$ −118.0 (*c* 0.73, $CHCl_3$), $[\alpha]_{435}$ −259.0 (*c* 0.73, $CHCl_3$), CD (cyclohexane) λ_{max} 315 ($[\theta]$ 2.0×10^4), 272 ($[\theta]$ -1.0×10^5), 230 ($[\theta]$ -1.4×10^5) nm; ^{1}H NMR, ^{13}C NMR, IR, MS, and UV spectra were almost the same as those of the racemic one.

(*R*)-(+)-8-Dimethylamino-1-naphthylphenylselenonium Trifluoromethanesulfonimide {(*R*)-(+)-2c}: White solid; mp 154–156 °C; 100% ee; $[\alpha]_D$ +147.6 (*c* 0.44, $CHCl_3$), $[\alpha]_{435}$ +245.5 (*c* 0.44, $CHCl_3$), CD (cyclohexane) λ_{max} 315 ($[\theta]$ -1.6×10^4), 230 ($[\theta]$ 1.5×10^5) nm; ^{1}H NMR, ^{13}C NMR, IR, MS, and UV spectra were almost the same as those of the racemic one.

(*S*)-(−)-8-Dimethylamino-1-naphthylphenylselenonium Trifluoromethanesulfonimide {(*S*)-(−)-2c}: White solid; mp 155–156 °C; 100% ee; $[\alpha]_D$ −145.4 (*c* 0.89, $CHCl_3$), $[\alpha]_{435}$ −243.6 (*c* 0.89, $CHCl_3$), CD (cyclohexane) λ_{max} 316 ($[\theta]$ 1.6×10^4), 228 ($[\theta]$ -1.7×10^5) nm, ^{1}H NMR, ^{13}C NMR; IR, MS, and UV spectra were almost the same as those of the racemic one.

Stability toward Racemization of Optically Active Selenonium Imides. The racemization of optically active selenonium imides (+)-**1a** and (*R*)-(+)-**2a–2c** was examined in 7 mM solution at 28 °C by means of their specific rotations.

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