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Thermodynamically Stabilized Chiral Chalcogen Oxides: Optical Resolution and Stereochemistry

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ABSTRACT: *Optical resolution of racemic selenoxides,* **1a, 1b***, and* **1c***, and telluroxide* **2b***, possessing an 8-dimethylamino-1-naphthyl group by liquid chromatography using optically active columns afforded the corresponding enantiomerically pure stereoisomers. Absolute configurations of the optically active chalcogen oxides were assigned by comparison of their specific rotations and CD spectra with those of the sulfur analog. All of the optically active chalcogen oxides obtained were stable toward racemization in their solid states; however, selenoxides* **1a** *and* **1b** *and telluroxide* **2b** *racemized in solutions. Kinetic studies of the racemization clarified that thermodynamic stabilization by intramolecular coordination of the nitrogen atom in the 8-dimethylamino-1-naphthyl group to the chalcogen atom was effective to prevent the racemization.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:227–237, 2001

INTRODUCTION

Our recent interest has focused on the synthesis and stereochemistry of optically active tricoordinate selenium and tellurium compounds [1–3]. Previously, we reported the isolation of optically active selenoxides [1,4] and telluroxides [5], which are stabilized by bulky substituents (kinetic stabilization) because the racemization of selenoxides and telluroxides had been considered to be very rapid. The kinetic stabilization was found to be effective; however, these chalcogen oxides were still unstable toward racemization, especially the optically active telluroxide, which racemized easily in solutions. Thermodynamic stabilization is also considered to be effective to stabilize unstable compounds, and there are many reports concerning stabilization by intramolecular coordination of an amino group [6]. For example, reactive and unstable divalent organoselenium and tellurium compounds [7–18], such as selenenyl [7–11] and tellurenyl [12–18] halides, selenolates [7,9–11], and tellurolates [12–18], have been isolated by using the stabilization by intramolecular coordination. Recently, we reported the isolation of optically active selenoxides [19] and telluroxides [20] possessing the 2-(*N,N*-dimethylaminomethyl)phenyl group; however, their configurational stabilities were not satisfactory in solutions, although the intramolecular coordination of the amino group to the chalcogen atoms certainly retarded the racemization.

We synthesized selenoxides and telluroxides possessing the 8-dimethylamino-1-naphthyl group, which are expected to facilitate the intramolecular coordination due to the restricted geometries of the molecules and we isolated the stereoisomers. In this article, optical resolution of the selenoxides and telluroxides by means of HPLC using optically active

Dedicated to Prof. Naoki Inamoto.
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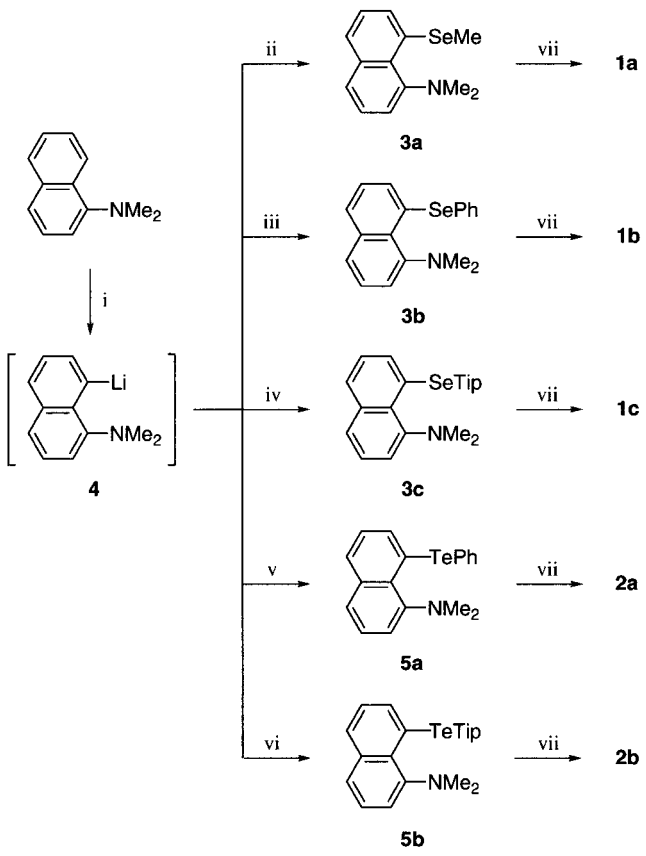
columns and their configurational stabilities will be reported [21].

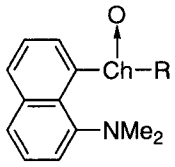
RESULTS AND DISCUSSION

Preparation of Racemic Selenoxides and Telluroxides

8-Dimethylamino-1-naphthyl methyl selenide (**3a**), precursor of selenoxide **1a**, was prepared in 53% yield by the reaction of 8-dimethylamino-1-naphthyllithium (**4**) with selenium powder followed by treatment with methyl iodide, as shown in Scheme 1 [22]. Diaryl selenides **3b** and **3c** and tellurides **5a** and **5b** were also synthesized by reacting the lithium reagent **4** with the corresponding diselenides or ditellurides in yields of 46, 41, 49, and 11%, respectively. Finally, racemic selenoxides **1a, 1b**, and **1c** and telluroxides **2a** and **2b** were obtained in 82–98% yields by oxidation [19,22] of the corresponding selenides or tellurides with *tert*-butyl hypochlorite, followed by treatment with aqueous sodium hydroxide.



SCHEME 1 Reagents and Conditions: i: BuLi, ether, r.t.; ii: Se powder, then MeI; iii: $(PhSe)_2$; iv: $(TipSe)_2$; v: $(PhTe)_2$; vi: $(TipTe)_2$; vii: Bu^tOCl, MeOH, CH_2Cl_2, −25°C, then NaOH(aq.)



1a: Ch = Se, R = Me
1b: Ch = Se, R = Ph
1c: Ch = Se, R = 2,4,6-$Pr^i_3C_6H_2$ (Tip)
2a: Ch = Te, R = Ph
2b: Ch = Te, R = 2,4,6-$Pr^i_3C_6H_2$ (Tip)

Optical Resolution of Selenoxides and Telluroxides by Means of HPLC Using Optically Active Columns

Optical resolution of racemic selenoxide **1a** was attempted by HPLC at an analytical scale using an optically active column packed with amylose carbamate derivative/silica gel (Daicel Chiralpak AS). As shown in Figure 1, selenoxide **1a** was resolved into two peaks corresponding to each enantiomer (eluent: hexane/ethanol = 90/10). Similarly, racemic selenoxide **1b** (eluent: hexane/ethanol = 90/10) and **1c** (eluent: hexane/2-propanol = 99/1) could also be resolved into the enantiomeric isomers, respectively.

Racemic telluroxides **2a** and **2b** were also subjected to HPLC using optically active columns at an analytical scale. Telluroxide **2b** was resolved into two peaks corresponding to each enantiomer on Chiralcel OD (packed with cellulose carbamate derivative/silica gel; eluent: hexane/2-propanol = 75/25), as shown in Figure 2. However, the first peak of the chromatogram did not return to the base line, and the phenomenon indicates that racemization is occurring in the column. When the chromatographic resolution was carried out under cooling the column to −3°C, telluroxide **2b** could be resolved completely. On the other hand, resolution of telluroxide **2a** was insufficient on Chiralcel OD (eluent: hexane/ethanol = 90/10), and **2a** also could not be resolved on Chiralpak AS.

The optical resolution of racemic selenoxides **1a, 1b**, and **1c** was carried out at a preparative scale on Daicel Chiralpak AS. Repeated resolution of the first and second fractions of selenoxide **1a** gave optically pure selenoxides, respectively, the optical purities of which were determined by HPLC analysis. The first eluted enantiomer had a positive specific rotation {(+)-**1a**: enantiomeric excess (ee) 100%; $[\alpha]_D$ +363.8 (c 0.10, $CHCl_3$)}, and the second eluted enantiomer had a negative one {(−)-**1a**: ee 100%; $[\alpha]_D$ −350.8 (c 0.19, $CHCl_3$)}. Similarly, optically pure selenoxides (−)-**1b** and (−)-**1c** were obtained from the first fractions. However, (+)-**1b** and (+)-**1c**, collected from the second fractions, were 80 and 90% ee, respectively. The results are summarized in Table 1. The reason why optically pure selenoxides (+)-**1b** and

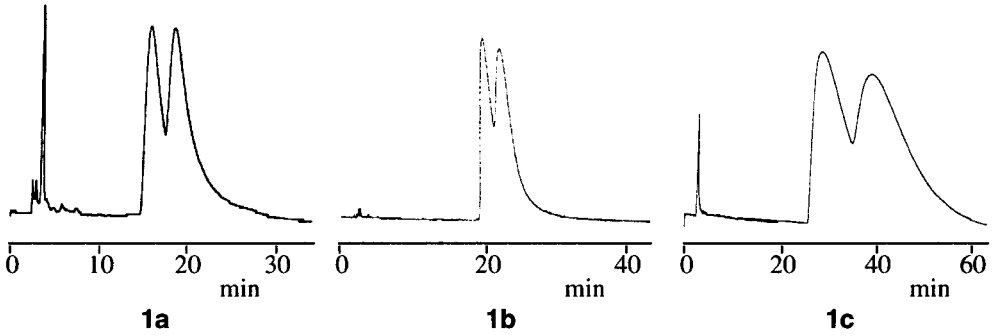


FIGURE 1 Chromatographic resolution of racemic selenoxides **1a, 1b**, and **1c** by means of HPLC using an optically active column (Daicel Chiralpak AS) at room temperature.

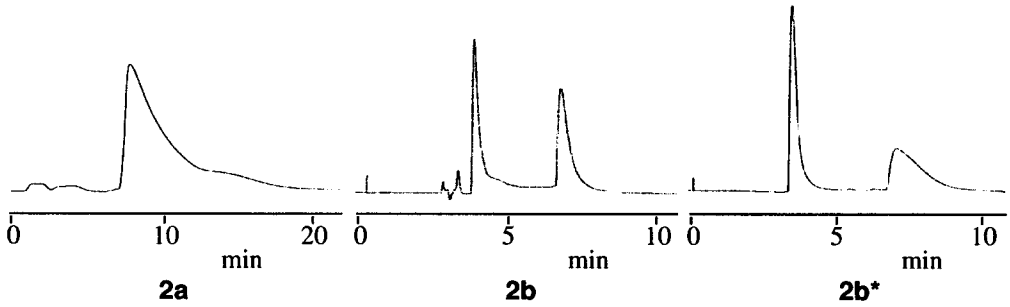


FIGURE 2 Chromatographic resolution of racemic telluroxides **2a** and **2b** by means of HPLC using an optically active column (Daicel Chiralcel OD) at room temperature. *At −3°C.

TABLE 1 Chromatographic Resolution of Selenoxides and Telluroxides

			First enantiomer		*Second enantiomer*	
Compound	*Column*[a]	*Alcohol/%*[b]	$[\alpha]_D$ *(c)*[c]	*ee/%*[d]	$[\alpha]_D$ *(c)*	*ee/%*
1a	AS	10[e]	+363.8 (0.10)	100	−350.8 (0.19)	100
1b	AS	10[e]	−165.4 (0.19)	100	+140.5 (0.50)	80
1c	AS	1[f]	−87.6 (0.58)	100	+78.7 (0.31)	90
2b	OD	25[f]	−46.0 (0.67)	100	+47.6 (0.23)	100

[a]AS, Daicel Chiralpak AS; OD, Daicel Chiralcel OD.
[b]The volume percentage of ethanol or 2-propanol in hexane used as mobile phase.
[c]Specific rotations were taken in chloroform at 25–27°C.
[d]Optical purities were determined by HPLC analysis.
[e]Ethanol.
[f]2-Propanol.

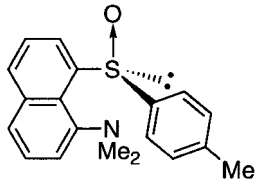
(+)-**1c** could not be obtained may be due to tailing of the first eluted enantiomer.

The optical resolution of racemic telluroxides **2a** and **2b** was also carried out by using an optically active column (Daicel Chiralcel OD) at a preparative scale at −3°C. In the case of **2b**, repeated resolution of the first and second fractions gave the optically pure stereoisomers, respectively. The first eluted enantiomer had a negative specific rotation, and the second enantiomer had a positive one. However, optically active telluroxides (−)-**2a** and (+)-**2a** could not be obtained, perhaps due to racemization that was occurring in the column.

Circular Dichroism Spectra and Absolute Configurations of Optically Active Selenoxides and Telluroxides

The CD spectra of optically active selenoxides (+)-**1a**, (+)-**1b**, and (+)-**1c**, showed negative first Cotton

effects at 317, 314, and 283 nm, respectively, and those of (−)-**1a**, (−)-**1b**, and (−)-**1c** showed positive Cotton effects in the same regions, as shown in Figure 3. The positive first Cotton effects of the (−)-selenoxides correspond well with that of optically active (*S*)-(−)-8-dimethylamino-1-naphthyl 4′-tolyl sulfoxide {(*S*)-(−)-**6**}, which was prepared by reacting $(S)_s$-(−)-menthyl-(−)-4-toluenesulfinate with lithium reagent **4** according to the modified Andersen's method [23,24]. Therefore, the absolute configuration of selenoxides (−)-**1a**, (−)-**1b**, and (−)-**1c** can be assigned to be the *S*-form, and that of (+)-**1a**, (+)-**1b**, and (+)-**1c** is *R*.



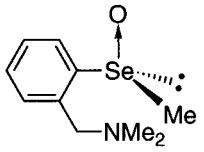
(*S*)-(-)-**6**

The CD spectrum of optically active telluroxide (+)-**2b** also showed a negative first Cotton effect at 339 nm, and that of (−)-**2b** showed a positive Cotton effect in the same region, as shown in Figure 4. The absolute configuration of optically active telluroxide (−)-**2b** was estimated to be the *S*-form by comparing the first Cotton effect with that of (*S*)-(−)-**6**.

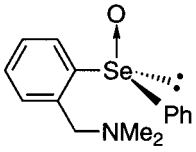
Configurational Stability of Optically Active Selenoxides and Telluroxides

Optically active selenoxides **1a, 1b**, and **1c** and telluroxide **2b** were stable toward racemization in the solid states even after two weeks when they were kept in a desiccator at room temperature. Selenoxides (+)-**1a**, (+)-**1b**, and (−)-**1c** were also stable in chloroform, and no racemization was observed after 5 days; however, (+)-**1a** and (+)-**1b** racemized in methanol solutions despite the careful purification of the solvent. On the other hand, selenoxide (−)-**1c**, having a bulky substituent, the 2,4,6-triisopropylphenyl group, was stable not only in chloroform but also in methanol. The rates of racemization for optically active selenoxides (+)-**1a** and (+)-**1b** in methanol showed a good linear relationship in first-order rate plots, and the rate constants were 1.84×10^{-5} and 2.21×10^{-6} s^{-1} (at 26°C), respectively, as summarized in Table 2. Addition of water to the methanol solution of (+)-**1a** and (+)-**1b** accelerated the racemization. These results indicate that the racemization of selenoxide occurs due to a trace amount of water that remains in the solvent. However, in the case of (−)-**1c**, no racemization was observed, even in methanol solution containing 20 vol % of water; showing that the combination of the kinetic and thermodynamic stabilization is effective to prevent the racemization of optically active selenoxides.

We had already reported that (*S*)-(−)-2-(*N,N*-dimethylaminomethyl)phenyl methyl selenoxide {(*S*)-(−)-**7**} and (*S*)-(−)-2-(*N,N*-dimethylaminomethyl)diphenyl selenoxide {(*S*)-(−)-**8**} were stabilized toward racemization by intramolecular coordination of the amino group to the selenium atom [19]. The rate constants of racemization for selenoxides (*S*)-(−)-**7** and (*S*)-(−)-**8** in methanol solutions were 2.28×10^{-4} and 5.58×10^{-6} s^{-1}, respectively. Therefore, selenoxide **1a** is more stable toward racemization in methanol solution than selenoxide **7**, and selenoxide **1b** is also more stable than selenoxide **8**. These results show that the thermodynamic stabilization of selenoxide by the intramolecular coordination of the amino group of 8-dimethylamino-1-naphthyl moiety to the selenium atom is more effective due to the restricted geometry than that of the 2-(*N,N*-dimethylaminomethyl)phenyl group.



(*S*)-(-)-**7**



(*S*)-(-)-**8**

The racemization of optically active telluroxide (+)-**2b** was observed, not only in methanol but also even in carefully purified and dried chloroform, whereas the corresponding optically active selenoxide (−)-**1c** did not racemize under these conditions, and the kinetics for racemization was also examined. The rate for the racemization of (+)-**2b** also showed a good linear relationship in first-order rate plots, and the rate constant was 9.08×10^{-5} s^{-1} at 26°C. Telluroxide **2b** is slightly more stable toward racemization in chloroform than is (*R*)-(+)-2-(*N,N*-dimethylaminomethyl)phenyl 2,4,6-triisopropylphenyl telluroxide {(*R*)-(+)-**9**} [20]. The intramolecular coordination of the amino group of the 8-dimethylamino-1-naphthyl moiety might be more effective to a certain extent than that of the 2-(*N,N*-dimethylaminomethyl)phenyl moiety; however, it was not enough to meet our initial expectation. Thus, telluroxide **2b** racemized completely within 1 minute in methanol solutions.

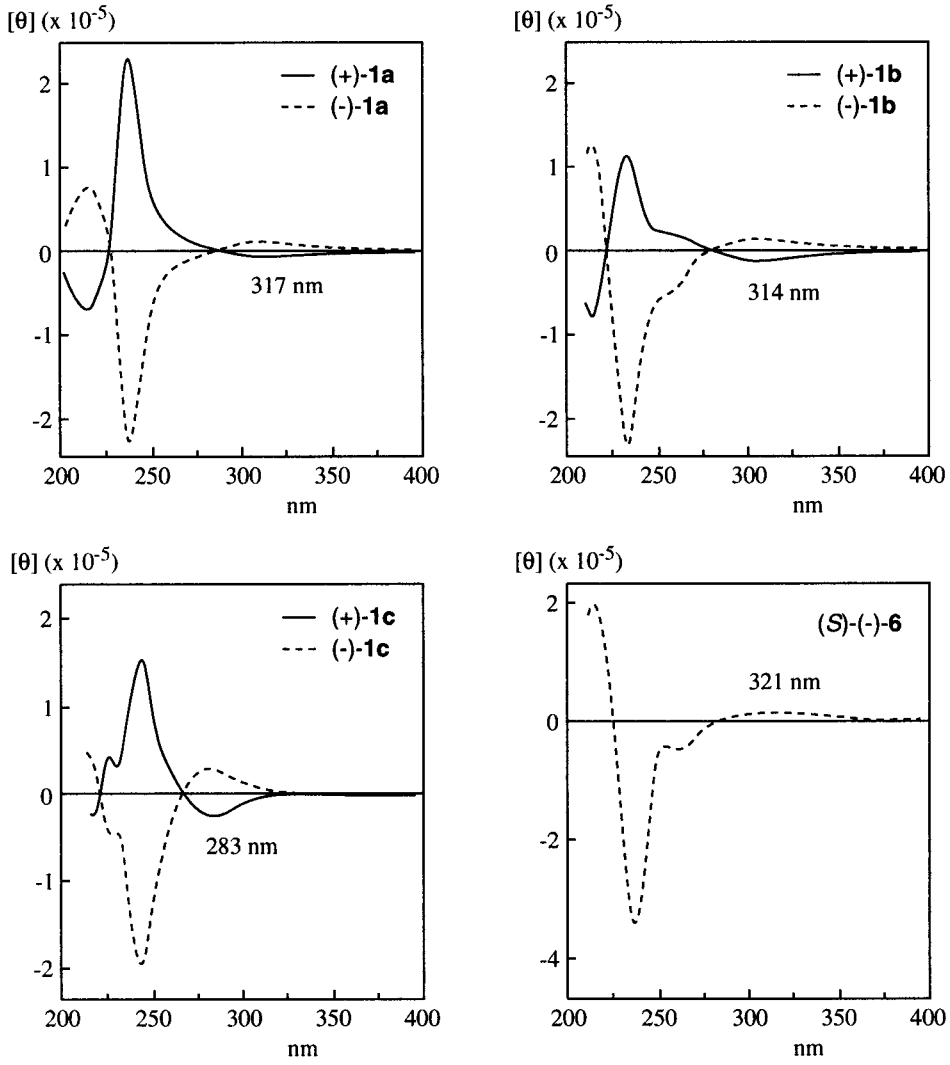
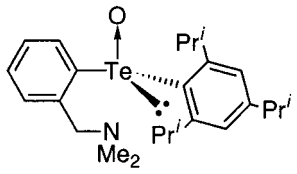


FIGURE 3 CD spectra of optically active selenoxides (+)- **1a–c** and (−)-**1a–c**, and sulfoxide (*S*)-(−)-**6** in cyclohexane.



(*R*)-(+)-**9**

CONCLUSION

Thermodynamically stabilized optically pure selenoxides **1a, 1b**, and **1c** and telluroxide **2b** possessing an 8-dimethylamino-1-naphthyl substituent were isolated by means of HPLC using optically active columns. These optically active chalcogen oxides were stable toward racemization in the solid state but racemized in solutions. Optically active telluroxides underwent racemization faster than selenoxides in solutions. Selenoxide **1c**, stabilized by the intramolecular coordination and bulky substituent, was very stable toward racemization even in solutions containing water. Selenoxide **1b** was more stable toward racemization than selenoxide **8**, and telluroxide **2b** was also more stable than telluroxide **9**. These results show that the coordination of the amino group of the 8-dimethylamino-1-naphthyl moiety to the chalcogen atom is more effective than that of the 2-(*N,N*-dimethylaminomethyl)phenyl group since the naphthyl group is considered to facilitate better intramolecular coordination due to the restricted geometry.

EXPERIMENTAL

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl before use. Cyclohexane,

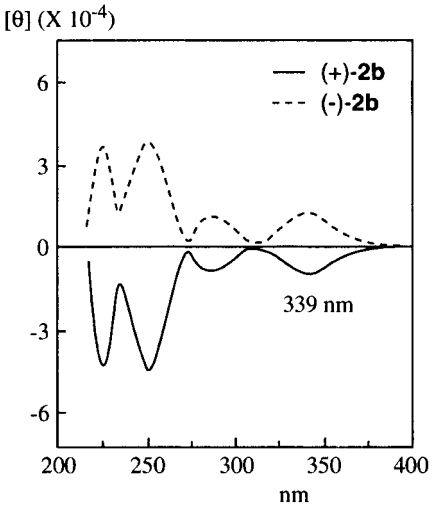


FIGURE 4 CD spectra of optically active telluroxides (+)-**2b** and (−)-**2b** in cyclohexane.

chloroform, dichloromethane, hexane and 2-propanol were distilled from calcium hydride before use. Methanol and ethanol were distilled from magnesium cake and stored with 3A molecular sieves under nitrogen. Thin-layer chromatography (TLC) was performed with Merck Art. 5554 DC-Alufolien Kieselgel 60 F_{254}. Column chromatography was performed with Merck 7734 Kieselgel 60.

*8-Dimethylamino-1-naphthyl Methyl Selenide (***3a***)*

To a stirred suspension of 8-(dimethylamino-1-naphthyl)lithium (**4**), prepared from *N,N*-dimethyl-1-naphthylamine (8.56 g, 50.0 mmol) and BuLi (1.53 M in hexane; 36.0 mL, 55.0 mmol) in anhydrous ether (150 mL), was added elemental selenium (3.9 g, 50.0 mmol) under nitrogen. After 1 hour, all of the selenium powder had been consumed to give a lithium naphthaleneselenolate, to which then was added an ether solution (20 mL) of methyl iodide (9.2 g, 65.0 mmol). The solution was stirred for an additional 2 hours. Saturated brine (100 mL) was added to the solution, and the organic layer was separated. The organic component remaining in the aqueous layer was extracted with ether (100 mL × 3), and the combined organic layer was washed with water and dried over anhydrous magnesium sulfate. The solution was concentrated under reduced pressure, and purification by silica gel column chromatography (eluent: hexane/ether = 2/1) gave selenide **3a** (6.98 g, 53%); m.p. 73–76°C (from benzene-hexane) (lit. 45°C) [22]; ν_{max} (KBr)/cm^{-1} 2360, 1560, 860, and 820; δ_H (500 MHz; $CDCl_3$; Me_4Si) 2.14 (3 H, s, SeMe), 2.68 (6 H, s, NMe_2), 7.28–7.44 (4 H, m, Ar-H), and 7.56–7.66 (2 H, m, Ar-H); δ_C (125 MHz; $CDCl_3$; Me_4Si) 7.2, 45.9, 119.0, 123.6, 124.8, 125.7, 125.8, 126.1, 129.9, 131.5, 135.8, and 151.6; *m/z* (EI) 265 (^{80}Se, M$^+$), 263 (^{78}Se, M$^+$), 250, 235, 168, 155, 127, 115, and 84.

*8-Dimethylamino-1-naphthyl Methyl Selenoxide (***1a***)*

Selenide **3a** (2.64 g, 10.0 mmol) was oxidized with *tert*-butyl hypochlorite (1.30 g, 12.0 mmol) to give racemic selenoxide **1a** (2.31 g, 82%) according to the procedures in the literature [22]; m.p. 123–125°C (lit. 128–129°C, decomp.) [22]; λ_{max} (cyclohexane)/nm 292 (ε/dm^3 mol^{-1} cm^{-3} 5.1 × 10^3) and 224 (2.9 × 10^4); ν_{max} (KBr)/cm^{-1} 2960, 2360, 1360, and 830; δ_H (500 MHz; $CDCl_3$; Me_4Si) 2.55 (3 H, s, SeMe), 2.60 (3 H, s, NMe), 2.88 (3 H, s, NMe), 7.48 (1 H, d, *J* 7.3, Ar-H), 7.55 (1 H, dd, *J* 7.9 and 7.9, Ar-H), 7.73 (1 H, dd, *J* 7.3 and 7.3, Ar-H), 7.80 (1 H, d, *J* 7.9, Ar-H), 7.98 (1 H, d, *J* 7.9, Ar-H) and 8.64 (1 H, d, *J* 7.3, Ar-H); δ_C (125 MHz, $CDCl_3$, Me_4Si) 39.3, 42.8, 49.0, 119.3, 124.6, 126.1, 126.3 (×2), 127.1, 130.7, 135.2, 137.6 and 148.8; *m/z* (EI) 281 (^{80}Se, M$^+$), 279 (^{78}Se, M$^+$), 264, 249, 235, 168, 127, and 86.

*8-Dimethylamino-1-naphthyl Phenyl Selenide (***3b***)*

To a stirred suspension of 8-dimethylamino-1-naphthyllithium (**4**), prepared from *N,N*-dimethyl-1-naphthylamine (8.56 g, 50.0 mmol) and BuLi (1.53 M in hexane; 36.0 mL, 55.0 mmol) in anhydrous ether (150 mL), was added an anhydrous ether solution (100 mL) of diphenyldiselenide (15.6 g, 50.0 mmol) under nitrogen at room temperature. The solution was stirred for an additional 2 hours. Saturated brine (50 mL) was added to the solution, and the organic layer was separated. The organic component remaining in the aqueous layer was extracted with ether (50 mL × 3), and the combined organic layer was washed with water and dried over anhydrous magnesium sulfate. The solution was concentrated under reduced pressure, and purification by silica gel column chromatography (eluent: hexane/ether = 2/1) gave selenide **3b** (7.45 g, 46%); m.p. 92–93°C; ν_{max} (KBr)/cm^{-1} 2970, 2350, 1700, and 820; δ_H (500 MHz, $CDCl_3$, Me_4Si) 2.76 (6 H, s, NMe_2), 6.87–6.94 (1 H, m, Ar-H), 7.03–7.14 (1 H, m, Ar-H), 7.35–7.45 (5 H, m, Ph), 7.52–7.65 (2 H, m, Ar-H) and 7.73–7.80 (2 H, m, Ar-H); δ_C (125 MHz; $CDCl_3$; Me_4Si) 46.1, 119.1, 125.1, 125.76, 125.79, 125.9, 126.1, 128.4, 129.39, 129.43, 132.79, 132.84, 135.9, 137.5, and 151.5; *m/z* (EI) 327 (^{80}Se, M$^+$), 325 (^{78}Se, M$^+$), 265, 250, 170, 154, and 84.

TABLE 2 First-Order Rate Constants for Racemization of Optically Active Selenoxides and Telluroxides in Solutions[a]

	k/s^{-1} ($t_{1/2}$/h)						
Solvent	*(R)-(+)*-**1a**	*(R)-(+)*-**1b**	*(S)-(−)*-**1c**	*(R)-(+)*-**2b**	*(S)-(−)*-**7**[b]	*(S)-(−)*-**8**[b]	*(R)-(+)*-**9**[c]
$CHCl_3$	A[e]	A	A	9.08×10^{-5} (2.12)	A	A	1.36×10^{-4} (1.41)
MeOH	1.84×10^{-5} (10.4)	2.21×10^{-6} (87.1)	A	B[f]	2.28×10^{-4} (0.844)	5.58×10^{-6} (34.5)	B
MeOH /H_2O[d]	5.21×10^{-5} (3.70)	3.70×10^{-6} (51.9)	A	B	1.23×10^{-3} (0.157)	5.13×10^{-5} (3.76)	B

[a]In ca. 5 mM solution at 26 ± 1°C.
[b]Ref. [19].
[c]Ref. [20].
[d]MeOH/H_2O = 4/1.
[e]A, No racemization was observed even after 5 days.
[f]B, Racemization was completed within 1 minute.

*8-Dimethylamino-1-naphthyl Phenyl Selenoxide (***1b***)*

To a stirred mixed solvent of dichloromethane (200 mL) and methanol (50 mL) containing selenide **3b** (3.27 g, 10.0 mmol) was added slowly a dichloromethane solution (50 mL) of *tert*-butyl hypochlorite (1.30 g, 12.0 mmol) at −25°C under nitrogen, and the solution was stirred for an additional 30 minutes and then was allowed to stand until it attained room temperature. After aqueous sodium hydroxide (0.60 g in 20 mL) was poured into the stirred reaction mixture, the organic layer was separated. The organic component remaining in the aqueous layer was extracted with dichloromethane (50 mL × 3), and combined with the organic layer and was dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure, and purification by silica gel column chromatography (eluent: dichloromethane/methanol = 100/6) gave racemic selenoxide **1b** (3.28 g, 88%); m.p. 152–155°C; λ_{max} (cyclohexane)/nm 295 (ε/dm^3 mol^{-1} cm^{-3} 4.5×10^3) and 218 (2.6×10^4); ν_{max} (KBr)/cm^{-1} 2980, 2360, 1440, 1360, and 815; δ_H (500 MHz; $CDCl_3$; Me_4Si) 2.13 (3 H, s, NMe), 2.51 (3 H, s, NMe), 7.13–7.18 (5 H, m, Ph), 7.22 (1 H, d, *J* 7.4, Ar-H), 7.35 (1 H, dd, *J* 7.9 and 7.9, Ar-H), 7.66 (1 H, d, *J* 7.9, Ar-H), 7.69 (1H, dd, *J* 7.4 and 7.4, Ar-H), 7.92 (1H, d, *J* 7.9, Ar-H) and 8.77 (1H, d, *J* 7.4, Ar-H); δ_C (125 MHz, $CDCl_3$, Me_4Si) 43.2, 49.4, 119.3, 125.9, 126.1, 126.3, 126.6 (×2), 127.7, 128.8, 129.8, 131.2, 134.2, 134.9, 145.7 and 148.9; *m/z* (EI) 343 (^{80}Se, M$^+$), 341 (^{78}Se, M$^+$, 341.0527, $C_{18}H_{17}NO^{78}Se$ requires 341.0483), 327, 235, 168, 121, and 86.

*8-Dimethylamino-1-naphthyl 2′,4′,6′-Triisopropylphenyl Selenide (***3c***)*

To a stirred suspension of 8-dimethylamino-1-naphthyllithium (**3**), prepared from *N,N*-dimethyl-1-naphthylamine (4.28 g, 25.0 mmol) and BuLi (1.53 M in hexane; 18.0 mL, 27.5 mmol) in anhydrous ether (75 mL), was added an anhydrous ether solution (75 mL) of bis(2,4,6-triisopropylphenyl)diselenide (14.1 g, 25.0 mmol) under nitrogen at room temperature. The solution was stirred for an additional 2 hours. Saturated brine (50 mL) was added to the solution, and the organic layer was separated. The organic component remaining in the aqueous layer was extracted with ether (50 mL × 3). The combined organic layer was washed with water, and dried over anhydrous magnesium sulfate. The solution was concentrated under reduced pressure, and purification by silica gel column chromatography (eluent: hexane/ether = 2/1) gave selenide **3c** (4.64 g, 41%); m.p. 119–122°C; ν_{max} (KBr)/cm^{-1} 2960, 2340, 1560, and 820; δ_H (500 MHz, $CDCl_3$, Me_4Si) 1.11 (6 H, br s, $CHMe_2$), 1.20 (6 H, br s, $CHMe_2$), 1.32 (6 H, d, *J* 7.0, $CHMe_2$), 2.80 (6 H, s, NMe_2), 2.96 (1 H, sep, *J* 7.0, $CHMe_2$), 3.74 (2 H, sep, *J* 7.0, $CHMe_2$), 6.75 (1 H, d, *J* 7.6, Ar-H), 7.07 (1 H, dd, *J* 7.6 and 7.6, Ar-H), 7.13 (2 H, s, Ar-H), 7.35–7.43 (2 H, m, Ar-H), 7.50 (1 H, d, *J* 7.6, Ar-H) and 7.61 (1 H, d, *J* 7.6, Ar-H); δ_C (125 MHz; $CDCl_3$; Me_4Si) 24.0, 25.2, 33.8, 34.3, 46.2, 118.6, 121.8, 124.7, 125.65, 125.70, 125.8, 126.1, 129.52, 129.54, 133.7, 136.1, 149.9, 151.7, and 154.0; *m/z* (EI) 453 (^{80}Se, M$^+$), 451 (^{78}Se, M$^+$), 250, 170, 155, and 84.

*8-Dimethylamino-1-naphthyl 2′,4′,6′-Triisopropylphenyl Selenoxide (***1c***)*

To a stirred mixed solvent of dichloromethane (40 mL) and methanol (10 mL) containing selenide **3c** (0.91 g, 2.0 mmol) was added slowly a dichloromethane solution (5 mL) of *tert*-butyl hypochlorite (0.26 g, 2.4 mmol) at −25°C under nitrogen, and the solution was stirred for an additional 30 minutes and

then was allowed to stand until it attained room temperature. After aqueous sodium hydroxide (0.30 g in 10 mL) had been poured into the stirred reaction mixture, the organic layer was separated. The organic component remaining in the aqueous layer was extracted with dichloromethane (50 mL × 3), and the combined organic layer was dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure, and purification by silica gel column chromatography (eluent: dichloromethane/methanol = 100/6) gave racemic selenoxide **1c** (0.83 g, 88%); m.p. 117–118°C; λ_{max} (cyclohexane)/nm 302 (ε/dm^3 mol^{-1} cm^{-3} 7.3 × 10^3) and 208 (5.6 × 10^4); ν_{max} (KBr)/cm^{-1} 2970, 2360, 1460, 1360, and 830; δ_H (500 MHz, $CDCl_3$, Me_4Si) 0.85 (6 H, d, *J* 6.7, $CHMe_2$), 1.20 (6 H, d, *J* 6.7, $CHMe_2$), 1.21 (6 H, d, *J* 6.7, $CHMe_2$), 2.26 (3 H, s, NMe), 2.77 (3 H, s, NMe), 2.81 (1 H, sep, *J* 6.7, $CHMe_2$), 3.56 (2 H, sep, *J* 6.7, $CHMe_2$), 6.97 (2 H, s, Ar-H), 7.39 (1 H, d, *J* 7.6, Ar-H), 7.47 (1 H, dd, *J* 7.6 and 7.6, Ar-H), 7.67 (1 H, dd *J* 7.6 and 7.6, Ar-H), 7.75 (1 H, d, *J* 7.6, Ar-H), 7.97 (1 H, d, *J* 7.6, Ar-H) and 8.65 (1 H, d, *J* 7.6, Ar-H); δ_C (125 MHz, $CDCl_3$, Me_4Si) 23.76, 23.83, 23.9, 24.8, 29.5, 34.1, 44.6, 48.1, 119.3, 122.5, 126.0, 126.3, 128.3, 128.4, 131.2, 135.6, 137.7, 139.4, 150.0, 150.3, and 151.0; δ_C (125 MHz, C_6D_6, Me_4Si) 23.9, 24.0, 24.1, 25.0, 29.8, 34.5, 44.1, 48.3, 119.1, 122.6, 126.1, 126.4, 128.3, 128.9, 129.0, 131.2, 136.0, 139.9, 141.5, 150.6, 150.9, and 151.0 [25]; *m/z* (EI) 469 (^{80}Se, M$^+$), 467 (^{78}Se, M$^+$, 467.1898, $C_{27}H_{35}NO^{78}Se$ requires 467.1892), 453, 250, 168, 127, and 91.

*8-Dimethylamino-1-naphthyl Phenyl Telluride (***5a***)*

To a stirred suspension of 8-dimethylamino-1-naphthyllithium (**4**), prepared from *N,N*-dimethyl-1-naphthylamine (4.28 g, 25.0 mmol) and BuLi (1.53 M in hexane; 18.0 mL, 27.5 mmol) in anhydrous ether (75 mL), was added an anhydrous ether solution (75 mL) of diphenylditelluride (10.2 g, 25.0 mmol) under nitrogen at room temperature. The solution was stirred for an additional 2 hours. Saturated brine (150 mL) was added to the solution, and the organic layer was separated. The organic component remaining in the aqueous layer was extracted with ether (50 mL × 3). The combined organic layer was washed with water, and then dried over anhydrous magnesium sulfate. The solution was concentrated under reduced pressure, and purification by silica gel column chromatography (eluent: hexane/ether = 2/1) gave telluride **5a** (4.59 g, 49%); m.p. 119–122°C (lit. 119°C) [18]; ν_{max} (KBr)/cm^{-1} 2970, 2350, 1700, and 820; δ_H (500 MHz, $CDCl_3$, Me_4Si) 2.78 (6 H, s, NMe_2), 7.07–7.15 (2 H, m, Ph), 7.31–7.35 (2 H, m, Ar-H), 7.39–7.45 (3 H, m, Ph), 7.56–7.60 (1 H, m, Ar-H), 7.63–7.68 (1 H, m, Ar-H) and 7.97–8.00 (2 H, m, Ar-H); δ_C (125 MHz; $CDCl_3$; Me_4Si) 47.2, 116.0, 119.0, 122.6, 125.5, 125.9, 126.6, 126.9, 128.1, 129.3, 130.9, 131.5, 135.4, 141.2, and 150.6; *m/z* (EI) 377 (^{130}Te, M$^+$), 375 (^{128}Te, M$^+$), 300, 170, 155, 127, and 77.

*8-Dimethylamino-1-naphthyl Phenyl Telluroxide (***2a***)*

To a stirred dichloromethane solution (50 mL) containing telluride **5a** (0.75 g, 2.0 mmol) and methanol (1 mL) was added slowly a dichloromethane solution (5 mL) of *tert*-butyl hypochlorite (0.26 g, 2.4 mmol) at −25°C under nitrogen, and the solution was stirred for an additional 30 minutes and was allowed to stand until it attained room temperature. After aqueous sodium hydroxide (0.30 g in 20 mL) had been poured into the stirred reaction mixture, the organic layer was separated. The organic component remaining in the aqueous layer was extracted with dichloromethane (50 mL × 3), and the combined organic layer was dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure, and purification by silica gel column chromatography (eluent: dichloromethane/methanol = 100/6) gave racemic telluroxide **2a** (0.77 g, 98%); m.p. 106–109°C; ν_{max} (KBr)/cm^{-1} 2980, 2360, 1440, 1360, and 815; δ_H (500 MHz, $CDCl_3$, Me_4Si) 2.38 (3 H, s, NMe), 2.72 (3 H, s, NMe), 7.18–7.37 (5 H, m, Ph), 7.39 (1H, d, *J* 7.3, Ar-H), 7.51 (1 H, dd, *J* 8.0 and 8.0, Ar-H), 7.84 (1 H, d, *J* 8.0, Ar-H), 7.86 (1 H, dd, *J* 7.3 and 7.3, Ar-H), 8.07 (1 H, d, *J* 8.0, Ar-H) and 8.84 (1 H, d, *J* 7.3, Ar-H); δ_C (125 MHz; $CDCl_3$; Me_4Si) 44.4, 49.6, 119.3, 126.4, 126.9, 127.1, 128.1, 129.4, 130.0, 130.5, 130.7, 131.1, 131.5, 135.3, 139.8, and 149.0; *m/z* (EI) 393 (^{130}Te, M$^+$, 393.0382, $C_{18}H_{17}NO^{130}Te$ requires 393.0377), 391 (^{128}Te, M$^+$), 377, 300, 170, 155, 127, and 77.

*8-Dimethylamino-1-naphthyl 2′,4′,6′-Triisopropylphenyl Telluride (***5b***)*

To a stirred suspension of 8-dimethylamino-1-naphthyllithium (**4**), prepared from *N,N*-dimethyl-1-naphthylamine (8.56 g, 50.0 mmol) and BuLi (1.53 M in hexane; 36.0 mL, 55.0 mmol) in anhydrous ether (150 mL), was added an anhydrous ether solution (100 mL) of bis(2,4,6-triisopropylphenyl) ditelluride (33.0 g, 50.0 mmol) under nitrogen at room temperature. The solution was stirred for an additional 30 minutes. Saturated brine (50 mL) was

added to the solution, and the organic layer was separated. The organic component remaining in the aqueous layer was extracted with ether (50 mL × 3), and the combined organic layer was washed with water and dried over anhydrous magnesium sulfate. The solution was concentrated under reduced pressure, and purification by silica gel column chromatography (eluent: hexane/ether = 2/1) gave telluride **5b** (2.85 g, 11%); m.p. 129–131°C; ν_{max} (KBr)/cm^{-1} 2975, 1580, 1460, 1130, 875, and 740; δ_H (500 MHz; $CDCl_3$; Me_4Si) 1.12 (6 H, br s, $CHMe_2$), 1.23 (6 H, br s, $CHMe_2$), 1.32 (6 H, d, *J* 7.8, $CHMe_2$), 2.83 (6 H, s, NMe_2), 2.96 (1 H, sep, *J* 7.8, $CHMe_2$), 3.80 (2 H, sep, *J* 7.8, $CHMe_2$), 7.00–7.10 (2 H, m, Ar-H), 7.13 (2 H, s, Ar-H), 7.42–7.47 (2 H, m, Ar-H), 7.75–7.63 (1 H, m, Ar-H), and 7.63–7.71 (1 H, m, Ar-H); δ_C (125 MHz, $CDCl_3$, Me_4Si) 24.0, 24.6, 25.4, 34.2, 39.0, 47.3, 117.6, 118.8, 121.0, 125.48, 125.54, 126.5, 126.9, 127.0, 131.2, 131.9, 135.5, 149.9, 150.8, and 155.5; *m/z* (EI) 503 (^{130}Te, M$^+$), 501 (^{128}Te, M$^+$), 300, 221, 170, 155, and 71.

*8-Dimethylamino-1-naphthyl 2′,4′,6′-Triisopropylphenyl Telluroxide (***2b***)*

To a stirred mixed solvent of dichloromethane (40 mL) and methanol (10 mL) containing telluride **5b** (1.50 g, 2.98 mmol) was added slowly a dichloromethane solution (10 mL) of *tert*-butyl hypochlorite (0.39 g, 3.6 mmol) at −25°C under nitrogen, the solution was stirred for an additional 30 minutes and allowed to stand until it attained room temperature. After aqueous sodium hydroxide (0.40 g in 20 mL) was poured into the stirred reaction mixture and the organic layer was separated. The organic component remaining in the aqueous layer was extracted with dichloromethane (50 mL × 3), and the combined organic layer the was dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure, and purification by silica gel column chromatography (eluent: dichloromethane/methanol = 100/6) gave racemic telluroxide **2b** (1.36 g, 88%); m.p. 180–182°C; λ_{max} (cyclohexane)/nm 293 (ε/dm^3 mol^{-1} cm^{-3} 1.2 × 10^4), 229 (sh, 6.2 × 10^4), and 212 (7.5 × 10^4) nm; ν_{max} (KBr)/cm^{-1} 2975, 1450, 1360, 870, and 840; δ_H (500 MHz, $CDCl_3$, Me_4Si) 0.90 (6 H, d, *J* 6.8, $CHMe_2$), 1.20 (6 H, d, *J* 6.8, $CHMe_2$), 1.25 (6 H, d, *J* 6.8, $CHMe_2$), 2.32 (3 H, s, NMe), 2.84 (1 H, sep, *J* 6.8, $CHMe_2$), 2.86 (3 H, s, NMe), 3.60 (2 H, sep, *J* 6.8, $CHMe_2$), 7.01 (2 H, s, Ar-H), 7.47–7.55 (2 H, m, Ar-H), 7.67 (1 H, dd, *J* 7.6 and 7.6, Ar-H), 7.79 (1 H, dd, *J* 7.6 and 1.6, Ar-H), 7.98 (1 H, d, *J* 7.6, Ar-H) and 8.54 (1 H, d, *J* 7.0, Ar-H); δ_C (125 MHz; $CDCl_3$; Me_4Si) 23.8, 24.3, 25.0, 25.4, 32.5, 34.2, 46.3, 47.8, 119.6, 122.6, 126.3, 126.8, 126.9, 130.1, 130.3, 131.2, 132.2, 135.3, 136.7, 149.5, 151.6, and 153.5; *m/z* (EI) 519 (^{130}Te, M$^+$, 519.1798, $C_{27}H_{35}NO^{130}Te$ requires 519.1781), 518 (^{128}Te, M$^+$ + 1), 502, 300, 170, 155, 127, and 91.

High-Performance Liquid Chromatography (HPLC) Analysis of Selenoxides **1a, 1b***, and* **1c** *and Telluroxides* **2a** *and* **2b** *Using Optically Active Columns*

The HPLC analysis of selenoxides **1a–c** was performed on a Daicel Chiralpak AS (250 × 4.6 mm) packed with amylose carbamate derivative/silica gel using hexane containing 10 vol % (for **1a** and **1b**) and 1 vol % (for **1c**) of ethanol as a mobile phase at a flow rate of 1.0 mL min^{-1}. The HPLC analysis of telluroxides **2a** and **2b** was performed on a Daicel Chiralcel OD (250 × 10 mm) packed with cellulose carbamate derivative/silica gel using hexane containing 10 vol % of ethanol (for **2a**) or 25 vol % of 2-propanol (for **2b**) as a mobile phase at a flow rate of 1.0 mL min^{-1}. The enantiomeric excess (ee) for each optically active selenoxide **1a, 1b**, and **1c** and telluroxide **2a** and **2b** was determined by HPLC with these optically active columns in an analytical scale.

Optical Resolution of Selenoxides **1a, 1b***, and* **1c** *and Telluroxides* **2a** *and* **2b** *at a Preparative Scale*

Typically, racemic selenoxide or telluroxide (50 mg) in eluent (0.5 mL) was charged to the same type of optically active columns (Daicel Chiralpak AS: 250 × 10 mm or Daicel Chiralcel OD: 250 × 10 mm) and eluted with hexane containing 10 vol % ethanol for **1a, 1b**, and **2a**, 1 vol % 2-propanol for **1c** and 25 vol % 2-propanol for **2b** at flow rate of 1.0 mL min^{-1}. Finally, ca. 15 mg of optically active selenoxides **1a, 1b**, and **1c** and telluroxide **2b** were obtained from the first eluate by repeated resolution (2–3 times) and ca. 10 mg from the second eluate by repeated resolution (4–5 times), respectively.

*Compound (+)-***1a**. 100% ee; m.p. 140–141°C; $[\alpha]_D$ + 363.8 (c 0.10, in $CHCl_3$), $[\alpha]_{435}$ +761.5 (c 0.10, in $CHCl_3$); CD (cyclohexane) nm 317 ($[\theta]$ −7.3 × 10^3), 237 ($[\theta]$ +2.3 × 10^5) and 214 ($[\theta]$ −7.1 × 10^4) nm; *m/z* (EI) 281.0291 (^{80}Se, M$^+$, $C_{13}H_{15}NO^{80}Se$ requires 281.0319). ^{1}H NMR, ^{13}C NMR, IR, UV, and MS spectra were almost the same as those of racemic one.

*Compound (−)-***1a**. 100% ee: m.p. 143–145°C; $[\alpha]_D$ −350.8 (c 0.19, in $CHCl_3$), $[\alpha]_{435}$ −752.9 (c 0.19,

in $CHCl_3$); CD (cyclohexane)/nm 318 ([θ] $+7.0 \times 10^3$), 237 ([θ] -2.3×10^5) and 213 ([θ] $+7.3 \times 10^4$); *m/z* (EI) 279.0331 (^{78}Se, M^+, $C_{13}H_{15}NO^{78}Se$ requires 279.0327). ^{1}H NMR, ^{13}C NMR, IR, UV, and MS spectra were almost the same as those of racemic one.

Compound (+)-**1b**. 80% ee; m.p. 155–159°C; $[\alpha]_D$ +140.5 (c 0.50, in $CHCl_3$), $[\alpha]_{435}$ +300.2 (c 0.50, in $CHCl_3$); CD (cyclohexane)/nm 314 ([θ] -1.4×10^4) and 234 ([θ] $+ 1.1 \times 10^5$); *m/z* (EI) 343.0464 (^{80}Se, M^+, $C_{18}H_{17}NO^{80}Se$ requires 343.0475). ^{1}H NMR, ^{13}C NMR, IR, UV, and MS spectra were almost the same as those of racemic one.

Compound (−)-**1b**. 100% ee; m.p. 159–160°C; $[\alpha]_D$ −165.4 (c 0.19, in $CHCl_3$), $[\alpha]_{435}$ −347.7 (c 0.19, in $CHCl_3$); CD (cyclohexane)/nm 310 ([θ] $+1.0 \times 10^4$) and 234 ([θ] -2.4×10^5); *m/z* (EI) 343.0473 (^{80}Se, M^+, $C_{18}H_{17}NO^{80}Se$ requires 343.0475). ^{1}H NMR, ^{13}C NMR, IR, UV, and MS spectra were almost the same as those of racemic one.

Compound (+)-**1c**. 90% ee; m.p. 59–62°C; $[\alpha]_D$ +78.7 (c 0.31, in $CHCl_3$), $[\alpha]_{435}$ +171.3 (c 0.31, in $CHCl_3$); CD (cyclohexane)/nm 283 ([θ] -2.0×10^4), 242 ([θ] $+1.5 \times 10^5$) and 225 ([θ] $+3.9 \times 10^4$); *m/z* (EI) 467.1891 (^{78}Se, M^+, $C_{27}H_{35}NO^{78}Se$ requires 467.1892). ^{1}H NMR, ^{13}C NMR, IR, UV, and MS spectra were almost the same as those of racemic one.

Compound (−)-**1c**. 100% ee; m.p. 63–64°C; $[\alpha]_D$ −87.6 (c 0.58, in $CHCl_3$), $[\alpha]_{435}$ −194.6 (c 0.58, in $CHCl_3$); CD (cyclohexane)/nm 284 ([θ] $+2.7 \times 10^4$), 242 ([θ] -1.9×10^5) and 224 ([θ] -5.2×10^4); *m/z* (EI) 469.1858 (^{80}Se, M^+, $C_{27}H_{35}NO^{80}Se$ 469.1884). ^{1}H NMR, ^{13}C NMR, IR, UV, and MS spectra were almost the same as those of racemic one.

Compound (+)-**2b**. 100% ee; m.p. 190–191°C; $[\alpha]_D$ +47.6 (c 0.23, in $CHCl_3$), $[\alpha]_{435}$ +105.6 (c 0.23, in $CHCl_3$); CD (cyclohexane)/nm 339 ([θ] -1.1×10^4), 287 ([θ] -1.0×10^4), 251 ([θ] $+4.3 \times 10^5$) and 225 ([θ] $+4.2 \times 10^5$); *m/z* (EI) 519.1805 (^{130}Te, M^+, $C_{27}H_{35}NO^{130}Te$ 519.1781). ^{1}H NMR, ^{13}C NMR, IR, UV, and MS spectra were almost the same as those of the racemic one.

Compound (−)-**2b**. 100% ee; m.p. 189–191°C; $[\alpha]_D$ −46.0 (c 0.67, in $CHCl_3$), $[\alpha]_{435}$ −104.6 (c 0.67, in $CHCl_3$); CD (cyclohexane)/nm 341 ([θ] $+1.4 \times 10^4$), 290 ([θ] $+1.3 \times 10^4$), 252 ([θ] -5.1×10^5) and 226 ([θ] -5.0×10^5); *m/z* (EI) 519.1803 (^{130}Te, M^+, $C_{27}H_{35}NO^{130}Te$ 519.1781). ^{1}H NMR, ^{13}C NMR, IR, UV, and MS spectra were almost same with those of racemic one.

Synthesis of (S)-(−)-8-Dimethylamino-1-naphthyl 4′-Tolyl Sulfoxide [(S)-(−)-6]

To a stirred ether solution (15 mL) of $(S)_s$-(−)-menthyl-(−)-4-toluenesulfinate [24] (100% ee; 0.29 g, 1.0 mmol) was added at 0°C 8-dimethylamino-1-naphthyllithium (**4**), prepared from *N,N*-dimethyl-1-naphthylamine (0.17 g, 1.0 mmol) and BuLi (1.53 M in hexane; 0.72 mL, 1.1 mmol) in anhydrous ether (10 mL). After additional stirring for 1 hour at room temperature, the mixture was poured into brine, and the organic layer was separated. The organic component remaining in the aqueous layer was extracted with ether (100 mL × 3), and the combined organic layer was washed with water and dried over anhydrous magnesium sulfate. The solution was concentrated under reduced pressure, and purification by silica gel column chromatography (eluent: dichloromethane/methanol = 100/6) gave (*S*)-(−)-**6** (0.26 g, 85%, 96% ee) as a pale yellow oil; λ_{max} (cyclohexane)/nm 298 (ε/dm^3 mol^{-1} cm^{-3} 5.3×10^3), 232 (2.3×10^4) and 215 (2.7×10^4) nm; ν_{max} (neat)/cm^{-1} 2951, 1452, 1182, 1038, and 830; δ_H (500 MHz; $CDCl_3$; Me_4Si) 2.17 (3 H, s, SMe), 2.25 (3 H, s, NMe), 2.62 (3 H, s, NMe), 7.04, and 7.09 (4H, ABq, *J* 8.1, Ar-H), 7.26 (1 H, d, *J* 7.6, Ar-H), 7.45 (1 H, dd, *J* 7.6 and 7.6, Ar-H), 7.74 (1 H, d, *J* 7.6, Ar-H), 7.78 (1 H, dd, *J* 7.6 and 7.6, Ar-H), 8.02 (1 H, d, *J* 7.6, Ar-H) and 8.72 (1 H, d, *J* 7.6, Ar-H); δ_c (125 MHz, $CDCl_3$, Me_4Si) 21.2, 42.8, 48.9, 119.6, 125.6, 125.73, 125.75, 126.0, 126.5, 127.5, 129.5, 131.3, 135.4, 138.7, 140.1, 145.6, and 149.9; *m/z* (EI) 309 (M^+, 309.1150, $C_{19}H_{19}NOS$ requires 309.1187), 292, 187, 168, 154, 127, 105, and 77; $[\alpha]_D$ −134.7 (c 1.27, in $CHCl_3$), $[\alpha]_{435}$ −220.1 (c 1.27, in $CHCl_3$); CD (cyclohexane)/nm 321 ([θ] $+1.4 \times 10^4$), 259 ([θ] -4.6×10^4), 234 ([θ] -3.4×10^5) and 210 ([θ] $+2.0 \times 10^5$).

Kinetic Studies on the Racemization of Optically Active Selenoxides and Telluroxide

Kinetic studies on the racemization of optically active selenoxides **1a, 1b**, and **1c** and telluroxide **2b** were examined in solutions (ca. 5 mM) at 26 ± 1°C. The rates of racemization were calculated based on their specific rotation and plotted according to the first-order rate equation.

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