Isolation of Stable Enantiomerically Pure Telluroxides and Their Stereochemistry

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Optical resolution of kinetically and thermodynamically stabilized diaryl telluroxides possessing bulky substituents (*rac*-**1a**−**d**) and amino group (*rac*-**2a**−**c**), respectively, by liquid chromatography using optically active columns yielded stable enantiomerically pure telluroxides. The absolute configurations of the optically active telluroxides were determined by comparing their specific rotations and CD spectra with those of sulfur or selenium analogues. The kinetics for the racemization of optically active telluroxides in solution was studied, and it was found that kinetic and thermodynamic stabilization were very effective preventing the racemization of telluroxides. The stabilization energy of telluroxides by intramolecular coordination of the amino group to the tellurium atom was estimated to be ca. 5 kcal mol^{-1} by variable temperature ^{1}H NMR measurement. The mechanism for the racemization of optically active telluroxides was studied by an isotope experiment using $H_2{}^{18}O$, and the results indicated that optically active telluroxides underwent racemization via an achiral tetracoordinated hydrate.

Introduction

Recently, our studies have focused on the synthesis and stereochemistry of optically active selenium and tellurium compounds.[1−3] Among tricoordinated optically active selenium and tellurium compounds, it had been thought that optically active selenoxides and telluroxides are too difficult to isolate because the racemization was estimated to be very rapid. Since the first synthesis of an optically active selenoxide (11% ee), stabilized against racemization by bulky substituents on the selenium atom, was reported by Davis et al. in 1983,[4] there have been several reports on the synthesis of optically active selenoxides, by means of optical resolution using fractional recrystallization of diastereomeric mixtures,[5] complexation with a chiral ligand,[6] chromatographic resolution of racemic mixtures using an optically active columns,[7] and asymmetric oxidation of selenides.[8,9] We first isolated an optically pure diaryl selenoxide (100% ee) that was stabilized by bulky substituents in 1986;[5] however, an optically pure alkyl aryl selenoxide had not been isolated until recently because optically active alkyl aryl selenoxides undergo racemization more rapidly than diaryl selenoxides.[9b] Fortunately, there is another technique for stabilizing molecular structures, i.e., thermodynamic stabilization by an electronic effect or coordination of intramolecular substituents, and there are many reports concerning stabilization through the intramolecular coordination of amino groups.[10] We previously reported the preparation of alkyl aryl selenoxides possessing an amino group, and the isolation of optically pure alkyl aryl selenoxides by chromatographic resolution using a chiral stationary phase.[11]

On the other hand, optically active telluroxides have not yet been isolated because they undergo racemization even more rapidly than optically active selenoxides, although optically active telluroxides have been proposed as intermediates in asymmetric reactions by Uemura et al.[12] We designed and synthesized configurationally stable telluroxides using two stabilizing methods; one is kinetic stabilization by bulky substituents[13] and the other is thermodynamic stabilization by the intramolecular coordination of the amino group to the tellurium atom and succeeded to resolve these racemic compounds into enantiomerically pure form by means of HPLC using a chiral stationary phase. The absolute configurations of the optically active telluroxides were determined on the basis of their specific rotations and CD spectra, and the

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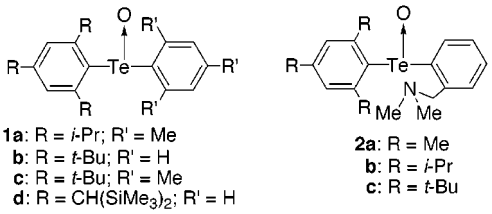
configurational stability of optically active telluroxides was studied.



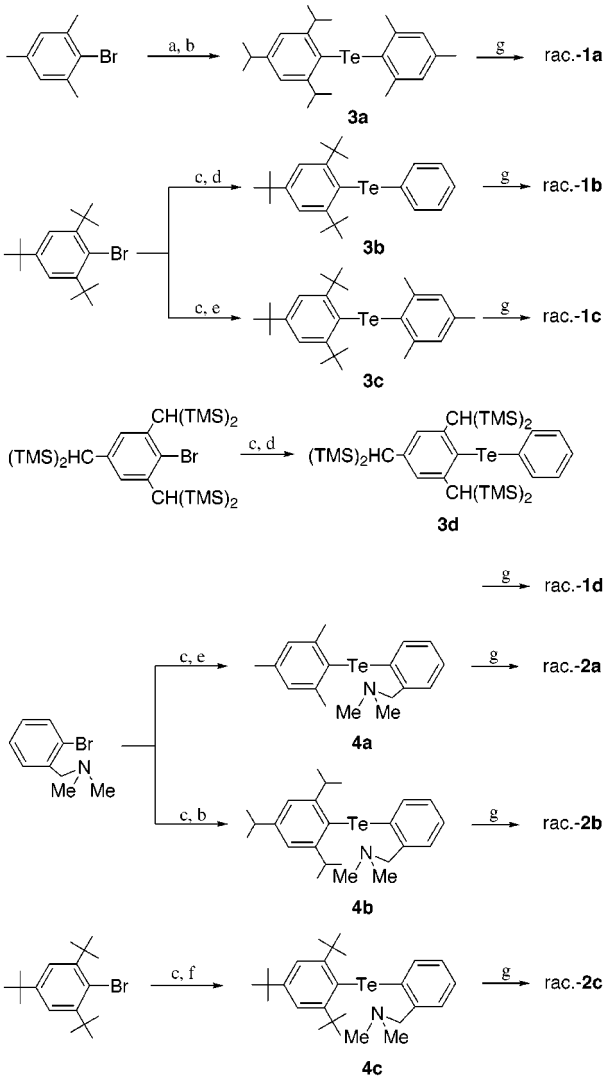
Results and Discussion

Previously, we isolated optically pure selenoxide that was stabilized against the racemization by bulky substituents.[5] Optically active telluroxides have been presumed to undergo racemization more rapidly than optically active selenoxides.[14] Therefore, substituents, bulkier than in the case of the selenoxides or some other stabilizing method, such as intramolecular coordination of amino group, will be necessary to isolate an optically active telluroxide.

Preparation of Racemic Telluroxides 1a−d and 2a−c. 2,4,6-Triisopropylphenyl mesityl telluride (**3a**) was synthesized in 77% yield by reacting mesitylmagnesium bromide and bis(2,4,6-triisopropylphenyl)ditelluride (Scheme 1). Similarly, 2,4,6-tri-*tert*-butyldiphenyl telluride (**3b**) and 2,4,6-tri-*tert*-butylphenyl mesityl telluride (**3c**) were synthesized in yields of 90 and 88% by reacting 2,4,6-tri-*tert*-butylphenyllithium with diphenyl ditelluride or dimesityl ditelluride, respectively. Telluride **3d** possessing a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group, which is known to be extremely bulky,[15,16] was synthesized in 62% yield by reacting 2,4,6-tris[bis(trimethylsilyl)methyl]phenyllithium[16] with diphenyl ditelluride. 2-(*N*,*N*-Dimethylaminomethyl)phenyl mesityl telluride (**4a**) and 2-[(*N*,*N*-dimethylamino)methyl]-2′,4′,6′-triisopropyldiphenyl telluride (**4b**) were synthesized in yields of 54 and 90% by reacting 2-(*N*,*N*-dimethylaminomethyl)phenyllithium with dimesityl ditelluride or bis(2,4,6-triisopropylphenyl) ditelluride, respectively. 2-[(*N*,*N*-Dimethylamino)methyl]-2′,4′,6′-tri-*tert*-butyldiphenyl telluride (**4c**) was synthesized in 64% yield by reacting 2,4,6-tri-*tert*-butylphenyllithium with bis[2-(*N*,*N*-dimethylaminomethyl)phenyl] ditelluride. Finally, asymmetric diaryl telluroxides **1a−d** possessing a bulky group and **2a−c** possessing an intramolecular amino group were obtained in yields of 72−99% by oxidation of the corresponding tellurides **3a−d** and **4a−c** with *tert*-butyl hypochlorite.

Optical Resolution of Telluroxides by Means of HPLC. Diaryl telluroxide (**1a**) was subjected to several columns with a chiral stationary phase using HPLC at an analytical scale. Racemic telluroxide **1a** was resolved into two peaks corresponding to the enantiomers when optically active columns, such as Daicel Chiralpak AS and AD, and Chiralcel OB, OJ, OC, OD, OF, and OJ, were used. Among these columns, the chromatogram of telluroxide **1a** using a column with amylose carbamate derivative/silica gel (Daicel Chiralpak AS) as a chiral stationary phase showed the best resolution on an analytical scale (eluent: hexane/isopropyl alcohol = 95/5) (Figure 1). Similarly, telluroxides **1b** (eluent: hexane/isopropyl alcohol = 95/5) and **1c** (eluent: hexane/isopropyl alcohol = 98/2) could also be resolved into their enantiomers. On the other hand, when telluroxide **1d** was subjected to several optically active columns at an analytical scale, optical resolution was not achieved, maybe because the very bulky Tbt group inhibited recognition of the asymmetry of the telluroxide moiety on the chiral stationary phase.

Scheme 1



Reagents and conditions: (a) Mg, THF, rt; (b) $(TipTe)_2$; (c) *n*-BuLi, THF, −60 °C; (d) $(PhTe)_2$; (e) $(MesTe)_2$; (f) $(DMAMPTe)_2$; (g) *t*-BuOCl, MeOH, CH_2Cl_2, −25 °C, then aq NaOH; Tip: 2,4,6-triisopropylphenyl; DMAMP: 2-{(*N*,*N*-dimethylamino)methyl}-phenyl.

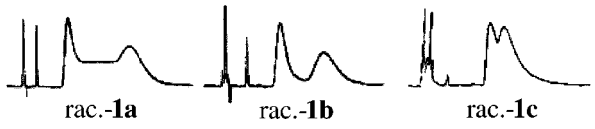


Figure 1. Chromatographic resolution of racemic diaryl telluroxides **1a−c** by means of HPLC using an optically active column (Daicel Chiralpak AS).

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Table 1. Chromatographic Resolution of Telluroxides

telluroxides	optically active column[a]	*i*-PrOH,[b] %	first enantiomer $[\alpha]_D$ ($CHCl_3$)[c]	first enantiomer ee (%)[d]	second enantiomer $[\alpha]_D$ ($CHCl_3$)	second enantiomer ee (%)
1c	AS	2	+25.3 (*c* 0.22)	100	−23.6 (*c* 0.11)	93
2b	OD	30	+39.5 (*c* 0.15)	100	−11.9 (*c* 0.13)	38
2c	OD	5	+166.2 (*c* 0.32)	100	−66.1 (*c* 0.12)	40

[a] AS: Daicel Chiralpak AS, AD: Daicel Chiralcel OD. [b] The volume percentage of isopropyl alcohol in hexane used as mobile phase. [c] Specific rotations were taken at 25−27 °C. [d] Enantiomeric purities were determined by HPLC analysis.

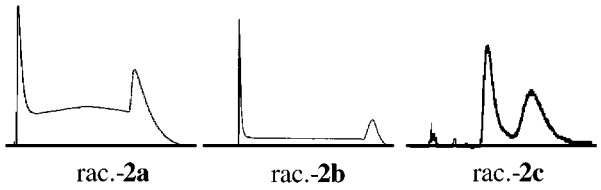


Figure 2. Chromatographic resolution of racemic diaryl telluroxides **2a**−**c** by means of HPLC using an optically active column (Daicel Chiralcel OD).

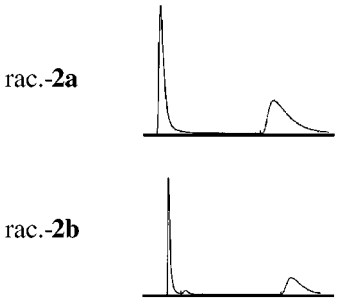


Figure 3. Chromatographic resolution of racemic diaryl telluroxides **2a** and **2b** by means of HPLC at −3 °C (Daicel Chiralcel OD).

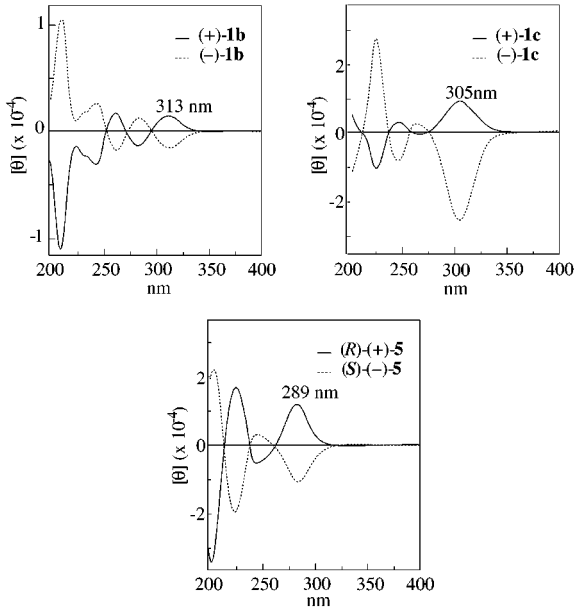


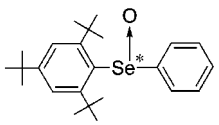
Figure 4. CD spectra of optically active telluroxides (+)-**1b**, (−)-**1b**, (+)-**1c**, and (−)-**1c** and selenoxides (*R*)-(+)-**5** and (*S*)-(−)-**5** in acetonitrile.

Chromatographic resolution of diaryl telluroxide **2a** possessing an intramolecular amino group was also examined using several chiral stationary phases at an analytical scale. Racemic telluroxide **2a** was resolved into two peaks corresponding to the enantiomers when a column with cellulose carbamate derivative/silica gel (Daicel Chiralcel OD, eluent: hexane/isopropyl alcohol = 60/40) was employed, as shown in Figure 2. Similarly, telluroxides **2b** (eluent: hexane/isopropyl alcohol = 70/30) and **2c** (eluent: hexane/isopropyl alcohol = 95/5) could also be resolved into their enantiomers.

The chromatograms of telluroxides **1a**, **2a**, and **2b** showed an unusual shape and indicated that racemization had occurred in the column, while the racemization of telluroxides **1b**, **1c**, and **2c** was not observed in the column. However, when chromatographic resolution was carried out at −3 °C, telluroxides **2a** and **2b** could be optically resolved very nicely into two peaks corresponding to the enantiomers without racemization in the column, as shown in Figure 3. These results show that bulky substituents effectively inhibited the racemization of telluroxides in the column.

The optical resolution of racemic telluroxides **1a**−**c** and **2a**−**c** was carried out by HPLC using the same type of optically active column at a preparative scale. For telluroxide **1c**, repeated resolution of the first and second fractions gave optically active telluroxides. The first eluted enantiomer had a positive specific rotation {(+)-**1c**: ee 100%; $[\alpha]_D$ +25.3 (*c* 0.22, $CHCl_3$)}, and the second eluted enantiomer had a negative specific rotation {(−)-**1c**: ee 93%; $[\alpha]_D$ −23.6 (*c* 0.11, $CHCl_3$)}, and their enantiomeric purities were determined by HPLC analysis. Our inability to isolate optically pure telluroxide (−)-**1c** is due to tailing of the first eluted enantiomer. Similarly, optically pure telluroxides (+)-**2b** and (+)-**2c** were isolated from the first eluent, and optically active telluroxides (−)-**2b** and (−)-**2c** were obtained from the second eluent. The results are summarized in Table 1. Optically active telluroxides **1a**, **1b**, and **2a** could not be isolated because racemization of these telluroxides occurred during concentration of the solution, and the CD spectra of optically active telluroxides (+)- and (−)-**1b** could be narrowly measured.

Circular Dichroism Spectra and Absolute Configuration of Optically Active Telluroxides. The CD spectra of optically active telluroxides (+)-**1b** and (+)-**1c** showed positive first Cotton effects at 313 and 305 nm, respectively, while those of (−)-**1b** and (−)-**1c** showed negative effects in the same region, as shown in Figure 4. These first Cotton effects correspond well with those of optically active 2,4,6-tri-*tert*-butyldiphenyl selenoxides {(*R*)-(+)-**5** and (*S*)-(−)-**5**}, for which the relationship



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between the absolute configurations and the CD spectra has been clarified.[14b] Therefore, the absolute configura-

Table 2. First Order Rate Constants for Racemization of Optically Active Telluroxides in Solutions[a]

	k/s^{-1} ($t_{1/2}$/h)					
solvent	(*R*)-(+)-**1b**	(*R*)-(+)-**1c**	(*R*)-(+)-**2b**	(*R*)-(+)-**2c**	(*S*)-(−)-**7**[b]	(*R*)-(+)-**8**[c]
$CHCl_3$	7.41×10^{-4} (0.260)	2.75×10^{-6} (69.3)	1.36×10^{-4} (1.41)	1.45×10^{-7} (1327)	A[e]	A
MeOH	B[f]	6.05×10^{-5} (3.18)	B	2.00×10^{-4} (0.963)	5.58×10^{-6} (34.5)	6.00×10^{-6} (32.1)
$MeOH/H_2O$[d]	B	B	B	1.18×10^{-3} (0.163)	5.13×10^{-5} (3.76)	3.34×10^{-5} (5.76)

[a] In ca. 5 mM solution at 26 ± 1 °C. [b] Reference 11. [c] Reference 14b. [d] $MeOH/H_2O$ = 4/1. [e] A: No racemization was observed even after 5 days. [f] B: Racemization was completed within 1 min.

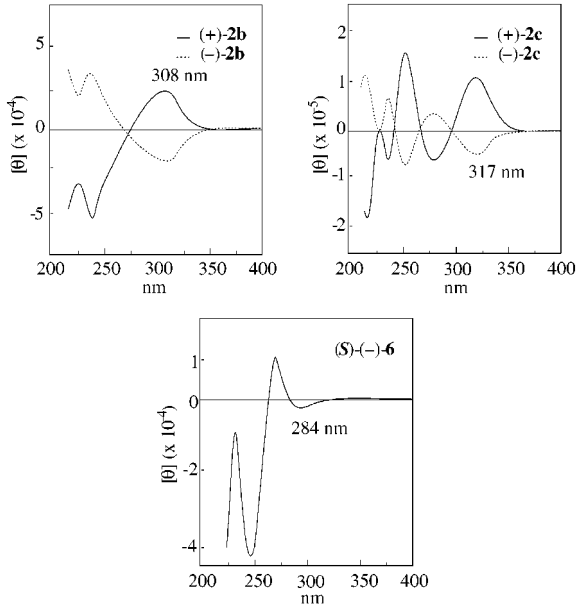
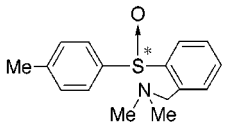


Figure 5. CD spectra of optically active telluroxides (+)-**2b**, (−)-**2b**, (+)-**2c**, and (−)-**2c** and sulfoxide (*S*)-(−)-**6** in cyclohexane.

tion of telluroxides (+)-**1b** and (+)-**1c** is determined to be *R* and that of (−)-**1b** and (−)-**1c** is *S*.

The CD spectra of optically active telluroxides (+)-**2b** and (+)-**2c** also showed positive first Cotton effects at 308 and 317 nm, respectively, and those of (−)-**2b** and (−)-**2c** showed negative effects in the same region, as shown in Figure 5. The absolute configuration of optically active telluroxides (−)-**2b** and (−)-**2c** was determined by comparing the first Cotton effects of their CD spectra with those of (*S*)-(−)-2-(*N*,*N*-dimethylaminomethyl)-4′-methyldiphenyl sulfoxide{(*S*)-(−)-**6**}.[11,17] Consequently, the absolute configuration of telluroxides (−)-**2b** and (−)-**2c** is determined to be *S*, and that of (+)-**2b** and (+)-**2c** is *R*.



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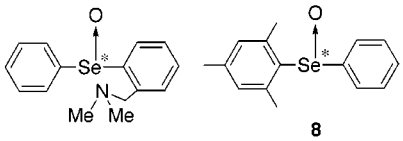
Configurational Stability of Optically Active Telluroxides. The kinetics for the racemization of optically active telluroxides was examined. The rates of racemization for optically active telluroxides (*R*)-(+)-**1b**, **1c**, **2b**, and **2c** showed a good linear relationship with first-order rate plots, and the rate constants are summarized in Table 2. The rate constants of telluroxides (*R*)-(+)-**1b** and -**1c** in chloroform were 7.41×10^{-4} and 2.75×10^{-6} s^{-1}, respectively. The racemization of optically active telluroxides (*R*)-(+)-**2b** and -**2c** was also observed, and the rate constants in chloroform were 1.36×10^{-4} and 1.45×10^{-7} s^{-1}, respectively. These results mean that telluroxides **1c** and **2c** are more stable than telluroxides **1b** and **2b**, respectively, against racemization in chloroform, and a bulky group on the tellurium atom was effective for preventing the racemization of telluroxide. On the other hand, (*S*)-(−)-2-(*N*,*N*-dimethylaminomethyl)diphenyl selenoxides{(*S*)-(−)-**7**}[11] and (*R*)-(+)-mesityl phenyl selenoxide {(*R*)-(+)-**8**}[14b] did not racemize even after 5 days in chloroform at room temperature. These results show that telluroxides racemize more easily than selenoxides in chloroform.



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The racemization of telluroxides (*R*)-(+)-**1b**, **1c**, **2b**, and **2c** proceeded faster in methanol than in chloroform. The addition of water to the methanol solution of (*R*)-(+)-**1c** and -**2c** accelerated their racemization. These results indicate that the racemization of telluroxide occurs due to a trace amount of water which remains in the solvent, despite careful purification of the solvent. Thus, a mechanism via an achiral hydrate formed by the addition of water to telluroxide for racemization is proposed. To confirm this mechanism involving an achiral tetracoordinated hydrate, the oxygen exchange reaction of telluroxide was investigated using $H_2{}^{18}O$. To a methanol solution of (*R*)-(+)-**1c** (ee 89%) was added $H_2{}^{18}O$ (97 atom % ^{18}O excess; 30 equiv), and the mixture was stirred at room temperature. The mass spectrum (FAB) showed 41 and 72% ^{18}O-enriched telluroxide at ee values of 34 and 12%, respectively, as shown in Figure 6. Similarly, the mass spectrum (FAB) of (*R*)-(+)-**2c** (ee 47%), showed 25, 47, and 60% ^{18}O-enriched telluroxide at ee values of 30, 20, and 8%, respectively.

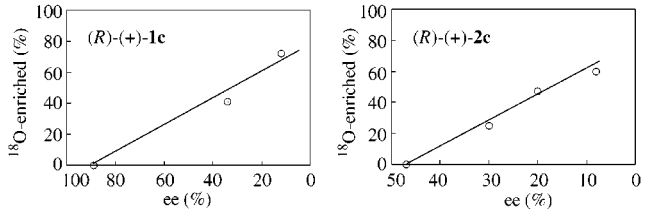
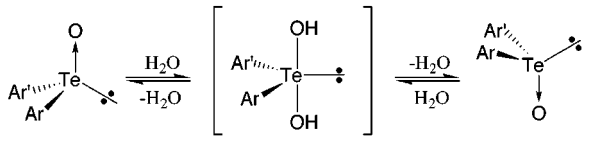


Figure 6. Correlation between enantiomeric purity and ^{18}O-labeled telluroxide for racemization of optically active telluroxides (*R*)-(+)-**1c** and **2c** in methanol in the presence of $H_2{}^{18}O$.

(17) (*S*)-(−)-2-(*N*,*N*-Dimethylaminomethyl)-4′-methyldiphenyl sulfoxide{(*S*)-(−)-**6**} was prepared by reacting (*S*)$_S$-(−)-menthyl-(−)-4-methylphenyl sulfinate and 2-(*N*,*N*-dimethylaminomethyl)phenylmagnesium bromide according to the Andersen's method: Andersen, K. K.; Gaffield, W.; Papanikolaou, N. E.; Foley, J. W.; Perkins, R. I. *J. Am. Chem. Soc.* **1964**, *86*, 5637.



Telluroxides (*R*)-(+)-**2b** and -**2c** with an intramolecular amino group were more stable against the racemization than the kinetically stabilized telluroxide (*R*)-(+)-**1b**. These results suggest that telluroxide is stabilized by the coordination of an intramolecular amino group to the tellurium atom. To obtain further experimental evidence for such intramolecular coordination, variable temperature ^{1}H NMR measurements were performed. As shown in Figure 7, methyl protons of the amino group of telluroxide *rac*-**2b** were observed as a singlet signal in chloroform-*d* at 298 K, however, two signals corresponding to the two methyl groups on the amino moiety of telluroxide were observed at 223 K (ν_{ab} = 108.4 Hz). These results suggest the tellurium and nitrogen atoms interact, and the two methyl groups are nonequivalent at low temperature. The coalescence temperature was 258 K, and the exchange energy of the two methyl groups of telluroxide *rac*-**2b** was calculated to be 12.2 kcal mol^{-1}. Similarly, the energy of *rac*-**2c** was calculated to be 11.6 kcal mol^{-1} (ν_{ab} = 259.7 Hz at 223 K; coalescence temperature = 258 K). These values include the coordination energy of the amino group to the tellurium atom and the rotation energy of the CH_2-N bond or the inversion energy on the nitrogen atom. The rotation energy of the CH_2-N bond (6.7 kcal mol^{-1}) and the inversion energy on the nitrogen atom (3.8 kcal mol^{-1}) for *N*-cyclohexyl-*N*-methylbenzylamine have been calculated by Iwaoka and Tomoda.[18] Therefore, the experimental values for *rac*-**2b** and -**2c** determined by ^{1}H NMR measurements were taken to be the sum of the coordination energy of the amino group to the tellurium atom and the rotation energy of the CH_2-N bond. Thus, the coordination energy for telluroxides *rac*-**2b** and -**2c** was estimated to be 5.5 and 4.9 kcal mol^{-1}, respectively. These estimated energies of telluroxides **2b** and **2c** are not so large that we have initially expected. Thus, we consider the reason why the optically active telluroxides **2b** and **2c** were stable against racemization despite the coordination energy values seemed to be insufficient as follows: the *N*,*N*-dimethylaminomethyl group is preventing the racemization not only by intramolecular coordination of the amino moiety to the tellurium atom (thermodynamic stabilization) but also steric protection by the bulkiness of the substituent in itself (kinetic stabilization).

Conclusion

We succeeded in isolating kinetically and thermodynamically stabilized optically pure telluroxides by HPLC using optically active columns. The absolute configurations of optically active telluroxides were determined by comparing the signs of their specific rotations and CD spectra with those of sulfur and selenium analogues, and optically active telluroxides (−)-**1** and -**2** were determined to be *S*. The results of kinetic studies indicated that a bulky group on the tellurium atom and intramolecular coordination by the amino group to the tellurium atom were very effective at preventing racemization, although optically active telluroxides underwent racemization faster than selenoxides in solution. The stabilization energies of telluroxides **2b** and **2c** by intramolecular coordination of the amino group to the tellurium atom were estimated to be ca. 5 kcal mol^{-1} on the basis of variable temperature ^{1}H NMR measurements.

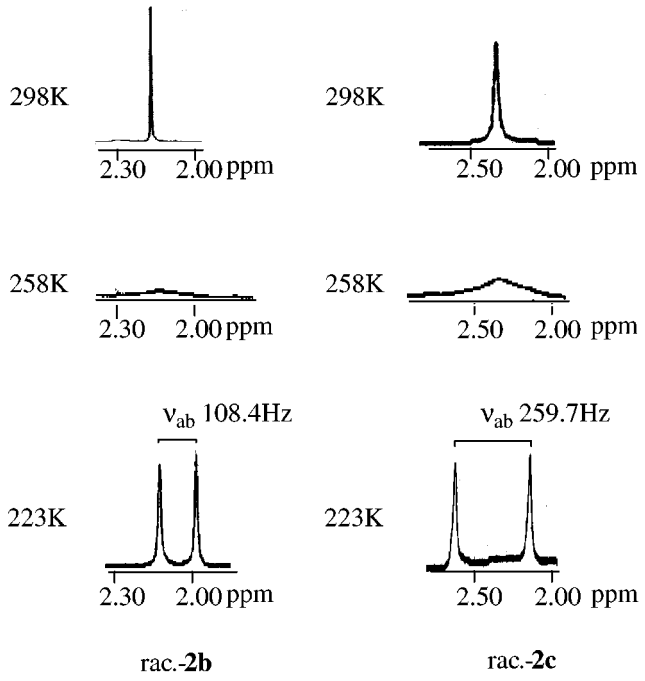


Figure 7. ^{1}H NMR signals of methyl protons of amino group of variable temperature NMR spectra for racemic telluroxides *rac*-**2b** and **2c** in $CDCl_3$.

Experimental Section

General. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl before use. Acetonitrile, cyclohexane, dichloromethane, hexane, and isopropyl alcohol were distilled from calcium hydride before use. Methanol was distilled from magnesium cake and stored with 3 A molecular sieves under nitrogen. TLC were performed with Merck Art. 5554 DC-Alufolien Kieselgel 60 F_{254}. Column chromatography was performed with Merck 7734 Kieselgel 60.

Materials. 2-(*N*,*N*-Dimethylaminomethyl)bromobenzene[11,19] and 2,4,6-tris[bis(trimethylsilyl)methyl]bromobenzene[16] were prepared according to the procedure in the literature.

General Procedure for Preparation of Diaryl Telluride 3a−d: 2,4,6-Triisopropylphenyl Mesityl Telluride (3a). To the Grignard reagent prepared from mesityl bromide (4.01 g, 20.0 mmol) and magnesium (0.49 g, 20.0 mmol) in anhydrous THF (60 mL) was slowly added an anhydrous THF solution (30 mL) of bis(triisopropylphenyl)ditelluride (11.55 g, 20.0 mmol) under nitrogen. The solution was stirred for an additional 2 h and was allowed to stand until room temperature. Saturated brine was added to the solution, and the organic layer was separated. The organic component remaining in the aqueous layer was extracted with ether, 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, pentane) gave telluride **3a** (6.89 g, 77%): oil; IR (KBr) 2975, 1450, 1360, 870, 840 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02 (12H, d, J = 6.3 Hz), 1.23 (6H, d, J = 6.8 Hz), 2.23 (3H, s), 2.36 (6H, s), 2.85 (1H, hep, J = 6.8

(18) Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1996**, *118*, 8077.

(19) (a) Yoshifuji, M.; Kamijo, K.; Toyota, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3440. (b) Yoshifuji, M.; Kamijo, K.; Toyota, K. *Tetrahedron Lett.* **1994**, *35*, 3971.

Hz), 3.59 (2H, hep, J = 6.3 Hz), 6.84 (2H, s), 6.94 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 24.0, 24.4, 28.2, 33.9, 39.4, 120.2, 120.8, 121.5, 127.7, 137.8, 144.0, 149.3, 154.1; mass (EI) m/z 452 (^{130}Te, M^+), 450 (^{128}Te, M^+), 333, 249, 203, 119.

2,4,6-Tri-*tert*-butyldiphenyl Telluride (3b). Yield 90%; mp 127−128 °C; IR (KBr) 2975, 1580, 1460, 1130, 875, 740 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (9H, s), 1.58 (18H, s), 6.56 (2H, m), 6.97 (3H, m), 7.52 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4, 33.1, 35.1, 40.1, 109.0, 122.5, 125.4, 125.7, 129.0, 131.4, 151.1, 157.1; MS (EI) m/z 452 (^{130}Te, M^+), 450 (^{128}Te, M^+), 375, 245, 77.

2,4,6-Tri-*tert*-butylphenyl Mesityl Telluride (3c). Yield 88%; pale yellow viscous oil; IR (KBr) 2975, 1590, 1455, 1120, 840 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (9H, s), 1.47 (18H, s), 1.83 (6H, s), 2.17 (3H, s), 6.70 (2H, s), 7.33 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.6, 25.2, 31.3, 31.6, 33.1, 39.8, 110.8, 119.4, 122.2, 128.7, 136.3, 141.7, 149.9, 156.5; MS (EI) m/z 494 (^{130}Te, M^+), 492 (^{128}Te, M^+), 250, 119.

2,4,6-Tris[bis(trimethylsilyl)methyl]diphenyl Telluride (3d). Yield 62%; mp 141.2−141.9 °C; IR (KBr) 2956, 1400, 1246, 690 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.03 (36H, s), 0.05 (18H, s), 1.33 (1H, s), 2.98 (1H, brs), 3.03 (1H, brs), 6.42 (1H, brs), 6.55 (1H, brs), 7.10−7.22 (3H, m), 7.57−7.62 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.6, 0.7, 30.3, 35.7, 117.0, 120.4, 123.7, 125.2, 127.2, 129.3, 137.3, 144.4; MS (EI, 70 eV) m/z 758 (^{130}Te, M^+), 756 (^{128}Te, M^+), 680, 552, 135, 73.

General Procedure for Preparation of Diaryl Telluride 4a and 4b: 2-(*N*,*N*-Dimethylaminomethyl)phenyl Mesityl Telluride (4a). To the lithium reagent prepared from 2-(*N*,*N*-dimethylaminomethyl)bromobenzene (1.07 g, 5.0 mmol) and *n*-BuLi (1.5 mol mL^{-1} in hexane; 4.1 mL, 6.0 mmol) in anhydrous THF (50 mL) was slowly added an anhydrous THF solution (50 mL) of dimesityl ditelluride (2.47 g, 5.0 mmol) under nitrogen at −60 °C. The solution was stirred for an additional 2 h and was allowed to stand until room temperature. Saturated brine was added to the solution, and the organic layer was separated. The organic component remaining in the aqueous layer was extracted with ether, 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 **4a** (1.02 g, 54%): pale yellow oil; IR (KBr) 2828, 1458, 1027, 846, 746 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.26 (6H, s), 2.30 (3H, s), 2.50 (6H, s), 3.50 (2H, s), 6.84 (1H, t, J = 7.4 Hz), 6.93 (1H, d, J = 7.6 Hz), 6.97 (2H, s), 7.01−7.08 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 29.0, 43.9, 66.6, 122.8, 123.5, 125.5, 127.2, 127.8, 128.7, 133.6, 138.4, 141.0, 145.5; MS (EI) m/z 383 (^{130}Te, M^+), 381 (^{128}Te, M^+), 263, 220, 134, 119, 91, 58.

2-(*N*,*N*-Dimethylaminomethyl)-2′,4′,6′-triisopropyldiphenyl Telluride (4b). Yield 90%; mp 108−109 °C; IR (KBr) 2969, 1458, 1032, 848, 742 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14 (12H, d, J = 7.0 Hz), 1.29 (6H, d, J = 7.0 Hz), 2.26 (6H, s), 2.92 (1H, hep, J = 7.0 Hz), 3.52 (2H, s), 3.76 (2H, hep, J = 7.0 Hz), 6.80−7.00 (4H, m), 7.07 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.7, 24.0, 24.7, 31.6, 34.2, 39.2, 44.0, 66.7, 121.0, 123.9, 125.0, 125.3, 127.6, 128.5, 134.5, 140.7, 149.8, 155.1; MS (EI) m/z 468 (^{130}Te, $M^+ + 1$), 466 (^{128}Te, $M^+ + 1$), 424, 377, 291, 264, 220, 135, 91.

2-(*N*,*N*-Dimethylaminomethyl)-2′,4′,6′-tri-*tert*-butyldiphenyl Telluride (4c). To the lithium reagent prepared from 2,4,6-tri-*tert*-butylbromobenzene (13.00 g, 40.0 mmol) and *n*-BuLi (1.54 mol mL^{-1} in hexane; 28.6 mL, 44.0 mmol) in anhydrous THF (200 mL) was slowly added an anhydrous THF solution (100 mL) of bis[2-(*N*,*N*-dimethylaminomethyl)phenyl] ditelluride (20.94 g, 40.0 mmol) under nitrogen at −60 °C. The solution was stirred for an additional 2 h and was allowed to stand until room temperature. Saturated brine was added to the solution, and the organic layer was separated. The organic component remaining in the aqueous layer was extracted with ether, and 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 **4c** (12.98 g, 64%): mp 139−140 °C; IR (KBr) 2948, 1583, 1456, 1340, 847, 751 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (9H, s), 1.56 (18H, s), 2.24 (6H, s), 3.44 (2H, s), 5.60 (1H, d, J = 7.5 Hz), 6.65 (1H, dd, J = 7.5 Hz), 6.89 (1H, dd, J = 7.5 Hz), 6.97 (1H, d, J = 7.5 Hz), 7.45 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4, 31.6, 33.2, 40.0, 43.9, 66.4, 117.5, 121.7, 124.5, 127.2, 128.1, 131.0, 132.9, 139.5, 149.9, 157.0; MS (EI) m/z 509 (^{130}Te, M^+), 507 (^{128}Te, M^+), 264, 134, 91, 57.

General Procedure for the Oxidation of Telluride Using *tert*-Butyl Hypochlorite: 2,4,6-Triisopropylphenyl Mesityl Telluroxide (*rac*-1a). To a dichloromethane solution (20 mL) containing telluride **3a** (0.90 g, 2.0 mmol) and methanol (20 mL) was slowly added a dichloromethane solution (10 mL) of *tert*-butyl hypochlorite (0.22 g, 2.0 mmol) at −25 °C under nitrogen, and the solution was stirred for an additional 30 min and was allowed to stand until room temperature. After aq sodium hydroxide (0.40 g in 20 mL) was poured into the reaction mixture, the organic layer was separated. The organic component remaining in the aqueous layer was extracted with dichloromethane, 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 telluroxide *rac*-**1a** (0.81 g, 86%): mp 165−167 °C; IR (KBr) 2960, 1590, 1560, 1460, 1360, 840, 740 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (6H, d, J = 6.8 Hz), 1.15 (6H, d, J = 6.8 Hz), 1.22 (6H, d, J = 6.8 Hz), 2.25 (3H, s), 2.53 (6H, s), 2.85 (1H, hep, J = 6.8 Hz), 3.75 (2H, hep, J = 6.8 Hz), 6.83 (2H, s), 7.03 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.9, 21.2, 23.8, 24.4, 24.7, 32.7, 34.1, 123.3, 130.5, 131.3, 131.7, 140.6, 142.3, 152.2, 153.6; MS (EI) m/z 468 (^{130}Te, M^+), 466 (^{128}Te, M^+), 452, 333, 249, 203, 119. Anal. Calcd for $C_{24}H_{34}OTe$: C, 61.84; H, 7.35. Found: C, 61.55; H, 7.65.

2,4,6-Tri-*tert*-butyldiphenyl Telluroxide (*rac*-1b). Yield 84%; mp 122−124 °C; IR (KBr) 2960, 1580, 1480, 1120, 880, 750 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (9H, s), 1.48 (18H, s), 6.94−6.96 (2H, m), 7.22−7.29 (3H, m), 7.51 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.1, 33.7, 35.1, 38.8, 124.0, 129.1, 130.1, 130.5, 133.7, 141.2, 152.7, 157.0; MS (EI) m/z 468 (^{130}Te, M^+), 466 (^{130}Te, M^+), 452, 375, 245, 77; UV (MeCN) λ_{max} 300.0 (ϵ 1.14 × 10^3) nm, 244.0 (ϵ 5.51 × 10^3), 215.0 (ϵ 1.01 × 10^4) nm. Anal. Calcd for $C_{24}H_{34}OTe$ C, 61.84; H, 7.35. Found: C, 62.05; H, 7.81.

2,4,6-Tri-*tert*-butylphenyl Mesityl Telluroxide (*rac*-1c). Yield 97%; mp 121−122 °C; IR (KBr) 2960, 1600, 1460, 800 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (9H, s), 1.34 (18H, s), 2.05 (6H, brs), 2.21 (3H, s), 6.75 (2H, s), 7.29 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.9, 31.1, 31.5, 33.0, 34.4, 39.3, 124.5, 130.1, 133.0, 138.3, 140.7, 142.2, 151.1, 157.4; FAB-MS (3-nitrobenzyl alcohol) m/z 511 (^{130}Te, $M^+ + 1$), 509 (^{130}Te, $M^+ + 1$), 391, 119; UV (MeOH) λ_{max} 236.0 (ϵ 1.77 × 10^4) nm; UV (MeCN) λ_{max} 243.0 (ϵ 2.80 × 10^4), 211.0 (ϵ 4.97 × 10^4) nm. Anal. Calcd for $C_{27}H_{40}OTe$: C, 63.81; H, 7.93. Found: C, 63.56; H 8.15.

2,4,6-Tris[bis(trimethylsilyl)methyl]diphenyl Telluroxide (*rac*-1d). Yield 74%; mp 172−174 °C; IR (KBr) 2950, 1400, 1250, 840, 690 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.10 (9H, s), −0.07 (9H, s), 0.039 (9H, s), 0.043 (9H, s), 0.11 (9H, s), 0.12 (9H, s), 1.35 (1H, s), 2.67 (1H, brs), 2.74 (1H, brs), 6.32 (1H, brs), 6.43 (1H, brs), 7.40−7.50 (3H, m), 7.78−7.82 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.4, 0.6, 0.7, 0.9, 1.1, 26.9, 27.0, 30.9, 123.4, 128.0, 128.2, 129.7, 130.8, 131.1, 135.1, 147.4, 151.0, 151.4; FAB-MS (3-nitrobenzyl alcohol) m/z 775 (^{130}Te, $M^+ + 1$), 773 (^{128}Te, $M^+ + H$). Anal. Calcd for $C_{33}H_{64}OSi_6Te$: C, 51.28; H, 8.35. Found: C, 51.49; H, 8.52.

2-(*N*,*N*-Dimethylaminomethyl)phenyl Mesityl Telluroxide (*rac*-2a). Yield 72%; mp 188−189 °C; IR (KBr) 2820, 1439, 1022, 756, 713 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.08 (6H, s), 2.25 (3H, s), 2.38 (6H, s),3.29 (1H, d, J = 13.8 Hz), 3.35 (1H, d, J = 13.8 Hz), 6.82 (2H, s), 7.18 (1H, d, J = 7.3 Hz), 7.40 (1H, dd, J = 7.3 Hz), 7.48 (1H, dd, J = 7.3 Hz), 8.33 (1H, d, J = 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 22.4, 44.3, 63.2, 128.0, 128.4, 129.4, 130.3, 131.7, 133.48, 133.50, 140.4, 140.5, 142.5; MS (EI) m/z 399 (^{130}Te, M^+), 397 (^{128}Te, M^+), 253, 207, 134, 119, 91, 77; UV (cyclohexane) λ_{max} 309.7 (sh, ϵ 2.48 × 10^3), 269.0 (sh, ϵ 7.92 × 10^3), 231.8 (sh, ϵ 3.85 × 10^4), 207.4

(ϵ 8.59 × 10^4) nm. Anal. Calcd for $C_{18}H_{23}NOTe$: C, 54.46; H, 5.84; N, 3.53. Found: C, 54.14; H, 5.92; N, 3.66.

2-(*N*,*N*-Dimethylaminomethyl)-2′,4′,6′-triisopropyldiphenyl Telluroxide (*rac*-2b). Yield 99%; mp 211−212 °C; IR (KBr) 2963, 1458, 1384, 1101, 741 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.00 (6H, d, J = 7.0 Hz), 1.24 (6H, d, J = 7.0 Hz), 1.25 (6H, d, J = 7.0 Hz), 2.21 (6H, s), 2.88 (1H, hep, J = 7.0 Hz), 3.31 (1H, d, J = 13.8 Hz), 3.59 (2H, hep, J = 7.0 Hz), 3.79 (1H, d, J = 13.8 Hz), 7.04 (2H, s), 7.12−7.20 (1H, m), 7.34−7.38 (2H, m), 7.86−7.90 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.67, 23.73, 24.5, 24.7, 32.5, 34.1, 44.3, 62.9, 122.4, 128.3, 128.6, 130.3, 132.1, 134.90, 134.93, 141.1, 151.6, 154.0; MS (EI) *m*/*z* 483 (^{130}Te, M^+), 481 (^{128}Te, M^+), 465, 438, 336, 291, 264, 175, 134, 91; UV (cyclohexane) λ_{max} 310 (sh, ϵ 2.48 × 10^3), 269 (sh, ϵ 7.92 × 10^3), 232 (sh, ϵ 3.85 × 10^4), 207 (ϵ 8.59 × 10^4) nm. Anal. Calcd for $C_{24}H_{35}NOTe$: C, 59.91; H, 7.33; N, 2.91. Found: C, 59.46; H, 7.31; N, 3.13.

2-(*N*,*N*-Dimethylaminomethyl)-2′,4′,6′-tri-*tert*-butyldiphenyl Telluroxide (*rac*-2c). Yield 97%; mp 143−145 °C; IR (KBr) 2963, 1597, 1460, 1362, 847, 764 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.37 (9H, s), 1.49 (18H, brs), 2.36 (6H, brs), 3.16 (1H, d, J = 13.0 Hz), 4.44 (1H, d, J = 13.0 Hz), 5.84 (1H, brs), 6.89 (1H, dd, J = 7.4 Hz), 7.11 (1H, d, J = 7.4 Hz), 7.20 (1H, dd, J = 7.4 Hz), 7.52 (2H, brs); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.2, 31.5, 34.0, 38.9, 43.6, 61.7, 119.3, 127.3, 128.7, 129.7, 133.3, 139.3, 140.6, 142.2, 149.8, 151.1; MS (EI) *m*/*z* 526 (^{130}Te, M^+ + 1), 524 (^{128}Te, M^+ + 1), 509, 280, 265, 245, 231, 134, 91, 57; UV (cyclohexane) λ_{max} 306 (sh, ϵ 2.07 × 10^3), 232 (sh, ϵ 2.18 × 10^4), 213 (ϵ 3.59 × 10^4) nm. Anal. Calcd for $C_{27}H_{41}NOTe$: C, 61.98; H, 7.90; N, 2.68. Found: C, 61.47; H, 8.01; N, 2.62.

HPLC Analysis of Telluroxides 1a−c and 2a−c. The HPLC analysis of telluroxides **1a**−**c** was performed on a Daicel Chiralpak AS (250 × 4.6 mm) packed with amylose carbamate derivative/silica gel using hexane containing 2−10 vol % of isopropyl alcohol as a mobile phase at a flow rate of 1.0 mL min^{-1}. The HPLC analysis of telluroxides **2a**−**c** was performed on a Daicel Chiralcel OD (250 × 4.6 mm) packed with cellulose carbamate derivative/silica gel using hexane containing 5−30 vol % of isopropyl alcohol as a mobile phase at a flow rate of 1.0 mL min^{-1}. The enantiomeric excess (ee) for each optically active telluroxides **1a**−**c** and **2a**−**c** was determined by HPLC with these columns in an analytical scale.

Optical Resolution of Telluroxides 1a−c and 2a−c at a Preparative Scale. Typically, the racemic telluroxide (100 mg) in eluent (0.5 mL) was charged to same type of optically active columns (Daicel Chiralpak AS: 250 × 10 mm, Daicel Chiralcel OD: 250 × 10 mm) and eluted with hexane containing 5 (for **1a**), 5 (for **1b**), 2 (for **1c**), 40 (for **2a**), 30 (for **2b**), and 5 (for **2c**) vol % isopropyl alcohol at flow rate of 1.0 mL min^{-1}. Finally, ca. 15 mg of optically active telluroxides **1c**, **2b**, and **2c** were obtained from the first eluent by repeated resolution (2−3 times) and ca. 10 mg from the second eluent by repeated resolution (usually, 4−5 times), respectively.

Compound (*R*)-(+)-1c. 100% ee; mp 96−97 °C; $[\alpha]_D$ +25.3 (*c* 0.22, $CHCl_3$), $[\alpha]_D$ +22.5 (c 0.36, MeCN), $[\alpha]_{435}$ +129.6 (*c* 0.22, $CHCl_3$), $[\alpha]_{435}$ +54.7 (*c* 0.36, MeCN); CD (MeCN) 313 ([θ] +1.7 × 10^4), 286 ([θ] −1.5 × 10^4), 264 ([θ] +1.9 × 10^4), 246 ([θ] −3.1 × 10^4), 236 (sh, [θ] −2.1 × 10^4), 212 ([θ] −1.2 × 10^5) nm. Anal. Calcd for $C_{27}H_{40}OTe$: C, 63.81; H, 7.93. Found: C, 63.83; H, 8.41. ^1H NMR, ^{13}C NMR, IR, UV, and MS spectra were almost same with those of racemic one.

Compound (*S*)-(−)-1c. 93% ee; mp 114−115 °C; $[\alpha]_D$ −23.6 (*c* 0.11, $CHCl_3$), $[\alpha]_D$ −21.3 (*c* 0.38, MeCN), $[\alpha]_{435}$ −118.2 (*c* 0.11, $CHCl_3$), $[\alpha]_{435}$ −54.4 (*c* 0.38, MeCN); CD (MeCN) 313 ([θ] −1.6 × 10^4), 286 ([θ] +1.4 × 10^4), 264 ([θ] −1.8 × 10^4), 246 ([θ] +2.9 × 10^4), 236 (sh, [θ] +1.9 × 10^4), 212 ([θ] +1.1 × 10^5) nm. Anal. Calcd for $C_{27}H_{40}OTe$: C, 63.81; H, 7.93. Found: C, 64.18; H, 8.24. ^1H NMR, ^{13}C NMR, IR, UV, and MS spectra were almost same with those of racemic one.

Compound (*R*)-(+)-2b. 100% ee; mp 189−191 °C; $[\alpha]_D$ +39.5 (*c* 0.15, $CHCl_3$), $[\alpha]_{435}$ +142.9 (c 0.15, $CHCl_3$); CD (cyclohexane) 308 ([θ] +2.50 × 10^4), 235 ([θ] −5.31 × 10^4) nm. Anal. Calcd for $C_{24}H_{35}NOTe$: C, 59.91; H, 7.33; N, 2.91. Found: C, 59.59; H, 7.13; N, 2.81. ^1H NMR, ^{13}C NMR, IR, UV, and MS spectra were almost same with those of racemic one.

Compound (*S*)−(−)-2b. 38% ee; mp 178−182 °C; $[\alpha]_D$ −11.9 (c 0.13, $CHCl_3$), $[\alpha]_{435}$ −58.5 (*c* 0.13, $CHCl_3$); CD (cyclohexane) 307 ([θ] −1.86 × 10^4), 236 ([θ] +3.69 × 10^4) nm. Anal. Calcd for $C_{24}H_{35}NOTe$: C, 59.91; H, 7.33; N, 2.91. Found: C, 59.52; H, 7.40; N, 3.16. ^1H NMR, ^{13}C NMR, IR, UV, and MS spectra were almost same with those of racemic one.

Compound (*R*)-(+)-2c. 100% ee; mp 140−141 °C; $[\alpha]_D$ +166.2 (*c* 0.32, $CHCl_3$), $[\alpha]_{435}$ +477.9 (*c* 0.32, $CHCl_3$); CD (cyclohexane) 317 ([θ] +1.15 × 10^5), 272 ([θ] −7.71 × 10^4), 245 ([θ] +1.63 × 10^5), 229 ([θ] −6.46 × 10^4), 219 ([θ] +1.96 × 10^4), 204 ([θ] −3.15 × 10^5) nm. Anal. Calcd for $C_{27}H_{41}NOTe$: C, 61.98; H, 7.90; N, 2.68. Found: C, 61.98; H, 7.51; N, 3.04. ^1H NMR, ^{13}C NMR, IR, UV, and MS spectra were almost same with those of racemic one.

Compound (*S*)-(−)-2c. 40% ee; mp 136−139 °C; $[\alpha]_D$ −66.1 (*c* 0.12, $CHCl_3$), $[\alpha]_{435}$ −193.3 (*c* 0.12, $CHCl_3$); CD (cyclohexane) 316 ([θ] −4.37 × 10^4), 273 ([θ] +3.15 × 10^4), 246 ([θ] −6.31 × 10^4), 229 ([θ] +2.65 × 10^4), 219 ([θ] −6.91 × 10^2), 204 ([θ] +1.27 × 10^5) nm. Anal. Calcd for $C_{27}H_{41}NOTe$: C, 61.98; H, 7.90; N, 2.68. Found: C, 62.08; H, 7.61; N, 3.02. ^1H NMR, ^{13}C NMR, IR, UV, and MS spectra were almost same with those of racemic one.

Kinetic Study for Racemization of Optically Active Telluroxides. Kinetic studies of optically active telluroxides **1b**, **1c**, **2b**, and **2c** for racemization were examined in solutions (ca. 5 mM) at 26 ± 1 °C. The rate of racemization were calculated based on their specific rotation and were plotted to the first-order rate equation.

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