Diastereoselective Synthesis and Stereochemical Research of Optically Pure Telluronium Salts

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The synthesis of optically pure telluronium salts **4a**−**i**, using the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand, has been achieved in high yield and selectivity by the reaction of chiral alkoxytelluranes **3a**−**i** with organolithium and Grignard reagents. Both diastereoisomers of ethyl(2-*exo*-hydroxy-10-bornyl)methyltelluronium chloride (**4a**,**b**) and butyl(2-*exo*-hydroxy-10-bornyl)methyltelluronium chloride (**4c**,**d**) have been synthesized in optically pure form in high yield and with excellent diastereoselectivity. The method has been used for the asymmetric synthesis of chiral benzyl- and allyltelluronium salts **5a**−**h**. Structures of these salts have been confirmed by X-ray analyses of **4a** and **4b**, which indicated that all of the salts have their pyramidal geometrical structures around the tellurium atom. The thermal and optical stability and the possible mechanisms of the reaction are also discussed.

Organochalcogenonium compounds such as chalcogenoxides, chalcogenonium imides, chalcogenonium ylides, chalcogenonium salts, and chalcogenuranes may become chiral when different substituents are attached to the chalcogen atom (Figure 1). Although many chiral organosulfur compounds have been prepared and the stereochemistry has been studied extensively,[1,2] the synthesis and stereochemistry of chiral organotellurium compounds have been studied to a lesser extent.[3,4] Kamigata et al. have reported recently on the first isolation of optically pure dialkylaryltelluronium salts **1** with defined stereochemistry by optical resolution.[4a−h] In contrast to the previous reports,[4c,d] they found that the telluronium salts were optically stable compounds and did not racemize easily.[4a,b] However, the number of chiral tellurium compounds with defined stereochemistry is still small, and further study is needed to develop synthetic methods and to establish the stereochemistry and optical stability of chiral organotellurium compounds.

In this paper, we describe the details of the first asymmetric synthesis and the structure of optically pure

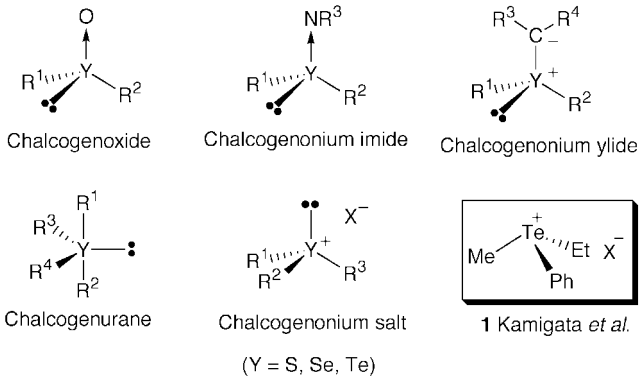

Figure 1.

telluronium salts by the reaction of chiral halooxatelluranes with alkyllithium or Grignard reagents.[5] The stereochemical study and possible mechanisms of the reaction will also be discussed.

Results and Discussion

Synthesis of Optically Pure Telluronium Salts. Chiral chlorooxatelluranes **3a**−**e** were synthesized by the treatment of tellurides **2a**−**e** with *t*-BuOCl. Bromotelluranes **3f**−**i** were obtained by halogen exchange reaction of chlorotelluranes with NaBr (Scheme 1).[6] Nucleophilic reaction of methylbromooxatellurane **3f** with 1.2 equiv of ethylmagnesium bromide in CH_2Cl_2 followed by work-up with NH_4Cl (aq) gave ethyl(2-*exo*-hydroxy-10-bornyl)-

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(5) A part of this work has been reported as a communication: Zhang, J.; Saito, S.; Koizumi, T. *Tetrahedron: Asymmetry* **1997**, *8*, 3357−3361. The structure of **5b** was also determined by X-ray crystallographic analysis.

(6) (a) Takahashi, T.; Kurose, N.; Kawanami, S.; Arai, Y.; Koizumi, T.; Shiro, M. *J. Org. Chem.* **1994**, *59*, 3262−3264. (b) Kurose, N.; Takahashi, T.; Koizumi, T. *J. Org. Chem.* **1996**, *61*, 2932−2933. (c) Zhang, J.; Takahashi, T.; Koizumi, T. *Heterocycles* **1997**, *44*, 325−339. (d) Takahashi, T.; Zhang, J.; Kurose, N.; Takahashi S.; Koizumi, T. Shiro, M. *Tetrahedron: Asymmetry* **1996**, *7*, 2797−2800. (e) Takahashi, T.; Kurose, N.; Kawanami, S.; Nojiro, A.; Arai, Y.; Koizumi, T.; Shiro, M. *Chem. Lett.* **1995**, 379−380.

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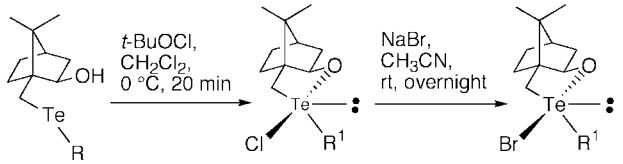
Scheme 1

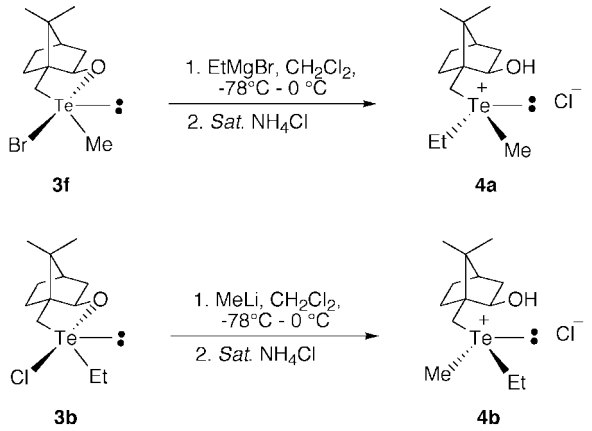


2a, R = Me
2b, R = Et
2c, R = *n*-Bu
2d, R = *n*-C_6H_{13}
2e, R = C_6H_5

3a, R = Me
3b, R = Et
3c, R = *n*-Bu
3d, R = *n*-C_6H_{13}
3e, R = C_6H_5

3f, R = Me
3g, R = Et
3h, R = *n*-Bu
3i, R = C_6H_5

Scheme 2



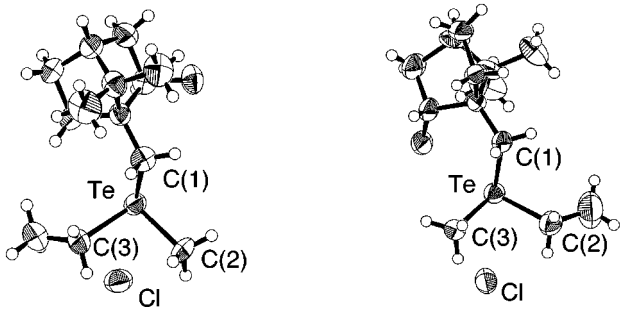
3f **4a**

3b **4b**

methyltelluronium chloride (**4a**) in 87% yield as a single diastereomer. Reaction of ethylchlorooxatellurane **3b** with methyllithium under the similar conditions gave ethyl(2-*exo*-hydroxy-10-bornyl)methyltelluronium chloride (**4b**) in 79% yield also as a single diastereomer (Scheme 2). No telluronium salts epimeric at tellurium were detected in these reactions. In the ^{1}H NMR spectrum of **4a**, an absorption for the methyl group bound to the tellurium atom was observed at 2.35 ppm, and an absorption for the methylene proton was observed at 2.75 and 2.83 ppm. In contrast, the corresponding absorption appeared at 2.32, 2.59, and 2.95 ppm in the ^{1}H NMR spectrum of **4b**. In the ^{125}Te NMR spectrum, an absorption was observed at 498 ppm for **4a** and at 488 ppm for **4b**. Obviously, their spectroscopic characteristics indicate that the two telluronium salts are quite different from each other.

The structures of the salt **4a** and **4b** were finally determined by X-ray crystallographic analyses as shown in Figure 2. Telluronium salt **4a** has a pyramidal geometrical structure with an *S* absolute configuration at the telluronium center (Figure 2). The bond distances of Te−C [2.16(2) Å, 2.083(8) Å, 2.139(7) Å] are of normal values, and the average value of C−Te−C angles of 94.2-(7)° is comparable with that of the reported ethylmethylphenyltelluronium salts.[4a,b] The X-ray crystallographic analysis of telluronium salt **4b** (Figure 2) proved that **4b** is a diastereoisomer of **4a**. Thus, we have succeeded in the stereoselective synthesis of both diastereoisomers of ethyl(2-*exo*-hydroxy-10-bornyl)methyltelluronium salts. At the same time, we confirmed that both diastereomers of the telluronium salts are optically stable compounds and they do not isomerize during workup.

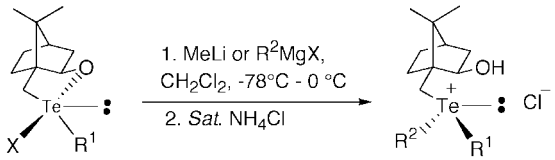
To study the generality of this reaction, we performed the reactions of various halooxatelluranes with alkyllithium and Grignard reagents as shown in Table 1. The two diastereomers of butyl(2-*exo*-hydroxy-10-bornyl)-



4a **4b**

Figure 2.

Table 1. Synthesis of Telluronium Salts 4a−i



3 **4**

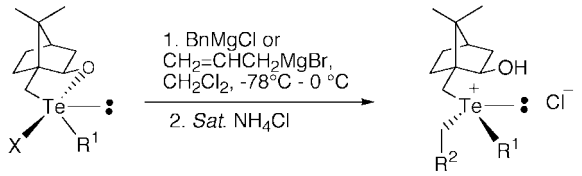
entry	telluranes	R^2Li or R^2MgX	tellurium salts	yield (%)
1	**3f**	EtMgBr	**4a**, R^1 = Me, R^2 = Et	87
2	**3b**	MeLi	**4b**, R^1 = Et, R^2 = Me	79
3	**3a**	*n*-BuMgCl	**4c**, R^1 = Me, R^2 = *n*-Bu	82
4	**3c**	MeLi	**4d**, R^1 = *n*-Bu, R^2 = Me	92
5	**3b**	*n*-BuMgCl	**4e**, R^1 = Et, R^2 = *n*-Bu	97
6	**3h**	EtMgBr	**4f**, R^1 = *n*-Bu, R^2 = Et	90
7	**3e**	MeLi	**4g**, R^1 = C_6H_5, R^2 = Me	79
8	**3i**	EtMgBr	**4h**, R^1 = C_6H_5, R^2 = Et	97
9	**3e**	*n*-BuMgCl	**4i**, R^1 = C_6H_5, R^2 = *n*-Bu	76

methyltelluronium chloride (**4c**, **d**) were also obtained by the reaction of butyltellurane with methyllithium or of methyltellurane with butylmagnesium chloride (Table 1, entries 3 and 4). The reactions of other halotelluranes also proceeded smoothly to afford chiral salts in high yield and with excellent diastereoselectivity. The reactivity of phenyltellurane was similar to that of alkyltelluranes, and reactions of phenyltellurane **3e** and **3i** with methyllithium or Grignard reagents gave phenyltelluronium salts **4g**−**i** in good yield and as sole products (Table 1, entries 7−9). The salts epimeric at tellurium atom were not detected in these reactions. Stereochemistry of these telluronium salts can be assigned as depicted in Scheme 2 by analogy with that of **4a** and **4b**.

The scope of the new method was extended to include the more synthetically attractive benzyl- and allyltelluronium salts. Nucleophilic reaction of a chiral chlorooxatellurane **3a** with 1.2 equiv of benzylmagnesium chloride in CH_2Cl_2 for ca. 2 h followed by usual workup gave chlorotelluronium salt **5a** (95% yield) as a single diastereomer.[7] The same reaction of benzylmagnesium

(7) The selectivity of the reaction of methyltellurane with benzylmagnesium chloride was found to be dependent on the amount of the Grignard reagent. When the methyltellurane was treated with 1.1 equiv of benzylmagnesium chloride, salt **5b** was obtained as the sole product, whereas an excess amount of the Grignard reagent gave the salt in low diastereoselectivity. This observation was reasonably explained in terms of the formation of the tetracoordinated tellurium complex under the basic conditions. Treatment of optically pure benzyltelluronium salt **5b** with excess benzylmagnesium chloride gave also isomerization at the tellurium atom to yield an approximately 1:1 mixture of diastereoisomers.

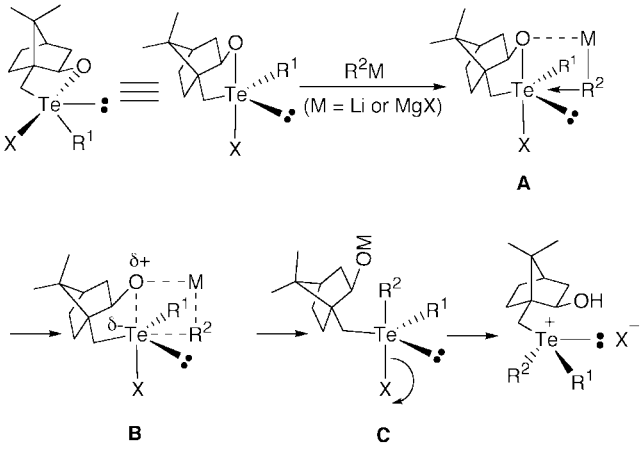
Table 2. Synthesis of Benzyl- and Allyltelluronium Salts 5a−h



3 **5**

entry	tellurane	telluronium salt	yield (%)
1	**3a**	**5a**, R^1 = Me, R^2 = Ph	95
2	**3b**	**5b**, R^1 = Et, R^2 = Ph	81
3	**3c**	**5c**, R^1 = *n*-Bu, R^2 = Ph	78
4	**3d**	**5d,** R^1 = *n*-C_6H_{13}, R^2 = Ph	67
5	**3e**	**5e**, R^1 = C_6H_5, R^2 = Ph	73
6	**3f**	**5f**, R = Me, R^2 = CH_2=CH	94
7	**3g**	**5g**, R = Et, R^2 = CH_2=CH	60
8	**3i**	**5h**, R = C_6H_5, R^2 = CH_2=CH	90

Scheme 3



chloride with telluranes **3b**−**e** was also performed and afforded telluronium salts **5b**−**e** as single diastereomers in good yield as shown in Table 2.[5] Reaction of bromotelluranes **3f**,**g**,**i** with allylmagnesium bromide gave allyl telluronium salts **5f**−**h** in moderate to good yields as single diastereomers after usual workup (Table 2).[5] These salts are precursors of the optically active telluronium ylides, which will be a useful building block in organic synthesis.

We found that the telluronium salts obtained in this study did not isomerize after the salts were allowed to stand at room temperature for several weeks. A solution ($CHCl_3$ or MeOH) of **4a** or **4b** was heated to reflux for 5 h to give only the starting materials recovered in almost quantitative yield. Thus, these trialkyltelluronium salts, as well as dialkylaryltelluronium salts,[4a,b] are highly stable toward pyramidal inversion.

Possible Mechanisms

Although the detailed stereochemical process of the reaction is not clear at the present time, the reaction may proceed through the pathway shown in Scheme 3. Initial chelation of Grignard reagents with the oxygen atom of the bornyl group induced the attack of the carbanion from the direction shown in Scheme 3. The coordinated metal induced the cleavage of the Te−O bond followed by the dissociation of the Te−Cl bond to afford telluronium salts with the observed configuration at the tellurium atom in high diastereoselectivity.[5,8,9]

Another possible pathway might involve an alkyloxotellurane, which is formed by the substitution of the halogen atom with the alkyl group, as an intermediate. However, it is difficult to explain the stereochemical results observed in the reaction, since it is likely that the pentacoordinated intermediate will be converted to a telluronium salt with different stereochemistry. Therefore, we consider the former pathway to be more reasonable. Further study is necessary to elucidate the mechanism of this reaction.[10]

Conclusion

In conclusion, we developed a facile method for the stereoselective synthesis of optically pure telluronium salts using the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand by the reaction of chiral alkoxytelluranes with alkyllithium or Grignard reagents. Optically pure benzyl- and allyltelluronium salts have also been synthesized. The optical stability of trialkyltelluronium salts was confirmed. We proposed a speculative mechanism of this reaction, which accounts for the observed stereochemistry.

Experimental Section

General Methods. Common experimental procedures and instrumentation have been described previously.[6c] Spectroscopic measurements were carried out with the following instruments: ^{125}Te NMR, Varian Unity 500 (157.9 MHz) for solutions in $CDCl_3$ with Ph_2Te_2 (0.5 M in CH_2Cl_2, 422 ppm) as an external standard. Coupling constants (*J*) are given in Hz. The ditelluride was synthesized according to the procedure reported in the literature.[11]

(1*S*)-10-Iodo-2-*exo*-borneol. To a solution of $NaBH_4$ (800 mg, 22.36 mmol) in EtOH (30 mL) was added a solution of (1*S*)-10-iodocamphor[12] (6.0 g, 22.86 mmol) in EtOH (60 mL) under N_2 atmosphere at 0 °C. The mixture was stirred at 0 °C to rt for 1 night. The reaction was quenched with saturated NH_4Cl (ca.10 mL) at rt followed by concentration of the solvent to one-fourth of its original volume. Then, the mixture was extracted with CH_2Cl_2 (100 mL × 2). The organic layer was washed with H_2O (15 mL × 2) followed by brine (15 mL × 1) and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the crude product, which was purified by column chromatography (hexane/EtOAc 19:1) to give the product (4.89 g, 76%) as a semisolid: $[\alpha]^{26}_D$ −31.22° (*c* 2.02, $CHCl_3$); IR (neat) 3478, 2953, 1306, 1188, 1070, 1019 cm^{-1}; ^{1}H NMR δ 0.87 (s, 3H), 1.06 (s, 3H), 1.22−1.49 (m, 2H), 1.50−1.86 (m, 4H), 2.00−2.09 (m, 2H), 3.18 (d, *J* = 9.3, 1H), 3.45 (d, *J* = 9.3, 1H), 3.78 (dd, *J* = 3.9, 7.7, 1H);^{13}C NMR δ 11.5, 20.4, 21.1, 26.7, 33.3, 39.5, 47.2, 47.8, 52.8, 78.4; MS *m*/*z* 280, 153; HRMS calcd for $C_{10}H_{17}IO$ 280.0326, found 280.0276.

(8) For nucleophilic reaction of halosulfuranes through a hexacoordinated transition state, see: (a) Balthazor, T. M.; Martin, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 5634−5635. (b) Martin, J. C.; Balthazor, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 152−162.

(9) We have suggested to use "retention" and "inversion" to describe the stereochemistry of the transformation of halooxachalcogenurane to chalcogenium compound; see ref 5.

(10) Andersen et al. have reported the synthesis of sulfonium salts by the reaction of Grignard reagents and alkylcadmium reagents with (alkyloxy)sulfonium salts derived by O-alkylation of sulfoxides. They have tried to prepare the optically active sulfonium salts via this reaction starting from chiral sulfoxides, but unfortunately, they have failed to get the sulfonium salts with high ee value, and the racemic sulfonium salts were often obtained because of the racemization of the products or because of other undentified reasons, according to the authors' explanation: see ref 2a,b.

(11) Ferreira, J. T. B.; de Oliveira, A. R. M.; Comasseto, J. V. *Synth. Commun.* **1989**, 239−244.

(12) Oae, S.; Togo, H. *Synthesis* **1981**, 371−373.

(1*S*)-10-(Methyltellurenyl)-2-*exo*-borneol (2a). To a solution of dimethyl ditelluride (400 mg, 1.40 mmol) and (1*S*)-10-iodo-2-*exo*-borneol (775 mg, 2.77 mmol) in absolute EtOH (15 mL) was added $NaBH_4$ (140 mg, 3.68 mmol) under N_2 atmosphere at −10 °C, and the mixture was stirred until the red color of the ditelluride disappeared (ca. 10 min). Then the whole solution was heated under reflux for 20 min. The reaction was quenched with H_2O (8 mL) at rt and the mixture was extracted with CH_2Cl_2 (40 mL × 2). The organic layer was washed with H_2O (6 mL × 2) followed by brine (6 mL × 1) and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the crude product, which was purified by column chromatography (hexane/EtOAc 40:1) to give **2a** (570 mg, 70%) as a red oil: $[\alpha]^{26}_D$ −30.26° (*c* 1.70, $CHCl_3$); IR (neat) 3467, 2949, 1454, 1386, 1070, 1018, 865 cm^{-1}; ^1H NMR δ 0.78 (s, 3H), 0.98 (s, 3H), 1.0−1.15 (m, 2H), 1.42−1.6 (m, 1H), 1.6−1.9 (m, 5H), 1.86 (s, 3H), 2.71 (d, J = 11.0, 1H), 2.75 (d, J = 10.5, 1H), 3.72 (dd, J = 3.9, 7.7, 1H); ^{13}C NMR δ −21.8, 4.9, 20.1, 20.8, 27.1, 33.5, 39.6, 45.6, 47.5, 53.2, 78.7; ^{125}Te NMR δ 628; MS *m*/*z* 298 (M^+, ^{130}Te), 296 (M^+,^{128}Te), 294 (M^+, ^{126}Te), 135, 109, 93, 81, 67, 55; HRMS calcd for $C_{11}H_{20}OTe$ 298.0582 (M^+, ^{130}Te), 296.0569 (M^+, ^{128}Te), found 298.0505, 296.0471.

(1*S*)-10-(Ethyltellurenyl)-2-*exo*-borneol (2b). To a solution of diethyl ditelluride (1.0 g, 3.18 mmol) and (1*S*)-10-iodo-2-*exo*-borneol (1.8 mg, 6.38 mmol) in absolute EtOH (15 mL) was added $NaBH_4$ (480 mg, 12.63 mmol) under N_2 atmosphere at 0 °C, and the mixture was stirred until the red color of the ditelluride disappeared (ca. 10 min). Then the solution was heated under reflux for 20 min. The reaction was quenched with H_2O (10 mL) at rt, and the mixture was extracted with CH_2Cl_2 (75 mL × 2). The organic layer was washed with H_2O (10 mL × 2) followed by brine (10 mL × 1) and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the crude product, which was purified by column chromatography (hexane/EtOAc 40:1) to give **2b** (1.33 g, 67%) as a red oil: $[\alpha]^{26}_D$ −33.95° (*c* 2.00, $CHCl_3$); IR (neat) 3390, 2950, 1368, 1071, 1019, 866 cm^{-1}; ^1H NMR δ 0.85 (s, 3H), 1.06 (s, 3H), 1.0−1.2 (m, 2H), 1.61 (t, J = 7.7, 3H), 1.40−1.85 (m, 5H), 2.66 (q, J = 7.7, 2H), 2.22−2.70 (br, 1H), 2.78 (d, J = 10.4, 1H), 2.84 (d, J = 10.4, 1H), 3.77 (dd, J = 3.8, 7.7, 1H); ^{13}C NMR δ −4.7, 3.5, 18.0, 20.2, 20.9, 26.9, 27.2, 33.7, 39.6, 45.7, 53.0, 78.7; ^{125}Te NMR δ 812; MS *m*/*z* 312 (M^+, ^{130}Te), 310 (M^+, ^{128}Te), 308 (M^+, ^{126}Te), 135, 107, 93, 67, 55; HRMS calcd for $C_{12}H_{22}OTe$ 312.0740 (M^+, ^{130}Te), found 312.0748.

(1*S*)-10-(Butyltellurenyl)-2-*exo*-borneol (2c). The procedure described in the preparation of **2b** was generally followed to prepare **2c** from (1*S*)-10-iodo-2-*exo*-borneol and ditelluride. **2c**: yield 40%; red oil; $[\alpha]^{26}_D$ −28.00° (*c* 2.05, $CHCl_3$); IR (neat) 3468, 2952, 1454, 1386, 1071, 1018, 864 cm^{-1}; ^1H NMR δ 0.83 (s, 3H), 0.91 (t, J = 7.1, 3H), 1.04 (s, 3H), 1.0−1.1 (m, 2H), 1.30−1.58 (m, 3H), 1.61−1.93 (m, 6H), 2.21−2.31 (br, 1H), 2.65 (t, J = 7.1, 2H), 2.75 (d, J = 10.4, 1H), 2.79 (d, J = 10.4, 1H), 3.76 (dd, J = 3.3, 7.7, 1H); ^{13}C NMR δ 3.5, 3.8, 13.7, 20.2, 20.9, 25.4, 27.2, 33.6, 34.6, 39.6, 45.7, 47.6, 53.1, 78.7; MS *m*/*z* 340 (M^+, ^{130}Te), 338 (M^+,^{128}Te), 336 (M^+, ^{126}Te), 135, 107, 93, 67, 55; HRMS calcd for $C_{14}H_{26}OTe$ 340.1035 (M^+, ^{130}Te), found 340.1035.

(1*S*)-10-(Hexyltellurenyl)-2-*exo*-borneol (2d). To a solution of dihexyl ditelluride (245 mg, 0.57 mmol) and (1*S*)-10-iodo-2-*exo*-borneol (324 mg, 1.15 mmol) in absolute EtOH (5 mL) was added $NaBH_4$ (76 mg, 2 mmol) under N_2 atmosphere at 0 °C. The mixture was stirred until the red color of the ditelluride disappeared (ca. 10 min), and the solution was heated under reflux for 20 min. The reaction was quenched with H_2O (2 mL) at rt, and the mixture was extracted with CH_2Cl_2 (30 mL × 2). The organic layer was washed with H_2O (6 mL × 2) followed by brine (6 mL × 1) and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the crude product, which was purified by column chromatography (hexane/EtOAc 9:1) to give **2d** (375 mg, 90%) as a red oil: $[\alpha]^{25}_D$ −22.48° (*c* 1.11, $CHCl_3$); IR (neat) 3467, 2926, 1454, 1070, 1040, 1018, 864 cm^{-1}; ^1H NMR δ 0.84 (s, 3H), 0.8−1.0 (m, 3H), 1.05 (s, 3H), 1.0−1.15 (m, 2H), 1.23−1.38 (m, 6H), 1.45−1.84 (m, 8H), 2.65 (t, J = 7.7, 2H), 2.75 (d, J = 10.5, 1H), 2.81 (d, J = 10.5, 1H), 3.76 (dd, J = 3.9, 7.7, 1H); ^{13}C NMR δ 3.7, 3.8, 14.3, 20.1, 20.8, 22.8, 27.1, 31.3, 31.9, 32.4, 33.6, 39.5, 45.6, 47.5, 53.0, 78.7; MS *m*/*z* 368 (M^+, ^{130}Te), 366 (M^+,^{128}Te), 364 (M^+, ^{126}Te), 214, 212, 135, 109, 93, 79, 67, 55; HRMS calcd for $C_{16}H_{30}OTe$ 368.1364 (M^+, ^{130}Te), 366.1351(M^+, ^{128}Te), found 368.1292, 366.1288.

General Procedure for the Synthesis of Halooxatelluranes 3a−i. To a solution of tellurides (1 mmol) in dry CH_2Cl_2 (8 mL) was added *t*-BuOCl (0.13 mL, 1.05 mmol) under a N_2 atmosphere at 0 °C, and the mixture was stirred at 0 °C for 20 min. Removal of the solvent under reduced pressure gave the crude product as a white solid. Purification of the residue by recrystallization from hexane and CH_2Cl_2 afforded chlorooxatelluranes **3a**−**e** as colorless crystals. Bromooxatelluranes **3f**−**i** were obtained by treatment of the corresponding chlorooxatelluranes with NaBr (3 equiv) in CH_3CN at rt overnight.

[2*R*-(2α,3aα,6α,7a*β*)]-2-Chloro-2,2,5,6,7,7a-hexahydro-8,8-dimethyl-2-methyl-4*H*-3a,6-methano-3*H*-1,2-benzoxatellurole (3a): $[\alpha]^{26}_D$ +85.22° (*c* 1.00, $CHCl_3$); IR (KBr) 2942, 1455, 1386, 1047, 989, 868 cm^{-1}; ^1H NMR δ 0.91 (s, 3H), 1.04 (s, 3H), 1.2−1.27 (m, 2H), 1.55−2.0 (m, 5H), 2.75 (s, 3H), 3.4 (d, J = 13.2, 1H), 3.59 (d, J = 13.2, 1H),4.19 (dd, J = 3.3, 7.1, 1H); ^{13}C NMR δ 20.4, 20.5, 22.2, 26.9, 31.7, 40,8, 41.9, 45.6, 46.6, 55.6, 93.7; MS *m*/*z* 334 (M^+, ^{130}Te, ^{37}Cl), 332 (M^+, ^{130}Te, ^{35}Cl/^{128}Te, ^{37}Cl), 330 (M^+, ^{128}Te, ^{35}Cl/^{126}Te, ^{37}Cl), 328 (M^+, ^{126}Te, ^{35}Cl), 297, 295, 293, 180, 178, 176, 107, 93, 81, 67, 55. Anal. Calcd for $C_{11}H_{19}ClOTe$: C, 40.00; H, 5.80. Found: C, 40.05; H, 5.69.

[2*R*-(2α,3aα,6α,7a*β*)]-2-Chloro-2,2,5,6,7,7a-hexahydro-8,8-dimethyl-2-ethyl-4*H*-3a,6-methano-3*H*-1,2-benzoxatellurole (3b): mp 130−132 °C (colorless prisms); $[\alpha]^{26}_D$ +93.1 ° (*c* 1.36, $CHCl_3$); IR (KBr) 3008, 2954, 2881, 1456, 1388, 1114, 1068, 1048, 1014 cm^{-1}; ^1H NMR δ 0.92 (s, 3H), 1.06 (s, 3H), 1.19 (dd, J = 9.9, 18.7, 2H), 1.63−1.95 (m, 5H), 1.71 (t, J = 7.7, 3H), 3.13−3.30 (m, 2H), 3.35 (d, J = 13.5, 1H), 3.50 (d, J = 13.5, 1H), 4.15 (dd, J = 3.3, 7.7, 1H); ^{13}C NMR δ 10.9, 20.5, 20.7, 26.8, 31.4, 35.0, 41.9, 44.0, 45.6, 46.7, 55.4, 93.9; ^{125}Te NMR δ 1852; MS *m*/*z* 348 (M^+, ^{130}Te, ^{37}Cl), 346 (M^+, ^{130}Te, ^{35}Cl/^{128}Te, ^{37}Cl), 344 (M^+, ^{128}Te, ^{35}Cl/^{126}Te, ^{37}Cl), 342 (M^+, ^{126}Te, ^{35}Cl). Anal. Calcd for $C_{12}H_{21}ClOTe$: C, 41.86; H, 6.15. Found: C, 41.71; H, 6.15.

[2*R*-(2α,3aα,6α,7a*β*)]-2-Chloro-2,2,5,6,7,7a-hexahydro-8,8-dimethyl-2-butyl-4*H*-3a,6-methano-3*H*-1,2-benzoxatellurole (3c): mp 164−165 °C; $[\alpha]^{26}_D$ +88.12° (*c* 1.22, $CHCl_3$); IR (neat) 2959, 1452, 1388, 1354, 1048, 584 cm^{-1}; ^1H NMR δ 0.91 (s, 3H), 0.99 (t, J = 7.1, 3H), 1.05 (s, 3H), 1.11−1.3 (m, 2H), 1.42−1.61 (m, 3H), 1.68−1.80 (m, 1H), 1.8−2.11 (m, 3H), 3.22 (t, J = 7.1, 2H), 3.35 (d, J = 13.2, 1H), 3.50 (d, J = 13.2, 1H), 4.13 (dd, J = 3.3, 7.7, 1H); ^{13}C NMR δ 13.8, 20.5, 20.7, 24.7, 27.0, 28.0, 31.7, 39.2, 42.2, 45.8, 46.8, 55.6, 93.9 (a signal will be overlapped with the signal of $CDCl_3$); ^{125}Te NMR δ 1838; MS *m*/*z* 376 (M^+, ^{130}Te, ^{37}Cl), 374 (M^+, ^{130}Te, ^{35}Cl/^{128}Te, ^{37}Cl), 372 (M^+, ^{128}Te, ^{35}Cl/^{126}Te, ^{37}Cl), 370 (M^+, ^{126}Te, ^{35}Cl) 339, 337, 335, 222, 220, 218, 135, 107, 9. Anal. Calcd for $C_{14}H_{25}ClOTe$: C, 45.15; H, 6.77. Found: C, 44.64; H, 6.46.

[2*R*-(2α,3aα,6α,7a*β*)]-2-Chloro-2,2,5,6,7,7a-hexahydro-8,8-dimethyl-2-hexyl-4*H*-3a,6-methano-3*H*-1,2-benzoxatellurole (3d): $[\alpha]^{26}_D$ +44.59° (*c* 1.00, $CHCl_3$); IR (neat) 2954, 1456, 1388, 1046, 987, 870 cm^{-1}; ^1H NMR δ 0.88 (s, 3H), 0.84−1.0 (m, 3H), 1.04 (s, 3H), 1.13−1.5 (m, 8H), 1.68−2.02 (m, 7H), 3.21 (t, J = 8.2, 2H), 3.34 (d, J = 13.2, 1H), 3.49 (d, J = 13.2, 1H), 4.12 (dd, J = 3.9, 8.8, 1H); ^{13}C NMR δ 20.4, 20.5, 22.6, 25.8, 26.9, 31.0, 31.3, 31.6, 39.1, 42.0, 42.4, 45.6, 46.7, 55.5, 93.3 (a signal will be overlapped with the signal of $CDCl_3$); MS *m*/*z* 404 (M^+, ^{130}Te, ^{37}Cl), 402 (M^+, ^{130}Te, ^{35}Cl/^{128}Te, ^{37}Cl), 400 (^{128}Te, ^{35}Cl/^{126}Te, ^{37}Cl), 398 (^{126}Te, ^{35}Cl) 367, 365, 363, 250, 248, 246, 135, 107, 85, 55; HRMS calcd for $C_{16}H_{29}ClOTe$ (^{130}Te, ^{37}Cl), (^{130}Te, ^{37}Cl), (^{130}Te, ^{37}Cl), found 404.0965, 402.1005, 402.0941, 400.0923.

[2*R*-(2α,3aα,6α,7a*β*)]-2-Chloro-2,2,5,6,7,7a-hexahydro-8,8-dimethyl-2-pheyl-4*H*-3a,6-methano-3*H*-1,2-benzoxatellurole (3e): mp 154−156 °C (colorless prisms); $[\alpha]^{26}_D$ +92.3° (*c* 0.993, $CHCl_3$); IR (KBr) 3048, 2984, 2947, 2871, 1481, 1453, 1436, 1017, 990, 734, 687 cm^{-1}; ^1H NMR δ 0.91 (s, 3H), 0.85−1.20 (m, 2H), 1.14 (s, 3H), 1.60−2.00 (m, 5H), 3.42 and 3.62

(ABq, J = 13.4, 2H), 3.81 (dd, J = 3.3, 1H), 7.50−7.60 (m, 3H), 8.10−8.20 (m, 2H); ^{13}C NMR δ: 20.5, 20.7, 26.8, 31.4, 41.9, 44.0, 45.6, 46.7, 55.4, 93.2, 130.2, 130.9, 131.4, 132.1; MS *m*/*z* 395 ($M^+ - 1$) (^{130}Te, ^{37}Cl), 394 (M^+) (^{130}Te, ^{35}Cl), 393 ($M^+ - 1$) (^{130}Te, ^{35}Cl/^{128}Te, ^{37}Cl), 392 (M^+) (^{128}Te, ^{35}Cl/^{126}Te, ^{37}Cl), 391 ($M^+ - 1$) (^{128}Te, ^{35}Cl/^{126}Te, ^{37}Cl), 390 (M^+) (^{126}Te, ^{35}Cl), 389 ($M^+ - 1$) (^{126}Te, ^{35}Cl). Anal. Calcd for $C_{16}H_{21}OClTe$: C, 48.97; H, 5.39. Found: C, 48.97; H, 5.36.

[2*R*-(2α,3aα,6α,7a*β*)]-2-Bromo-2,2,5,6,7,7a-hexahydro-8,8-dimethyl-2-methyl-4*H*-3a,6-methano-3*H*-1,2-benzoxatellurole (3f): mp 156−157 °C; $[\alpha]^{26}_D$ +106.36° (*c* 1.00, $CHCl_3$); IR (KBr) 2953, 1454, 1389, 1042, 868 cm^{-1}; ^{1}H NMR δ 0.89 (s, 3H), 1.03 (s, 3H), 1.16−1.27 (m, 2H), 1.59−2.0 (m, 5H), 2.86 (s, 3H), 3.52 (d, J = 14.0, 1H), 3.69 (d, J = 14.0, 1H), 4.22 (dd, J = 3.3, 7.2, 1H); ^{13}C NMR δ 20.5, 20.6, 21.8, 26.9, 31.7, 41,8, 42.2, 45.7, 46.7, 55.7, 94.3; MS *m*/*z* 378 (M^+, ^{130}Te, ^{81}Br), 376 (M^+, ^{130}Te, ^{79}Br/^{128}Te, ^{81}Br), 374 (M^+, ^{128}Te, ^{79}Br/^{126}Te, ^{81}Br), 372 (M^+, ^{126}Te, ^{79}Br), 297, 295, 293, 226, 224, 222, 107, 93, 81, 67, 55; HRMS calcd for $C_{11}H_{19}BrOTe$ 375.9688 (^{130}Te, ^{79}Br), 375.9654 (^{128}Te, ^{81}Br), found 375.9704, 375.9628.

[2*R*-(2α,3aα,6α,7a*β*)]-2-Bromo-2,2,5,6,7,7a-hexahydro-8,8-dimethyl-2-ethyl-4*H*-3a,6-methano-3*H*-1,2-benzoxatellurole (3g): mp 114−116 °C; $[\alpha]^{26}_D$ +93.68° (*c* 0.62, $CHCl_3$); IR (KBr) 2956, 1455, 1048, 869 cm^{-1}; ^{1}H NMR δ 0.91 (s, 3H), 1.06 (s, 3H), 1.17−1.23 (m, 2H), 1.59−1.98 (m, 5H), 1.71 (t, J = 7.7, 3H), 3.2−3.38 (m, 2H), 3.42 (d, J = 13.7, 1H), 3.56 (d, J = 13.7, 1H), 4.17 (dd, J = 3.3, 7.2, 1H); ^{13}C NMR δ 11.4, 20.6, 20.7, 27.0, 31.6, 35.0, 39.5, 42.3, 45.7, 46.8, 55.6, 94.4; ^{125}Te NMR δ 1865; MS *m*/*z* 392 (M^+, ^{130}Te, ^{81}Br), 390 (M^+, ^{130}Te, ^{79}Br/^{128}Te, ^{81}Br), 388 (M^+, ^{128}Te, ^{79}Br/^{126}Te, ^{81}Br), 386 (M^+, ^{126}Te, ^{79}Br), 346, 344, 342, 311, 309, 307, 238, 236, 234, 194, 192, 190, 107, 93, 81, 67, 55; HRMS calcd for $C_{12}H_{21}BrOTe$ 389.9844 (^{130}Te, ^{79}Br), 389.9811 (^{128}Te, ^{81}Br), found 389.9799.

[2*R*-(2α,3aα,6α,7a*β*)]-2-Bromo-2,2,5,6,7,7a-hexahydro-8,8-dimethyl-2-butyl-4*H*-3a,6-methano-3*H*-1,2-benzoxatellurole (3h): mp 172−173.5 °C; $[\alpha]^{26}_D$ +106.96° (*c* 1.06, $CHCl_3$); IR (KBr) 2957.8, 1354.1, 1047.4 cm^{-1}; ^{1}H NMR δ 0.88 (s, 3H), 0.97 (t, J = 7.1, 3H), 1.04 (s, 3H), 1.11−1.25 (m, 2H), 1.42−1.59 (m, 2H), 1.63−2.05 (m, 7H), 3.2−3.4 (m, 2H), 3.48 (d, J = 13.2, 1H), 3.59 (d, J = 13.2, 1H), 4.17 (dd, J = 3.3, 7.2, 1H); ^{13}C NMR δ 13.8, 20.4, 20.6, 24.6, 26.9, 28.2, 31.5, 39.9, 41.5, 42.3, 45.6, 46.7, 55.6, 94.5; ^{125}Te NMR δ 1851; MS *m*/*z* 420 (M^+, ^{130}Te, ^{81}Br), 418 (M^+, ^{130}Te, ^{79}Br/^{128}Te, ^{81}Br), 416 (M^+, ^{128}Te, ^{79}Br/^{126}Te, ^{81}Br), 414 (M^+, ^{126}Te, ^{79}Br), 339, 337, 335, 266, 264, 262, 222, 220, 218, 135, 107, 93.

[2*R*-(2α,3aα,6α,7a*β*)]-2-Bromo-2,2,5,6,7,7a-hexahydro-8,8-dimethyl-2-phenyl-4*H*-3a,6-methano-3*H*-1,2-benzoxatellurole (3i): mp 143−144 °C (colorless prisms, recrystallized from hexane−AcOEt); $[\alpha]^{25}_D$ +143.5° (*c* 1.00, $CHCl_3$); IR (KBr) 3047, 2939, 2868, 1435, 1045, 733 cm^{-1}; ^{1}H NMR δ 0.89 (s, 3H), 0.80−1.20 (m, 2H), 1.13 (s, 3H), 1.60−1.95 (m, 5H), 3.58 and 3.74 (ABq, J = 13.2, 2H), 3.80−3.85 (m, 1H), 7.50−7.60 (m, 3H), 8.10−8.20 (m, 2H); ^{13}C NMR δ 20.4, 20.6, 26.7, 31.4, 42.1, 44.9, 45.5, 46.7, 55.5, 93.8, 129.4, 130.2, 131.4 132.5; MS *m*/*z* 441 ($M^+ + 1$) (^{130}Te, ^{81}Br), 440 (M^+) (^{130}Te, ^{81}Br), 439 ($M^+ + 1$) (^{130}Te, ^{79}Br/^{128}Te, ^{81}Br)/($M^+ - 1$) (^{130}Te, ^{81}Br), 438 (M^+) (^{130}Te, ^{79}Br/^{128}Te, ^{81}Br), 437 ($M^+ + 1$) (^{128}Te, ^{79}Br/^{126}Te, ^{81}Br)/($M^+ - 1$) (^{130}Te, ^{79}Br/^{130}Te, ^{81}Br), 436 (M^+) (^{128}Te, ^{79}Br/^{126}Te, ^{81}Br), 435 ($M^+ + 1$) (^{126}Te, ^{79}Br)/($M^+ - 1$) (^{128}Te, ^{79}Br/^{126}Te, ^{81}Br), 434 (M^+) (^{126}Te, ^{79}Br), 433 (M^+ - 1) (^{126}Te, ^{79}Br). Anal. Calcd for $C_{16}H_{21}OBrTe$: C, 43.99; H, 4.85. Found: C, 44.04; H, 4.79.

General Procedure for Synthesis of Telluronium Salts 4a−i and 5a−h. To a solution of tellurane (0.2 mmol) in CH_2Cl_2 (6 mL) was added RLi (or RMgX) (0.24 mmol, 1.2 equiv) dropwise at −78 °C under N_2. The reaction mixture was stirred and allowed to warm to 0 °C during ca. 1 h. Then the mixture was stirred at 0 °C for another 1 h. The reaction was quenched with saturated aqueous NH_4Cl solution (4 mL), followed by extraction with CH_2Cl_2 (35 mL × 2). The combined organic layers were washed with H_2O (5 mL × 2) and brine (5 mL × 1), dried over $MgSO_4$, and then concentrated to dryness. Purification of the residue by recrystallization from hexane and CH_2Cl_2 afforded colorless crystalline products.

(S_{Te})-(−)-Ethyl[[(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl]methyl]methyltelluronium chloride (4a): mp 135−136 °C; $[\alpha]^{26}_D$ −34.75° (*c* 1.467, $CHCl_3$); IR (KBr) 3312, 3257, 1475, 1388, 1220, 1078, 868 cm^{-1}; ^{1}H NMR δ 0.86 (s, 3H), 1.11 (s, 3H), 1.0−1.24 (m, 2H), 1.55 (t, J = 7.69, 3H), 1.61−2.1 (m, 5H), 2.35 (s, 3H), 2.75 (d, J = 12.09, 1H), 2.83 (d, J = 12.09, 1H), 2.97−3.02 (m, 2H), 3.91 (m, 1H), 5.92 (br, 1H); ^{13}C NMR δ 8.1, 10.2, 20.8, 21.0, 21.4, 25.1, 27.5, 34.5, 40.8, 45.6, 48.4, 51.0, 77.1; ^{125}Te NMR δ 498; MS *m*/*z* 312, 310, 308, 298, 296, 294, 174, 172, 170, 135, 108, 93, 79, 67, 55. Anal. Calcd for $C_{13}H_{25}ClOTe$: C, 43.33; H, 6.99. Found: C, 43.37; H, 7.03.

Crystallographic data for **4a**: orthorhombic, space group, $P2_12_12_1$ (#19) with a = 7.76(8) Å, b = 25.8(1) Å, c = 7.60(7) Å, V = 1522(18) Å^3, and Z = 4 (d_{calcd} = 1.572 g cm^{-3}), μ (MoKα) = 21.11 cm^{-1} absorption corrected by ω scans; 2083 unique reflections; 1621 with $I > 3.00\sigma(I)$ were used in refinement; R = 2.8%, R_w = 2.9%. Selected bond lengths (Å) and angles (deg) are as follows: Te−C(1), 2.16(2); Te−C(2), 2.083(8); Te−C(3), 2.139(7); C(1)−Te−C(2), 92.9(6); C(1)−Te-C(3), 96.4(3); C(2)−Te−C(3), 93.4(3). Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, on quoting the full journal citation.

(R_{Te})-(−)-Ethyl[[(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl]methyl]methyltelluronium chloride (4b): mp 159−160 °C; $[\alpha]^{26}_D$ −29.72° (*c* 1.133, $CHCl_3$); IR (KBr) 3213, 2953, 1456, 1252, 1207, 1069 cm^{-1}; ^{1}H NMR δ 0.84 (s, 3H), 1.0−1.2 (m, 2H), 1.10 (s, 3H), 1.55 (t, J = 7.69, 3H), 1.59−2.1 (m, 5H), 2.32 (s, 3H), 2.59 (d, J = 11.54, 1H), 2.95 (d, J = 12.09, 1H), 3.13 (q, 7.69, 2H), 3.90 (dd, J = 3.3, 7.14, 1H), 5.83 (d, J = 3.85, 1H); ^{13}C NMR δ 8.0, 10.1, 20.8, 20.9, 22.7, 26.3, 27.5, 34.3, 40.6, 45.5, 48.5, 51.1 (a signal will be overlapped with the signal of $CDCl_3$); ^{125}Te NMR δ 488; MS *m*/*z* 312, 310, 308, 298, 296, 294, 174, 172, 170, 135, 108, 93, 81, 67, 55. Anal. Calcd for $C_{13}H_{25}ClOTe$: C, 43.33; H, 6.99. Found: C, 43.24; H, 7.00.

Crystallographic data for **4b**: orthorhombic, space group, $P2_12_12_1$ (#19) with a = 9.655(3) Å, b = 24.241(5) Å, c = 6.719-(4) Å, V = 1572(1) Å^3, and Z = 4 (d_{calcd} = 1.522 g cm^{-3}), μ (MoKα) = 20.44 cm^{-1} absorption corrected by ω scans; 2122 unique reflections; 1352 with $I > 3.00\sigma(I)$ were used in refinement; R = 3.3%, R_w = 3.4%. Selected bond lengths (Å) and angles (deg) are as follows: Te−C(1), 2.153(1); Te−C(2), 2.14(1); Te−C(3), 2.093(8); C(1)−Te−C(2), 92.1(4); C(1)−Te−C(3), 96.5(4); C(2)−Te−C(3), 94.4(4). Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, on quoting the full journal citation.

(S_{Te})-(−)-Butyl[[(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl]methyl]methyltelluronium chloride (4c): mp 146−148 °C; $[\alpha]^{26}_D$ −37.24° (*c* 2.53, $CHCl_3$); IR (KBr) 3328, 2955, 1456, 1073, 868 cm^{-1}; ^{1}H NMR δ 0.85 (s, 3H), 0.95 (t, J = 7.14, 3H), 1.09 (s, 3H), 1.0−1.22 (m, 2H), 1.42−1.60 (m, 3H), 1.68−1.84 (m, 6H), 2.0−2.2 (m, 1H),2.41 (s, 3H), 2.75 (d, J = 12.09, 1H), 2.90 (d, J = 12.64, 1H), 2.91−3.31 (m 1H), 3.90 (dd, J = 3.3, 7.7, 1H), 5.80−5.85 (br, 1H); ^{13}C NMR δ 9.0, 13.8, 20.8, 20.8, 24.8, 26.2, 27.2, 27.5, 27.6, 34.4, 40.7, 45.5, 48.4, 51.1, 77.0; ^{125}Te NMR δ 481; MS *m*/*z* 340, 338, 336, 298, 296, 294, 202, 200, 198, 135, 108, 93, 79, 57. Anal. Calcd for $C_{15}H_{29}ClOTe$: C, 46.39; H, 7.53. Found: C, 46.09; H, 7.47.

(R_{Te})-(−)-Butyl[[(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl]methyl]methyltelluronium chloride (4d): mp 165−166 °C; $[\alpha]^{26}_D$ −25.69° (*c* 1.80, $CHCl_3$); IR (KBr) 3212, 2953, 1454, 1209, 1069 cm^{-1}; ^{1}H NMR δ 0.87 (s, 3H), 0.98 (s, 3H), 1.0−1.2 (m, 2H), 1.14 (s, 3H), 1.4−1.6 (m, 3H), 1.42−1.92 (m, 6H), 1.62−1.92 (m, 6H), 2.38 (s, 3H), 2.69 (d, J = 12.09, 1H), 2.98 (d, J = 12.09, 1H), 2.97−3.12 (m, 2H), 3.94 (dd, J = 3.85, 7.7, 1H), 6.0 (d, J = 3.85, 1H); ^{13}C NMR δ 9.00, 13.84, 20.8, 21.1, 24.9, 27.1, 27.5, 27.6, 28.8, 34.5, 40.7, 45.6, 48.4, 51.1, 76.8; ^{125}Te NMR δ 477; MS *m*/*z* 338, 336, 334, 298, 296, 294, 202, 200, 198, 146, 144, 142, 108, 93, 79, 57.

Anal. Calcd for $C_{15}H_{29}ClOTe$: C, 46.38; H, 7.53. Found: C, 46.65; H, 7.53.

(S_{Te})-(−)-Butylethyl[[(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]-heptan-1-yl]methyl]telluronium chloride (4e): oil; $[\alpha]^{26}_D$ −23.05° (*c* 1.14, $CHCl_3$); IR (KBr) 3269, 2956, 1456, 1075, 730 cm^{-1}; ^1H NMR δ 0.88 (s, 3H), 0.98 (t, J = 7.14, 3H), 1.12 (s, 3H), 0.8−1.24 (m, 2H), 1.44−1.55 (m, 3H), 1.60 (t, J = 7.69, 3H), 1.71−1.88 (m, 6H), 2.2−2.4 (m, 1H),2.63 (d, J = 11.54, 1H), 2.8−3.21 (m, 5H), 3.93 (dd, J = 3.3, 7.1, 1H); ^{13}C NMR δ 10.7, 13.8, 20.7, 20.8, 22.4, 24.9, 25.0, 26.1, 27.4, 28.1, 28.3, 34.4, 40.8, 45.5, 48.5, 50.9 (a signal will be overlapped with the signal of $CDCl_3$); MS *m*/*z* 340, 338, 336, 298, 296, 294, 202, 200, 198, 135, 108, 93, 79, 57.

(R_{Te})-(−)-Butylethyl[[(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]-heptan-1-yl]methyl]telluronium chloride (4f): mp 99−101.5 °C; $[\alpha]^{26}_D$ −45.30° (*c* 2.10, $CHCl_3$); IR (KBr) 3328, 2954, 1454, 1074, 868 cm^{-1}; ^1H NMR δ 0.86 (s, 3H), 0.95 (t, J = 7.14, 3H), 1.12 (s, 3H), 1.0−1.23 (m, 2H), 1.40−1.50 (m, 2H), 1.57 (t, J = 7.69, 3H), 1.62−2.03 (m, 7H), 2.69 (d, J = 12.09, 1H), 2.77 (d, J = 12.64, 1H), 2.75−2.83 (m 1H), 2.96−3.20 (m, 3H), 3.91 (m, 1H), 6.1−6.2 (br, 1H); ^{13}C NMR δ 10.7, 10.8, 13.8, 20.8, 21.3, 23.8, 25.0, 27.1, 27.4, 28.0, 34.8, 40.9, 45.7, 48.3, 50.6, 76.9; ^{125}Te NMR δ 549; MS *m*/*z* 340, 338, 336, 312, 310, 308, 216, 214, 212, 160, 158, 156, 135, 108, 93, 79, 57.

(S_{Te})-(+)-[[(1*S*,2*R*,4*R*)-2-Hydroxy-7,7-dimethylbicyclo-[2.2.1]heptan-1-yl]methyl]methylphenyltelluronium chloride (4g): mp 138−139 °C; $[\alpha]^{26}_D$ +9.76° (*c* 1.00, $CHCl_3$); IR (KBr) 3424, 2950, 1456, 1071, 735 cm^{-1}; ^1H NMR δ 0.76 (s, 3H), 0.95−1.20 (m, 2H), 1.07 (s, 3H), 1.2−1.4 (m, 1H), 1.58−1.97 (m, 5H), 2.83 (s, 3H), 2.94 (d, J = 12.6, 1H), 3.30 (d, J = 12.6, 1H), 4.07 (dd, J = 3.3, 7.7, 1H), 7.4−7.6 (m, 3H), 7.70−7.85 (m, 2H); ^{13}C NMR δ 15.8, 20.6, 21.5, 27.5, 33.1, 35.3, 40.7, 44.5, 45.9, 47.9, 51.1, 130.2, 130.3, 131.5, 131.7; ^{125}Te NMR δ 564; MS *m*/*z* 360, 358, 356, 222, 220, 218, 207, 205, 203, 135, 93, 77. Anal. Calcd for $C_{17}H_{25}ClOTe$: C, 49.99; H, 6.17. Found: C, 50.21; H, 5.92.

(S_{Te})-(−)-Ethyl[[(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl]methyl]phenyltelluronium chloride (4h): mp 117−119 °C; $[\alpha]^{26}_D$ −0.045° (*c* 1.16, $CHCl_3$); IR (KBr) 3187, 2956, 1438, 1068, 742 cm^{-1}; ^1H NMR δ 0.74 (s, 3H), 0.9−1.15 (m, 1H), 1.05 (s, 3H), 1.27−1.34 (m, 1H), 1.44 (t, J = 7.7, 3H), 1.66−1.86 (m, 6H), 2.95 (d, J = 12.09, 1H), 3.35−3.41 (m, 2H), 3.56−3.60 (m, 1H), 4.05 (dd, J = 3.3, 7.1, 1H), 7.47−7.55 (m, 3H), 7.78−7.80 (m, 2H); ^{13}C NMR δ 11.1, 20.6, 21.6, 27.4, 28.3, 29.2, 35.3, 40.8, 45.9, 47.9, 50.7, 77.4, 123.6, 130.2, 131.5, 134.0; MS *m*/*z* 360, 358, 356, 284, 282, 280, 236, 234, 232, 208, 206, 204, 135, 109, 93, 77. Anal. Calcd for $C_{18}H_{27}ClOTe$: C, 51.18; H, 6.44. Found: C, 51.01; H, 6.40.

(S_{Te})-(−)-Butyl[[(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl]methyl]phenyltelluronium chloride (4i): oil; $[\alpha]^{26}_D$ −6.47° (*c* 1.66, $CHCl_3$); IR (KBr) 3236, 2956, 1436, 1072, 738 cm^{-1}; ^1H NMR δ 0.73 (s, 3H), 0.84−1.20 (m, 2H), 0.86 (t, J = 7.1, 3H), 1.04 (s, 3H), 1.31−1.46 (m, 4H), 1.66−1.88 (m, 6H), 3.06 (d, J = 12.09, 1H), 3.31−3.40 (m, 1H), 3.51 (d, J = 12.09, 1H), 3.60−3.75 (m 1H), 4.09 (dd, J = 3.3, 7.1, 1H), 7.3−7.54 (m, 3H), 7.79−7.82 (m, 2H); ^{13}C NMR δ 13.7, 20.5, 21.4, 24.6, 27.4, 28.2, 35.3, 35.4, 40.6, 45.9, 46.0, 47.8, 50.8, 77.5, 130.3, 130.4, 131.7, 133.9; MS *m*/*z* 360, 358, 356, 264, 262, 260, 242, 240, 238, 208, 206, 204, 135, 93, 77, 57.

(S_{Te})-(−)-Benzyl[[(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl]methyl]methyltelluronium chloride (5a): mp 134−135 °C; $[\alpha]^{26}_D$ −70.60° (*c* 1.47, $CHCl_3$); IR (KBr) 3386, 2950, 1454, 1073, 758 cm^{-1}; ^1H NMR δ 0.82 (s, 3H), 1.0−1.20 (m, 2H), 1.09 (s, 3H), 1.4−1.5 (m, 1H), 1.65−1.93 (m, 5H), 2.12 (s, 3H), 2.38 (d, J = 12.6, 1H), 2.46 (d, J = 12.4, 1H), 3.96 (dd, J = 3.3, 7.7, 1H), 4.48 (d, J = 11.5, 1H), 4.60 (d, J = 11.5, 1H), 7.27−7.42 (m, 5H); ^{13}C NMR δ 9.9, 20.8, 21.1, 25.6, 27.4, 33.1, 34.5, 40.9, 45.6, 48.3, 50.6, 128.4, 129.0, 130.5, 132.3 (a signal will be overlapped with the signal of $CDCl_3$); ^{125}Te NMR δ 522; MS *m*/*z* 374, 372, 370, 298, 296, 294, 135, 91, 79, 57. Anal. Calcd for $C_{18}H_{27}ClOTe$: C, 51.18; H, 6.44. Found: C, 51.02; H, 6.43.

(S_{Te})-(−)-Benzylethyl[[(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl]methyl]telluronium chloride (5b): mp 145−146 °C; $[\alpha]^{26}_D$ −93.30° (*c* 2.30, $CHCl_3$); IR (KBr) 3204, 2943, 1454, 1073, 755 cm^{-1}; ^1H NMR δ 0.80 (s, 3H), 0.9−1.1 (m, 2H), 1.27−1.34 (m, 1H), 1.48 (t, J = 7.7, 3H), 1.61−1.95 (m, 5H), 2.24 (d, J = 12.6, 1H), 2.49 (d, J = 12.4, 1H), 2.45−2.60 (m, 1H), 3.04−3.20 (m, 1H), 3.94 (dd, J = 3.3, 7.7, 1H), 4.53 (d, J = 11.5, 1H), 4.63 (d, J = 11.5, 1H), 7.28−7.41 (m, 5H); ^{13}C NMR δ 10.8, 20.7, 21.4, 22.9, 23.8, 27.3, 33.0, 34.5, 41.0, 45.6, 48.2, 50.1, 76.9, 128.2, 129.0, 130.4, 132.6; ^{125}Te NMR δ 588; MS *m*/*z* 374, 372, 370, 312, 310, 308, 135, 91, 79, 57. Anal. Calcd for $C_{19}H_{29}ClOTe$: C, 52.28; H, 6.70. Found: C, 52.05; H, 6.67.

Crystallographic data for **5b**: monoclinic, space group, *C*2 (#5) with a = 26.128(2) Å, b = 6.694(2) Å, c = 12.842(1) Å, V = 1998.1(6) $Å^3$, and Z = 4 (d_{calcd} = 1.451 g cm^{-3}), μ (MoKα) = 16.23 cm^{-1} absorption corrected by ω scans; 2479 unique reflections; 2056 with $I > 3.00\sigma(I)$ were used in refinement; R = 6.1%, R_w = 7.9%. Selected bond lengths (Å) and angles (deg) are as follows: Te−C(1), 2.16(1); Te−C(2), 2.13(2); Te−C(3), 2.15(1); Te···O, 2.84(1); Te···Cl, 3.150(3); C(1)−Te−C(2), 93.5-(7); C(1)−Te−C(3), 95.8(6); C(2)−Te−C(3), 80.1(7); Cl···Te···O, 87.8(3); Cl···Te−C(1), 90.9(4); Cl···Te−C(2), 110.7(5); Cl···Te−C(3), 167.0(5); O···Te−C(1), 69.4(6); O···Te−C(2), 155.4(6); O···Te−C(3), 84.1(5). Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, on quoting the full journal citation.

(S_{Te})-(−)-Benzylbutyl[[(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl]methyl]telluronium chloride (5c): mp 113−115 °C; $[\alpha]^{26}_D$ −84.34° (*c* 1.20, $CHCl_3$); IR (KBr) 3328, 2956, 1455, 1074, 701 cm^{-1}; ^1H NMR δ 0.80 (s, 3H), 0.85−1.1 (m, 2H), 0.92 (t, J = 7.1, 3H), 1.11 (s, 3H), 1.31−1.45 (m, 4H), 1.62−1.88 (m, 6H), 2.20 (d, J = 12.6, 1H), 2.40 (d, J = 12.4, 1H), 2.34−2.41 (m, 1H), 2.95−3.01 (m, 1H), 3.96 (dd, J = 3.3, 7.7, 1H), 4.60 (d, J = 11.5, 1H), 4.67 (d, J = 11.5, 1H), 7.26−7.41 (m, 5H); ^{13}C NMR δ 13.8, 20.7, 21.6, 23.9, 25.1, 27.3, 27.9, 28.5, 33.3, 34.6, 41.0, 45.5, 45.7, 48.1, 50.0, 77.0, 128.2, 129.0, 130.5, 132.6; MS *m*/*z* 340, 338, 336, 188, 186, 184, 135, 91, 79, 57.

(S_{Te})-(−)-Benzylhexyl[[(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl]methyl]telluronium chloride (5d): mp 100−102 °C; $[\alpha]^{26}_D$ −59.96° (*c* 0.40, $CHCl_3$); IR (KBr) 3420, 2953, 1455, 1074, 701 cm^{-1}; ^1H NMR δ 0.71 (s, 3H), 0.82−1.0 (m, 2H), 0.77 (t, J = 6.7, 3H), 1.00 (s, 3H), 1.22−1.49 (m, 6H), 1.51−1.82 (m, 8H), 2.21 (d, J = 12.6, 1H), 2.34−2.44 (m, 1H), 2.46 (d, J = 12.1, 1H), 2.83−2.92 (m, 1H), 3.85 (dd, J = 3.3, 7.7, 1H), 4.38 (d, J = 11.5, 1H), 4.43 (d, J = 11.5, 1H), 7.16−7.31 (m, 5H); ^{13}C NMR δ 14.2, 20.8, 21.5, 22.7, 25.3, 26.1, 27.4, 29.3, 31.5, 31.7, 33.0, 34.6, 41.0, 45.7, 48.3, 50.4, 76.9, 128.3, 129.1, 130.3, 132.7; MS *m*/*z* 366, 364, 362, 306, 304, 302, 214, 212, 210, 135, 91, 79, 57.

(S_{Te})-(+)-Benzyl[[(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl]methyl]phenyltelluronium chloride (5e): mp 132−133 °C; $[\alpha]^{26}_D$ +14.02° (*c* 0.65, $CHCl_3$); IR (KBr) 3448, 2948, 1454, 1077, 690 cm^{-1}; ^1H NMR δ 0.73 (s, 3H), 0.87−1.10 (m, 2H), 1.12 (s, 3H), 1.51−1.60 (m, 6H), 1.74−1.88 (m, 5H), 3.08 (d, J = 11.5, 1H), 3.80 (d, J = 11.5, 1H), 4.00 (dd, J = 3.3, 7.7, 1H), 4.66 (d, J = 11.0, 1H), 4.85 (d, J = 11.0, 1H), 7.08−7.10 (m, 1H), 7.2−7.28 (m, 1H), 7.35−7.40 (m, 1H), 7.43−7.47 (m, 1H), 7.52−7.55 (m, 1H); ^{13}C NMR δ 20.3, 20.8, 27.8, 33.8, 33.9, 39.9, 41.5, 45.4, 49.3, 52.2, 76.9, 124.0, 128.7, 130.1, 131.7, 131.8, 133.6, 133.9; ^{125}Te NMR δ 361; MS *m*/*z* 366, 364, 362, 306, 304, 302, 214, 212, 210, 135, 91, 79, 57. Anal. Calcd for $C_{23}H_{29}ClOTe$: C, 57.01; H, 6.03. Found: C, 56.98; H, 5.70.

(S_{Te})-(−)-Allyl[[(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl]methyl]methyltelluronium chloride (5f): mp 144−145 °C; $[\alpha]^{26}_D$ −27.12° (*c* 1.8, $CHCl_3$); IR (KBr) 3431, 2947, 1627, 1388, 1072 cm^{-1}; ^1H NMR δ 0.85 (s, 3H), 1.0−1.2 (m, 2H), 1.11 (s, 3H), 1.5−2.1 (m, 6H), 2.26 (s, 3H), 2.69 (d, J = 12.09, 1H), 2.75 (d, J = 12.09, 1H), 3.68−3.75 (m, 1H), 3.85−3.95 (m, 2H), 5.30−5.41 (m, 2H), 5.82−5.91 (m, 1H); ^{13}C NMR δ 8.9, 20.9, 20.9, 25.3, 27.5, 30.5, 34.5, 40.7, 45.5, 48.4, 51.0, 77.1, 123.2, 128.3; MS *m*/*z* 324, 322, 320,

298, 296, 294, 265, 263, 261, 135, 107, 93, 79, 67, 55. Anal. Calcd for $C_{14}H_{25}ClOTe$: C, 45.15; H, 6.77. Found: C, 45.50; H, 6.73.

(S_{Te})-(−)-Allylethyl[[(1*S*, 2*R*, 4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1] heptan-1-yl]methyl]telluronium chloride (5g): oil; $[\alpha]^{26}_D$ −29.62° (*c* 1.65, $CHCl_3$); IR (KBr) 3270, 2952, 1628, 1388, 1074 cm^{-1}; ^{1}H NMR δ 0.87 (s, 3H), 1.0−1.3 (m, 2H), 1.13 (s, 3H), 1.58 (t, *J* = 7.4, 3H), 1.5−2.0 (m, 6H), 2.70 (d, *J* = 12.1, 1H), 2.77 (d, *J* = 12.1, 1H), 2.8−2.9 (m, 1H), 2.99−3.18 (m, 1H), 3.65−3.97 (m, 3H), 5.30−5.42 (m, 2H), 5.82−6.04 (m, 1H); ^{13}C NMR δ 10.9, 20.9, 21.2, 22.2, 27.5, 30.2, 34.7, 40.8, 45.6, 45.7, 48.5, 50.8, 76.9, 122.9, 128.7; MS *m*/*z* 337, 335, 333, 324, 322, 320, 312, 310, 308, 135, 109, 93, 79.

(S_{Te})-(−)-Allyl[[(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl]methyl]phenyl telluronium chloride (5h): mp 106−108 °C; $[\alpha]^{26}_D$ +33.36° (*c* 1.05, $CHCl_3$); IR (KBr) 3398, 2950, 1436, 1047 cm^{-1}; ^{1}H NMR δ 0.80 (s, 3H), 1.0−1.38 (m, 2H), 1.10 (s, 3H), 1.61−2.0 (m, 6H), 2.81 (d, *J* = 12.1, 1H), 3.20 (d, *J* = 12.1, 1H), 4.01 (dd, *J* = 3.85, 7.14, 1H), 4.12−4.38 (m, 2H), 5.22−5.38 (m, 2H), 5.65−5.82 (m, 1H), 7.44−7.54 (m, 3H), 7.77−7.80 (m, 2H); ^{13}C NMR δ 20.7, 21.7, 27.5, 29.3, 35.5, 37.8, 40.8, 46.0, 47.8, 50.9, 77.5, 124.0, 128.2, 130.2, 130.3, 131.6, 133.8; ^{125}Te NMR δ 482; MS *m*/*z* 358, 356, 354, 283, 281, 279, 130, 128, 126, 59.

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