4, 115981-41-4; 5, 115981-42-5; 6, 115981-43-6; 7, 115981-44-7; 8, 115981-45-8; 9, 115981-46-9; 10, 115981-47-0; 11, 115981-48-1; bpy, 366-18-7; $NiMe_2$(bpy), 32370-42-6; $NiEt_2$(bpy), 15218-76-5; $NiMe_2$(dpe), 31387-22-1; $PeMe_2$(dpe), 63455-39-0; $HOCH(CF_3)_2$, 920-66-1; $HOCH_2CF_3$, 75-89-8; $HOCH(CF_3)C_6H_5$, 340-04-5; HSC_6H_5, 108-98-5; HSC_6H_4-*p*-CH_3, 106-45-6; CH_4, 74-82-8; C_2H_4, 74-85-1; C_2H_6, 74-84-0; $CF_3COC_6H_5$, 434-45-7; $CH_3COOCH(CF_3)_2$, 6919-79-5; $CH_3CH_2COOCH(CF_3)_2$, 24499-62-5; $CH_3COSC_6H_5$, 934-87-2; $CH_3COSC_6H_4$-*p*-CH_3, 10436-83-6; $CH_3COOCH(CF_3)C_6H_5$, 84194-69-4; $CH_3COOCH_2CF_3$, 406-95-1.

Preparation of "Unnatural" Tellurium Analogues of Naturally Occurring Chromones and Flavones. The Control of Ipso vs Ortho Acylation, Selective Demethylation, and Olefin-Forming Condensation Reactions in Benzo[*b*]tellurapyranones

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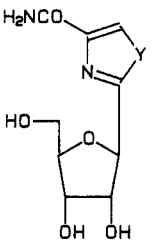
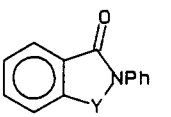
Several factors controlling the intramolecular acylations of β-(arylchalcogeno)cinnamoyl chlorides were examined. Aryltelluro groups were more highly activated toward electrophilic attack than the corresponding arylthio and arylseleno groups. Tellurium analogues of several naturally occurring, highly oxygenated chromones and flavones were prepared including eugenin (2-methyl-5-hydroxy-7-methoxy-4*H*-1-benzo[*b*]pyran-4-one), techtochrysin (2-phenyl-5-hydroxy-7-methoxy-4*H*-1-benzo[*b*]pyran-4-one), dimethylapigenin [2-(4-methoxyphenyl)-5-hydroxy-7-methoxy-4*H*-1-benzo[*b*]pyran-4-one], and trimethylluteolin [2-(3,4-dimethoxyphenyl)-5-hydroxy-7-methoxy-4*H*-1-benzo[*b*]pyran-4-one]. These compounds were prepared from the corresponding 5-methoxy-4*H*-1-benzo[*b*]tellurapyran-4-ones by reaction with boron trifluoride etherate to give difluoroboronate complexes of the 4*H*-1-benzo[*b*]tellurapyran-4-ones by demethylation at the 5-position and difluoroboronate complexation at the 5-oxo substituent and the 4*H*-1-benzo[*b*]tellurapyran-4-one carbonyl oxygen. The difluoroboronate complexes were isolable and represent novel heterocyclic structures. 5-Methoxy-4*H*-1-benzo[*b*]tellurapyran-4-thione (**36**) formed difluoroboronate complex **37** upon treatment with boron trifluoride etherate. Hydrolysis of the difluoroboronates gave the phenolic 5-hydroxy-4*H*-1-benzo[*b*]tellurapyran-4-ones. The difluoroboronate complex **34a**, bearing a 2-methyl substituent, was activated toward condensation reactions of the 2-methyl substituent with various aldehydes and ketones to give styryltellurachromones **38–41** allowing synthetic entry to the hormothamnione (**6**) skeletal framework. In 2-methyl-4*H*-1-benzo[*b*]tellurapyran-4-ones lacking a 5-methoxy substituent, the 2-methyl substituent was activated toward condensation reactions by reaction with ethyl fluorosulfonate. 2-Methyl-4-ethoxy-7-methoxy-4*H*-1-benzo[*b*]tellurapyrylium fluorosulfonate (**44**) reacted with various aldehydes and ketones to give styryl-4*H*-1-benzo[*b*]tellurapyrylium salts **45–48**. Both the difluoroboronate complexes and the 4-ethoxy-4*H*-1-benzo[*b*]tellurapyrylium salts could be hydrolyzed to the corresponding styrylchromones. 2-Methyl substituents in 4*H*-1-benzo[*b*]tellurapyrylium species were much more reactive in condensation reactions than the corresponding 4*H*-1-benzo[*b*]pyrylium species.

The biological activity of heterocyclic systems containing the heavier chalcogen atoms selenium and tellurium have been little explored. The recent literature contains examples of heterocyclic systems in which the heavier chalcogens impart a biological activity not observed with the oxygen and/or sulfur analogues. Tiazofurin [**1**, 2-(β-D-ribofuranosyl)-thiazole-4-carboxamide][1] and selenazofurin [**2**, 2-(β-D-ribofuranosyl)selenazole-4-carboxamide][2] have been shown to be effective antitumor agents in animals. Selenazofurin has been shown to possess broad-spectrum antiviral activity in cell culture experiments, as well.[3] The oxazole analogue **3** does not display such biological activity. 2-Phenyl-1,2-benzisoselenazol-3(2*H*)-one (**4**, ebselen) exhibits GSH-peroxidase-like activity in vitro while its sulfur analogue, **5**, is inactive.[4]

We have been interested in developing synthetic routes to selenium and tellurium analogues of the naturally occurring chromones and flavones in order to compare the effects of chalcogen substitution on biological activity. The chromones, flavones, pyranones, and related compounds are widespread in the plant kingdom from algae[5] to conifers.[6] Flavones and chromones have been found to be



1, Y=S
2, Y=Se
3, Y=O



4, Y=Se
5, Y=S

(1) Robins, R. K.; Srivastiva, P. C.; Narayanan, V. L.; Plowman, J.; Paull, K. D. *J. Med. Chem.* **1982**, *25*, 107.
(2) Srivastava, P. C.; Robins, R. K. *J. Med. Chem.* **1983**, *26*, 445.
(3) Kirsi, J. J.; North, J. A.; McKernan, P. A.; Murry, B. K.; Canonico, P. G.; Huggins, J. W.; Srivastava, P. C.; Robins, R. K. *Antimicrob. Agents Chemother.* **1983**, *24*, 353.
(4) (a) Dereu, N.; Romer, A.; Sies, H. *Proc. 5th International Symposium on the Chemistry of Selenium and Tellurium* **1987**, 000. (b) Lambert, C.; Cantineau, R.; Christiaens, L.; Biedermann, J.; Dereu, N. *Bull. Soc. Chim. Belg.* **1987**, *96*, 383.
(5) Gerwick, W. H.; Lopez, A.; Van Duyne, G. D.; Clardy, J.; Ortiz, W.; Baez, A. *Tetrahedron Lett.* **1986**, *27*, 1979.
(6) (a) Dean, F. M. *Naturally Occurring Oxygen Ring Compounds*, Butterworths: London, 1963. (b) Ellis, G. P., Ed. *Heterocyclic Compounds: Chromenes, Chromanones and Chromones*; Wiley: New York, 1977. (c) Swain, T. "Nature and Properties of Flavanoids", In *Chemistry and Biochemistry of Plant Pigments*; Goodwin, T. W., Ed.; Academic: London, 1976.

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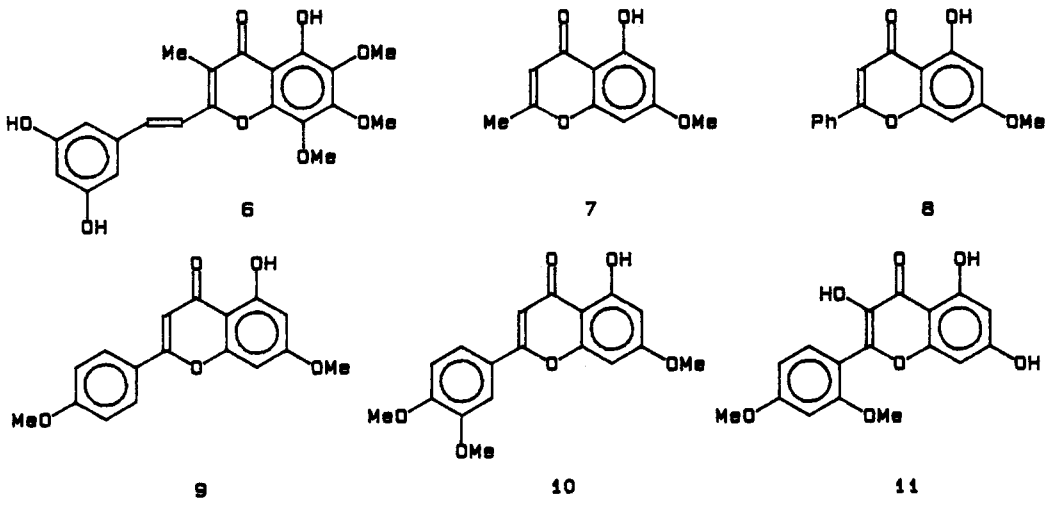
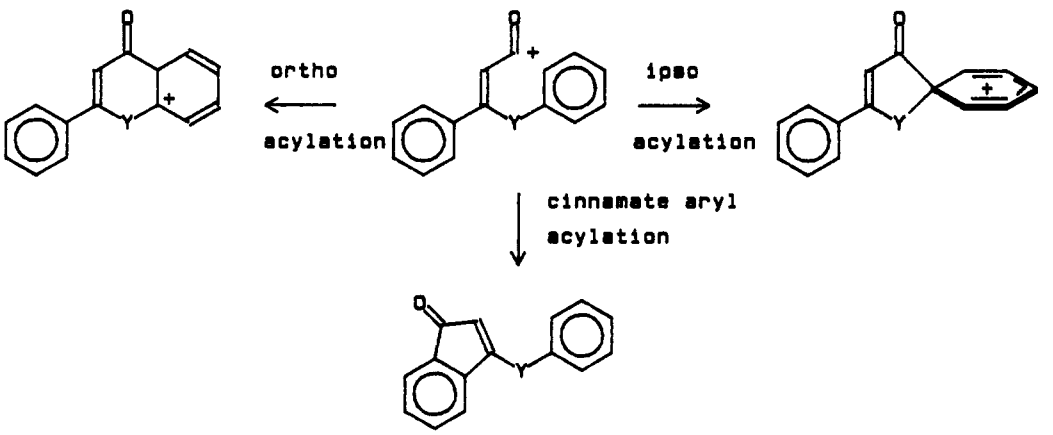
Chart I



Scheme I



active in a number of plant cycles, including growth regulation,[7] indoleacetic acid oxidation,[8] and dormancy inhibition,[9] as well as exhibiting cytokinin-type behavior[10] and stimulating oxygen uptake in plant tissues.[11] The furochromone khellin has lipid-altering capabilities,[12] while the styrylchromone hormothamnione (**6**) has been found to be a potent cytotoxic agent for P388 lymphocytic leukemia and HL-60 human promyelocytic cell lines in vitro.[5]

The naturally occurring chromones and flavones are characterized by highly oxygenated aromatic A rings fused to the pyranone ring as represented by hormothamnione (**6**), eugenin (**7**, the first alkoxychromone identified in nature, from wild clove, *Eugenia caryophyllata*),[13] and techtochrysin (**8**) (Chart I). In the flavone and flavanoid systems, the B ring (the 2-substituent) is often oxygenated as well. Dimethylapigenin (**9**) bears a *p*-anisyl substituent at the 2-position while 3′,4′,7-trimethylluteolin (**10**) bears a 3,4-dimethoxyphenyl substituent at the 2-position (Chart I). The flavanoid morin (**11**) carries a 2,4-dimethoxyphenyl substituent at the 2-position (Chart I).

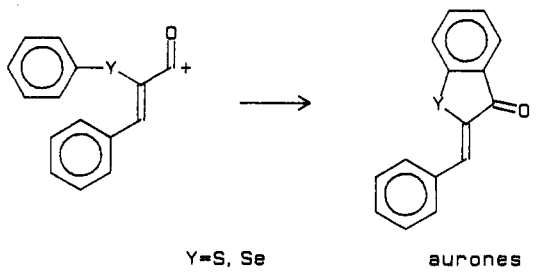
We have reported the intramolecular cyclizations of β-(arylchalcogeno)cinnamates to benzo[*b*]thia-, benzo[*b*]selena-, and benzo[*b*]tellurapyranones—the chalcogenachromones and -flavones.[14,15] The presence of highly activated rings in either the cinnamate aryl group or the chalcogen-bearing aryl group can lead to unwanted side reactions. Intramolecular acylation of the cinnamate aryl group has been observed[14] while ipso acylation into the arylchalcogeno group has complicated intramolecular acylations of β-(aryltelluro) and β-(arylseleno)cinnamoyl chlorides.[15] These cyclization pathways are illustrated in Scheme I.

In cyclizations of this type, substituent effects in both the cinnamate aryl group and the arylchalcogeno group have not been well-defined. However, the ease of preparation of β-(arylchalcogeno)cinnamates from propiolate esters[16] makes this an attractive route to chromone and flavone analogues.

We report the total syntheses of several tellurium analogues of naturally occurring chromones and flavones and introduce synthetic methodology to prepare styryltellurachromones with the skeletal carbon framework of hormathamnione (**6**). In completing this study, several aspects of the chemistry of tellurium relative to the other chalcogens were investigated including the ability of a

(7) Mandava, N. B. In *Plant Growth Substances*; Mandava, N. B., Ed.; ACS Symposium Series 136; American Chemical Society: Washington, DC, 1979; p 135.
(8) Thiman, K. V. In *Plant Physiology*; Steward, F. C., Ed.; Academic: New York, 1972; Vol. VIb.
(9) Isogi, Y.; Komoda, Y.; Okamoto, T. *Chem. Pharm. Bull.* **1970**, *18*, 1872.
(10) Hendershott, C. H.; Walker, D. R. *Science (Washington, D.C.)* **1959**, *130*, 798.
(11) Greimal, A.; Koch, H. *Biochem. Physiol. Pflan.* **1977**, *171*, 425.
(12) (a) Yamashita, A. *J. Am. Chem. Soc.* **1985**, *107*, 5823. (b) Gammill, R. B.; Day, C. E.; Schurr, P. Ed. *J. Med. Chem.* **1983**, *26*, 1672.
(13) (a) Meijer, T. M. *Recl. Trav. Chim. Pays-Bas* **1946**, *65*, 843. (b) Schmid, H.; Meijer, T. M. *Helv. Chim. Acta* **1948**, *31*, 748.
(14) Wadsworth, D. H.; Detty, M. R. *J. Org. Chem.* **1980**, *45*, 4611.
(15) Detty, M. R.; Murray, B. J. *J. Am. Chem. Soc.* **1983**, *105*, 883.
(16) The preparation of methoxylated arylpropiolates has been recently described: Wadsworth, D. H.; Geer, S. M.; Detty, M. R. *J. Org. Chem.* **1987**, *52*, 3662.

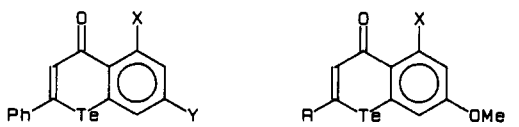
Scheme II



tellurium atom to activate aromatic rings to electrophilic attack and the ability of a tellurapyrylium nucleus to "activate" a 2-methyl substituent to condensation reactions. The benzo[*b*]tellurapyrylium boronates described herein are novel heterocyclic structures. This method of making analogues of compounds of biological interest illustrates the challenge of introducing the heavier main-group elements to the hydrocarbon backbone and of controlling the more varied reaction pathways available to the heavier main-group elements.

Results and Discussion

Construction of the Benzo[*b*]tellurapyranone Ring System. The approach to tellurium analogues of the naturally occurring chromones and flavones is illustrated by the preparation of **12** and **13**,[15] involving the intramo-



12a, X=OMe, Y=H
12b, X=H, Y=OMe
12c, X=Y=OMe

13a, R=H, X=OMe
13b, R=Me, X=OMe
13c, R=H, X=H
13d, R=Me, X=H

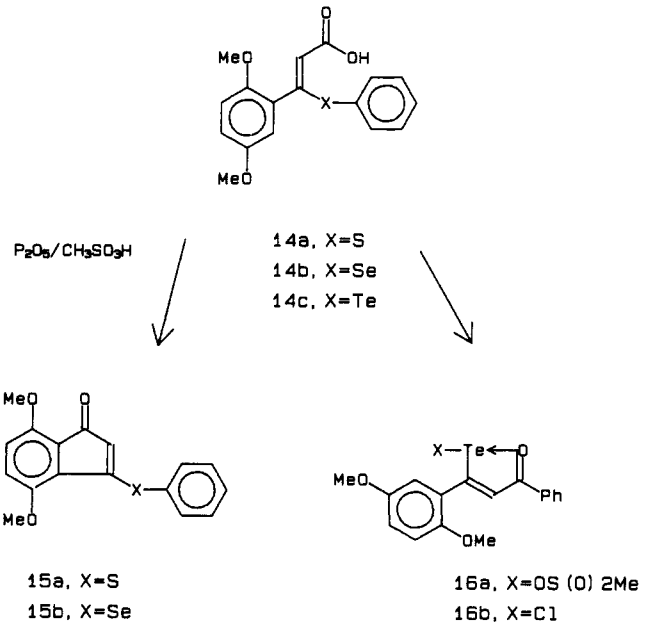
lecular acylation of a β-(aryltelluro)cinnamate or -butenoate ester to give the benzo[*b*]tellurapyranone ring. Similar cyclizations with highly activated cinnamate aryl groups would allow entry to several classes of tellurium analogues of naturally occurring flavones.

We have reported the intramolecular cyclizations of α-(arylchalcogeno)cinnamates (Scheme II) to thio- and selenoaurones[14] and of β-(arylchalcogeno)cinnamates to benzo[*b*]thia-, benzo[*b*]selena-, and benzo[*b*]tellurapyranones.[14,15] In (arylthio)- and (arylseleno)cinnamates of this type, where the cinnamate aryl group is highly activated with one or more methoxy substituents, intramolecular cyclization into the cinnamate aryl group or onto a methoxy oxygen leads to indenone-, coumarin-, or phenalenone-type products[14] instead of aurone or benzo[*b*]-pyranone products. Since many of the flavone B rings are highly activated to electrophilic attack with 2,4-, 3,4-, 2,5-, or 3,5-dihydroxy and/or 2,4-, 3,4-, 2,5-, or 3,5-dimethoxy substituents, competitive acylation of the cinnamate aryl group was viewed as a potential problem.

Cyclizations of β-(arylseleno)- and β-(aryltelluro)-cinnamates and -butenoates have also been complicated by the formation of oxaselenolylium halides and oxatellurolylium halides, respectively, through ipso attack on the arylchalcogeno ring by the acylium ion intermediate.[17]

(17) Detty, M. R.; Murray, B. J.; Smith, D. L.; Zumbulyadis, N. *J. Am. Chem. Soc.* **1983**, *105*, 875.
(18) The isolation of the flavone products is described in: Jaipetch, T.; Reutrakul, V.; Tuntiwachwuttikul, T.; Santisuk, T. *Phytochemistry* **1983**, *22*, 625.

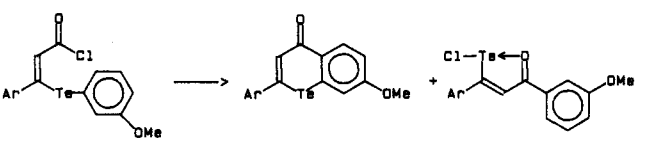
Scheme III



15a, X=S
15b, X=Se

16a, X=OS (O) 2Me
16b, X=Cl

Scheme IV



17a, Ar=4-Methoxyphenyl
17b, Ar=3, 4-Dimethoxyphenyl
17c, Ar=2, 5-Dimethoxyphenyl

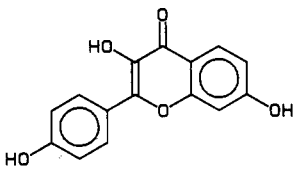
18 19

The judicious choice of substituents on the chalcogen-bearing aryl group gives some control over the ratio of ipso to ortho acylation.[15] The choice of substituents in both the A and B rings of the flavone analogues might limit synthetic routes to these compounds.

The addition of phenyl chalcogenide anions to ethyl 2,5-dimethoxyphenylpropiolate[14] gives β-(phenylchalcogeno)cinnamic acids **14** following saponification of the esters. Treatment of the acids **14** with phosphorus pentoxide in methanesulfonic acid gave benzocyclopentenones **15** for the phenylthio and phenylseleno derivatives but gave the oxatellurolylium mesylate **16a**, as an unstable oil, for the phenyltelluro derivative **14c** (Scheme III). The more stable oxatellurolylium chloride **16b** could be prepared by converting acid **14c** to the cinnamoyl chloride with oxalyl chloride followed by the aluminum chloride promoted rearrangement of the cinnamoyl chloride to **16b**. Apparently, the phenyl group bearing tellurium is much more activated to electrophilic attack than the phenyl groups bearing sulfur or selenium.

Since tellurium appears to activate strongly an aryl ring, competitive cyclization into the cinnamate aryl group should not be problematic in cyclization of β-(aryltelluro)cinnamates. Cyclization of β-((3-methoxyphenyl)telluro)cinnamates **17** should produce telluraflavones **18** with methoxy-substituted B rings by analogy with the cyclizations to give flavones **12** and chromones **13** (although substituted cinnamate aryl groups have not been utilized in this context).[15] As shown in Scheme IV, these cyclizations produce the telluraflavones **18** in good yield. Small amounts (5%) of the oxatellurolylium chlorides **19** could be detected in the ^{1}H NMR spectra of the crude reaction mixtures although these materials were not isolated.

Compounds **18a** and **18b** are analogues of the naturally occurring 3,4′,7-trihydroxyflavone (**20**) and 3,3′,4′,7-tetrahydroxyflavone (**21**, fisetin).[6b] The natural products have been shown to possess anti-inflammatory activity.[19]



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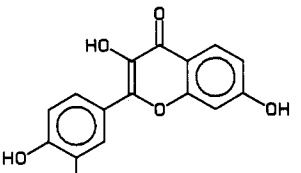
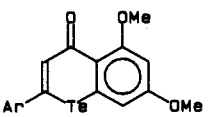
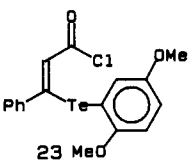


21

The importance of substituent control in the cyclization of β-(aryltelluro)cinnamates can be illustrated by comparing the cyclization of different disubstituted (aryltelluro)cinnamates. (3,5-Dimethoxyphenyl)telluro-substituted cinnamates and alkenoates cyclize to give benzo[*b*]tellurapyranones **12**[15] and **22**. The aluminum chloride catalyzed cyclization of β-((2,5-dimethoxyphenyl)telluro)cinnamoyl chloride (**23**), on the other hand, gave oxatelurolylium chloride **24** as the only product. None of the telluraflavone could be detected by ^{1}H NMR. The factors that determine the ratio of ipso and ortho acylation appear to be balanced delicately in these systems.





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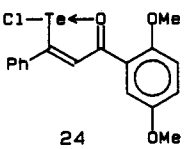
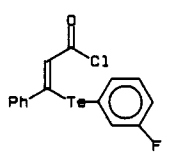


24

22a, Ar=4-Methoxyphenyl
22b, Ar=3, 4-Dimethoxyphenyl
22c, Ar=2, 5-Dimethoxyphenyl

β-(3-Fluorophenyl)telluro)cinnamoyl chloride (**25**) gave 7-fluorotelluraflavone (**26**) in 5% yield and oxatellurolylium chloride **27** in 78% yield.[15] We had hoped



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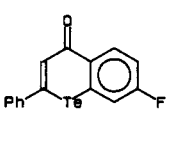

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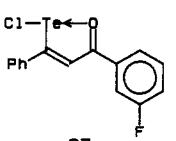
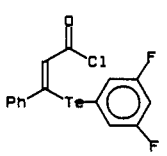


27

that the addition of a second fluoro group in the cinnamoyl chloride would produce much more of the flavone during cyclization. β-((3,5-difluorophenyl)telluro)cinnamoyl chloride (**28**) upon treatment with aluminum chloride at 0 °C gave telluraflavone **29** in only 18% isolated yield. The major product of this cyclization was oxatellurolylium chloride **30**.



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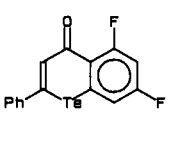

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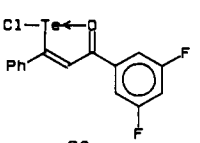
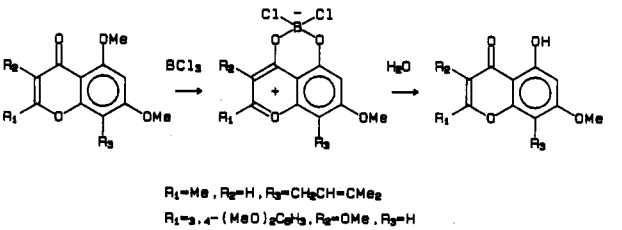


30

The benzo[*b*]tellurapyranones **12b**, **12c**, **22a**, and **22b** all have chromone and flavone analogues that are naturally occurring.[18] However, we were more interested in preparing tellurium analogues of the phenolic chromones and flavones (which have been found to have greater biological activity than their methyl ether counterparts).[19]

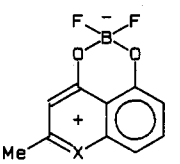
(19) Gabor, M. *Prog. Clin. and Bio. Res.* **1986**, *213*, 471.

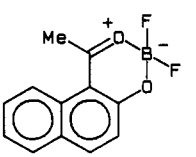
Scheme V

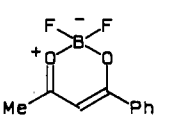


Preparation of Boronate Complexes of Benzo[*b*]-tellurapyranones. Demethylation at the 5-position of the tellurachromones and telluraflavones appeared to be the most direct route to the phenolic analogues. A few 5-methoxychromones and 5-methoxyflavones have been converted to the phenolic chromones and flavones, as shown in Scheme V, by treatment with boron trichloride followed by rapid hydrolysis of the intermediate dichloroboronate.[20] The dichloroboronate intermediates were not isolated. In these systems, boron trichloride appears to be specific for the formation of the boronate to the oxygen functionality at the 4- and 5-positions.

We were interested in forming boronates that would be more stable to hydrolysis in order to accomplish two transformations with one intermediate. In a boronate structure such as **31**, the formal positive charge in the benzo[*b*]chalcogenapyrylium ring should activate the 2-methyl substituent toward condensation reactions by decreasing the pK_α of the carbon acid. Boronates **32** and **33**,







31, X=O, S, Se, Te **32** **33**

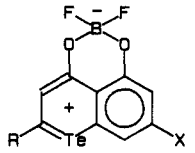
bearing a methyl group adjacent to a ketone functionality, condense with various aldehydes and ketones to give boronate dyes.[21] Boronates of tellurachromone **13b**, in addition to demethylating the 5-methoxy substituent, should condense with aldehydes and ketones to give 2-styryltellurachromones following hydrolysis.

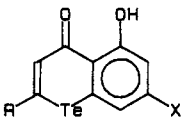
Boronate complexes from boron trifluoride have been found to be more stable hydrolytically than those from boron tribromide and boron trichloride.[21,22] We prepared a series of difluoroboronate complexes **34** be heating 5-methoxy-bearing benzo[*b*]tellurapyranones in boron trifluoride etherate. The benzo[*b*]tellurapyrylium boronate complexes **34** were isolated as crystalline solids in good yield (Table I) and were bright yellow to orange dyes in solution (Table I). These compounds are the first heavier chalcogen analogues of boronate complexes of chromones and flavones to be prepared.

The solid difluoroboronates could be stored at ambient temperature in glass vials on the shelf without any significant hydrolysis after several months. However, stirring acetonitrile solutions of the difluoroboronates with saturated sodium bicarbonate gave the phenolic benzo[*b*]tellurapyranones **35** in quantitative yield.

Compound **35a** is the tellurium analogue of the chromone eugenin (**7**), compound **35c** is the tellurium analogue

(20) Dean, F. M.; Goodchild, J.; Houghton, L. E.; Martin, J. A.; Morton, R. B.; Parton, B.; Price, A. W.; Somvichien, N. *Tetrahedron Lett.* **1966**, 4153.
(21) VanAllan, J. A.; Reynolds, G. A. *J. Heterocycl. Chem.* **1969**, *6*, 29.
(22) Kaestner, D. *Newer Methods of Preparative Organic Chemistry*; Interscience: London, 1948; p 249.



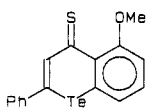


35

34a, R=Me, X=OMe
34b, R=Ph, X=H
34c, R=Ph, X=OMe
34d, R=4-Methoxyphenyl, X=OMe
34e, R=3, 4-Dimethoxyphenyl, X=OMe
34f, R=2, 5-Dimethoxyphenyl, X=OMe

of the flavone techtochrysin (8), and compound **35d** is the tellurium analogue of the flavone dimethylapigenin (9). Dimethylapigenin (9) has been found to exhibit anti-inflammatory behavior.[23] Compound **35e** is the tellurium analogue of naturally occurring 3′,4′,7-trimethylluteolin (10). Luteolin derivatives have been examined for their mutagenic activity.[24,25]

The formation of boronate esters of benzo[*b*]tellurapyranones could be extended to thione analogues of these compounds. 2-Phenyl-5-methoxybenzo[*b*]tellurapyranone was converted to its thione analogue **36** with the Lawesson reagent.[26] When **36** was heated with boron trifluoride etherate, boronate **37** was isolated in excellent yield (Table I).



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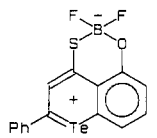

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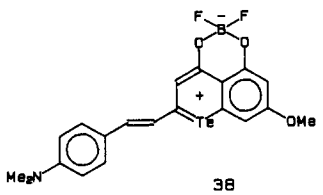
Preparation of Styrylchromones. The condensation of **34a** with various aldehydes and ketones in acetic anhydride gave dyes **38–41** in modest yield (Table II) as very



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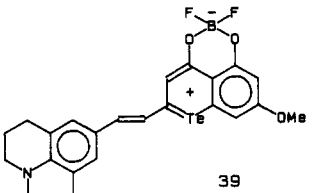

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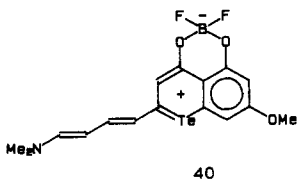

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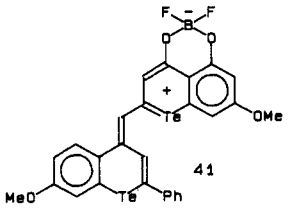


41

insoluble crystalline solids. Hydrolysis of **38** and **39** with sodium carbonate in aqueous acetonitrile gave styrylchromones **42** and **43**. The overall conversions of **34a** to **42** and **43** demonstrate the selective demethylation of a 5-methoxy substituent and the activation of a 2-methyl

(23) Fourie, T. G.; Snyckers, F. O. *J. Nat. Prod.* **1984**, *47*, 1057.
(24) Ulubelan, A.; Miski, M.; Johansson, C. *Doga Bilim Derg., Seri C* **1984**, *8*, 109.
(25) Elliger, C. A.; Henika, P. R.; MacGregor, J. T. *Mutat. Res.* **1984**, *135*, 77.
(26) (a) Schiebye, S.; Kristensen, J.; Lawesson, S. O. *Tetrahedron* **1979**, *35*, 1339. (b) Detty, M. R.; Murray, B. J. *J. Org. Chem.* **1982**, *47*, 1146.

Table I. Physical and Spectral Properties of Benzo[*b*]tellurapyrylium Difluoroboronates

compd	isolated yield, %	mp, °C	λ_{max},[a] nm	log ε
34a	91	239–242	480	3.93
34b	73	204–205	505	3.85
34c	72	224.5–226.5	488	3.84
34d	66	246–249	492	3.96
34e	96	240–243	490	3.95
34f	83	304–306	491	4.03
37	95	182 dec	518	3.96

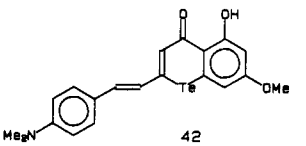
[a] In CH_2Cl_2 solution.

Table II. Physical and Spectral Properties of Benzo[*b*]tellurapyrylium Species with Extended Chromophores

compd	isolated yield, %	mp, °C	λ_{max},[a] nm	log ε
38	20	200–206 dec	715	4.93
39	53	190–195 dec	822	4.57
			744	4.80
40	46	188–192	588	4.81
41	25	160–166 dec	742	4.33
43	59	163–167 dec	695	4.98
44	17	175–178 dec	780	4.95
45	67	175–179	753	4.97
46	16	204 dec	720	4.60

[a] In CH_2Cl_2 solution.

substituent to condensation reactions in 2-methyl-5-methoxybenzo[*b*]tellurapyranones through a boronate intermediate.



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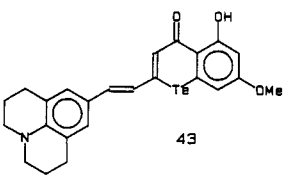
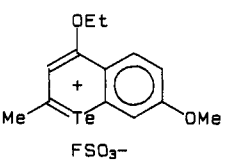


43

In tellurachromones lacking the oxygen functionality in the 5-position, a 2-alkyl substituent could be activated toward condensation reactions by generating a 4-alkoxybenzo[*b*]tellurapyrylium salt. The addition of ethyl fluorosulfonate to chromone **13a** generated benzo[*b*]tellurapyrylium salt **44**. Compound **44** condensed with several different aldehydes to generate dyes **45–48** (Table II). Hydrolysis of **45** generated styrylchromone **49**.



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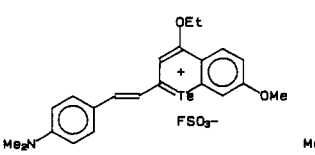

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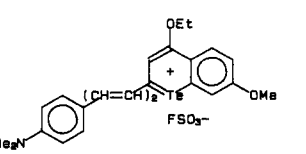
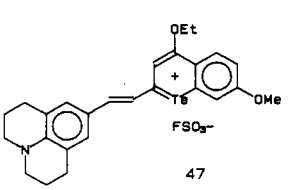


46



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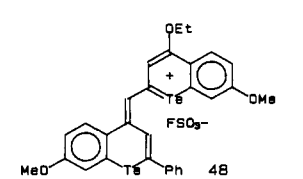
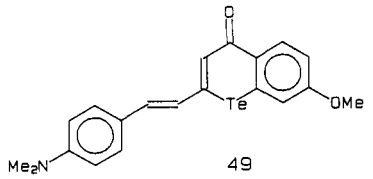


48

The reactivity of the 2-methylbenzo[*b*]tellurapyrylium compounds **34a** and **44** toward condensation reactions with



49

aldehydes and ketones is much greater than the corresponding 2-methylbenzo[*b*]pyrylium compounds **50** and **51**. Condensation reactions of **34a** and **44** were complete within 3–10 min while condensation reactions of **50** and **51** (with identical substrates) required 3–10 h for completion.[27]

Summary and Conclusions

The syntheses of several tellurium analogues of naturally occurring chromones and flavones have been completed. The tellurium atom in these molecules relative to an oxygen atom limits the general applicability of intramolecular acylation approaches to the tellurium derivatives. Ipso acylation of the tellurium-bearing ring complicates cyclization of β-(aryltelluro)cinnamates if substituents other than 5-methoxy or 5,7-dimethoxy are present.

The generation of styryltellurachromones from condensation reactions of 2-alkylbenzo[*b*]tellurapyrylium compounds is facilitated by the presence of the tellurium atom relative to an oxygen atom. The organotellurium compounds are approximately 60 times more reactive than the corresponding 2-alkylbenzo[*b*]pyrylium compounds.

The conversion of a 2-methyl-5-methoxybenzo[*b*]tellurapyranone to a 2-styryl-5-hydroxybenzo[*b*]tellurapyranone via a benzo[*b*]tellurapyrylium boronate intermediate allows both a selective demethylation of a 5-methoxy substituent and the activation of a 2-methyl substituent toward condensation reactions. This approach should have general utility in the construction of styrylchromones. In particular, the construction of the styryl unit of hormothamnione (**6**) and the introduction of the 5-hydroxy substituent might be accomplished via this sequence.

The biological properties of organotellurium compounds are being investigated. The synthetic techniques described for styrylchromone formation are being applied to the total syntheses of hormothamnione (**6**) and its sulfur, selenium, and tellurium analogues.

Experimental Section

Melting points were determined on a Thomas-Hoover melting-point apparatus and are corrected. ^{1}H NMR spectra were recorded on a General Electric QE-300 spectrometer. Infrared spectra were recorded on a Beckman IR 4250 instrument. UV–visible spectra were recorded on a Cary 17 spectrophotometer. Solvents were obtained from Kodak Laboratory Chemicals and were stored over 3A molecular sieves prior to use. Tetrahydrofuran (THF) and diethyl ether were dried over sodium benzophenone ketyl prior to use. Microanalyses were performed at Kodak on a Perkin-Elmer C, H, and N analyzer. Tellurium analyses were performed by atomic absorption spectroscopy with ±1% accuracy.

Preparation of β-(Phenylthio)-2,5-dimethoxycinnamic Acid (14a). Phosphorus Pentoxide–Methanesulfonic Acid Cyclization[28] to Benzocyclopentenone 15a. Sodium methoxide (0.27 g, 5 mmol) was added to a solution of thiophenol (0.50 g, 4.55 mmol) in 10 mL of methanol. After the solution was stirred 0.5 h at ambient temperature, methyl (2,5-dimethoxyphenyl)-propiolate (1.00 g, 4.55 mmol) in 5 mL of methanol was added. The resulting solution was stirred 1 h at ambient temperature. The methanolic solution was diluted with 5 mL of water, and solid potassium hydroxide (0.6 g) was added. The resulting mixture was heated on a steam bath for 1 h. The reaction mixture was diluted with 50 mL of water. The aqueous solution was extracted with ether (3 × 25 mL). The aqueous phase was acidified with 10% HCl. A white solid precipitate that was collected by filtration and washed with several portions of water. The acid was recrystallized from acetonitrile to give 0.96 g (64%) of 2,5-dimethoxycinnamic acid: mp 152–155 °C (lit.[14] mp 141–144 °C); ^{1}H NMR ($CDCl_3$) δ 10.4 (br s, 1 H), 5.90 (s, 1 H), 3.65 (s, 3 H), 3.60 (s, 3 H); IR (KBr) 3000, 1680 cm^{-1} (br). Anal. Calcd for $C_{17}H_{16}O_4S$: C, 64.5; H, 5.1; S, 10.1. Found: C, 64.5; H, 5.0; S, 9.9.

The cinnamic acid was dissolved in a mixture of phosphorus pentoxide (1 g) and methanesulfonic acid.[28] The resulting solution was stirred at ambient temperature for 3 h. The reaction mixture was slowly added to 200 mL of saturated sodium bicarbonate. The products were extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with brine, were dried over sodium sulfate, and were concentrated. The residue was recrystallized from methanol to give 0.81 g (92%) of **15a** as yellow needles: mp 132–134 °C (lit.[1] mp 132–134 °C); ^{1}H NMR ($CDCl_3$) δ 7.75 (m, 2 H), 7.60 (m, 3 H), 7.07 (m, 2 H), 5.08 (s, 1 H), 3.99 (s, 1 H), 3.97 (s, 3 H); FDMS, m^+/e 298 ($C_{17}H_{14}O_3S$).

Preparation of β-(Phenylseleno)-2,5-dimethoxycinnamic Acid (14b). Phosphorus Pentoxide–Methanesulfonic Acid Cyclization[28] to Benzocyclopentenone 15b. The procedure described for the preparation of **14a** was followed with sodium methoxide (0.27 g, 5 mmol), benzeneselenol (0.72 g, 4.55 mmol), and methyl (2,5-dimethoxyphenyl)propiolate. Product yield was 0.96 g (58%) of β-(phenylseleno)-2,5-dimethoxycinnamic acid: mp 166–170 °C (lit.[14] mp 167–171 °C); ^{1}H NMR ($CDCl_3$) δ 10.4 (br s, 1 H), 7.40 (m, 2 H), 7.20 (m, 3 H), 6.65 (m, 2 H), 6.45 (s, 1 H), 6.40 (m, 1 H), 3.60 (s, 3 H), 3.55 (s, 3 H); IR (KBr) 2950 (br), 1670, 1580, 1250, 1050 cm^{-1}; FDMS, m^+/e 364 ($C_{17}H_{16}O_4{}^{80}Se$). Calcd for $C_{17}H_{16}O_4Se$: C, 56.2; H, 4.4; Se, 21.7. Found: C, 55.9; H, 4.4; Se, 21.4.

A 0.95-g sample of the cinnamic acid was converted to **15b** as described for the preparation of **15a**. Workup as described for the preparation of **15a** gave 0.57 g (70%) of **15b** as yellow needles: mp 129–133 °C (lit.[14] mp 129–133 °C); ^{1}H NMR ($CDCl_3$) δ 7.81 (m, 2 H), 7.56 (m, 3 H), 7.07 (m, 2 H), 5.26 (s, 1 H), 4.00 (s, 3 H), 3.95 (s, 3 H); FDMS, m^+/e 346 ($C_{17}H_{14}O_3{}^{80}Se$).

Preparation of β-(Phenyltelluro)-2,5-diphenylcinnamic Acid (14c). Phosphorus Pentoxide–Methanesulfonic Acid Cyclization to Oxatellurolylium Mesylate 16a. Sodium borohydride (1.5 g, 40 mmol) was added as a powder in several portions to a stirred solution of diphenyl ditelluride (4.11 g, 10.0 mmol) in 20 mL of THF and 20 mL of ethanol until the characteristic red color of the ditelluride disappeared. Methyl (2,5-dimethoxyphenyl)propiolate (4.68 g, 20 mmol) in 10 mL of ethanol was added via syringe. The resulting mixture was stirred at ambient temperature for 0.5 h and was then concentrated to approximately 10 mL. Ethanol (20 mL) and 20 mL of 10% aqueous KOH were added. The resulting mixture was heated at reflux for 1 h. The reaction mixture was diluted with 200 mL of water and extracted with ether (2 × 50 mL). The aqueous phase was acidified with 10% HCl, and the products were extracted with dichloromethane (3 × 50 mL). The combined dichloromethane extracts were washed with brine, dried over sodium sulfate, and concentrated. The residue was recrystallized from acetonitrile to give 7.90 g (96%) of the acid: mp 176–179 °C; ^{1}H NMR ($CDCl_3$) δ 7.05 (m, 5 H), 7.03 (d, 1 H, J = 3.1 Hz), 6.84 (s, 1 H), 6.71 (d × d, 1 H, J = 3.1, 8.9 Hz), 6.49 (d, 1 H, J = 8.9 Hz), 3.63 (s, 3 H), 3.55 (s, 3 H); IR (KBr) 3420, 1655, 1490, 1215 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_4Te$: C, 49.6; H, 3.9. Found: C, 49.6; H, 3.9.

A 1.0-g sample of the cinnamic acid was cyclized as described for the preparation of **15a**. Workup and ^{1}H NMR analysis of the crude reaction mixture showed no evidence for the formation of benzocyclopentenone **15c**. ^{1}H NMR analysis and mass spectral analysis were consistent with the oxatellurolylium mesylate **16a**: ^{1}H NMR ($CDCl_3$) δ 8.51 (s, 1 H), 8.32 (m, 2 H), 7.57 (m, 3 H), 6.97 (m, 2 H), 6.79 (m, 1 H), 3.86 (s, 3 H), 3.85 (s, 3 H), 2.60 (s, 3 H); FDMS, m^+/e 492 ($C_{18}H_{18}O_6S^{130}Te$).

(27) The condensation reactions of **48** and **49** will be reported as part of our work toward the total synthesis of hormothamnione (**6**): McGarry, L. W.; Detty, M. R., manuscript in preparation.

(28) Eaton, P. E.; Carlson, G. R.; Lee, J. T. *J. Org. Chem.* **1973**, *38*, 4071.

Preparation of Oxatellurolylium Chloride 16b. A 1.0-g sample of cinnamic acid **14c** (2.6 mmol) was dissolved in 2 mL of dichloromethane. Five milliliters of oxalyl chloride was added, and the resulting solution was heated at reflux for 1.0 h. The reaction mixture was concentrated, and the crude cinnamoyl chloride was dried under high vacuum for 15 h. The cinnamoyl chloride was dissolved in 10 mL of dry dichloromethane under an argon atmosphere. The resulting solution was cooled to −78 °C, and anhydrous aluminum chloride (0.40 g, 3.0 mmol) was added. The resulting mixture was stirred 3.0 h at −78 °C and was then warmed to ambient temperature. The reaction mixture was poured into approximately 100 g of ice water. The products were extracted with dichloromethane (3 × 25 mL). The combined organic extracts were dried over sodium sulfate and were concentrated. The residue was recrystallized from acetonitrile to give 0.68 g (70%) of **16b**: mp 163–164 °C; ^{1}H NMR ($CDCl_3$) δ 8.49 (s, 1 H), 8.30 (m, 2 H), 7.55 (m, 3 H), 6.97 (m, 2 H), 6.79 (m, 1 H), 3.862 (s, 3 H), 3.855 (s, 3 H); IR (KBr) 1595, 1533, 1495, 1489, 1452, 1225 cm^{-1}; FDMS, m^+/e 432 ($C_{17}H_{15}{}^{35}ClO_3{}^{130}Te$).

Preparation of β-((2,5-Dimethoxyphenyl)telluro)cinnamic Acid and Its Conversion to Acid Chloride 23. Bis(2,5-dimethoxyphenyl) ditelluride (5.30 g, 10.0 mmol) was dissolved in 20 mL of THF and 20 mL of ethanol. Sodium borohydride (1.5 g, 40 mmol) was added in several portions as a powder. After the characteristic red color of the ditelluride faded, ethyl phenylpropiolate (3.48 g, 20.0 mmol) in 5 mL of THF was added. The resulting mixture was stirred for 0.5 h and was then concentrated to approximately 10 mL. Ethanol (20 mL) was added followed by 20 mL of 10% aqueous KOH. The resulting mixture was heated for 1 h at reflux. The reaction mixture was diluted with 200 mL of water. The aqueous mixture was extracted with dichloromethane (2 × 50 mL). The aqueous phase was acidified with 10% HCl, and the products were extracted with dichloromethane (3 × 25 mL). The combined extracts were washed with brine, were dried over sodium sulfate, and were concentrated. The residue was recrystallized from acetonitrile to give 7.90 g (96%) of the acid as golden needles: mp 176–179 °C dec; IR (KBr) 3440, 1645, 1559, 1548, 1480, 1301, 1270, 1229, 1215 cm^{-1}. Calcd for $C_{17}H_{16}O_4Te$: C, 49.6; H, 3.9. Found: C, 49.6; H, 3.9.

The cinnamic acid (4.39 g, 10.0 mmol) was dissolved in 25 mL of dichloromethane, and 10 mL of oxalyl chloride was added. The resulting solution was heated at reflux under argon for 1 h. The reaction mixture was concentrated and the crude acid chloride **23** was dried under high vacuum for 15 h.

Preparation of Oxatellurolylium Chloride 16b. The crude acid chloride **23** as prepared above was dissolved in 25 mL of dry dichloromethane. The resulting solution was cooled to −78 °C under an argon atmosphere, and anhydrous aluminum chloride (1.33 g, 10 mmol) was added as a powder. The resulting mixture was warmed to 0 °C where stirring was continued for 1.0 h. The reaction mixture was poured into approximately 100 g of ice water, and the product was extracted with dichloromethane (3 × 25 mL). The combined organic extracts were dried over sodium sulfate and were concentrated. The ^{1}H NMR spectrum of the crude reaction mixture showed no evidence for the formation of flavone products. The residue was recrystallized from acetonitrile to give 3.01 g (70%) of oxatellurolylium chloride **24** as orange needles: mp 167.5–169 °C; ^{1}H NMR ($CDCl_3$) δ 8.78 (s, 1 H), 7.62 (d, 1 H, J = 3.2 Hz), 7.49 (m, 5 H), 7.48 (d × d, 1 H, J = 3.2, 9.1 Hz), 7.01 (d, 1 H, J = 9.1 Hz), 3.94 (s, 3 H), 3.90 (s, 3 H); IR (KBr) 1580, 1520, 1495, 1483, 1460, 1425, 1350, 1230, 1201, 1179, 1042 cm^{-1}; FDMS, m^+/e 432 ($C_{17}H_{15}{}^{35}ClO_3{}^{130}Te$).

Preparation of β-((3-Methoxyphenyl)telluro)-4-methoxycinnamoyl Chloride (17a). The procedure described for the preparation of β-((2,5-dimethoxyphenyl)telluro)cinnamic acid was followed with methyl (4-methoxyphenyl)propiolate (0.76 g, 4.0 mmol) and bis(3-methoxyphenyl) ditelluride (0.94 g, 2.0 mmol). Recrystallization of the crude acid from acetonitrile gave 0.78 g (48%) of the cinnamic acid as a yellow, crystalline powder: mp 130–135 °C dec (gas evolution); ^{1}H NMR ($CDCl_3$) δ 7.59 (d, 2 H, J = 8.5 Hz), 6.93 (m, 4 H), 6.88 (s, 1 H), 6.70 (d, 1 H, J = 8.5 Hz), 3.72 (s, 3 H), 3.62 (s, 3 H); FDMS, m^+/e 414 ($C_{17}H_{16}O_4{}^{130}Te$). Anal. Calcd for $C_{17}H_{16}O_4Te$: C, 49.6; H, 3.9; Te, 31.0. Found: C, 49.5; H, 3.9; Te, 29.6.

The cinnamic acid was converted to cinnamoyl chloride **17a** by dissolving the acid (0.41 g, 1.0 mmol) in 5 mL of dichloromethane and 5 mL of oxalyl chloride. The resulting solution was heated at reflux for 1.5 h. The reaction mixture was concentrated, and the crude **17a** was dried under high vacuum for 15 h.

Preparation of 2-((4-Methoxyphenyl)telluro)-7-methoxybenzo[*b*]tellurapyranone (18a). Acid chloride **17a** (0.44 g, 1.0 mmol) was dissolved in 10 mL of dry dichloromethane under argon. The resulting solution was cooled to 0 °C, and anhydrous aluminum chloride (0.15 g, 1.1 mmol) was added. The cooling bath was removed, and the reaction mixture was stirred at ambient temperature for 3 h. The reaction mixture was poured into approximately 100 g of ice water. The products were extracted with dichloromethane (3 × 25 mL). The combined organic extracts were dried over sodium sulfate and were concentrated. The residue was purified by chromatography on silica gel (5% ethyl acetate–dichloromethane). The crude **17a** was recrystallized from acetonitrile to give 0.17 g (44%) of **17a** as yellow needles: mp 140–5–142 °C; ^{1}H NMR ($CDCl_3$) δ 8.66 (d, 1 H, J = 9.0 Hz), 7.48 (d, 2 H, J = 8.7 Hz), 7.42 (s, 1 H), 7.20 (d, 1 H, J = 2.5 Hz), 7.03 (d × d, 1 H, J = 2.5, 9.0 Hz), 6.97 (d, 2 H, J = 8.7 Hz), 3.89 (s, 3 H), 3.86 (s, 3 H); IR (KBr) 1601, 1580, 1506, 1270, 1235, 1188, 1178, 1027, 820 cm^{-1}; FDMS, m^+/e 396 ($C_{17}H_{14}O_3{}^{130}Te$). Anal. Calcd for $C_{17}H_{14}O_3Te$: C, 51.8; H, 3.6. Found: C, 51.8; H, 3.6.

Preparation of β-((3-Methoxyphenyl)telluro)-3,4-dimethoxycinnamoyl Chloride (17b). The procedure described for the preparation of β-((2,5-dimethoxyphenyl)telluro)cinnamic acid was followed with methyl (3,4-dimethoxyphenyl)propiolate (0.88 g, 4.0 mmol) and bis(3-methoxyphenyl) ditelluride (0.94 g, 2.0 mmol) to give yellow crystals of the cinnamic acid (1.24 g, 70%): mp 145–148 °C dec (gas evolution); ^{1}H NMR ($CDCl_3$) δ 7.20–6.5 (m, 7 H), 6.93 (s, 1 H), 3.92 (s, 3 H), 3.82 (s, 3 H), 3.82 (s, 3 H); IR (KBr) 3000 (br, s), 1675, 1652, 1595, 1582, 1560, 1510 cm^{-1}.

The cinnamic acid (0.66 g, 1.5 mmol) was converted to cinnamoyl chloride **17b** as described for the preparation of **17a**.

Preparation 2-(3,4-Dimethoxyphenyl)benzo[*b*]tellurapyranone (18b). Cinnamoyl chloride **17b** (0.69 g, 1.5 mmol) was treated with aluminum chloride (0.20 g, 1.5 mmol) as described for the preparation of **18a** to give 0.43 g (68%) of **18b**: mp 173.5–175.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.68 (d, 1 H, J = 9.0 Hz), 7.46 (s, 1 H), 7.23 (d, 1 H, J = 2.3 Hz), 7.11 (s, 2 H), 7.06 (d × d, 1 H, J = 2.3, 9.0 Hz), 3.98 (s, 3 H), 3.96 (s, 3 H), 3.92 (s, 3 H); IR (KBr) 1595, 1580, 1505, 1267, 1233, 1140, 1020, 844 cm^{-1}; FDMS, m^+/e 246 ($C_{18}H_{16}O_4{}^{130}Te$). Anal. Calcd for $C_{18}H_{16}O_4Te$: C, 51.0; H, 3.8. Found: C, 51.1; H, 4.3.

Preparation of β-((3-Methoxyphenyl)telluro)-2,5-dimethoxycinnamic Acid (19). The procedure described for the preparation of β-((2,5-diphenyltelluro))cinnamic acid was followed with methyl (2,5-dimethoxyphenyl)propiolate (0.44 g, 2.0 mmol) and bis(3-methoxyphenyl) ditelluride (0.47 g, 1.0 mmol) to give 0.61 g (69%) of **19** as a yellow powder: mp 151.5–154 °C dec (gas evolution); ^{1}H NMR ($CDCl_3$) δ 7.09 (d, 1 H, J = 7.5 Hz), 6.91 (t, 1 H, J = 7.5 Hz), 6.91 (s, 1 H), 6.82 (s, 1 H), 6.67 (d × d, 1 H, J = 2.3, 7.2 Hz), 6.57 (d, 1 H, J = 7.2 Hz), 6.56 (s, 1 H), 6.33 (d × d, 1 H, J = 2.1, 7.5 Hz), 3.71 (s, 3 H), 3.64 (s, 3 H), 3.52 (s, 3 H); IR nKBr) 3000 (br, s), 1653, 1584, 1560, 1490, 1305, 1215 cm^{-1}.

Cyclization of 19. Preparation of Benzo[*b*]tellurapyranones 18c and 18d. Phosphorus pentoxide (1 g) was dissolved in 10 mL of methanesulfonic acid under an argon atmosphere. Cinnamic acid **19** (0.48 g, 1.0 mmol) was added as a powder. The resulting mixture was stirred 4 h at ambient temperature. The reaction mixture was slowly added to 200 mL of saturated sodium bicarbonate. The products were extracted with dichloromethane (3 × 50 mL). The combined organic extracts were dried over sodium sulfate and concentrated. The ^{1}H NMR of the crude reaction mixture showed an 80:20 mixture of **18d**/**18c**. Recrystallization of the crude product from acetonitrile gave 0.21 g (50%) of **18d** as yellow needles: mp 130.5–132.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.35 (d, 1 H, J = 8.0 Hz), 7.63 (s, 1 H), 7.46 (t, 1 H, J = 8.0 Hz), 7.10 (broadened s, 1 H), 6.98 (d, 1 H, J = 8.0 Hz), 6.95 (broadened s, 2 H), 4.02 (s, 3 H), 3.91 (s, 3 H), 3.84 (s, 3 H); IR (KBr) 1596, 1583, 1491, 1285, 1246, 1048 cm^{-1}; FDMS, m^+/e 426 ($C_{18}H_{16}O_4{}^{130}Te$). Anal. Calcd for $C_{18}H_{16}O_4Te$: C, 51.0; H, 3.8. Found: C, 50.9; H, 3.9.

For **18c**: ^{1}H NMR ($CDCl_3$) δ 8.64 (d, 1 H, J = 9.0 Hz), 7.67 (s, 1 H), 7.21 (d, 1 H, J = 2.1 Hz), 7.10 (s, 1 H), 7.01 (d × d, 1 H, J = 2.1, 9.0 Hz), 6.94 (s, 2 H), 3.93 (s, 3 H), 3.92 (s, 3 H), 3.82 (s, 3 H).

Preparation of 2-(4-Methoxyphenyl)-5,7-dimethoxybenzo[*b*]tellurapyranone (22a). The procedure described for the preparation of β-((2,5-dimethoxyphenyl)telluro)cinnamic acid was followed with bis(3,5-dimethoxyphenyl) ditelluride (0.32 g, 0.60 mmol) and methyl (4-methoxyphenyl)propiolate (0.23 g, 1.2 mmol) to give 0.32 g (60%) of β-((3,5-dimethoxyphenyl)-telluro)-4-methoxycinnamic acid: mp 143–147 °C dec (gas evolution); ^{1}H NMR ($CDCl_3$) δ 6.96 (d, 2 H, J = 8.6 Hz), 6.77 (s, 1 H), 6.59 (d, 2 H, J = 8.6 Hz), 6.53 (d, 2 H, J = 2.1 Hz), 6.20 (t, 1 H, J = 2.1 Hz), 3.71 (s, 3 H), 3.59 (s, 6 H); IR (KBr) 2950 (br, s), 1641, 1600, 1583, 1550, 1501, 1419, 1291, 1245, 1210, 1159, 1038, 83 cm^{-1}.

The acid (0.20 g, 0.45 mmol) was dissolved in 2 mL of dichloromethane and 2 mL of oxalyl chloride. The resulting solution was heated at reflux for 1.5 h. The reaction mixture was concentrated, and the crude acid chloride was dried under high vacuum for 15 h. The acid chloride was dissolved in 10 mL of dry dichloromethane under an argon atmosphere. The resulting solution was cooled to 0 °C, and anhydrous aluminum chloride (0.10 g, 0.75 mmol) was added as a powder. The reaction mixture was warmed to ambient temperature where stirring was maintained for 3 h. The reaction mixture was poured over approximately 25 g of ice water. The products were extracted with dichloromethane (3 × 20 mL). The combined organic extracts were dried over sodium sulfate and concentrated. The residue was recrystallized from acetonitrile to give 0.11 g (58%) of **22a** as yellow needles: mp 131–132.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.48 (d, 2 H, J = 8.7 Hz), 7.35 (s, 1 H), 6.97 (d, 2 H, J = 8.7 Hz), 6.83 (d, 1 H, J = 2.0 Hz), 6.53 (d, 1 H, J = 8.7 Hz), 3.96 (s, 3 H), 3.90 (s, 3 H), 3.88 (s, 3 H); IR (KBr) 1600, 1575, 1395, 1300, 1278, 1252, 1178, 1073, 1020, 831 cm^{-1}; FDMS, m^+/e 426 ($C_{18}H_{16}O_4{}^{130}Te$). Anal. Calcd for $C_{18}H_{16}O_4Te{\cdot}H_2O$: C, 49.8; H, 4.4. Found: C, 49.7; H, 4.2.

Preparation of 2-(3,4-Dimethoxyphenyl)-5,7-dimethoxybenzo[*b*]tellurapyranone (22b). The procedure described for the preparation of **22a** was followed with bis(3,5-dimethoxy) ditelluride (0.32 g, 0.60 mmol) and methyl (3,4-dimethoxyphenyl)propiolate (0.26 g, 1.2 mmol) to give 0.22 g (39%) of β-((3,5-dimethoxyphenyl)telluro)-3,4-dimethoxycinnamic acid: mp 146–149 °C; ^{1}H NMR ($CDCl_3$) δ 6.80 (s, 1 H), 6.72 (d × d, 1 H, J = 1.5, 8.4 Hz), 6.64 (d, 1 H, J = 8.4 Hz), 6.56 (d, 2 H, J = 2.1 Hz), 6.46 (d, 1 H, J = 1.5 Hz), 6.20 (t, 1 H, J = 2.1 Hz), 3.80 (s, 1 H), 3.59 (s, 9 H); IR (KBr) 2950 (br, s), 1642, 1597, 1585, 1510, 1324, 1257, 1223, 1158, 1022 cm^{-1}.

The cinnamic acid (0.15 g, 0.32 mmol) was converted to **22b** as described for the preparation of **22a** to give 0.081 g (57%) of the benzo[*b*]tellurapyranone **22b**: mp 187.5–188.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.36 (s, 1 H), 7.11 (m, 2 H), 6.94 (m, 1 H), 6.84 (d, 1 H, J = 2.1 Hz), 6.54 (d, 1 H, J = 2.1 Hz), 3.97 (s, 3 H), 3.96 (s, 3 H), 3.95 (s, 3 H), 3.90 (s, 3 H); IR (KBr) 1599, 1584, 1505, 1397, 1255, 1235, 1070, 1024, 830 cm^{-1}; FDMS, m^+/e 456 ($C_{19}H_{18}O_5{}^{130}Te$). Anal. Calcd for $C_{19}H_{18}O_5Te$: C, 50.3; H, 4.0. Found: C, 50.1; H, 4.4.

Preparation of 2-(2,5-Dimethoxyphenyl)-5,7-dimethoxybenzo[*b*]tellurapyranone (22c). The procedure described for the preparation of **22a** was followed with bis(3,5-dimethoxyphenyl) ditelluride (1.72 g, 3.26 mmol) and isopropyl (2,5-dimethoxyphenyl)propiolate (1.62 g, 6.53 mmol) to give 2.85 g (93%) of β-((3,5-dimethoxyphenyl)telluro)-2,5-dimethoxycinnamic acid as a tan powder: mp 158–162 °C dec (gas evolution); ^{1}H NMR ($CDCl_3$) δ 6.60 (s, 1 H), 6.47 (m, 5 H), 6.17 (t, 1 H, J = 2.1 Hz), 3.59 (s, 3 H), 3.55 (s, 6 H), 3.42 (s, 3 H); IR (KBr) 2950 (br s), 1660, 1585, 1560 cm^{-1}; FDMS, m^+/e 474 ($C_{19}H_{20}O_6{}^{130}Te$).

The cinnamic acid (2.80 g, 5.94 mmol) was converted to **22c** as described for the preparation of **22a**. Product yield was 1.95 g (72%) of **22c** as a tan powder: mp 79–81 °C; ^{1}H NMR ($CDCl_3$) δ 7.47 (s, 1 H), 7.03 (t, 1 H, J = 0.8 Hz), 6.83 (d, 2 H, J = 0.8 Hz), 6.75 (d, 1 H, J = 2 Hz), 6.43 (d, 1 H, J = 2 Hz), 3.90 (s, 3 H), 3.83 (s, 6 H), 3.75 (s, 3 H); IR (KBr) 1598, 1500, 1285 cm^{-1}; FDMS, m^+/e 456 ($C_{19}H_{18}O_5{}^{130}Te$). Anal. Calcd for $C_{19}H_{18}O_5Te{\cdot}H_2O$: C, 48.3; H, 4.3; Te, 26.9. Found: C, 48.2; H, 4.4; Te, 26.1.

Compound **22c** was quite insoluble for NMR studies. The benzo[*b*]tellurapyranone was protonated with HPF_6 in acetic acid, and the ^{1}H NMR spectrum of the protonated salt was run in CD_3CN: δ 8.47 (s, 1 H), 7.80 (d, 1 H, J = 2.1 Hz), 7.62 (m, 1 H), 7.35 (m, 2 He, 7.01 (d, 1 H, J = 2.1 Hz), 4.32 (s, 3 H), 4.22 (s, 3 H), 4.13 (s, 3 H), 3.98 (s, 3 H).

Preparation of β-((3,5-Difluorophenyl)telluro)cinnamoyl Chloride (28). Bis(3,5-difluorophenyl) ditelluride n4.81 g, 10.0 mmol) was dissolved in 150 mL of ethanol. Powdered sodium borohydride (1.5 g, 40.0 mmol) was added in three 0.5-g portions. When the ditelluride solution changed color from red to pale yellow, ethyl phenylpropiolate (3.48 g, 20.0 mmol) in 10 mL of ethanol was added. The resulting solution was stirred 15 min at ambient temperature. The reaction mixture was poured into 400 mL of water. The excess sodium borohydride was quenched by the addition of 50 mL of 10% HCl. The products were extracted with dichloromethane (3 × 150 mL). The combined organic extracts were washed with brine, dried over sodium sulfate, and concentrated. The residue was recrystallized from ethanol to give 6.84 g (82%) of ethyl β-((3,5-difluorophenyl)telluro)cinnamate: mp 66–68 °C; ^{1}H NMR ($CDCl_3$) δ 7.06 (m, 2 H), 6.8–7.0 (m, 5 H), 6.75 (s, 1 H), 6.48 (m, 1 H), 4.32 (q, 2 H, J = 7.1 Hz), 1.35 (t, 1 H, J = 7.1 Hz); FDMS, m^+/e 418 ($C_{17}H_{14}F_2O_2{}^{130}Te$). Anal. Calcd for $C_{17}H_{14}F_2O_2Te$: C, 49.1; H, 3.4; F, 9.1. Found: C, 49.2; H, 3.4; F, 9.1.

The ester (6.60 g, 15.9 mmol) was dissolved in 100 mL of hot ethanol. Twenty milliliters of 25% aqueous KOH was added. The resulting mixture was heated for 15 min on a steam bath and was then diluted with 300 mL of water. The aqueous solution was extracted with dichloromethane (3 × 50 mL). The aqueous phase was acidified with 10% HCl. The acidified solution was extracted with dichloromethane (3 × 50 mL). These extracts were dried over sodium sulfate and concentrated to give the acid. The acid was recrystallized from acetonitrile to give 5.73 g (93%) of the acid as yellow needles: mp 160–163 °C; ^{1}H NMR ($CDCl_3$) δ 11.2 (br s, 1 H), 7.10 (m, 3 H), 6.98 (m, 2 H), 6.91 (d × d, 2 H, J = 2.0, 6.4 Hz), 6.85 (s, 1 H), 6.51 (t × t, 1 H, J = 2.0, 9.0 Hz); FDMS, m^+/e 390 ($C_{15}H_{10}F_2O_2{}^{130}Te$).

The acid (1.94 g, 5.00 mmol) was added to 15 mL of oxalyl chloride. The resulting mixture was stirred 1 h at 40 °C and was then concentrated under vacuum. The crude acid chloride was dried under high vacuum for 15 h.

Preparation of 2-Phenyl-5,7-difluorobenzo[*b*]tellurapyranone (29). The acid chloride **28** (2.02 g, 5.00 mmol) was dissolved in 25 mL of dry dichloromethane under an argon atmosphere. The resulting solution was cooled to 0 °C, and anhydrous aluminum chloride (0.67 g, 5.00 mmol) was added as a powder. The cooling bath was removed, and the reaction mixture was stirred 1.5 h at ambient temperature. The reaction mixture was poured into approximately 100 g of ice water. The products were extracted with dichloromethane (3 × 50 mL). The combined organic extracts were dried over sodium sulfate and were concentrated. The residue was purified by chromatography on silica gel (2% ethyl acetate–dichloromethane) to give 0.34 g (18%) of the flavone **29** (following recrystallization from methanol) as yellow needles: mp 174–175 °C; ^{1}H NMR ($CDCl_3$) δ 7.47 (m, 5 H), 7.38 (s, 1 H), 7.32 (m, 1 H), 6.93 (d × d × d, 1 H, J = 2.5, 7.7, 8.7 Hz); FDMS, m^+/e 372 ($C_{15}H_8F_2O^{130}Te$). Anal. Calcd for $C_{15}H_8F_2OTe$: C, 48.7; H, 2.2. Found: C, 48.7; H, 2.4.

For oxatellurolylium chloride **30**: ^{1}H NMR ($CDCl_3$) δ 8.38 (s, 1 H), 7.60 (m, 2 H), 7.43 (m, 3 H), 7.05 (m, 2 H), 6.88 (m, 1 H); FDMS, m^+/e 408 ($C_{15}H_9{}^{35}ClF_2O^{130}Te$).

Preparation of Boronate 34a. 2-Phenyl-5-methoxybenzo-[*b*]tellurapyranone (0.30 g, 0.83 mmol) was dissolved in 3 mL of freshly distilled boron trifluoride etherate. The resulting solution was heated on a steam bath for 1.0 h. The reaction mixture was diluted with 10 mL of ether. The dark red solid was collected by filtration and recrystallized from acetonitrile to give 0.24 g (73%) of **34a** as red needles: mp 204–205 °C; ^{1}H NMR ($CDCl_3$) δ 7.90 (s, 1 H), 7.60 (m, 7 H), 7.17 (m, 1 H); IR (KBr) 1600, 1555, 1497, 1449, 1435, 1290 cm^{-1}; FDMS, m^+/e 400 ($C_{15}H_9BF_2O_2{}^{130}Te$). Anal. Calcd for $C_{15}H_9BF_2O_2Te$: C, 45.3; H, 2.3; B, 2.7; Te, 32.1. Found: C, 45.3; H, 2.4; B, 2.8; Te, 29.7.

Preparation of Boronate 34b. 2-Methyl-5,7-dimethoxybenzo[*b*]tellurapyranone (0.40 g, 1.2 mmol) in 10 mL of boron trifluoride etherate was treated as described for the preparation

of **34a**. The orange-red solid was recrystallized from acetonitrile to give 0.40 g (91%) of **34b**: mp 239–242 °C; ^{1}H NMR ($CDCl_3$) δ 7.42 (q, 1 H, J = 1.2 Hz), 7.40 (d, 1 H, J = 2 Hz), 6.58 (d, 1 H, J = 2 Hz), 3.90 (s, 3 H), 3.80 (d, 3 H, J = 1.2 Hz); IR (KBr) 1600, 1555, 1290 cm^{-1}; FDMS, m^+/e 368 ($C_{11}H_9BF_2O_3{}^{130}Te$). Anal. Calcd for $C_{11}H_9BF_2O_3Te$: C, 36.1; H, 2.5; Te, 34.9. Found: C, 36.5; H, 2.4; Te, 34.1.

Preparation of Boronate 34c. 2-Phenyl-5,7-dimethoxybenzo[*b*]tellurapyranone (0.85 g, 2.2 mmol) in 5 mL of boron trifluoride etherate was treated as described for the preparation of **34a**. The red crystalline solid was recrystallized from acetonitrile to give 0.66 g (72%) of red needles of **34c**: mp 224.5–226.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.70 (s, 1 H), 7.55 (s, 1 H), 7.15 (d, 1 H, J = 2 Hz), 6.62 (d, 1 H, J = 2 Hz), 3.92 (s, 3 H); IR (KBr) 1600, 1535, 1450, 1435, 1283 cm^{-1}; FDMS, m^+/e 430 ($C_{16}H_{11}BF_2O_3{}^{130}Te$). Anal. Calcd for $C_{16}H_{11}BF_2O_3Te$: C, 44.9; H, 2.6; B, 2.5; Te, 29.8. Found: C, 45.3; H, 2.4; B, 2.5; Te, 30.6.

Preparation of Boronate 34d. 2-(4-Methoxyphenyl)-5,7-dimethoxybenzo[*b*]tellurapyranone (0.13 g, 0.31 mmol) in 2 mL of boron trifluoride etherate was treated as described for the preparation of **34a**. The red solid was recrystallized from acetonitrile to give 0.093 g (66%) of red needles of **34d**: mp 246–249 °C; ^{1}H NMR (CD_2Cl_2) δ 7.72 (s, 1 H), 7.61 (d, 2 H, J = 8.4 Hz), 7.23 (d, 1 H, J = 2 Hz), 7.07 (d, 2 H, J = 8.4 Hz), 6.66 (d, 1 H, J = 2 Hz), 3.95 (s, 3 H), 3.91 (s, 3 H); IR (KBr) 1602, 1543, 1440, 1292, 1177 cm^{-1}; FDMS, m^+/e 460 ($C_{17}H_{13}BF_2O_4{}^{130}Te$).

Preparation of 34e. 2-(3,4-Dimethoxyphenyl)-5,7-dimethoxybenzo[*b*]tellurapyranone (0.045 g, 0.10 mmol) in 1 mL of boron trifluoride etherate was treated as described for the preparation of **34a**. The red crystalline solid was recrystallized from acetonitrile to give 0.047 g (96%) of red needles of **34e**: mp 240–243 °C; ^{1}H NMR (CD_2Cl_2) δ 7.80 (s, 1 H), 7.25 (m, 2 H), 7.16 (m, 1 H), 7.03 (d, 1 H, J = 2 Hz), 6.66 (d, 1 H, J = 2 Hz), 3.962 (s, 3 H), 3.957 (s, 3 H), 3.945 (s, 3 H); IR (KBr) 1601, 1545, 1510, 1449, 1440, 1300, 1260 cm^{-1}; FDMS, m^+/e 490 ($C_{18}H_{15}BF_2O_5{}^{130}Te$).

Preparation of Boronate 34f. 2-(2,5-Dimethoxyphenyl)-5,7-dimethoxybenzo[*b*]tellurapyranone (0.38 g, 0.84 mmol) in 10 mL of boron trifluoride etherate was treated as described for the preparation of **34a**. The red solid was recrystallized from acetonitrile to give 0.34 g (83%) of **34f**: mp 304–306 °C; ^{1}H NMR [$(CF_3)_2CHOH$] δ 8.00 (s, 1 H), 7.43 (s, 1 H), 7.27 (s, 1 H), 7.10 (d, 1 H, J = 2 Hz), 6.60 (d, 1 H, J = 2 Hz), 4.43 (s, 3 H), 4.37 (s, 3 H), 4.30 (s, 3 H); IR (KBr) 1605, 1550, 1445, 1300 cm^{-1}; FDMS, m^+/e 490 ($C_{18}H_{15}BF_2O_5{}^{130}Te$). Anal. Calcd for $C_{15}H_{18}BF_2O_5Te$: C, 44.3; H, 3.1; Te, 26.2. Found: C, 44.1; H, 3.1; Te, 25.7.

Hydrolysis of Boronate 34a. Preparation of 2-Phenyl-5-hydroxybenzo[*b*]tellurapyranone (35a). Boronate **34a** (0.78 g, 2.0 mmol) was slurried in 20 mL of acetone and 20 mL of water with 1 g of potassium carbonate. The resulting mixture was heated at reflux for 0.5 h. The reaction mixture was acidified with 10% HCl, precipitating an orange solid that was collected by filtration. The crude product was recrystallized from methanol to give 0.62 g (90%) of **35a**: mp 139–142 °C; ^{1}H NMR ($CDCl_3$) δ 7.55 (s, 1 H), 7.50 (narrow multiplet, 5 H), 6.80–7.50 (m, 3 H), 4.70 (br s, 1 H); IR (KBr) 3400, 1600, 1550, 1445, 1175, 870, 785, 743 cm^{-1}; FDMS, m^+/e 352 ($C_{15}H_{10}O_2{}^{130}Te$). Anal. Calcd for $C_{15}H_{10}O_2Te$: C, 51.5; H, 2.9; Te, 36.5. Found: C, 51.3; H, 2.8; Te, 34.4.

Hydrolysis of Boronate 34b. Preparation of 2-Methyl-5-hydroxy-7-methoxybenzo[*b*]tellurapyranone (35b, Telluraeugenin). Boronate **34b** (0.072 g, 0.20 mmol) was slurried in 5 mL of acetonitrile and 2 mL of 10% potassium carbonate solution. The resulting mixture was heated at reflux for 0.5 h. The reaction mixture was diluted with water, and the products were extracted with dichloromethane (3 × 25 mL). The combined organic extracts were dried over sodium sulfate and concentrated. The residue was purified by chromatography on silica gel eluted with dichloromethane to give 0.053 g (84%) of **35b**: mp 137–140 °C; ^{1}H NMR ($CDCl_3$) δ 7.39 (q, 1 H, J = 0.8 Hz), 7.11 (d, 1 H, J = 3 Hz), 6.63 (d, 1 H, J = 3 Hz), 3.91 (s, 3 H), 2.79 (d, 3 H, J = 0.8 Hz); FDMS, m^+/e 320 ($C_{11}H_{10}O_3{}^{130}Te$).

Hydrolysis of Boronate 34c. Preparation of 2-Phenyl-5-hydroxy-7-methoxybenzo[*b*]tellurapyranone (35c). Boronate **34c** (0.43 g, 1.0 mmol) was treated as described for the hydrolysis of **34a**. Product yield was 0.34 g (90%) of **35c**: mp 150–152 °C; ^{1}H NMR ($CDCl_3$) δ 7.56 (m, 2 H), 7.53 (s, 1 H), 7.50 (m, 3 H), 6.83 (d, 1 H, J = 2.3 Hz), 6.47 (d, 1 H, J = 2.3 Hz), 3.86 (s, 3 H); FDMS, m^+/e 382 ($C_{16}H_{12}O_3{}^{130}Te$).

Hydrolysis of Boronate 34d. Preparation of 2-(4-Methoxyphenyl)-5-hydroxy-7-methoxybenzo[*b*]tellurapyranone (35d). Boronate **34d** (0.046 g, 0.10 mmol) was slurried in 1 mL of acetonitrile and 1 mL of saturated sodium bicarbonate solution. The resulting mixture was heated at reflux for 0.5 h. The reaction mixture was diluted with 30 mL of water, and the product was extracted with dichloromethane (3 × 15 mL). The combined organic extracts were dried over sodium sulfate and were concentrated. The residue was purified by chromatography on silica gel eluted with 10% ethyl acetate–dichloromethane. Flavone **35d** was recrystallized from acetonitrile to give 0.038 g (93%) of yellow needles: mp 173–176 °C; ^{1}H NMR ($CDCl_3$) δ 7.46 (d, 2 H, J = 8.7 Hz), 7.33 (s, 1 H), 6.97 (d, 2 H, J = 8.7 Hz), 6.83 (d, 1 H, J = 2.3 Hz), 6.46 (d, 1 H, J = 2.3 Hz), 3.86 (s, 3 H), 3.85 (s, 3 H); IR (KBr) 1610, 1559, 1510, 1258, 1188, 983, 825 cm^{-1}; FDMS, m^+/e 412 ($C_{17}H_{14}O_4{}^{130}Te$).

Hydrolysis of Boronate 34e. Preparation of 2-(3,4-Dimethoxyphenyl)-5-hydroxy-7-methoxybenzo[*b*]tellurapyranone (35e). Boronate **34e** (0.049 g, 0.10 mmol) was treated as described for the hydrolysis of **34d**. Product yield was 0.040 g (91%) of **35e** as orange needles: mp 208.5–210.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.35 (s, 1 H), 7.07 (m, 2 H), 6.92 (d, 1 H, J = 8.1 Hz), 6.83 (d, 1 H, J = 2.3 Hz), 6.46 (d, 1 H, J = 2.3 Hz), 3.95 (s, 3 H), 3.94 (s, 3 H), 3.86 (s, 3 H); IR (KBr) 1612, 1561, 1509, 1263 cm^{-1}; FDMS, m^+/e 442 ($C_{18}H_{16}O_5{}^{130}Te$). Anal. Calcd for $C_{18}H_{16}O_5Te$: C, 49.1; H, 3.7. Found: C, 49.1; H, 3.9.

Hydrolysis of Boronate 34f. Preparation of 2-(2,5-Dimethoxyphenyl)-5-hydroxy-7-methoxybenzo[*b*]tellurapyranone (35f). Boronate **34f** was treated as described for the hydrolysis of **34d**. Product yield was 0.038 g (86%) of **35f** mp 176–178 °C; ^{1}H NMR ($CDCl_3$) δ 7.57 (s, 1 H), 7.16 (d, 1 H, J = 2.7 Hz), 6.99 (d × d, 1 H, J = 2.7, 8.7 Hz), 6.95 (d, 1 H, J = 8.7 Hz), 6.84 (d, 1 H, J = 2.3 Hz), 6.46 (d, 1 H, J = 2.3 Hz), 3.92 (s, 3 H), 3.87 (s, 3 H), 3.85 (s, 3 H); IR (KBr) 1610, 1565, 1489, 1440, 1278 cm^{-1}; FDMS, m^+/e 442 ($C_{18}H_{16}O_5{}^{130}Te$). Anal. Calcd for $C_{18}H_{16}O_5Te$: C, 49.1; H, 3.7. Found: C, 49.1; H, 3.9.

Preparation of Tellurapyrylium Difluoroboronate 38. Boronate **34a** (0.15 g, 0.41 mmol) and *p*-(*N*,*N*-Dimethylamino)-benzaldehyde (0.15 g, 1.0 mmol) in 3 mL of acetic anhydride were heated on a steam bath for 6 min. The reaction mixture was diluted with 5 mL of acetonitrile and chilled, precipitating a brown solid which was collected by filtration to give 0.051 g (25%) of **38**, mp 200–206 °C. Anal. Calcd for $C_{20}H_{18}bf_2NO_3Te$: C, 58.4; H, 3.6; N, 3.8. Found: C, 48.5; H, 3.8; N, 2.8.

Preparation of Tellurapyrylium Difluoroboronate 39. 9-Formyljulolyldine (0.25 g, 1.0 mmol) and **34a** (0.10 g, 0.27 mmol) in 5 mL of acetic anhydride were heated on a steam bath for 10 min. Ether (10 mL) was added, and the resulting mixture was chilled, precipitating a copper solid. The solid was recrystallized from acetonitrile to give 0.080 g (53%) of **39**, mp 190–195 °C dec. Anal. Calcd for $C_{24}H_{22}BF_2NO_3Te$: C, 52.5; H, 4.0; N, 2.6. Found: C, 52.6; H, 4.1; N, 2.3.

Preparation of Tellurapyrylium Difluoroboronate 40. 3-(*N*,*N*-Diethylamino)propenal (0.15 g, 1.2 mmol) and **34a** in 1 mL of acetic anhydride were stirred for 1 h at ambient temperature. Acetic acid (2 mL) and ether (3 mL) were added, precipitating a copper solid. The solid was collected by filtration, washed with ether, and dried to give 0.060 g (46%) of **40**, mp 188–192 °C. Anal. Calcd for $C_{18}H_{20}BF_2NO_3Te$: C, 46.4; H, 4.3; N, 3.0. Found: C, 46.3; H, 4.3; N, 2.8.

Preparation of Tellurapyrylium Difluoroboronate 41. Benzo[*b*]tellurapyranone **12a** (0.15 g, 0.41 mmol) and **34a** (0.12 g, 0.33 mmol) in 5 mL of acetic anhydride were heated for 15 min on a steam bath. The reaction mixture was diluted with 50 mL of ether, precipitating a jet-black solid, which was recrystallized from acetonitrile to give 0.060 g (25%) of **41**, 160–166 °C dec. Anal. Calcd for $C_{27}H_{19}BF_2O_4Te_2$: C, 45.6; H, 2.7. Found: C, 45.5; H, 2.7.

Preparation of 2-Methyl-4-ethoxy-7-methoxybenzo[*b*]-tellurapyrylium Fluorosulfonate (44). Tellurachromone **13b** (1.00 g, 3.31 mmol) was added in one portion to 10 mL of freshly distilled ethyl fluorosulfonate under argon at 75 °C. After being stirred for 0.5 h, the reaction was diluted with 10 mL of dry ether and was chilled. The product was collected by filtration, was washed with ether, and was dried to give 1.31 g (92%) of **44** as

a yellow solid which was air-sensitive and thermally sensitive (decomposition above 100 °C: ^{1}H NMR (CD_3CN) δ 9.20 (d, 1 H, J = 9 Hz), 8.15 (q, 1 H, J = 1.2 Hz), 8.03 (d, 1 H, J = 2.5 Hz), 7.50 (d × d, 1 H, J = 2.5, 9 Hz), 4.80 (q, 2 H, J = 7 Hz), 4.10 (s, 3 H), 3.00 (d, 3 H, J = 1.2 Hz), 1.83 (t, 3 H, J = 7 Hz).

Preparation of Tellurapyrylium Fluorosulfonate 45. *p*-(*N*,*N*-Dimethylamino)benzaldehyde (0.30 g, 2.0 mmol) and **44** (0.43 g, 1.0 mmol) in 3 mL of acetic anhydride were heated on a steam bath for 2 min. The reaction mixture was chilled to 0 °C, precipitating a green solid. The solid was recrystallized from acetonitrile to give 0.33 g (59%) of **45** as a metallic, green solid: 163–167 °C; λ_{max} (CH_2Cl_2) 695 nm (log ϵ 4.98). Anal. Calcd for $C_{22}H_{24}FNO_5STe$: C, 47.0; H, 4.3; N, 2.5. Found: C, 47.0; H, 4.1; N, 2.5.

Preparation of Tellurapyrylium Fluorosulfonate 46. 2-Methyl-4-ethoxybenzo[*b*]tellurapyrylium salt **44** (0.43 g, 1.0 mmol) and *p*-(*N*,*N*-dimethylamino)benzaldehyde (0.35 g, 2.0 mmol) in 3 mL of acetic anhydride were heated 15 min on a steam bath. The reaction mixture was chilled, precipitated a brown powder. Recrystallization from acetonitrile gave 0.10 g (17%) of **46** as a brown crystals with a metallic luster: mp 175–178 °C; λ_{max} (CH_2Cl_2) 780 nm (log ϵ 4.95). Anal. Calcd for $C_{24}H_{26}FNO_5STe$: C, 49.1; H, 4.5; N, 2.4. Found: C, 49.1; H, 4.2; N, 2.1.

Preparation of Tellurapyrylium Fluorosulfonate 47. 2-Methyl-4-ethoxybenzo[*b*]tellurapyrylium salt **44** (0.43 g, 1.0 mmol) and 9-formyljulolylidine (0.26 g, 1.4 mmol) in 3 mL of acetic anhydride were heated on a steam bath for 3.0 min. The reaction mixture was chilled precipitating the dye. The dye was recrystallized from acetonitrile to give 0.41 g (67%) of **47** as metallic, purple crystals: mp 175–179 °C; λ_{max} (CH_2Cl_2) 753 nm (log ϵ 4.97). Anal. Calcd for $C_{26}H_{28}FNO_5STe$: C, 50.9; H, 4.6; N, 2.3; S, 5.2; F, 3.1; Te, 20.8. Found: C, 50.9; H, 4.7; N, 2.0; S, 5.2; F, 2.2; Te, 19.4.

Preparation of Tellurapyrylium Fluorosulfonate 48. Benz[*b*]tellurapyranone **12a** (0.37 g, 1.0 mmol) and 2-methyl-4-ethoxybenzo[*b*]tellurapyrylium salt **44** (0.40 g, 0.93 mmol) in 3 mL of acetic anhydride were heated on a steam bath for 5 min. The reaction mixture was diluted with 5 mL of acetonitrile and chilled. The precipitate was collected by filtration and recrystallized from acetonitrile to give 0.15 g (16%) of **48**: mp 204 °C: λ_{max} (CH_2Cl_2) 720 (log ϵ 4.60). Anal. Calcd for $C_{29}H_{25}FO_6STe_2$: C, 44.9; H, 3.2; Te, 32.9. Found: C, 45.2; H, 2.9; Te, 34.4.

Hydrolysis of 45. Preparation of Styrylchromone 49. Dye **45** (0.12 g, 0.21 mmol) was dissolved in 10 mL of acetonitrile and 10 mL of 10% aqueous potassium carbonate was added. The resulting mixture was warmed on a steam bath for 15 min and was cooled. The product crystallized as fine yellow needles to give 0.09 g (100%) of **49**: mp 123–127 °C; ^{1}H NMR ($CDCl_3$) δ 8.55 (d, 1 H, J = 9 Hz), 7.35 (d, 2 H, J = 9 Hz), 7.20 (d, 1 H, J = 15 Hz), 7.10 (s, 1 H), 7.00 (d × d, 1 H, J = 2.5, 9 Hz), 6.80 (d, 1 H, J = 15 Hz), 6.65 (d, 1 H, J = 2.5 Hz), 6.62 (d, 2 H, J = 9 Hz), 3.85 (s, 3 H), 3.00 (s, 6 H); IR (KBr) 1595, 1575, 1540 cm^{-1}; FDMS, m^+/e 435 ($C_{20}H_{19}NO_2{}^{130}Te$). Anal. Calcd for $C_{20}H_{19}NO_2Te$: C, 55.5; H, 4.4; N, 3.2. Found: C, 55.1; H, 4.5; N, 3.3.

Hydrolysis of 38. Preparation of Phenolic Styrylchromone 42. Dye **38** (0.050 g, 0.10 mmol) was treated as described for **34d**. Product yield was 0.044 g (90%) of an orange solid: ^{1}H NMR ($CDCl_3$) δ 7.35 (d, 2 H, J = 9 Hz), 7.20 (d, 1 H, J = 15 Hz), 7.10 (s, 1 H), 6.83 (d, 1 H, J = 2.3 Hz), 6.80 (d, 1 H, J = 15 Hz), 6.62 (d, 2 H, J = 9 Hz), 6.46 (d, 1 H, J = 2.3 Hz), 3.86 (s, 3 H), 3.01 (s, 6 H); FDMS, m^+/e 451 ($C_{20}H_{19}NO_3{}^{130}Te$). Anal. Calcd for $C_{20}H_{19}NO_3Te$: C, 53.5; H, 4.3; N, 3.1. Found: C, 53.4; H, 4.4; N, 3.2.

Preparation of Difluoroboronate 37. Thione **36** (0.38 g, 1.0 mmol) in 3 mL of boron trifluoride etherate was heated on a steam bath for 15 min. Chilling the reaction mixture precipitated the product as a dark red solid. The solid was collected by filtration, washed with ether, and dried to give 0.39 g (95%) of **37**: mp 182 °C dec; IR (KBr) 1670, 1565, 1540, 1450, 1410, 1060 cm^{-1}; FDMS, m^+/e 416 ($C_{15}H_9BF_2OS^{130}Te$). Anal. Calcd for $C_{15}H_9BF_2OSTe$: C, 43.5; H, 2.2; S, 7.8. Found: C, 43.5; H, 2.2; S, 7.9.

Registry No. **14a**, 116006-41-8; **14b**, 74877-30-8; **14c**, 116006-42-9; **15a**, 74877-54-6; **15b**, 74877-53-5; **16a**, 116025-58-2; **17a**, 116006-48-5; **17a** (acid), 116006-47-4; **17b**, 116006-51-0; **17b** (acid), 116006-50-9; **17c**, 116006-54-3; **17c** (acid), 116006-53-2; **18a**, 116006-49-6; **18b**, 116006-52-1; **18c**, 116006-55-4; **18d**, 116006-56-5; **19**, 116025-60-6; **22a**, 116006-59-8; **22b**, 116006-62-3; **22c**, 116006-66-7; **22c**·HPF_6, 116006-67-8; **23**, 116006-46-3; **23** (acid), 116006-46-3; **24**, 116052-44-9; **28**, 116006-71-4; **28** (acid), 116006-70-3; **29**, 116006-72-5; **30**, 116025-61-7; **34a**, 84798-04-9; **34b**, 84798-05-0; **34c**, 116025-52-6; **34d**, 116025-53-7; **34e**, 116025-54-8; **34f**, 116025-55-9; **35a**, 116006-73-6; **35b**, 84790-47-6; **35c**, 116006-74-7; **35d**, 116006-75-8; **35e**, 116006-76-9; **35f**, 116006-77-0; **36**, 116006-86-1; **37**, 84798-03-8; **38**, 116025-56-0; **39**, 116025-57-1; **40**, 116006-78-1; **41**, 84805-36-7; **42**, 116006-85-0; **44**, 84144-71-8; **45**, 84144-73-0; **46**, 116006-80-5; **47**, 116006-82-7; **48**, 116006-84-9; **49**, 84144-74-1; methyl (2,5-dimethoxyphenyl)-propiolate, 71797-96-1; β-(phenyltelluro)-2,5-dimethoxycinnamoyl chloride, 116006-43-0; bis(2,5-dimethoxyphenyl) ditelluride, 116006-44-1; ethyl phenylpropiolate, 2216-94-6; methyl (4-methoxyphenyl)propiolate, 7515-17-5; bis(3-methoxyphenyl) ditelluride, 92720-48-4; methyl (3,4-dimethoxyphenyl)propiolate, 62497-24-9; bis(3,5-dimethoxyphenyl) ditelluride, 84144-31-0; β-(3,5-dimethoxyphenyl)telluro-4-methoxycinnamic acid, 116006-57-6; β-(3,5-dimethoxyphenyl)telluro-4-methoxycinnamoyl chloride, 116006-58-7; β-(3,5-dimethoxyphenyl)telluro-3,4-dimethoxycinnamic acid, 116006-60-1; β-(3,5-dimethoxyphenyl)telluro-3,4-dimethoxycinnamoyl chloride, 116006-61-2; isopropyl (2,5-dimethoxyphenyl)propiolate, 116006-63-4; β-(3,5-dimethoxyphenyl)telluro-2,5-dimethoxycinnamic acid, 116006-64-5; β-(3,5-dimethoxyphenyl)telluro-2,5-dimethoxycinnamoyl chloride, 116006-65-6; bis(3,5-difluorophenyl) ditelluride, 116006-68-9; ethyl β-(3,5-diphenyl)tellurocinnamate, 116006-69-0; 2-phenyl-5-methoxybenzo[*b*]tellurapyranone, 84144-54-7; 2-methyl-5,7-dimethoxybenzo[*b*]tellurapyranone, 84144-59-2; 2-phenyl-5,7-dimethoxybenzo[*b*]tellurapyranone, 84144-55-8; *p*-(*N*,*N*-dimethylamino)-benzaldehyde, 100-10-7; 9-formyljvlolylidine, 33985-71-6; 3-(*N*,*N*-diethylamino)propenal, 927-63-9; *p*-(*N*,*N*-dimethylamino)-cinnamaldehyde, 6203-18-5.