Cyclofunctionalization of Hydroxyolefins Induced by Arenetellurinyl Acetate[1]

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Treatment of arenetellurinic anhydride (1) with acetic acid or anhydride readily formed arenetellurinyl acetate (2). It underwent not only oxytellurinylation of an olefin but also intramolecular cyclofunctionalization of various hydroxyolefins to cyclic ethers. The latter reaction was effectively accelerated by addition of boron trifluoride etherate or tin(IV) chloride and highly regio- and stereoselective. The tellurium functional group introduced in the cyclic ethers could be manipulated into other versatile groups by telluroxide elimination, halogenolysis, and reductive detelluration.

Cyclofunctionalization of olefins provides a useful synthetic methodology that combines intramolecular ring closure leading to a cyclic system with simultaneous introduction of a useful function into it. This reaction has the particular advantage of being applicable to complex natural product syntheses. Although much recent attention has been paid to synthetic methodology based on organotelluriums,[2] cyclofunctionalization using tellurium species has little been studied. This is ascribable to the lesser development of effective electrophilic tellurium reagents toward unsaturated compounds. Only a few tellurium-based cyclofunctionalizations have so far been reported. Petragnani and co-workers first reported the lactonization of unsaturated acids with aryltellurium monohalide, trihalides, or tellurium tetrachloride.[3] Furthermore, they recently found cycloetherification of hydroxyolefins with aryltellurium trihalide.[4] Bergman and Engman also described the formation of bis(cyclic ethers) on treatment of hydroxyolefins with tellurium dioxide in acetic acid containing lithium chloride.[5]

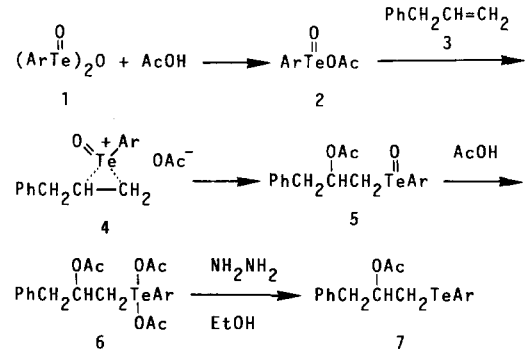
During the course of recent studies on organotelluriums as new synthetic agents, Barton et al. reported that arenetellurinic anhydride (1) mildly oxidized thiols, hydroquinones, and xanthates.[6] We found independently that

1 2

a: Ar = phenyl
b: Ar = p-methoxyphenyl
c: Ar = 2-naphthyl

1 also has a versatile oxidizing property for phosphines, thioamides, thioureas, thionoesters, and benzylic alcohols.[7] In addition, it can act as a catalyst for selective hydration of terminal alkynes in refluxing acetic acid.[7] In the latter case, arenetellurinyl acetate (2) was postulated as the active species, which underwent acetoxytellurinylation of the alkynes followed by hydrolysis. We have, therefore, expected that compound 2 would be an effective electrophile toward unsaturated compounds. Pant reported the first formation of benzenetellurinyl acetate (2a) by hydrolysis of phenyltellurium triacetate,[8] but its synthetic details and properties are still unknown. In this paper we report that arenetellurinyl acetate (2) can be, in fact, generated from treatment of arenetellurinic anhydride (1) with acetic acid or acetic anhydride and be a useful agent not only for acetoxytellurinylation of an olefin but also for cyclofunctionalization of various hydroxyolefins.[9] In addition, the chemical manipulations of the introduced tellurinyl function are described.

Scheme I



Results and Discussion

Acetoxytellurinylation. Sonoda and co-workers reported that treatment of olefins with benzenetellurinic anhydride (1a) in refluxing acetic acid containing a catalytic amount of sulfuric acid gave *vic*-diacetate.[10] This diacetoxylation was proposed to proceed via acetoxytellurenylation of olefin with benzenetellurenyl acetate (PhTeOAc) generated reductively from 1a, followed by acetolysis of the phenyltelluro group. On the other hand, we have found that benzenetellurinic anhydride (1a) reacted with allylbenzene (3) in acetic acid under reflux for 15 h to give tellurium-containing compound 6a, which was difficult to purify and on reduction with hydrazine hydrate was isolated as its telluride form (7a) in 58% yield. No *vic*-diacetoxylation was detected. *p*-Methoxybenzene-

(1) Organotelluriums. Part 19.
(2) For reviews on the chemistry of organotelluriums, see: (a) Engman, L. *Acc. Chem. Res.* **1985**, *18*, 274-279. (b) Petragnani, N.; Comasseto, J. V. *Synthesis* **1986**, 1-30. (c) Engman, L. *Phosphorus Sulfur* **1988**, *38*, 105-119.
(3) (a) Campos, M. M.; Petragnani, N. *Chem. Ber.* **1960**, *93*, 317-320. (b) Campos, M. M.; Petragnani, N. *Tetrahedron* **1962**, *18*, 521-526. (c) Comasseto, J. V.; Petragnani, N. *Synth. Commun.* **1983**, *13*, 889-899.
(4) Comasseto, J. V.; Ferraz, M. M. C.; Petragnani, N.; Brandt, C. A. *Tetrahedron Lett.* **1987**, *28*, 5611-5614.
(5) Bergman, J.; Engman, L. *J. Am. Chem. Soc.* **1981**, *103*, 5196-5200.
(6) Barton, D. H. R.; Finet, J. P.; Thomas, M. *Tetrahedron* **1986**, *42*, 2319-2324.
(7) Hu, N. X.; Aso, Y.; Otsubo, T.; Ogura, F. *Tetrahedron Lett.* **1986**, *27*, 6099-6102.
(8) Pant, B. C. *Tetrahedron Lett.* **1972**, 4779-4780.
(9) A preliminary communication has appeared: Hu, N. X.; Aso, Y.; Otsubo, T.; Ogura, F. *Tetrahedron Lett.* **1987**, *28*, 1281-1284.
(10) (a) Kambe, N.; Tsukamoto, T.; Miyoshi, N.; Murai, S.; Sonoda, N. *Chem. Lett.* **1987**, 269-272. (b) Kambe, N.; Fujioka, T.; Ogawa, A.; Miyoshi, N.; Sonoda, N. *Phosphorus Sulfur* **1988**, *38*, 167-175.

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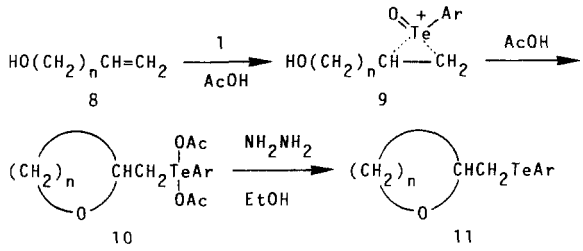
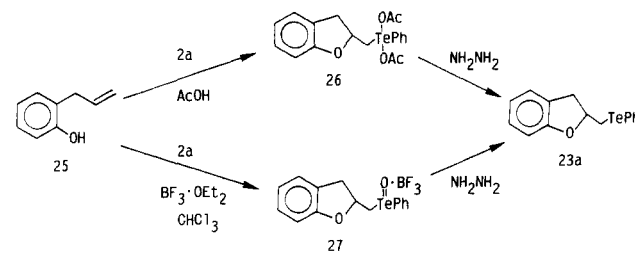
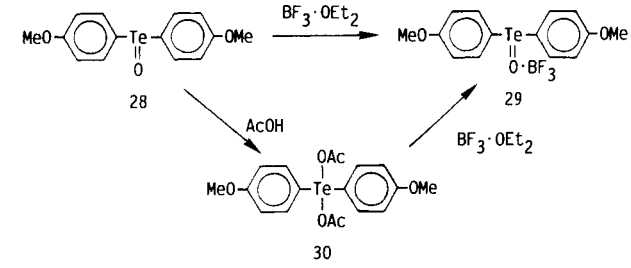
Scheme II



Scheme III



Scheme IV



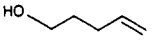
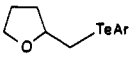
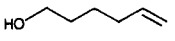
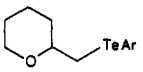
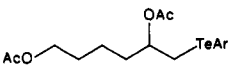
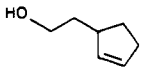
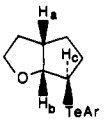
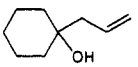
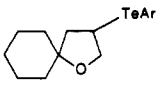
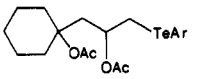
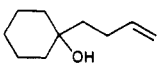
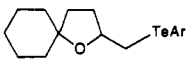
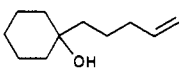
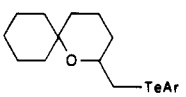
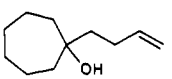
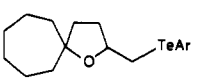
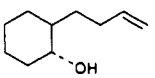
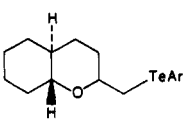
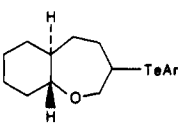
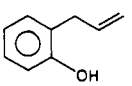
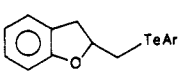
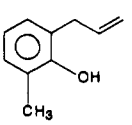
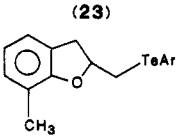
tellurinic anhydride (**1b**) behaved similarly, giving **7b** in 68% yield. These reactions are quite different from that in the presence of catalytic sulfuric acid reported by Sonoda et al. It is therefore suggested that arenetellurinyl acetate (**2**) is the actual active species that reacts with allylbenzene (**3**) leading to telluroxide **5** via an epioxytelluronium intermediate (**4**) as shown in Scheme I. In fact, the quantitative formation of benzenetellurinyl acetate (**2a**), *p*-methoxybenzenetellurinyl acetate (**2b**), and 2-naphthalenetellurinyl acetate (**2c**) was confirmed on heating the corresponding arenetellurinic anhydride (**1**) with acetic acid. Because of high hygroscopicity, they could be better isolated in pure solid states by treatment of **1** with an equivalent of acetic anhydride in refluxing chloroform. On considering that the telluroxide function with acetic acid is readily convertible into tetravalent tellurium diacetate,[11] it is reasonable to assume that the product of the acetoxytellurinylation exists as tetravalent tellurium compound **6** rather than telluroxide **5**. This was actually confirmed by the spectroscopic analyses of the crude product prior to reduction: the ^{1}H NMR spectrum showed three singlets at δ 1.92, 1.95, and 2.00, corresponding to two magnetically nonequivalent acetoxy groups attached to the tellurium and one acetoxy group attached to the chiral carbon, and the IR spectrum showed two distinct carbonyl stretching vibrations at 1645 cm^{-1} for the tellurium diacetate and at 1740 cm^{-1} for the normal acetate.

Cyclofunctionalization. The above acetoxytellurinylation proceeds slowly owing to the low nucleophilicity of acetate anion or acetic acid. If an effective nucleophilic group is disposed at the suitable position of an olefinic molecule, an intramolecular cyclization might occur in preference to the acetoxylation. Thus, treatment of hydroxyolefin **8** with benzenetellurinic anhydride (**1a**) (1.1 equiv) in acetic acid at reflux for 15 h gave cyclic ether **10** bearing a tellurium functional group (Scheme II). *p*-Methoxybenzenetellurinic anhydride (**1b**) and 2-naphthalenetellurinic anhydride (**1c**) behaved similarly. Because of its intractability, compound **10** was isolated as the corresponding telluride **11** after reduction with hydrazine hydrate in ethanol for 10 min. Table I summarizes a variety of examples, of which the yields depicted by method A indicate some features of this cyclization reaction. The ring closure generally follows Baldwin's rules.[12] Thus the five-membered cyclic ether is favored over the four- or six-membered one, and the six-membered cyclic ether over the seven-membered one. Example 4 demonstrates that the five-membered ring is formed in preference to the four-membered one in spite of anti Markovnikov addition. As shown in examples 2 and 4, sluggish cyclization often competes with acetoxylation. An attempted preparation of three- or four-membered rings from allyl alcohol was unsuccessful. The addition is highly stereoselective, anti on the basis of the stereochemistry of the bicyclic ether **15** (example 3), which has the same configuration as already reported for the selenium analogue.[13] That is, the ^{1}H NMR spectrum of **15a** showed a doublet of doublets at δ 4.55 due to H_b proton. The coupling constants 5.9 Hz and 1.4 Hz were assigned to J_{ab} and J_{bc}, respectively, by a decoupling technique. The larger value of 5.9 Hz for J_{ab} indicates cis ring fusion for the bicyclic system, and the smaller value of 1.4 Hz for J_{bc} supports trans configuration of the phenyltelluro group to the ethereal oxygen.

Although the above cyclization reaction provides a novel and convenient method for the syntheses of cyclic ethers bearing aryltelluro group from γ- or δ-hydroxyolefins, it requires a high reaction temperature (110 °C) and often competes with acetoxytellurinylation, restricting greatly the scope of its synthetic utilization. In order to overcome these problems, we have examined further modifications of reaction conditions. Table II summarizes the effects of several additional Lewis acids on cyclofunctionalization of *o*-allylphenol (**25**) to 2,3-dihydro-2-[(phenyltelluro)-methyl]benzofuran (**23a**) in chloroform (Scheme III). Of them, boron trifluoride etherate and tin(IV) chloride were most effective, causing the reactions to be complete within 30 min at room temperature. The reactions with the other Lewis acids such as zinc iodide and ferric(III) chloride required reflux temperature and prolonged time. The use of aluminum chloride or titanium tetrachloride resulted in considerable decomposition, and zinc acetate was quite inefficient. When the catalyst was omitted, no reaction occurred even in refluxing chloroform. In addition, an equimolar amount of catalyst was needed for the reaction to smoothly proceed. When the amount of boron trifluoride etherate was reduced to 20% molar equiv, the reaction took 15 h at reflux to go to completion. This suggests that Lewis acid coordinates not only to the tellurinyl acetate so as to enhance the activity but also to the product. The above reaction in acetic acid led to the formation of tetravalent tellurium diacetate **26** prior to reduction with hydrazine as confirmed by spectroscopic measurements: ^{1}H NMR δ = 1.88 (s, 3 H, TeOAc), 1.96 (s, 3 H, TeOAc), 2.7–3.7 (m, 4 H, CH_2), 4.8–5.6 (m, 1 H,

(11) Tamagaki, S.; Hatanaka, I.; Kozuka, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2501–2502.
(12) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734–736.
(13) Clive, D. L. J.; Chittattu, G.; Wong, C. K. *Can. J. Chem.* **1977**, *55*, 3894–3897.

Table I. Cyclofunctionalization of Hydroxyolefins with Arenetellurinyl Acetate (2)

run	substrate	product	method[a]	yield, %
1		 (12)	A B	80,[a] 77,[b] 73[c] 92[a]
2		 (13)	A B	62,[a] 38,[b] 26[c] 85[a]
		 (14)	A	23,[a] 26,[b] 23[c]
3		 (15)	A B	55,[a] 42[b] 91[a]
4		 (16)	A B	15[b] 63[a]
		 (17)	A	29[b]
5		 (18)	A B	86[b] 85[a]
6		 (19)	A	90[b]
7		 (20)	A	94[b]
8		 (21)	A B	45[b] 53[a]
		 (22)	A B	22[b] 35[a]
9		 (23)	A B	80,[a] 94,[b] 92[c] 92[a]
10		 (24)	A B	91,[a] 90,[b] 89[c] 96[a]

[a] Ar = phenyl. [b] Ar = *p*-methoxyphenyl. [c] Ar = 2-naphthyl. [d] Method A: hydroxyolefin was treated with arenetellurinic anhydride (1) in acetic acid at reflux for 15 h. Method B: hydroxyolefin was treated with arenetellurinyl acetate (2) in chloroform containing equivalent boron trifluoride etherate at room temperature for 0.5 h.

CH), 6.7–7.2 (m, 4 H, Ar H), 7.2–7.5 (m, 3 H, Ar H), 7.6–8.0 (m, 2 H, Ar H); IR 1645 cm^{-1} (TeOAc). On the other hand, the NMR and IR measurements of the cyclization product in the boron trifluoride promoted reaction in chloroform indicated no signal due to acetoxy groups of **26**, even though equimolar acetic acid is considered to exist in the reaction medium. In order to understand these observations, we examined the behavior of bis(*p*-methoxyphenyl) telluroxide (**28**) on ^1H NMR spectroscopy (Scheme IV). Compound **28** showed a singlet at δ 3.75 due to the methoxy protons and two doublets at δ 6.80 and 7.50 due to the aromatic protons in deuteriochloroform. When

Table II. Effect of Lewis Acids on Cyclofunctionalization of *o*-Allylphenol (25) to 2,3-Dihydro-2-[(phenyltelluro)methyl]benzofuran (23a) by Benzenetellurinyl Acetate (2a) in Chloroform

run	Lewis acid[a]	temp	time, h	yield, %
1	BF_3·OEt_2	RT[c]	0.5	92
2	BF_3·OEt_2[b]	reflux	15	88
3	$SnCl_4$	RT	0.5	96
4	$FeCl_3$	reflux	2	74
5	ZnI_2	reflux	12	94
6	$AlCl_3$	reflux	0.5	20
7	$TiCl_4$	reflux	1	26
8	$Zn(OAc)_2$·H_2O	reflux	12	0

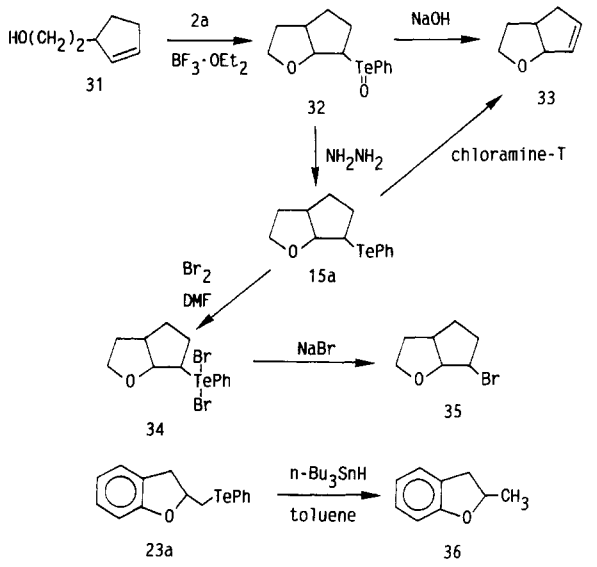
[a] An equivalent amount of Lewis acid was used unless otherwise stated. [b] A 20% equimolar amount of Lewis acid was used. [c] RT = room temperature.

boron trifluoride etherate was added into its solution, the two aromatic signals shifted to lower fields (δ 6.91, 7.54) in contrast to the small shift of the methoxy signal (δ 3.76), indicating BF_3 to coordinate to the tellurinyl oxygen as shown in **29**. On the other hand, addition of acetic acid to **28** led to ready formation of bis(*p*-methoxyphenyl)-tellurium diacetate (**30**) (δ 1.94, 3.78, 6.91, 7.70), which was then treated with boron trifluoride etherate, generating the BF_3 complex **29** together with acetic acid. These results evidently support the BF_3 complex of telluroxide **27** for the structure of the cyclization product from **25** in the presence of boron trifluoride etherate.

Table I also demonstrates the successful application of boron trifluoride promoted cyclofunctionalization depicted by method B to other hydroxyolefins. This modified reaction not only proceeds very mildly but also completely avoids competitive acetoxylation. Therefore the yields are much higher than those in method A. High regioselectivity and stereoselectivity also hold in these cases.

Transformation of Tellurium Functional Group. Another important point in demonstrating the utilization of the present tellurium-based methodology is the manipulation of the introduced tellurium moiety following cyclofunctionalization. There have been so far developed a number of chemical transformations of the phenyltelluro group such as reductive detelluration,[14] oxidative elimination,[15,16] halogenolysis,[17] and methanolysis.[18] Scheme V shows some examples applying such reactions to the present tellurium-containing cyclic ethers. Although the syn elimination reaction of secondary alkyl phenyl telluroxide was observed to readily occur at room temperature,[15b] it was not the case with the present telluroxide (**32**) prepared by cyclofunctionalization of 2-(2-cyclopentenyl)ethanol (**31**). This is presumably because **32** is stabilized by complexation with BF_3. The elimination reaction of **32** was then carried out in refluxing tetrahydrofuran with aqueous sodium hydroxide, giving 8-oxabicyclo[3.3.0]oct-2-ene (**33**) in 53% overall yield based on **31**. This sequence provides a convenient alternative to

Scheme V



selenium-based methodology using an oxidant for the similar conversion.[19] In addition, 8-(phenyltelluro)-2-oxabicyclo[3.3.0]octane (**15a**), obtained by reduction of **32**, was treated with chloramine-T in refluxing tetrahydrofuran, giving the same allylic ether in 82% yield by way of tellurimide elimination.[16] The telluride compound **15a** on treatment with bromine dimethylformamide at 0 °C was quantitatively converted into the tellurium dibromide **34**, which was then heated at 90 °C in the same solvent containing 1.5 equiv of sodium bromide, giving 8-bromo-2-oxabicyclo[3.3.0]octane (**35**) in 87% yield.[17] Finally, 2,3-dihydro-2-[(phenyltelluro)methyl]benzofuran (**23a**) was reduced with commercial tributyltin hydride in refluxing toluene to give 2,3-dihydro-2-methylbenzofuran (**36**) in 95% yield.[14] The same reductive detelluration also occurred in 83% yield from 2,3-dihydro-2-[[(*p*-methoxyphenyl)telluro]methyl]benzofuran (**23b**).

Conclusion. The present results demonstrate that arenetellurinyl acetate (**2**), readily available from arenetellurinic anhydride (**1**), has a potential of an effective electrophile toward olefins. That is, it can induce novel regio- and stereoselective cyclofunctionalization of hydroxyolefins to cyclic ethers bearing a tellurium functional group. Since the introduced tellurium functional group is transformable into other appropriate groups by telluroxide elimination, tellurimide elimination, halogenolysis, and reductive detelluration, this cyclization reaction constitutes a useful new approach to functionalized cyclic ethers.

Experimental Section

General Methods and Materials. Elemental analyses were measured by Mr. Hideaki Iwatani, Microanalytical Laboratory in Department of Applied Chemistry, Faculty of Engineering, Hiroshima University. Melting points were determined with a Yanaco micro-melting-point determination apparatus and are uncorrected. IR spectra were recorded with a Hitachi 260-30 spectrometer. Characteristic absorption peaks are reported in cm^{-1}. ^1H NMR spectra were recored on a JEOL JNM-PMX 60 (60 MHz) spectrometer in deuteriochloroform. The spectrum measured at 90 MHz was taken on a JEOL FX-90A spectrometer. Chemical shifts are reported in δ (ppm) downfield from tetramethylsilane as an internal standard. Mass spectra were measured on a Shimadzu GCMS-QP1000 spectrometer using a 70-eV ion-

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ization potential. Molecular ion peaks and fragment peaks involving a typical isotopic pattern of tellurium are reported on the basis of its isotope mass number 130.

All reactions were carried out under a nitrogen atmosphere. All chemicals are of reagent grade. 4-Penten-1-ol, 5-hexen-1-ol, 2-allylphenol, and 2-allyl-6-methylphenol were commercially available. The other hydroxyolefins were prepared according to the literature procedures.[20] *p*-Methoxybenzenetellurinic anhydride (**1b**) and 2-naphthalenetellurinic anhydride (**1c**) were prepared from alkaline hydrolysis of the corresponding aryltellurium trichloride according to the method of Barton et al.[6] Benzenetellurinic anhydride (**1a**) was similarly prepared from phenyltellurium tribromide.[21]

Arenetellurinyl Acetate (2). When benzenetellurinic anhydride (**1a**) (0.457 g, 1.0 mmol) was treated with acetic anhydride (0.112 g, 1.1 mmol) in chloroform (10 mL) under reflux, the solid tellurinic anhydride disappeared within 30 min, indicating smooth conversion to benzenetellurinyl acetate (**2a**). Concentration under reduced pressure left quantitatively a solid of **2a**, which was recrystallized from benzene–hexane to give colorless crystals: mp 150–152 °C (sealed); IR (KBr disk) 3055, 3000, 2945, 1580 (C=O), 1480, 1440, 1372, 1310, 1182, 1065, 1020, 1000, 922, 740, 692, 660, 620; ^{1}H NMR 1.87 (s, 3 H, CH_3), 7.2–7.5 (m, 3 H, Ar H), 7.6–8.0 (m, 2 H, Ar H). Anal. Calcd for $C_8H_8O_3Te$: C, 34.34; H, 2.89. Found: C, 34.25; H, 2.90. When acetic acid was used instead of acetic anhydride, crystallization of **2a** was very difficult because of its hygroscopicity.

p-Methoxybenzenetellurinyl acetate (**2b**) and 2-naphthalenetellurinyl acetate (**2c**) were similarly obtained from the corresponding tellurinic anhydrides.

2b: white crystals from benzene–hexane, mp 155–156 °C (sealed); IR (KBr disk) 3060, 3010, 2950, 2845, 1580 (C=O), 1490, 1460, 1440, 1400, 1370, 1300, 1255, 1180, 1068, 1025, 800, 790; ^{1}H NMR 1.92 (s, 3 H, CH_3), 3.78 (s, 3 H, CH_3), 6.88 (d, J = 8 Hz, 2 H, Ar H), 7.80 (d, J = 8 Hz, 2 H, Ar H). Anal. Calcd for $C_9H_{10}O_4Te$: C, 34.89; H, 3.26. Found: C, 34.71; H, 3.24.

2c: white crystals from benzene–hexane, mp 148–150 °C; IR (KBr disk) 3055, 1585 (C=O), 1500, 1375, 1310, 1200, 1160, 1140, 1062, 1020, 960, 905, 862, 820, 740, 670; ^{1}H NMR 2.03 (s, 3 H, CH_3), 7.2–8.1 (m, 6 H, Ar H), 8.50 (s, 1 H, Ar H). Anal. Calcd for $C_{12}H_{10}O_3Te$: C, 43.70; H, 3.06. Found: C, 43.27; H, 3.55.

Acetoxytellurinylation of Allylbenzene (3). To a magnetically stirred solution of benzenetellurinic anhydride (**1a**) (0.252 g, 0.55 mmol) in acetic acid (4 mL) was added allylbenzene (**3**) (0.118 g, 1 mmol), and the resulting mixture was heated at reflux for 15 h. The solution was concentrated under reduced pressure. The spectroscopic analysis of the residual oil showed that it consisted mainly of **6a**: ^{1}H NMR 1.92 (s, TeOAc), 1.95 (s, TeOAc), 2.00 (s, OAc), 2.7–3.6 (m, CH_2), 5.0–5.3 (m, CH), 7.0–7.5 (m, Ar H), 7.5–7.9 (m, Ar H); IR (liquid film) 1740 (OAc), 1645 (TeOAc), 1370, 1285 cm^{-1}. It was then reduced at 60 °C with hydrazine hydrate (0.1 g, 2 mmol) in ethanol (4 mL) for 15 min. The cooled solution was then poured into water and extracted with dichloromethane (25 mL × 2). The organic layer was washed with brine and dried over $MgSO_4$. Evaporation of the solvent left a yellow oil, which was subjected to column chromatography (silica gel) with dichloromethane as eluant to give **7a** (0.22 g, 58%) as a yellow oil: IR (liquid film) 3050, 2925, 1739, 1570, 1470, 1430, 1370, 1240, 1020, 735, 700; ^{1}H NMR 1.80 (s, 3 H, OAc), 2.8–3.1 (m, 2 H, CH_2), 2.93 (d, J = 6 Hz, 2 H, CH_2), 5.17 (quin, J = 6 Hz, 1 H, OCH), 7.0–7.3 (m, 8 H, Ar H), 7.5–7.8 (m, 2 H, Ar H). Anal. Calcd for $C_{17}H_{18}O_2Te$: C, 53.45; H, 4.76. Found: C, 53.42; H, 4.69.

A similar reaction with *p*-methoxybenzenetellurinic anhydride (**1b**) as tellurinylating reagent gave **7b** as a pale yellow oil in 68% yield: IR (liquid film) 3040, 2945, 2850, 1740, 1590, 1490, 1460, 1370, 1283, 1240, 1180, 1030, 825, 750, 705; ^{1}H NMR 1.90 (s, 3 H, OAc), 2.8–3.1 (m, 2 H, CH_2), 2.93 (d, J = 6 Hz, 2 H, CH_2), 3.73 (s, 3 H, OCH_3), 5.10 (quint, J = 6 Hz, 1 H, CH), 6.63 (d, J = 8.5 Hz, 2 H, Ar H), 6.9–7.3 (m, 5 H, Ar H), 7.58 (d, J = 8.5 Hz, 2 H, Ar H). Anal. Calcd for $C_{18}H_{20}O_3Te$: C, 52.47; H, 4.90. Found: C, 52.30; H, 4.83.

General Procedure for Cyclofunctionalization of Hydroxyolefins. Method A: Induced by Arenetellurinic Anhydride (1). To a solution of *p*-methoxybenzenetellurinic anhydride (**1b**) (0.285 g, 0.55 mmol) in acetic acid (5 mL) was added *o*-allylphenol (**25**) (0.134 g, 1 mmol) in one portion. The resulting mixture was heated at reflux for 15 h and then concentrated under reduced pressure. The residue was reduced with hydrazine hydrate (0.1 g, 2 mmol) in ethanol (5 mL) at 60 °C for 15 min. The reaction mixture was cooled to room temperature, poured into water, and extracted with dichloromethane (25 mL × 2). The organic layer was washed with brine and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the residue was chromatographed on silica gel with dichloromethane as eluant to afford a solid of 2,3-dihydro-2-[[(*p*-methoxyphenyl)telluro]methyl]benzofuran (**23b**) (0.346 g, 94%). Recrystallization from methanol gave white needles: mp 85–86 °C; IR (KBr disk) 2935, 1600, 1580, 1280, 1240, 1180, 940, 822, 750; ^{1}H NMR 2.7–3.6 (m, 4 H, CH_2), 3.75 (s, 3 H, OCH_3), 4.7–5.2 (m, 1 H, CH), 6.70 (d, J = 8 Hz, 2 H, Ar H), 6.5–7.3 (m, 4 H, Ar H), 7.66 (d, J = 8 Hz, 2 H, Ar H); MS, m/z (rel intensity) 370 (M^+, 12), 237 ($CH_3OC_6H_4Te^+$, 52), 222 (14), 133 ($M^+ - CH_3OC_6H_4Te$, base peak), 131 (39), 105 (55). Anal. Calcd for $C_{16}H_{16}O_2Te$: C, 52.23; H, 4.39. Found: C, 52.02; H, 4.33.

Method B: Induced by Arenetellurinyl Acetate (2) and Boron Trifluoride. Benzenetellurinyl acetate (**2a**) (1.1 mmol) was in situ generated by treatment of benzenetellurinic anhydride (**1a**) (0.252 g, 0.55 mmol) with acetic anhydride (0.056 g, 0.55 mmol) in chloroform (6 mL) at reflux for 30 min. Into the cooled solution were successively added *o*-allylphenol (**25**) (0.134 g, 1.0 mmol) in chloroform (2 mL) and boron trifluoride etherate (0.170 g, 1.2 mmol). The resulting mixture was stirred at room temperature for 0.5 h and then concentrated under reduced pressure. The product mixture was worked up as described in method A to give 2,3-dihydro-2-[(phenyltelluro)methyl]benzofuran (**23a**) (0.311 g, 92%). Recrystallization from methanol gave white needles: mp 46.5–47.0 °C; IR (KBr disk) 3045, 2960, 1600, 1575, 1480, 1460, 1330, 1225, 1160, 1100, 1020, 915, 860, 760, 740, 695; ^{1}H NMR 2.6–3.6 (m, 4 H, CH_2), 4.6–5.2 (m, 1 H, CH), 6.5–7.3 (m, 7 H, Ar H), 7.5–7.8 (m, 2 H, Ar H); MS, m/z (rel intensity) 340 (M^+, 52), 207 ($PhTe^+$, 25), 133 (M^+ – PhTe, base peak), 132 (14), 105 (55), 77 (52), 51 (14). Anal. Calcd for $C_{15}H_{14}OTe$: C, 53.32; H, 4.18. Found: C, 53.12; H, 4.11.

2-[(Phenyltelluro)methyl]tetrahydrofuran (12a): a pale yellow oil; IR (liquid film) 3050, 2965, 2850, 1565, 1470, 1430, 1095, 1045, 1019, 905, 730, 690; ^{1}H NMR 1.3–2.3 (m, 4 H, CH_2), 3.08 (d, J = 6 Hz, 2 H, $TeCH_2$), 3.5–4.3 (m, 3 H, OCH_2 and OCH), 7.0–7.3 (m, 3 H, Ar H), 7.5–7.8 (m, 2 H, Ar H); MS, m/z (rel intensity) 292 (M^+, 37), 207 ($PhTe^+$, 17), 130 (6), 91 (11), 85 (M^+ – PhTe, 40), 77 (45), 71 (39), 43 (base peak). Anal. Calcd for $C_{11}H_{14}OTe$: C, 45.58; H, 4.88. Found: C, 45.53; H, 4.87.

2-[[(*p*-Methoxyphenyl)telluro]methyl]tetrahydrofuran (12b): a pale yellow oil; IR (liquid film) 2965, 2860, 1582, 1482, 1460, 1282, 1240, 1175, 1050, 1025, 820; ^{1}H NMR 1.3–2.3 (m, 4 H, CH_2), 3.00 (d, J = 6 Hz, 2 H, $TeCH_2$), 3.5–4.2 (m, 3 H, OCH_2 and OCH), 3.70 (s, 3 H, OCH_3), 6.66 (d, J = 8 Hz, 2 H, Ar H), 7.60 (d, J = 8 Hz, 2 H, Ar H); MS, m/z (rel intensity) 322 (M^+, 7), 108 (9), 85 ($M^+ - TeC_6H_4OCH_3$, 11), 71 (10), 63 (8), 55 (9), 43 (base peak). Anal. Calcd for $C_{12}H_{16}O_2Te$: C, 45.05; H, 5.05. Found: C, 45.05; H, 4.93.

2-[(2-Naphthyltelluro)methyl]tetrahydrofuran (12c): a yellow oil; IR (liquid film) 3050, 2975, 2865, 1620, 1580, 1500, 1130, 1050, 940, 859, 820, 745; ^{1}H NMR 1.3–2.3 (m, 4 H, CH_2), 3.09 (d, J = 5 Hz, 2 H, $TeCH_2$), 3.5–4.3 (m, 3 H, OCH_2 and OCH), 7.2–7.5 (m, 3 H, Ar H), 7.5–7.8 (m, 3 H, Ar H), 8.13 (s, 1 H, Ar H); MS, m/z (rel intensity) 342 (M^+, 8), 257 ($C_{10}H_7Te^+$, 4), 127 (26), 85 ($M^+ - C_{10}H_7Te$, 11), 71 (13), 43 (base peak). Anal. Calcd for $C_{15}H_{16}OTe$: C, 53.00; H, 4.75. Found: C, 53.00; H, 4.74.

2-[(Phenyltelluro)methyl]tetrahydropyran (13a): a yellow oil; IR (liquid film) 3065, 2950, 2855, 1580, 1480, 1440, 1220, 1175, 1090, 1055, 1022, 902, 740, 700; ^{1}H NMR 1.2–2.0 (m, 6 H, CH_2), 2.7–3.2 (m, 2 H, $TeCH_2$), 3.2–3.6 (m, 2 H, OCH_2), 3.8–4.2 (m, 1 H, OCH), 7.0–7.3 (m, 3 H, Ar H), 7.5–7.8 (m, 2 H, Ar H); MS, m/z (rel intensity) 306 (M^+, 11), 207 ($PhTe^+$, 16), 99 (M^+ – PhTe, 31), 91 (16), 85 (61), 77 (base peak). Anal. Calcd for $C_{12}H_{16}OTe$:

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C, 47.43; H, 5.32. Found: C, 47.67; H, 5.30.

2-[[(*p*-Methoxyphenyl)telluro]methyl]tetrahydropyran (13b): a pale yellow oil; IR (liquid film) 2945, 2840, 1585, 1560, 1485, 1460, 1440, 1280, 1240, 1175, 1082, 1045, 1030, 965, 900, 820; ^{1}H NMR 1.1–2.2 (m, 6 H, CH_2), 2.7–4.2 (m, 5 H, $TeCH_2$, OCH_2, and OCH), 3.73 (s, 3 H, OCH_3), 6.67 (d, J = 8 Hz, 2 H, Ar H), 7.60 (d, J = 8 Hz, 2 H, Ar H); MS, m/z (rel intensity) 336 (M^+, 19), 237 ($CH_3C_6H_4Te^+$, 11), 121 (9), 108 (32), 99 ($M^+ - CH_3O$-C_6H_4Te, 24), 92 (13), 85 (31), 81 (24), 77 (20), 63 (24), 55 (55), 43 (base peak). Anal. Calcd for $C_{13}H_{18}O_2Te$: C, 46.76; H, 5.44. Found: C, 46.51; H, 5.38.

2-[(2-Naphthyltelluro)methyl]tetrahydropyran (13c): a pale yellow oil; IR (liquid film) 3050, 2945, 2850, 1582, 1500, 1440, 1380, 1340, 1270, 1215, 1130, 1085, 1050, 1020, 970, 940, 900, 855, 815, 800, 770, 743; ^{1}H NMR 1.0–2.1 (m, 6 H, CH_2), 2.9–3.2 (m, 2 H, $TeCH_2$), 3.47 (t, J = 7 Hz, 2 H, OCH_2), 3.8–4.2 (m, 1 H, OCH), 7.2–7.9 (m, 6 H, Ar H), 8.13 (s, 1 H, Ar H); MS, m/z (rel intensity) 356 (M^+, 16), 257 ($C_{10}H_7Te^+$, 19), 85 (28). Anal. Calcd for $C_{16}H_{18}OTe$: C, 54.29; H, 5.14. Found: C, 54.23; H, 5.10.

2,6-Diacetoxyhexyl phenyl telluride (14a): a pale yellow oil; IR (liquid film) 3050, 2950, 2860, 1740, 1570, 1470, 1430, 1370, 1245, 1020, 735, 690; ^{1}H NMR 1.1–2.2 (m, 6 H, CH_2), 1.93 (s, 3 H, OAc) 2.00 (s, 3 H, OAc), 3.06 (d, J = 5 Hz, 2 H, $TeCH_2$), 3.8–4.2 (m, 2 H, OCH_2), 4.8–5.2 (m, 1 H, OCH), 7.0–7.3 (m, 3 H, Ar H), 7.6–7.9 (m, 2 H, Ar H). Anal. Calcd for $C_{16}H_{22}O_4Te$: C, 47.33; H, 5.47. Found: C, 47.16; H, 5.35.

2,6-Diacetoxyhexyl *p*-methoxyphenyl telluride (14b): a pale yellow oil; IR (liquid film) 2945, 2860, 1735, 1720, 1605, 1490, 1280, 1250, 1180, 1030, 825, 790; ^{1}H NMR 1.1–2.3 (m, 6 H, CH_2), 1.97 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 3.00 (d, J = 6 Hz, 2 H, $TeCH_2$), 3.73 (s, 3 H, OCH_3), 3.5–4.3 (m, 2 H, OCH_2), 4.7–5.2 (m, 1 H, OCH), 6.70 (d, J = 8 Hz, 2 H, Ar H), 7.62 (d, J = 8 Hz, 2 H, Ar H). Anal. Calcd for $C_{17}H_{24}O_5Te$: C, 46.83; H, 5.56. Found: C, 46.34; H, 5.41.

2,6-Diacetoxyhexyl 2-naphthyl telluride (14c): a pale yellow oil; IR (liquid film) 3055, 2955, 2875, 1740, 1615, 1585, 1500, 1440, 1375, 1240, 1140, 1050, 1025, 942, 860, 820, 750; ^{1}H NMR 1.1–2.3 (m, 6 H, CH_2), 1.90 (s, 3 H, OAc), 2.00 (s, 3 H, OAc), 3.13 (d, J = 6 Hz, 2 H, $TeCH_2$), 3.95 (t, J = 6 Hz, 2 H, OCH_2), 4.8–5.2 (m, 1 H, OCH), 7.2–7.5 (m, 3 H, Ar H), 7.5–7.9 (m, 3 H, Ar H), 8.18 (s, 1 H, Ar H). Anal. Calcd for $C_{20}H_{24}O_4Te$: C, 52.67; H, 5.32. Found: C, 52.52; H, 5.28.

8-(Phenyltelluro)-2-oxabicyclo[3.3.0]octane (15a): a pale yellow oil; IR (liquid film) 3060, 2950, 2865, 1575, 1470, 1430, 1300, 1218, 1165, 1060, 1035, 1018, 995, 730, 690; ^{1}H NMR (90 MHz) 1.2–2.3 (m, 6 H, CH_2), 2.77 (m, 1 H, H_a), 3.6–4.0 (m, 2 H, OCH_2), 3.87 (m, 1 H, H_c), 4.55 (dd, J_{ab} = 5.9 Hz, J_{bc} = 1.4 Hz, 1 H, H_b), 7.1–7.3 (m, 3 H, Ar H), 7.7–7.9 (m, 2 H, Ar H); MS, m/z (rel intensity) 318 (M^+, 3), 207 ($PhTe^+$, 8), 160 (24), 111 (M^+ – PhTe, 29), 93 (59), 84 (79), 77 (40), 67 (55), 56 (63), 51 (base peak). Anal. Calcd for $C_{13}H_{16}OTe$: C, 49.43; H, 5.12. Found: C, 49.63; H, 5.12.

8-[(*p*-Methoxyphenyl)telluro]-2-oxabicyclo[3.3.0]octane (15b): a pale yellow oil; IR (liquid film) 2950, 2865, 1585, 1565, 1490, 1460, 1285, 1250, 1180, 1065, 1030, 915, 820, 790; ^{1}H NMR 1.2–2.4 (m, 6 H, CH_2), 2.70 (m, 1 H, H_a), 3.5–4.0 (m, 3 H, OCH_2 and H_c), 3.73 (s, 3 H, OCH_3), 4.67 (dd, J_{ab} = 6 Hz, J_{bc} = 1.5 Hz, 1 H, H_b), 6.70 (d, J = 8 Hz, 2 H, Ar H), 7.63 (d, J = 8 Hz, 2 H, Ar H); MS, m/z (rel intensity) 348 (M^+, 5), 137 ($CH_3OC_6H_4Te^+$, 6), 111 ($M^+ - CH_3OC_6H_4Te$, 5), 108 (30), 93 (31), 77 (29), 67 (43), 63 (21), 55 (base peak). Anal. Calcd for $C_{14}H_{18}O_2Te$: C, 48.61; H, 5.26. Found: C, 48.37; H, 5.51.

3-(Phenyltelluro)-1-oxaspiro[4.5]decane (16a): a pale yellow oil; IR (liquid film) 3075, 2945, 2855, 1570, 1475, 1445, 1430, 1305, 1230, 1145, 1105, 1020, 925, 850, 825, 730, 695; ^{1}H NMR 1.1–1.8 (m, 10 H, CH_2), 1.8–2.4 (m, 2 H, CH_2), 3.3–4.3 (m, 3 H, OCH_2 and TeCH), 7.0–7.3 (m, 3 H, Ar H), 7.5–7.8 (m, 2 H, Ar H); MS, m/z (rel intensity) 346 (M^+, 2), 207 ($PhTe^+$, 11), 139 (M^+ – PhTe, 22), 121 (91), 109 (18), 95 (base peak), 81 (61), 67 (56), 56 (72). Anal. Calcd for $C_{15}H_{20}OTe$: C, 52.38; H, 5.87. Found: C, 52.30; H, 5.87.

3-[(*p*-Methoxphenyl)telluro]-1-oxaspiro[4.5]decane (16b): a pale yellow oil; IR (liquid film) 2945, 2860, 1585, 1560, 1490, 1445, 1290, 1250, 1180, 1030, 930, 820; ^{1}H NMR 1.0–2.4 (m, 12 H, CH_2), 3.2–4.2 (m, 3 H, OCH_2 and TeCH), 3.77 (s, 3 H, OCH_3), 6.73 (d, J = 8 Hz, 2 H, Ar H), 7.67 (d, J = 8 Hz, 2 H, Ar H); MS, m/z (rel intensity) 376 (M^+, 5), 237 ($CH_3OC_6H_4Te^+$, 16), 139 ($M^+ - CH_3OC_6H_4Te$, 22), 121 (91), 108 (86), 95 (base peak), 81 (74), 67 (57), 56 (67). Anal. Calcd for $C_{16}H_{22}O_2Te$: C, 51.38; H, 5.94. Found: C, 51.37; H, 5.94.

1-[2-Acetoxy-3-[(*p*-methoxyphenyl)telluro]propyl]cyclohexyl acetate (17b): a yellow oil; IR (liquid film) 2940, 2855, 1740, 1585, 1490, 1440, 1370, 1280, 1245, 1175, 1030, 965, 825, 760; ^{1}H NMR 1.2–2.0 (m, 12 H, CH_2), 1.93 (s, 3 H, OAc), 1.97 (s, 3 H, OAc), 2.8–3.2 (m, 2 H, $TeCH_2$), 3.73 (s, 3 H, OCH_3), 5.0–5.3 (m, 1 H, OCH), 6.70 (d, J = 8 Hz, 2 H), 7.73 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_{20}H_{28}O_5Te$: C, 50.45; H, 5.94. Found: C, 50.60; H, 5.96.

2-[(Phenyltelluro)methyl]-1-oxaspiro[4.5]decane (18a): a pale yellow oil; IR (liquid film) 3075, 2960, 2875, 1580, 1480, 1450, 1420, 1355, 1140, 1065, 1050, 1000, 905, 720, 680; ^{1}H NMR 1.2–2.2 (m, 14 H, CH_2), 3.10 (d, J = 6 Hz, 2 H, $TeCH_2$), 4.0–4.5 (m, 1 H, CH), 7.0–7.3 (m, 3 H, Ar H), 7.5–7.8 (m, 2 H, Ar H); MS, m/z (rel intensity) 360 (M^+, 12), 207 ($PhTe^+$, 26), 153 (M^+ – PhTe, 24), 139 (38), 135 (88), 121 (base peak), 109 (25), 95 (94), 77 (54), 67 (54), 56 (99). Anal. Calcd for $C_{16}H_{22}OTe$: C, 53.68; H, 6.21. Found: C, 53.57; H, 6.22.

2-[[(*p*-Methoxyphenyl)telluro]methyl]-1-oxaspiro[4.5]decane (18b): a pale yellow oil; IR (liquid film) 2930, 2850, 1582, 1562, 1485, 1448, 1280, 1240, 1175, 1030, 820; ^{1}H NMR 1.0–2.2 (m, 14 H, CH_2), 3.00 (d, J = 6 Hz, 2 H, $TeCH_2$), 3.70 (s, 3 H, OCH_3), 3.8–4.3 (m, 1 H, CH), 6.63 (d, J = 8 Hz, 2 H, Ar H), 7.57 (d, J = 8 Hz, 2 H, Ar H); MS, m/z (rel intensity) 390 (M^+, 49), 237 ($CH_3OC_6H_4Te^+$, 51), 153 ($M^+ - CH_3OC_6H_4Te$, 14), 139 (15), 136 (14), 135 (base peak), 121 (79), 108 (49), 95 (95), 79 (30), 67 (49), 55 (86). Anal. Calcd for $C_{17}H_{24}O_2Te$: C, 52.68; H, 6.25. Found: C, 52.91; H, 6.23.

2-[[(*p*-Methoxyphenyl)telluro]methyl]-1-oxaspiro[5.5]undecane (19b): a pale yellow oil; IR (liquid film) 2940, 2855, 1585, 1483, 1440, 1280, 1240, 1175, 1070, 1030, 995, 820, 755; ^{1}H NMR 0.8–2.2 (m, 16 H, CH_2), 2.6–4.0 (m, 3 H, $TeCH_2$ and OCH), 3.70 (s, 3 H, OCH_3), 6.63 (d, J = 8 Hz, 2 H, Ar H), 7.57 (d, J = 8 Hz, Ar H); MS, m/z (rel intensity) 404 (M^+, 42), 254 (15), 237 ($CH_3OC_6H_4Te^+$, 51), 222 (14), 149 (70), 135 (77), 108 (43), 93 (28), 81 (40), 67 (83), 55 (70), 41 (base peak). Anal. Calcd for $C_{18}H_{24}O_2Te$: C, 54.04; H, 6.06. Found: C, 54.01; H, 6.00.

2-[[(*p*-Methoxyphenyl)telluro]methyl]-1-oxaspiro[4.6]undecane (20b): a pale yellow oil; IR (liquid film) 2930, 2852, 1583, 1485, 1460, 1280, 1240, 1175, 1030, 820, 760; ^{1}H NMR 1.2–2.2 (m, 16 H, CH_2), 3.00 (d, J = 6 Hz, 2 H, $TeCH_2$), 3.73 (s, 3 H, OCH_3), 3.9–4.3 (m, 1 H, OCH), 6.65 (d, J = 8 Hz, 2 H, Ar H), 7.60 (d, J = 8 Hz, 2 H, Ar H). Anal. Calcd for $C_{18}H_{26}O_2Te$: C, 53.77; H, 6.53. Found: C, 53.54; H, 6.64.

3-[(Phenyltelluro)methyl]-2-oxabicyclo[4.4.0]decane (21a): a pale yellow oil; IR (liquid film) 3050, 2930, 2855, 1570, 1480, 1450, 1440, 1365, 1240, 1110, 1060, 1020, 965, 885, 730; ^{1}H NMR 0.9–2.1 (m, 13 H, CH_2 and CH), 2.7–3.3 (m, 2 H, $TeCH_2$), 3.3–4.0 (m, 2 H, OCH), 7.0–7.3 (m, 3 H, Ar H), 7.6–7.9 (m, 2 H, Ar H); MS, m/z (rel intensity) 360 (M^+, 15), 207 ($PhTe^+$, 22), 153 (M^+ – PhTe, 11), 139 (31), 135 (64), 121 (base peak), 95 (78), 77 (47), 67 (56), 56 (46). Anal. Calcd for $C_{16}H_{22}OTe$: C, 53.68; H, 6.21. Found: C, 53.45; H, 6.21.

3-[[(*p*-Methoxyphenyl)telluro]methyl]-2-oxabicyclo[4.4.0]decane (21b): a pale yellow oil; IR (liquid film) 2940, 2855, 1585, 1490, 1450, 1280, 1240, 1180, 1060, 1020, 820, 755; ^{1}H NMR 0.8–2.2 (m, 13 H, CH_2 and CH), 2.6–3.2 (m, 2 H, $TeCH_2$), 3.2–4.1 (m, 2 H, OCH), 3.70 (s, 3 H, OCH_3), 6.63 (d, J = 8 Hz, 2 H, Ar H), 7.58 (d, J = 8 Hz, 2 H, Ar H); MS, m/z (rel intensity) 390 (M^+, 50), 254 (10), 237 ($CH_3OC_6H_4Te^+$, 31), 153 ($M^+ - CH_3O$-C_6H_4Te, 2), 135 (67), 121 (41), 108 (24), 107 (12), 95 (68), 93 (27), 79 (23), 67 (41), 55 (32), 43 (57), 28 (base peak). Anal. Calcd for $C_{17}H_{24}O_2Te$: C, 52.62; H, 6.25. Found: C, 52.54; H, 6.23.

4-(Phenyltelluro)-2-oxabicyclo[5.4.0]undecane (22a): a pale yellow oil; IR (liquid film) 3070, 2940, 2860, 1575, 1480, 1455, 1440, 1375, 1240, 1110, 1085, 1020, 1000, 920, 880, 735, 700; ^{1}H NMR 0.9–2.1 (m, 13 H, CH_2 and CH), 2.8–3.9 (m, 3 H, $TeCH_2$ and OCH), 4.0–4.5 (m, 1 H, OCH), 7.0–7.3 (m, 3 H, Ar H), 7.5–7.8 (m, 2 H, Ar H); MS, m/z (rel intensity) 360 (M^+, 11), 224 (11), 207 ($PhTe^+$, 25), 153 (M^+ – PhTe, 7), 135 (95), 121 (base peak), 95 (96), 77 (48), 67 (58), 56 (45). Anal. Calcd for $C_{16}H_{22}OTe$: C, 53.68; H, 6.21. Found: C, 53.42; H, 6.21.

4-[[(*p*-Methoxyphenyl)telluro]methyl]-2-oxabicyclo[5.4.0]undecane (22b): a pale yellow oil; IR (liquid film) 2940, 2850, 1585, 1485, 1450, 1280, 1240, 1175, 1105, 1080, 1065, 1030,

820, 760; ^{1}H NMR 0.8–2.5 (m, 13 H, CH_2 and CH), 2.7–3.2 (m, 1 H, TeCH), 3.3–4.3 (m, 3 H, OCH_2 and OCH), 3.67 (s, 3 H, OCH_3), 6.63 (d, J = 8 Hz, 2 H, Ar H), 7.58 (d, J = 8 Hz, 2 H, Ar H); MS, m/z (rel intensity) 390 (M^+, 21), 237 ($CH_3OC_6H_4Te^+$, 16), 153 ($M^+ - CH_3OC_6H_4Te$, 2.5), 135 (34), 121 (38), 95 (36), 79 (38), 67 (25), 55 (29), 28 (base peak). Anal. Calcd for $C_{17}H_{24}O_2Te$: C, 52.62; H, 6.25. Found: C, 52.54; H, 6.23.

2,3-Dihydro-2-[(2-naphthyltelluro)methyl]benzofuran (23c): white crystals from methanol, mp 71–72 °C; IR (KBr disk) 3050, 2940, 1600, 1580, 1480, 1240, 1015, 950, 930, 820, 741; ^{1}H NMR 2.7–3.6 (m, 4 H, CH_2), 4.7–5.2 (m, 1 H, CH), 6.5–7.2 (m, 4 H, Ar H), 7.2–7.8 (m, 6 H, Ar H), 8.16 (s, 1 H, Ar H); MS, m/z (rel intensity) 390 (M^+, 44), 257 ($C_{10}H_7Te^+$, 47), 133 ($M^+ - C_{10}H_7Te$, base peak), 127 (60), 105 (25), 77 (16). Anal. Calcd for $C_{19}H_{16}OTe$: C, 58.82; H, 4.17. Found: C, 58.54; H, 4.11.

2,3-Dihydro-7-methyl-2-[(phenyltelluro)methyl]benzofuran (24a): a pale yellow oil; IR (liquid film) 3050, 2910, 2850, 1595, 1570, 1460, 1430, 1260, 1185, 1068, 1015, 925, 860, 760, 730, 690; ^{1}H NMR 2.13 (s, 3 H, CH_3), 2.7–3.6 (m, 4 H, CH_2), 4.7–5.2 (m, 1 H, CH), 6.5–7.0 (m, 3 H, Ar H), 7.0–7.3 (m, 3 H, Ar H), 7.6–7.9 (m, 2 H, Ar H); MS, m/z (rel intensity) 354 (M^+, 3), 207 ($PhTe^+$, 10), 154 (27), 147 ($M^+ - PhTe$, base peak), 131 (29), 119 (31), 115 (21), 91 (31), 77 (47). Anal. Calcd for $C_{16}H_{16}OTe$: C, 54.60; H, 4.59. Found: C, 54.11; H, 4.39.

2,3-Dihydro-2-[[(*p*-methoxyphenyl)telluro]methyl]-7-methylbenzofuran (24b): a pale yellow oil; IR (liquid film) 3025, 2950, 2845, 1580, 1465, 1490, 1460, 1440, 1280, 1245, 1180, 1025, 910, 825, 760, 725, 590, 519; ^{1}H NMR 2.13 (s, 3 H, CH_3), 2.8–3.5 (m, 4 H, CH_2), 3.73 (s, 3 H, OCH_3), 4.7–5.2 (m, 1 H, CH), 6.68 (d, J = 8 Hz, 2 H, Ar H), 6.5–7.0 (m, 3 H, Ar H), 7.65 (d, J = 8 Hz, 2 H, Ar H); MS, m/z (rel intensity) 384 (M^+, 32), 237 ($CH_3OC_6H_4Te^+$, 66), 222 (12), 220 (11), 147 ($M^+ - CH_3OC_6H_4Te$, base peak), 145 (22), 119 (20), 108 (11), 91 (16), 77 (12). Anal. Calcd for $C_{17}H_{18}O_2Te$: C, 53.45; H, 4.76. Found: C, 53.31; H, 4.52.

Synthesis of 8-Oxabicyclo[3.3.0]oct-2-ene (33) by Telluroxide Elimination of 8-(Phenyltellurinyl)-2-oxabicyclo[3.3.0]octane (32). The cyclofunctionalization of 2-cyclopent-2-enylethanol (**31**) (0.152 g, 1.35 mmol) with benzenetellurinyl acetate (**2a**) (1.48 mmol) in chloroform (6 mL) was carried out by the general method B. The reaction solution containing crude telluroxide **32** was diluted with chloroform (25 mL), washed with brine, and evaporated under reduced pressure. To the residue were successively added tetrahydrofuran (5 mL) and aqueous sodium hydroxide solution (0.5 M, 10 mL). The resulting mixture was stirred at reflux for 5 h, poured into water, and extracted with ether (20 mL × 2). The extract was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on silica gel with dichloromethane–hexane (5:2) to give 8-oxabicyclo[3.3.0]oct-2-ene (**33**)[19] (0.079 g, 53%) as a colorless oil: IR (liquid film) 3077, 2950, 2850, 1460, 1360, 1240, 1175, 1060, 1035, 990, 935, 900, 717; ^{1}H NMR 1.6–3.0 (m, 5 H, CH and CH_2), 3.5–4.0 (m, 2 H, OCH_2), 5.12 (d, J = 6 Hz, 1 H, OCH), 5.65 (m, 1 H, =CH), 5.85 (m, 1 H, =CH).

Synthesis of 8-Oxabicyclo[3.3.0]oct-2-ene (33) by Reaction of 8-(Phenyltelluro)-2-oxabicyclo[3.3.0]octane (15a) with Chloramine-T. To a solution of **15a** (0.32 g, 1.01 mmol) in tetrahydrofuran (6 mL) was added anhydrous chloramine-T (0.34 g, 1.5 mmol), and the resulting mixture was stirred at reflux for 1 h. After evaporation of the solvent, the residue was taken up with ether (25 mL), and the ethereal solution was washed with water and dried over $MgSO_4$. After removal of the solvent the residue was chromatographed on silica gel with dichloromethane–hexane (5:2) as eluant to afford 8-oxabicyclo[3.3.0]-oct-2-ene (**33**) (0.091 g, 82%) as a colorless oil, which was consistent in all respects with the product from telluroxide elimination of **32**.

Synthesis of 8-Bromo-2-oxabicyclo[3.3.0]octane (35) from 15a. Into a stirred solution of **15a** (0.316 g, 1.0 mmol) in 5 mL of dimethylformamide was slowly added a solution of bromine (0.32 g, 2 mmol) in dimethylformamide (2 mL) at 0 °C. The solution was stirred for 10 min at room temperature, and sodium bromide (0.155 g, 1.5 mmol) was added. The resulting mixture was then heated with stirring at 90 °C for 3 h. After the mixture was cooled to room temperature, it was quenched with water and extracted with ether. The organic layer was washed with brine and dried over $MgSO_4$. Evaporation of the solvent left a red oil, which was subjected to column chromatography (silica gel) with dichloromethane–hexane (5:2) as eluant to give 8-bromo-2-oxabicyclo[3.3.0]octane (**35**) (0.166 g, 87%) as a colorless oil: IR (liquid film) 2950, 2860, 1450, 1300, 1260, 1220, 1180, 1170, 1070, 1040, 980, 930, 905, 865, 730; ^{1}H NMR (90 MHz) 1.1–2.5 (m, 6 H, CH_2), 2.5–3.0 (m, 1 H, CH), 3.7–4.7 (m, 4 H, OCH_2, OCH, and BrCH); MS, m/z (rel intensity) 192 ($M^+ + 2$, 9), 190 (M^+, 10), 83 (base peak), 56 (17), 46 (46); exact mass calcd for $C_7H_{11}BrO$ 189.9993, found (high-resolution mass spectrum) 189.9952.

Synthesis of 2,3-Dihydro-2-methylbenzofuran (36) by Reduction of 2,3-Dihydro-2-[(phenyltelluro)methyl]benzofuran (23a). To a solution of **23a** (0.338 g, 1 mmol) in toluene (6 mL) was injectd tributyltin hydride (0.67 mL, 2.5 mmol) at room temperature, and the resulting solution was stirred at reflux for 1 h. The solution was evaporated under a reduced pressure and the residual yellow oil was subjected to column chromatography (silica gel) with benzene–hexane (3:1) as eluant to give pure 2,3-dihydro-2-methylbenzofuran (**36**)[5] (0.128 g, 95%) as a colorless oil, bp 93–94 °C/23 mmHg: IR (liquid film) 3045, 2975, 2920, 1595, 1475, 1460, 1375, 1330, 1225, 1030, 1015, 905, 860, 820, 750, 710; ^{1}H NMR 1.42 (d, J = 6 Hz, 3 H, CH_3), 3.02 (dq due to ABX, J_1 = 9 Hz, J_2 = 15 Hz, 2 H, CH_2), 4.5–5.1 (m, 1 H, OCH), 6.5–7.2 (m, 4 H, Ar H).

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