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Isolation and Racemization Mechanism of Optically Active Benzylmethylphenyltelluronium Salts

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Diastereomeric benzylmethylphenyltelluronium (1*S*)-(+)- and (1*R*)-(–)-camphor-10-sulfonates were synthesized and resolved by fractional recrystallization. The absolute configurations of the isomers were determined by X-ray crystallographic analysis. Enantiomerically pure telluronium salts with achiral counteranions, such as tetrafluoroborate, 4-chlorobenzenesulfonate, bromide, iodide, and tetraphenylborate, were also obtained by anion-exchange reactions of the separated diastereomers. The optically active telluronium salts possessing counteranions with a high nucleophilicity, such as bromide and iodide, were found to racemize in solution. The racemization of the telluronium salts was found to proceed either through the formation of a tellurane by the nucleophilic addition of a counteranion to the tellurium atom followed by decomposition into methyl phenyl telluride and benzyl halide or by several pseudorotations of the tellurane.

Introduction

Optically active tricoordinate chalcogen compounds have been the subject of considerable interest, particularly regarding their synthesis, stability, and role as intermediates in organic synthesis. Chiral sulfur compounds, in particular, have been widely investigated.[1,2] We have been interested in the isolation and stereochemistry of optically active selenium and tellurium compounds. Some optically active selenium and tellurium compounds have been synthesized and their stereochemistry has been studied.[2–4] Among the chiral chalcogen compounds, optically active telluronium salts were isolated for the first time as early as 1929,[5] and the next paper appeared in 1945.[6] In those papers, it was described that the chiral telluronium salts decomposed or racemized in solution. Previously, we isolated optically active dialkylaryltelluronium salts but observed no racemization even in solution.[7–9] Koizumi and co-workers also isolated stable optically active dialkyl- or alkylaryl(2-*exo*-hydroxy-10-bornyl)telluronium salts.[10] Recently, we synthesized benzylmethylphenyltelluronium salts and isolated their optically active isomers with several counteranions. We also found that some isomers racemized in solution. We report herein the isolation, stereochemistry, and racemization of optically active benzylmethylphenyltelluronium salts, and clarify the racemization mechanism.[11]

Results and Discussion

Optical Resolution of Diastereomeric Benzylmethylphenyltelluronium Salts

A racemic sample of benzylmethylphenyltelluronium bromide was prepared by reacting methyl phenyl telluride with benzyl bromide. A diastereomeric mixture of benzylmethylphenyltelluronium (1*S*)-(+)-camphor-10-sulfonate (dia.-**1**) {$[\alpha]_D^{25}$ = +15.8 (*c* = 1.00, MeOH). $[\alpha]_D^{25}$ = +33.5 (*c* = 1.00, $CHCl_3$)} was synthesized by counteranion-exchange reaction of the bromide.[11] The diastereomeric mixture was separated roughly into acetone-soluble and -insoluble fractions. Repeated recrystallization (four times) of the acetone-soluble fraction from acetone/hexane afforded the diastereomerically pure (+)-telluronium salt (+)-**1** as colorless needles. In the case of the previously synthesized dialkylaryltelluronium salt, ethylmethylphenyltelluronium (1*S*)-(+)-camphor-10-sulfonate, the (*R*)-isomer was dextrorotatory in methanol and levorotatory in chloroform,[8] whereas (+)-**1** showed dextrorotatory rotation due to the chirality of the tellurium atom in both methanol and chloroform {$[\alpha]_D^{25}$ = +80.0 (*c* = 1.00, MeOH). $[\alpha]_D^{25}$ = +88.8 (*c* = 1.00, $CHCl_3$)}. Recrystallization (once) of the acetone-insoluble fraction from dichloromethane/acetone yielded the diastereomerically pure (–)-telluronium salt (–)-**1** {$[\alpha]_D^{25}$ = –57.3 (*c* = 1.00, MeOH). $[\alpha]_D^{25}$ = –21.2 (*c* = 1.00, $CHCl_3$)} as colorless prisms. The optical purities were determined by ^{1}H NMR spectroscopic measurements (the methyl signals of the telluronium cations for (+)-**1** and (–)-**1** showed different chemical shifts). (+)-Benzylmethylphenyltelluronium (1*R*)-(–)-camphor-10-sulfonate possessing an enantiomeric counteranion was also prepared in a similar manner as its

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enantiomer (–)-**1**, by counteranion-exchange of the racemic telluronium bromide followed by recrystallization of the acetone-insoluble fraction from dichloromethane/acetone.

Absolute Configuration of Diastereomeric Telluronium Salts

The absolute configuration around the tellurium atom of (–)-**1** was determined to be *S* by X-ray crystallographic analysis based on the known configuration of (1*S*)-(+)-camphor-10-sulfonate as an internal standard.[11] Therefore, the absolute configuration of (+)-**1** was assigned to be *R* around the tellurium atom. The tellurium atom of (*S*)-(–)-**1** was also found to interact with two oxygen atoms of the different sulfonate anions in the crystalline state, and the distances between the tellurium atom and the oxygen atoms were 2.84 and 3.01 Å, respectively (Figure 1). Through these tellurium–oxygen interactions, the salts are arranged in a zigzag manner.

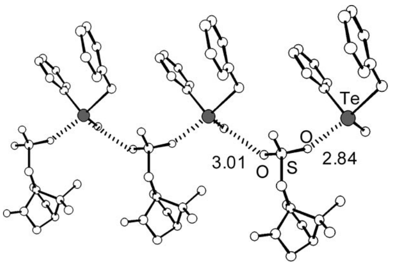
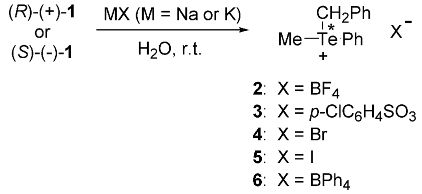


Figure 1. Crystal structure of (*S*)-(–)-**1** with cation–anion interactions. Hydrogen atoms are omitted for clarity.

Transformation of Diastereomerically Pure Telluronium Salts into Enantiomerically Pure Telluronium Salts

Enantiomeric (*R*)- and (*S*)-benzylmethylphenyltelluronium tetrafluoroborates (*R*)-(+)-**2** and (*S*)-(–)-**2** were obtained in 60 and 65% yields, respectively, by the anion-exchange reactions of diastereomerically pure telluronium salts (*R*)-(+)-**1** and (*S*)-(–)-**1** with sodium tetrafluoroborate (Table 1). The optical purities of (*R*)-(+)-**2** and (*S*)-(–)-**2** were determined to be 100% *ee* on the basis of the ^{1}H NMR spectra by using (*S*)-(–)-1,1′-bi-2-naphthol as the chiral shift reagent; singlet signals of methyl groups for (*R*)-(+)-**2** and (*S*)-(–)-**2** were observed at different chemical shifts in the presence of the chiral reagent. Optically active (*R*)- and (*S*)-benzylmethylphenyltelluronium *p*-chlorobenzenesulfonates (*R*)-(+)-**3** and (*S*)-(–)-**3**, bromides (*R*)-(+)-**4** and (*S*)-(–)-**4**, iodides (*R*)-(+)-**5** and (*S*)-(–)-**5**, and tetraphenylborates (*R*)-(+)-**6** and (*S*)-(–)-**6** were also obtained by similar anion-exchange reactions of (*R*)-(+)-**1** and (*S*)-(–)-**1**. The telluronium salts (*R*)- and (*S*)-**3**–**5** were also found to be optically pure, but the optical purities of (*R*)- and (*S*)-**6** could not be determined because the split of the ^{1}H NMR signals of the racemic sample was not observed in the presence of several chiral shift reagents. The specific rotations are also summarized in Table 1. The chiral ethylmethylphenyltelluronium *p*-chlorobenzenesulfonate previously obtained showed opposite signs of the specific rotations in methanol and chloroform.[8] However, the chiral benzylmethylphenyltelluronium salt **3** with the same counteranion did not show such a phenomenon.

Table 1. Anion exchange reactions of (*R*)-(+)-**1** and (*S*)-(–)-**1** and their specific rotations.



Compound	Yield [%]	$[\alpha]_D$[a] in MeOH	in $CHCl_3$
(*R*)-(+)-**2**	60	+96.3	+143.5
(*S*)-(–)-**2**	65	–94.1	–158.3
(*R*)-(+)-**3**	90	+80.3	+71.4
(*S*)-(–)-**3**	94	–81.8	–74.9
(*R*)-(+)-**4**	63	+64.9[b]	+93.8[b]
(*S*)-(–)-**4**	73	–66.5	–96.5
(*R*)-(+)-**5**	67	+76.5[b]	+105.6[b]
(*S*)-(–)-**5**	80	–77.3	–107.4
(*R*)-(+)-**6**	79	+58.0[b]	+22.5
(*S*)-(–)-**6**	89	–30.5[c]	–14.0

[a] Specific rotations were measured at 25 °C and *c* = 1.00. [b] *c* = 0.50. [c] *c* = 0.67.

Circular Dichroism Spectra of Optically Active Telluronium Salts

Diastereomerically pure telluronium salt (*R*)-(+)-**1** showed a positive first Cotton effect at 298 nm and a positive second Cotton effect at 247 nm in the circular dichroism spectrum in methanol (Figure 2). Telluronium salt (*S*)-(–)-**1** also showed a similar positive first Cotton effect at 297 nm, but the corresponding second Cotton effect was negative. Therefore, the observed first Cotton effects of (*R*)-(+)-**1** and (*S*)-(–)-**1** were found to be derived from the common chiral counteranion, (1*S*)-(+)-camphor-10-sulfonate bearing a carbonyl group, and the second Cotton effect must be caused by the chirality on the tellurium atoms. In chloroform, both diastereomers gave Cotton effects with the same respective signs as those in methanol, but the second Cotton effects shifted to 268 nm. Enantiomerically pure telluronium salt (*R*)-(+)-**2** showed a positive Cotton effect at 247 nm in methanol similar to that of (*R*)-(+)-**1**, and no Cotton effect around 300 nm, as observed in the cases of **1**. Telluronium salt (*S*)-(–)-**2** showed a symmetrical spectrum to that of (*R*)-(+)-**2**. Other enantiomeric telluronium salts with *R*-configuration, (*R*)-(+)-**3**–**6**, also showed positive Cotton effects. The circular dichroism spectra of (*R*)-(+)-**2**–**6** looked very similar to one another (the maxima of the Cotton effects appeared at 246–247 nm) in methanol (compounds **2**–**6** showed absorption maxima or shoulder in the range of 237–249 nm in methanol corresponding to π–π* transitions), while the corresponding Cotton effects in chloroform were observed in the range of 268–276 nm. These results indicate that the Cotton effects in methanol are not affected by the different counteranions, possibly due to the strong solvation by methanol, and the Cotton effects in methanol are mainly derived from the telluronium cation moiety.

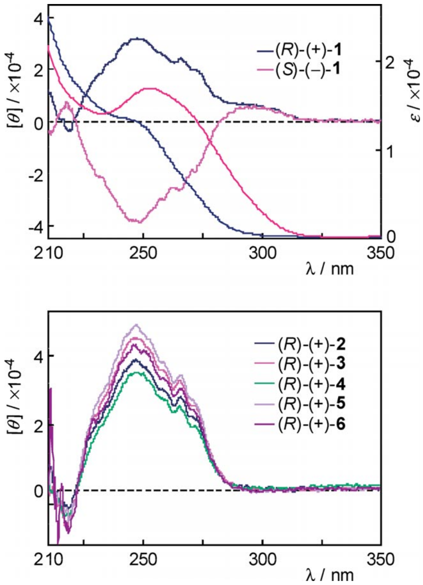


Figure 2. Circular dichroism spectra of optically active telluronium salts **1**–**6** in methanol.

Configurational Stability and Racemization Mechanism of Optically Active Telluronium Salts

Diastereomerically pure telluronium salt (*S*)-**1** was stable both in the crystalline state and in chloroform at room temperature. However, in boiling chloroform, the racemization of (*S*)-**1** was observed together with the formation of trace amounts of methyl phenyl telluride and benzyl (1*S*)-(+)-camphor-10-sulfonate. The racemization obeyed first-order kinetics, and the rate constant k and the half-life $t_{1/2}$ were 4.46×10^{-5} s^{-1} and 4.32 h, respectively. In the case of enantiomerically pure telluronium salts, (*S*)-**4** and (*S*)-**5** were found to racemize in several solvents, such as chloroform, ethanol, methanol, and DMSO, even at room temperature, whereas salts (*S*)-**2**, (*S*)-**3**, and (*S*)-**6** were stable in the above-mentioned solvents. In addition, all of the telluronium salts were stable in MeOH/H_2O (4:1) solution or in the crystalline state. The results indicate that telluronium salts possessing counteranions with a high nucleophilicity racemize in solution. The first-order rate constants and half-lives for the racemization of (*S*)-**4** and (*S*)-**5** at 25 °C are summarized in Table 2. The results show that the racemization proceeds more rapidly in less polar solvents. To examine the cation-anion interaction of the telluronium salts, ^{125}Te NMR spectra were measured in several solvents (Table 3). The ^{125}Te NMR signals of **4** and **5** appeared at a higher field than those of telluronium salts **1**–**3** in chloroform, whereas in methanol, the signals of **1**–**5** were observed in a narrow region, as shown in Figure 3, indicating that the interaction between the tellurium atom of the salts and bromide or iodide is stronger than those with the other counteranions. These experimental findings may indicate the occurrence of nucleophilic attack of the counteranion on the positive tellurium atom to yield a tellurane.

Table 2. First-order rate constants and half-lives for racemization of enantiomeric telluronium salts (*S*)-**4** and (*S*)-**5**.[a]

Solvent	$k \times 10^5$ [s^{-1}] ($t_{1/2}$ [h])			
	(*S*)-**4**		(*S*)-**5**	
$CHCl_3$	10	(1.9)	440	(0.044)
EtOH	1.1	(17)	31	(0.63)
MeOH	0.49	(39)	7.4	(2.6)
DMSO	0.26	(75)	5.7	(3.4)

[a] Racemizations were measured at 25 °C.

Table 3. ^{125}Te NMR chemical shifts of telluronium salts **1**–**6**.

Solvent	Chemical shift [ppm]					
	(*S*)-**1**	**2**	**3**	**4**	**5**	**6**
$CDCl_3$	629	626	631	608	585	–[a]
[D$_6$]acetone	654	647	656	616	626	633
[D$_6$]DMSO	660	656	658	634	646	655
CD_3OD	655	654	655	638	640	–[a]

[a] Insoluble.

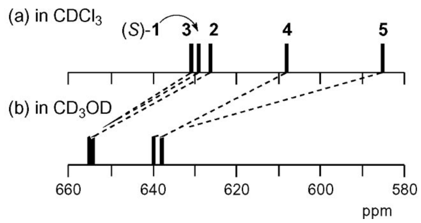
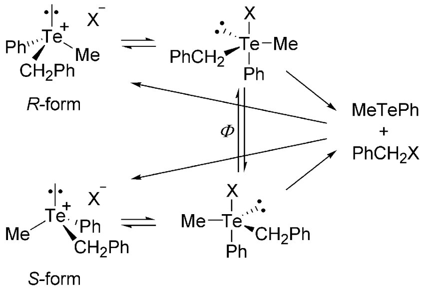


Figure 3. ^{125}Te NMR spectra of telluronium salts **1**–**5**.

Two plausible mechanisms for the racemization of the telluronium salts having a benzyl group are considered, as shown in Scheme 1. A pyramidal inversion mechanism for the racemization of many telluronium species has been ruled out by theoretical studies at least at room temperature.[12,13] The first mechanism is as follows. The counteranion attacks the positive tellurium atom of the telluronium salt to give a tellurane, which yields achiral methyl phenyl telluride and benzyl halide by the ligand-coupling reaction, then the telluronium salt is reproduced. The second mechanism involves Berry pseudorotation[14] of the tellurane (5 pseudorotations (Φ) result in the enantiomeric tellurane), which is known to occur easily. When the reaction of racemic benzylmethylphenyltelluronium bromide **4** with *p*-methylbenzyl bromide was carried out in chloroform at room temperature, methyl(*p*-methylbenzyl)phenyltelluronium bromide **7** was obtained together with benzyl bromide and a small amount of methyl phenyl telluride (Figure 4). The reverse reaction was also observed in the reaction that used telluronium salt **7** and benzyl bromide. These results strongly support the existence of the first mechanism. These ligand-exchange reactions, however, are slow compared to the racemization of **4** in chloroform. Therefore, the Berry pseudorotation of the tellurane is considered to take place concurrently.



Scheme 1. Plausible racemization mechanism of benzylmethylphenyltelluronium salts.

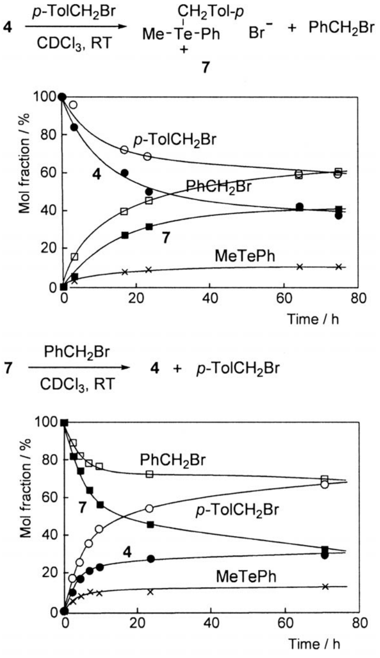


Figure 4. Ligand exchange reactions of telluronium salts **4** and **7**.

The mutarotation observed in chiral 2-*p*-chlorophenacyltelluroisochromanium salts having a benzyl moiety, which was previously reported,[6] is speculated to be due to racemization by a similar mechanism.

Conclusions

Through the optical resolution of diastereomeric benzylmethylphenyltelluronium salts, followed by anion-exchange reactions, several enantiomeric benzylmethylphenyltelluronium salts could be isolated in an optically pure form. The absolute configurations were determined on the basis of X-ray analysis of a diastereomerically pure compound, specific rotations, and circular dichroism spectra. Telluronium salts possessing counteranions with a high nucleophilicity were found to racemize in solution, and the racemization of telluronium salts with a benzyl substituent was found to proceed through two pathways involving the nucleophilic addition of a counteranion to the tellurium atom.

Experimental Section

Synthesis of Benzylmethylphenyltelluronium (1*S*)-(+)-Camphor-10-sulfonate (dia.-1): A mixture of methyl phenyl telluride[15] (6.5 g, 30 mmol) and benzyl bromide (4.6 mL, 39 mmol) was stirred for 1 d under nitrogen. The resulting precipitate was collected by filtration and washed with hexane to yield benzylmethylphenyltelluronium bromide (rac.-**4**) (10.2 g, 87%). Silver (1*S*)-(+)-camphor-10-sulfonate (8.5 g, 25 mmol) was added to a dichloromethane solution (250 mL) of the telluronium bromide (9.0 g, 23 mmol), and the mixture was stirred for 1 d. Precipitated silver bromide was filtered off, and the filtrate was concentrated. The residue was subjected to chromatography on a short alumina column (MeOH/acetone = 1:5) to give a diastereomeric mixture of benzylmethylphenyltelluronium (1*S*)-(+)-camphor-10-sulfonate (dia.-**1**) (11.7 g, 94%).

Benzylmethylphenyltelluronium Bromide (rac.-4): M.p. 105–106 °C (decomp, white powder). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.19 (s, 3 H, Me), 4.46 (d, J = 11.7 Hz, 1 H, CH_2), 4.68 (d, J = 11.6 Hz, 1 H, CH_2), 6.86–6.88 (m, 2 H, Ar), 7.09–7.10 (m, 3 H, Ar), 7.25–7.28 (m, 2 H, Ar), 7.33–7.36 (m, 1 H, Ar), 7.89 (d, J = 7.5 Hz, 2 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.8, 37.7, 122.9, 127.7, 128.1, 129.3, 129.8, 130.3 ppm. 133.1, 134.6. ^{125}Te NMR (158 MHz, $CDCl_3$): δ = 607 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3028, 2359, 2340, 1480, 1454, 1437, 1058, 998, 844, 739 cm^{-1}. UV (MeOH): λ_{max} (ε, L mol^{-1} cm^{-1}) = 201 (3.0×10^4), 241 (1.1×10^4) nm. $C_{14}H_{15}BrTe$ (390.78): calcd. C 43.03, H 3.87; found C 42.87, H 3.86.

Benzylmethylphenyltelluronium (1*S*)-(+)-Camphor-10-sulfonate (dia.-1): M.p. 97–99 °C (pale yellow powder, decomp). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.80 (s, 3 H, Me), 1.06 (s, 3 H, Me), 1.30–1.34 (m, 1 H, CH_2), 1.61–1.67 (m, 1 H, CH_2), 1.84 (d, J = 18.3 Hz, 1 H, CH_2), 1.93–1.99 (m, 1 H, CH), 2.00–2.03 (m, 1 H, CH_2), 2.27–2.33 (m, 1 H, CH_2), 2.41 (s, 3/2 H, CH_2), 2.42 (s, 3/2 H, CH_2), 2.63–2.70 (m, 1 H, CH_2), 2.75 (d, J = 14.7 Hz, 1 H, CH_2), 3.28 (d, J = 14.7 Hz, 1 H, CH_2), 4.50 (d, J = 11.0 Hz, 1/2 H, CH_2), 4.52 (d, J = 11.0 Hz, 1/2 H, CH_2), 4.65 (d, J = 11.3 Hz, 1 H, CH_2), 6.96–6.98 (m, 2 H, Ar), 7.17–7.18 (m, 3 H, Ar), 7.36–7.42 (m, 4 H, Ar), 7.45–7.48 (m, 1 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.7, 19.6, 19.8, 24.3, 26.9, 35.5, 42.4, 42.7, 47.3, 47.7, 58.4, 121.6, 127.9, 128.2, 129.6, 130.1, 131.1, 131.9, 133.7, 216.6 ppm. ^{125}Te NMR (158 MHz, $CDCl_3$): δ = 630.8, 631.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2962, 2359, 2341, 1737, 1192, 1036, 868, 740 cm^{-1}. UV (MeOH): λ_{max} (ε, L mol^{-1} cm^{-1}) = 201 (3.6×10^4), 241 (sh, 1.4×10^4) nm. UV ($CHCl_3$): λ_{max} (ε, L mol^{-1} cm^{-1}) = 235 (1.3×10^4), 254 (1.3×10^4) nm. $[\alpha]_D^{25}$ = +15.8 (c = 1.00, MeOH). $[\alpha]_D^{25}$ = +18.5 (c = 1.00, EtOH). $[\alpha]_D^{25}$ = +21.3 (c = 1.00, AcOEt). $[\alpha]_D^{25}$ = +22.2 (c = 1.00, MeCN). $[\alpha]_D^{25}$ = +23.2 (c = 1.00, acetone). $[\alpha]_D^{25}$ = +29.5 (c = 1.00, CH_2Cl_2). $[\alpha]_D^{25}$ = +33.5 (c = 1.00, $CHCl_3$). CD (MeOH): λ = 296 ($[\theta]$ $+6.5 \times 10^3$) nm. CD ($CHCl_3$): λ = 297 ($[\theta]$ $+1.1 \times 10^4$) nm. $C_{24}H_{30}O_4STe$ (542.17): calcd. C 53.17, H 5.58; found C 53.18, H 5.51.

Optical Resolution of Benzylmethylphenyltelluronium (1*S*)-(+)-Camphor-10-sulfonate (dia.-1): Diastereomeric telluronium salt dia.-**1**

(22.7 g, 42 mmol) was added to acetone (10 mL); a portion dissolved and a portion was insoluble. The insoluble fraction (13.5 g) was collected by filtration and recrystallized from CH_2Cl_2/acetone to give diastereomerically pure (*S*)-(–)-**1** (5.2 g, 9.6 mmol) as colorless prisms. The acetone-soluble fraction (8.9 g) was recrystallized from acetone/hexane, and the resulting crystals were recrystallized a further three times to yield diastereomerically pure (*R*)-(+)-**1** (0.68 g, 1.3 mmol) as colorless needles.

(*R*)-(+)-Benzylmethylphenyltelluronium (1*S*)-(+)-Camphor-10-sulfonate {(*R*)-(+)-1}: 100% de; m.p. 113–115 °C (decomp). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.85 (s, 3 H, Me), 1.11 (s, 3 H, Me), 1.36–1.41 (m, 1 H, CH_2), 1.74–1.78 (m, 1 H, CH_2), 1.89 (d, J = 18.3 Hz, 1 H, CH_2), 1.99–2.06 (m, 1 H, CH), 2.31–2.35 (m, 1 H, CH_2), 2.46 (s, 3 H, Me), 2.73–2.78 (m, 1 H, CH_2), 2.86 (d, J = 14.7 Hz, 1 H, CH_2), 3.36 (d, J = 14.7 Hz, 1 H, CH_2), 4.48 (d, J = 11.3 Hz, 1 H, CH_2), 4.69 (d, J = 11.3 Hz, 1 H, CH_2), 4.69 (d, J = 11.3 Hz, 1 H, CH_2), 6.97–6.98 (m, 2 H, Ar), 7.20–7.22 (m, 3 H, Ar), 7.26–7.28 (m, 2 H, Ar), 7.40 (t, J = 7.7 Hz, 2 H, Ar), 7.52 (t, J = 7.5 Hz, 1 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.9, 19.8, 19.9, 24.5, 27.0, 35.8, 42.6, 42.9, 47.4, 47.8, 58.5, 121.6, 128.1, 128.4, 129.8, 130.2, 131.3, 131.7, 133.8, 216.8 ppm. ^{125}Te NMR (158 MHz, $CDCl_3$): δ = 627 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2956, 1735, 1180, 1039, 736, 700 cm^{-1}. UV (MeOH): λ_{max} (ε, $L\,mol^{-1}cm^{-1}$) = 199 (3.4×10^4), 244 (sh, 1.3×10^4) nm. UV ($CHCl_3$): λ_{max} (ε, $L\,mol^{-1}cm^{-1}$) = 236 (1.3×10^4), 256 (1.2×10^4) nm. $[\alpha]_D^{25}$ = +80.0 (c = 1.00, MeOH). $[\alpha]_D^{25}$ = +88.8 (c = 1.00, $CHCl_3$). CD (MeOH): λ = 247 ([θ] $+3.7\times10^4$), 298 ([θ] $+5.6\times10^3$) nm. CD ($CHCl_3$): λ = 268 ([θ] $+2.3\times10^4$), 294 ([θ] $+1.1\times10^4$) nm. $C_{24}H_{30}O_4STe$ (542.17): calcd. C 53.17, H 5.58; found C 53.40, H 5.53.

(*S*)-(–)-Benzylmethylphenyltelluronium (1*S*)-(+)-Camphor-10-sulfonate {(*S*)-(–)-1}: 100% de; m.p. 125–126 °C (decomp). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.80 (s, 3 H, Me), 1.05 (s, 3 H, Me), 1.30–1.34 (m, 1 H, CH_2), 1.60–1.66 (m, 1 H, CH_2), 1.85 (d, J = 18.3 Hz, 1 H, CH_2), 1.91–1.97 (m, 1 H, CH), 2.00–2.02 (m, 1 H, CH_2), 2.27–2.32 (m, 1 H, CH_2), 2.42 (s, 3 H, Me), 2.63–2.69 (m, 1 H, CH_2), 2.73 (d, J = 14.7 Hz, 1 H, CH_2), 3.27 (d, J = 14.7 Hz, 1 H, CH_2), 4.52 (d, J = 11.3 Hz, 1 H, CH_2), 4.62 (d, J = 11.3 Hz, 1 H, CH_2), 6.96–6.98 (m, 2 H, Ar), 7.17–7.19 (m, 3 H, Ar), 7.37–7.42 (m, 4 H, Ar), 7.46 (t, J = 7.0 Hz, 1 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.8, 19.7, 19.9, 24.4, 26.9, 35.6, 42.5, 42.8, 47.4, 47.7, 58.4, 121.6, 128.0, 128.3, 129.7, 130.2, 131.2, 131.9, 133.8, 216.7 ppm. ^{125}Te NMR (158 MHz, $CDCl_3$): δ = 629 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2968, 1740, 1192, 1035, 868, 740 cm^{-1}. UV (MeOH): λ_{max} (ε, $L\,mol^{-1}cm^{-1}$) = 200 (3.3×10^4), 253 (sh, 1.7×10^4) nm. UV ($CHCl_3$): λ_{max} (ε, $L\,mol^{-1}cm^{-1}$) = 237 (1.2×10^4), 255 (1.2×10^4) nm. $[\alpha]_D^{25}$ = –57.3 (c = 1.00, MeOH). $[\alpha]_D^{25}$ = –52.9 (c = 1.00, EtOH). $[\alpha]_D^{25}$ = –17.1 (c = 1.00, MeCN). $[\alpha]_D^{25}$ = –23.8 (c = 1.00, acetone). $[\alpha]_D^{25}$ = –8.5 (c = 1.00, CH_2Cl_2). $[\alpha]_D^{25}$ = –21.2 (c = 1.00, $CHCl_3$). CD (MeOH): λ = 247 ([θ] -3.9×10^4), 297 ([θ] $+5.7\times10^3$) nm. CD ($CHCl_3$): λ = 268 ([θ] -4.1×10^4), 297 ([θ] $+1.0\times10^4$) nm. $C_{24}H_{30}O_4STe$ (542.17): calcd. C 53.17, H 5.58; found C 53.03, H 5.51.

Optical Resolution of Benzylmethylphenyltelluronium (1*R*)-(–)-Camphor-10-sulfonate: A diastereomeric mixture of benzylmethylphenyltelluronium (1*R*)-(–)-camphor-10-sulfonate (13.3 g, 25 mmol), prepared in a similar way to dia.-**1** by the reaction of rac.-**4** with silver (1*R*)-(–)-camphor-10-sulfonate, was added to hot acetone (10 mL), a portion dissolved and a portion was insoluble. The insoluble fraction was collected by filtration and recrystallized from CH_2Cl_2/acetone to give diastereomerically pure (*R*)-(+)-benzylmethylphenyltelluronium (1*R*)-(–)-camphor-10-sulfonate (1.47 g, 2.7 mmol) as colorless prisms.

(*R*)-(+)-Benzylmethylphenyltelluronium (1*R*)-(–)-Camphor-10-sulfonate: 100% *de*; m.p. 122–124 °C (decomp). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.81 (s, 3 H, Me), 1.07 (s, 3 H, Me), 1.31–1.37 (m, 1 H, CH_2), 1.65–1.71 (m, 1 H, CH_2), 1.86 (d, J = 18.0 Hz, 1 H, CH_2), 1.94–2.00 (m, 1 H, CH), 2.02–2.03 (m, 1 H, CH_2), 2.28–2.33 (m, 1 H, CH_2), 2.43 (s, 3 H, Me), 2.66–2.72 (m, 1 H, CH_2), 2.78 (d, J = 14.7 Hz, 1 H, CH_2), 3.30 (d, J = 14.7 Hz, 1 H, CH_2), 4.53 (d, J = 11.3 Hz, 1 H, CH_2), 4.65 (d, J = 11.3 Hz, 1 H, CH_2), 6.97–6.99 (m, 2 H, Ar), 7.19–7.20 (m, 3 H, Ar), 7.36–7.41 (m, 4 H, Ar), 7.48 (t, J = 7.2 Hz, 1 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.0, 19.8, 20.0, 24.5, 27.0, 36.2, 42.6, 42.9, 47.5, 47.9, 58.6, 121.7, 128.2, 128.5, 129.9, 130.3, 131.4, 131.7, 133.7, 216.9 ppm. ^{125}Te NMR (158 MHz, $CDCl_3$): δ = 632 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2966, 1737, 1191, 1035, 866, 738 cm^{-1}. UV (MeOH): λ_{max} (ε, $L\,mol^{-1}cm^{-1}$) = 199 (3.3×10^4), 244 (sh, 1.3×10^4) nm. $[\alpha]_D^{25}$ = +51.0 (c = 1.00, MeOH). CD (MeOH): λ = 247 ([θ] $+4.0\times10^4$), 298 ([θ] $+6.5\times10^3$) nm. $C_{24}H_{30}O_4STe$ (542.17): calcd. C 53.17, H 5.58; found C 52.99, H 5.55.

General Procedure for Transformation of Diastereomerically Pure Telluronium Salts into Enantiomerically Pure Telluronium Salts: An aqueous solution (13 mL) of diastereomerically pure telluronium salt (*R*)-(+)-**1** or (*S*)-(–)-**1** (0.41 g, 0.75 mmol) and sodium tetrafluoroborate, sodium 4-chlorobenzenesulfonate, potassium bromide, potassium iodide, or sodium tetraphenylborate (10 equiv.) was stirred for 2 h. When using sodium tetrafluoroborate, sodium 4-chlorobenzenesulfonate, or sodium tetraphenylborate, the products were extracted with dichloromethane followed by recrystallization from CH_2Cl_2/diethyl ether. When using potassium bromide and potassium iodide, the resulting precipitates were collected by filtration.

(*R*)-(+)-Benzylmethylphenyltelluronium Tetrafluoroborate {(*R*)-(+)-2}: 60%; 100% *ee*; m.p. 101–103 °C (decomp, colorless needles). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.33 (s, 3 H, Me), 4.46 (d, J = 11.6 Hz, 1 H, CH_2), 4.54 (d, J = 11.6 Hz, 1 H, CH_2), 6.90 (d, J = 7.3 Hz, 2 H, Ar), 7.17–7.24 (m, 3 H, Ar), 7.36–7.43 (m, 4 H, Ar), 7.51–7.54 (m, 1 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 6.0, 34.3, 117.2, 128.7, 128.8, 130.3, 130.36, 130.42, 132.3, 133.7 ppm. ^{125}Te NMR (158 MHz, $CDCl_3$): δ = 626 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3032, 2359, 1701, 1577, 1494, 1483, 1437, 1020, 871, 737, 702, 689 cm^{-1}. UV (MeOH): λ_{max} (ε, $L\,mol^{-1}cm^{-1}$) = 199 (3.1×10^4), 245 (sh, 1.3×10^4) nm. UV ($CHCl_3$): λ_{max} (ε, $L\,mol^{-1}cm^{-1}$) = 237 (1.3×10^4), 260 (1.4×10^4) nm. $[\alpha]_D^{25}$ = +96.3 (c = 1.00, MeOH). $[\alpha]_D^{25}$ = +143.5 (c = 1.00, $CHCl_3$). CD (MeOH): λ = 247 ([θ] $+3.7\times10^4$) nm. CD ($CHCl_3$): λ = 274 ([θ] $+3.7\times10^4$) nm. $C_{14}H_{15}BF_4Te$ (397.68): calcd. C 42.28, H 3.80; found C 42.07, H 3.78.

(*S*)-(–)-Benzylmethylphenyltelluronium Tetrafluoroborate {(*S*)-(–)-2}: 65%; 100% *ee*; m.p. 102–104 °C (decomp, colorless prisms). $[\alpha]_D^{25}$ = –94.1 (c = 1.00, MeOH). $[\alpha]_D^{25}$ = –93.2 (c = 1.00, EtOH). $[\alpha]_D^{25}$ = –87.9 (c = 1.00, MeCN). $[\alpha]_D^{25}$ = –110.5 (c = 1.00, acetone). $[\alpha]_D^{25}$ = –108.1 (c = 1.00, CH_2Cl_2). $[\alpha]_D^{25}$ = –158.3 (c = 1.00, $CHCl_3$). CD (MeOH): λ = 247 ([θ] -4.1×10^4) nm. CD ($CHCl_3$): λ = 275 ([θ] -3.1×10^4) nm. $C_{14}H_{15}BF_4Te$ (397.68): calcd. C 42.28, H 3.80; found C 42.01, H 3.76. The ^1H NMR and ^{13}C NMR spectra were almost the same as those for (*R*)-(+)-**2**.

(*R*)-(+)-Benzylmethylphenyltelluronium 4-Chlorobenzenesulfonate {(*R*)-(+)-3}: 90%; 100% *ee*; m.p. 125–127 °C (decomp, colorless needles). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.34 (s, 3 H, Me), 4.47 (d, J = 11.3 Hz, 1 H, CH_2), 4.60 (d, J = 11.3 Hz, 1 H, CH_2), 6.85 (d, J = 7.1 Hz, 2 H, Ar), 7.11–7.19 (m, 3 H, Ar), 7.25 (d, J = 8.4 Hz, 2 H, Ar), 7.31 (t, J = 7.4 Hz, 2 H, Ar), 7.36 (d, J = 7.4 Hz, 2 H, Ar), 7.44 (d, J = 7.4 Hz, 1 H, Ar), 7.71 (d, J =

8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.3, 35.2, 120.7, 127.5, 128.17, 128.23, 128.4, 129.8, 130.1, 131.4, 131.6, 133.7, 135.5, 144.2 ppm. ^{125}Te NMR (158 MHz, $CDCl_3$): δ = 630 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2359, 1474, 1438, 1224, 1178, 1120, 1085, 1030, 1006, 832, 755 cm^{-1}. UV (MeOH): λ_{max} (ε, L mol^{-1} cm^{-1}) = 223 (2.9×10^4), 249 (1.2×10^4) nm. UV ($CHCl_3$): λ_{max} (ε, L mol^{-1} cm^{-1}) = 236 (1.5×10^4), 260 (1.3×10^4) nm. $[\alpha]_D^{25}$ = +80.3 (*c* = 1.00, MeOH). $[\alpha]_D^{25}$ = +71.4 (*c* = 1.00, $CHCl_3$). CD (MeOH): λ = 246 ([θ] +4.3×10^4) nm. CD ($CHCl_3$): λ = 268 ([θ] +4.2×10^4) nm. $C_{20}H_{19}ClO_3STe$ (502.49): calcd. C 47.81, H 3.81; found C 47.58, H 3.80.

(*S*)-(–)-Benzylmethylphenyltelluronium 4-Chlorobenzenesulfonate {(*S*)-(–)-3}: 94%; 100% *ee*; m.p. 123–125 °C (decomp, colorless needles). $[\alpha]_D^{25}$ = –81.8 (*c* = 1.00, MeOH). $[\alpha]_D^{25}$ = –82.4 (*c* = 1.00, EtOH). $[\alpha]_D^{25}$ = –59.8 (*c* = 1.00, MeCN). $[\alpha]_D^{25}$ = –65.2 (*c* = 1.00, acetone). $[\alpha]_D^{25}$ = –50.8 (*c* = 1.00, CH_2Cl_2). $[\alpha]_D^{25}$ = –74.9 (*c* = 1.00, $CHCl_3$). CD (MeOH): λ = 248 ([θ] –4.5×10^4) nm. CD ($CHCl_3$): λ = 269 ([θ] –4.1×10^4) nm. $C_{20}H_{19}ClO_3STe$ (502.49): calcd. C 47.81, H 3.81; found C 48.03, H 3.92. The ^{1}H NMR and ^{13}C NMR spectra were almost the same as those for (*R*)-(+)-**3**.

(*R*)-(+)-Benzylmethylphenyltelluronium Bromide {(*R*)-(+)-4}: 63%; 100% *ee*; m.p. 101–103 °C (decomp, white powder). $[\alpha]_D^{25}$ = +64.9 (*c* = 0.50, MeOH). $[\alpha]_D^{25}$ = +93.8 (*c* = 0.50, $CHCl_3$). CD (MeOH): λ = 247 ([θ] +3.3×10^4) nm. CD ($CHCl_3$): λ = 275 ([θ] +2.6×10^4) nm. $C_{14}H_{15}BrTe$ (390.78): calcd. C 43.03, H 3.87; found C 42.98, H 3.88. The ^{1}H NMR and ^{13}C NMR spectra were almost the same as those for rac.-**4**.

(*S*)-(–)-Benzylmethylphenyltelluronium Bromide {(*S*)-(–)-4}: 73%; 100% *ee*; m.p. 108–110 °C (decomp, white powder). $[\alpha]_D^{25}$ = –66.5 (*c* = 1.00, MeOH). $[\alpha]_D^{25}$ = –96.5 (*c* = 1.00, $CHCl_3$). CD (MeOH): λ = 249 ([θ] –3.1×10^4) nm. CD ($CHCl_3$): λ = 275 ([θ] –2.7×10^4) nm. $C_{14}H_{15}BrTe$ (390.78): calcd. C 43.03, H 3.87; found C 42.97, H 4.14. The ^{1}H NMR and ^{13}C NMR spectra were almost the same as those for rac.-**4**.

(*R*)-(+)-Benzylmethylphenyltelluronium Iodide {(*R*)-(+)-5}: 67%; 100% *ee*; m.p. 78–80 °C (decomp, pale yellow powder). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.20 (s, 3 H, Me), 4.46 (s, 2 H, CH_2), 7.18–7.21 (m, 2 H, Ar), 7.23–7.26 (m, 2 H, Ar), 7.28–7.30 (m, 2 H, Ar), 7.37–7.38 (m, 2 H, Ar), 7.63–7.65 (m, 2 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.8, 38.7, 121.2, 127.9, 128.1, 129.1, 129.6, 129.9 ppm. 134.7, 136.7. ^{125}Te NMR (158 MHz, $CDCl_3$): δ = 586 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3027, 1598, 1573, 1492, 1479, 1453, 1435, 1059, 997, 853, 760, 738, 700 cm^{-1}. UV (MeOH): λ_{max} (ε, L mol^{-1} cm^{-1}) = 199 (5.2×10^4), 217 (3.7×10^4), 249 (sh, 2.2×10^4) nm. $[\alpha]_D^{25}$ = +76.5 (*c* = 0.50, MeOH). $[\alpha]_D^{25}$ = +105.6 (*c* = 0.50, $CHCl_3$). CD (MeOH): λ = 247 ([θ] +4.7×10^4) nm. $C_{14}H_{15}ITe$ (437.78): calcd. C 38.41, H 3.45; found C 38.51, H 3.47.

(*S*)-(–)-Benzylmethylphenyltelluronium Iodide {(*S*)-(–)-5}: 80%; 100% *ee*; m.p. 77–78 °C (decomp, pale yellow powder). $[\alpha]_D^{25}$ = –77.3 (*c* = 1.00, MeOH). $[\alpha]_D^{25}$ = –107.4 (*c* = 1.00, $CHCl_3$). CD (MeOH): λ = 249 ([θ] –4.9×10^4) nm. $C_{14}H_{15}ITe$ (437.78): calcd. C 38.41, H 3.45; found C 38.34, H 3.42. The ^{1}H NMR and ^{13}C NMR spectra were almost the same as those for (*R*)-(+)-**5**.

(*R*)-(+)-Benzylmethylphenyltelluronium Tetraphenylborate {(*R*)-(+)-6}: 79%; m.p. 131–133 °C (decomp, colorless prisms). ^{1}H NMR (500 MHz, [D$_6$]acetone, 25 °C): δ = 2.40 (s, 3 H, Me), 4.51 (s, 2 H, CH_2), 6.78 (t, *J* = 7.3 Hz, 4 H, Ar), 6.93 (t, *J* = 7.3 Hz, 8 H, Ar), 7.01–7.03 (m, 2 H, Ar), 7.23–7.27 (m, 3 H, Ar), 7.36–7.37 (m, 8 H, Ar), 7.49–7.54 (m, 4 H, Ar), 7.60–7.63 (m, 1 H, Ar) ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone): δ = 7.7, 34.8, 119.9, 122.3, 126.05, 126.09, 129.4, 129.6, 130.8, 131.2, 132.2, 133.1, 134.6, 137.0 ppm. ^{125}Te NMR (158 MHz, [D$_6$]acetone): δ = 638 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3054, 1579, 1479, 1437, 1427, 1160, 1131, 856, 744, 731, 709 cm^{-1}. UV (MeOH): λ_{max} (ε, L mol^{-1} cm^{-1}) = 201 (1.3×10^4) nm. UV ($CHCl_3$): λ_{max} (ε, L mol^{-1} cm^{-1}) = 237 (3.8×10^4) nm. $[\alpha]_D^{25}$ = +58.0 (*c* = 0.50, MeOH). $[\alpha]_D^{25}$ = +22.5 (*c* = 1.00, $CHCl_3$). CD (MeOH): λ = 246 ([θ] +4.1×10^4) nm. CD ($CHCl_3$): λ = 276 ([θ] +1.6×10^4), 305 ([θ] –6.1×10^3) nm. $C_{38}H_{35}BTe$ (630.11): calcd. C 72.43, H 5.60; found C 72.31, H 5.66.

(*S*)-(–)-Benzylmethylphenyltelluronium Tetraphenylborate {(*S*)-(–)-6}: 89%; m.p. 132–133 °C (decomp, colorless prisms). $[\alpha]_D^{25}$ = –30.5 (*c* = 0.67, MeOH). $[\alpha]_D^{25}$ = –30.5 (*c* = 1.67, MeOH). $[\alpha]_D^{25}$ = –17.6 (*c* = 0.50, EtOH). $[\alpha]_D^{25}$ = –52.8 (*c* = 1.00, MeCN). $[\alpha]_D^{25}$ = –61.9 (*c* = 1.00, acetone). $[\alpha]_D^{25}$ = –34.4 (*c* = 1.00, CH_2Cl_2). $[\alpha]_D^{25}$ = –14.0 (*c* = 1.00, $CHCl_3$). CD (MeOH): λ = 246 ([θ] –4.5×10^4) nm. CD ($CHCl_3$): λ = 276 ([θ] +1.0×10^4), 301 ([θ] +4.0×10^3) nm. $C_{38}H_{35}BTe$ (630.11): calcd. C 72.43, H 5.60; found C 72.13, H 5.65. The ^{1}H NMR and ^{13}C NMR spectra were almost the same as those for (*R*)-(+)-**6**.

Reaction of Benzylmethylphenyltelluronium Bromide (4) with *p*-Methylbenzyl Bromide: In an NMR tube, racemic benzylmethylphenyltelluronium bromide (**4**) (20 mg, 0.051 mmol) and *p*-methylbenzyl bromide (9.5 mg, 0.051 mmol) were dissolved in $CDCl_3$ (0.8 mL), and the sample was left at room temperature and monitored by ^{1}H NMR spectroscopy. The reaction of methyl(*p*-methylbenzyl)phenyltelluronium bromide (**7**) with benzyl bromide was carried out similarly.

Methyl(*p*-methylbenzyl)phenyltelluronium Bromide (rac.-7): M.p. 141–142 °C (decomp, colorless powder). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.24 (s, 3 H, Me), 2.27 (s, 3 H, Me), 4.51 (d, *J* = 11.6 Hz, 1 H, CH_2), 4.71 (d, *J* = 11.6 Hz, 1 H, CH_2), 6.81 (d, *J* = 7.7 Hz, 2 H, Ar), 6.94 (d, *J* = 7.7 Hz, 2 H, Ar), 7.29–7.40 (m, 3 H, Ar), 7.76 (d, *J* = 7.7 Hz, 2 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.7, 21.1, 37.2, 123.0, 128.9, 129.4, 129.6, 129.8, 130.4, 134.5, 137.7 ppm. ^{125}Te NMR (158 MHz, $CDCl_3$): δ = 620 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3051, 1575, 1510, 1480, 1436, 1404, 999, 824, 734, 689, 565, 456 cm^{-1}. UV (MeOH): λ_{max} (ε, L mol^{-1} cm^{-1}) = 253 (1.0×10^4), 241 (1.1×10^4) nm. $C_{15}H_{17}BrTe$ (404.80): calcd. C 44.51, H 4.23; found C 44.75, H 4.25.

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