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Studies on chalcogen-containing heterocycles. Part 37: *m*-CPBA oxidation of isotellurochromenes and isoselenochromenes☆

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ABSTRACT

The oxidation of the 1-unsubstituted isotellurochromenes and isoselenochromenes with *m*-CPBA resulted in a novel ring-opening reaction to give the *o*-formyl distyryl ditellurides and diselenides as the sole products in good yields, respectively. The *o*-benzoyl distyryl ditelluride and diselenide were also produced from the corresponding 1-phenylisochromenes. In contrast, the 1-benzyl and 1-*n*-butylisochromenes were oxidized to afford the (*Z*)-1-benzylideneisochromenes and (*Z*)-1-butylideneisochromenes under similar conditions; no distyryl compounds were obtained. The distyryl compounds were also obtained by the hydrolysis of the corresponding 2-benzochalcogenopyrylium salts, which were easily converted from the 2-benzoisochromenes by treatment with triphenylcarbenium tetrafluoroborate ($Ph_3C^+BF_4^-$).

1. Introduction

The breakthrough of the synthesis, structure, physical properties, and reactions of the heterocycles containing of chalcogen (sulfur, selenium and tellurium) elements has lately been attracted increasing interest in both the fields of heterocyclic[1] and organosulfur, -selenium, and -tellurium chemistry,[2] but more investigations remain. We have studied the syntheses and reactions of the novel tellurium- and selenium-containing heterocyclic compounds[3] over the past 20 years. Our synthetic strategy[4] for the preparation of these compounds is based on the intramolecular cyclization of the tellurol or selenol moieties and related compounds to a triple bond. As part of our continuing studies, we have previously focused on the synthesis of the isotellurochromenes[5a] and isoselenochromenes[5b] as the precursors for the preparation of the corresponding novel 2-benzopyrylium salts.[6] In addition, several reactivities of these isochromenes have been investigated: (1) the transformation of the isotellurochromenes into the 1,2-dihydro-2-metalanaphthalenes via a tellurium–lithium exchange reaction;[7] (2) the alkylation (phenylation) and halogenations;[3b] (3) the oxidation of the isotellurochromenes.[8]

The synthetic utility of the *m*-CPBA of acylic alkyl phenyl selenides and tellurides has been reviewed by Uemura,[9] and there are several reports concerning the oxidation of the mono and benzene ring fused six-membered heterocycles containing a chalcogen atom (Scheme 1). The selenium dioxide oxidation of 4*H*-thiopyrans and 4*H*-selenopyrans undergoes a ring contraction to give the 2-aroylthiophenes and selenophenes, respectively (Eq. 1).[10] The oxidation of the 3,6-dihydro-2*H*-selenopyrans having an electron-withdrawing group at the 2-position with sodium periodate is also known to produce selenophenes (Eq. 2).[11] Furthermore, the oxidation of thiochromenes,[12] selenochromenes,[12] and tellurochromenes[13,14] with selenium dioxide, trityl perchlorate or K_2CrO_7 produced the corresponding 2-formylbenzo[*b*]-thiophenes, -selenophenes, and -tellurophenes, respectively (Eq. 3). Whereas the normal isothiochromene *S*-oxide[15] is easily isolated as the thermally stable *m*-CPBA oxidation products (Eq. 4), a similar oxidation of the highly substituted isoselenochromenes[16] gives the benzo[*b*] selenophene derivatives as the main product (Eq. 5). These facts prompted us to examine the oxidation of the simple isotellurochromenes and isoselenochromenes. In this report, we describe the oxidative one-pot conversion of the isotellurochromenes and isoselenochromenes to the corresponding distyryl dichalcogenides and others as additional reactivities for these isochromenes involving an X-ray crystallographic analysis of the oxidation product.

Vinylic tellurides[17] and selenides[18] involving styryl compounds have been widely studied and used in organic syntheses. Most of the vinyl derivatives have been synthesized by the addition of the

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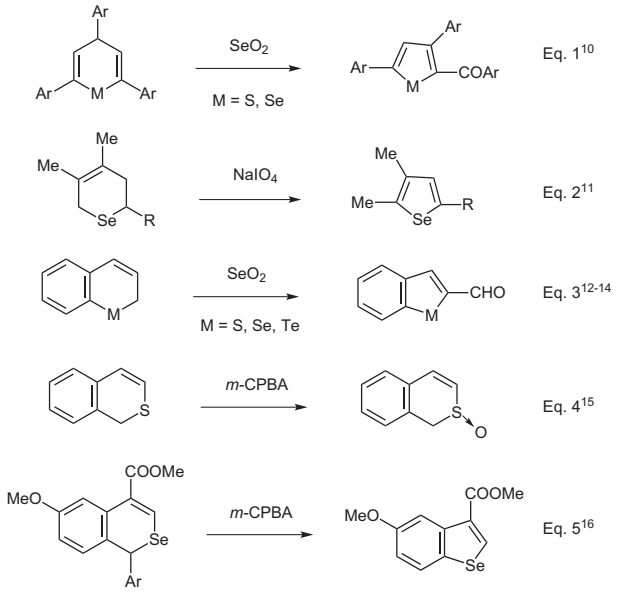


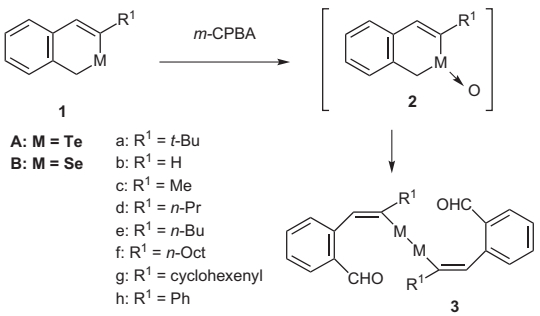
Scheme 1.

tellurols or selenols and related compounds to an acetylene. Thus, the result described in this paper provides a new practical access for the preparation of the vinylic tellurides and selenides.

2. Results and discussion

2.1. *m*-CPBA oxidation of 1-unsubstituted isotellurochromenes and isoselenochromenes: formation of distyryl ditellurides and diselenides

The oxidation of the 1-unsubstituted isotellurochromenes with *m*-CPBA is shown in Scheme 2 and the results are summarized in Table 1. When 1.2 equiv of *m*-CPBA was added to a solution of 3-*tert*-butyl-1*H*-isotellurochromene **1Aa** in $CHCl_3$ at 0 °C, the starting material immediately disappeared; the reddish yellow solution turned colorless. The (*Z*)-bis(*o*-formylstyryl) ditelluride **3Aa** was isolated as red prisms in 83% yield as the sole product after the usual workup. No telluroxide **2Aa** was produced (Table 1, entry 1). The MS spectrum of this compound suggested the ditelluride molecular formula of $C_{26}H_{30}O_2Te_2$ with a molecular ion at *m*/*z*=634 (^{130}Te) and the expected isotope pattern for Te_2. The HRMS of **3Aa** also showed the same exact molecular formula. The IR spectrum showed the characteristic absorption due to the formyl carbonyl group at 1690 cm^{-1}. In the NMR spectrum, the benzyl singlet 2H proton signals disappeared at ca. 3.8 ppm, and the olefinic 1H proton remains at ca. 6.9 ppm. These spectroscopic data were consistent with the **3Aa** structure. A similar *m*-CPBA oxidation of the unsubstituted isotellurochromene **1Ab**



Scheme 2.

Table 1
(*Z*)-Bis(*o*-formylstyryl) ditellurides **3A** and diselenides **3B**

Entry	M	R^1	Product	Yield[a] (%)
1	Te	*t*-Bu	**3Aa**	83
2	Te	H	**3Ab**	43
3	Te	Me	**3Ac**	57
4	Te	*n*-Pr	**3Ad**	60
5	Te	*n*-Bu	**3Ae**	70
6	Te	*n*-Oct	**3Af**	62
7	Te	1-Cyclohexenyl	**3Ag**	83
8	Te	Ph	**3Ah**	78
9	Se	*t*-Bu	**3Ba**	88
10	Se	H	**3Bb**	77
11	Se	Me	**3Bc**	55
12	Se	*n*-Pr	**3Bd**	61
13	Se	*n*-Bu	**3Be**	76
14	Se	*n*-Oct	**3Bf**	65
15	Se	1-Cyclohexenyl	**3Bg**	73

[a] Isolated yield.

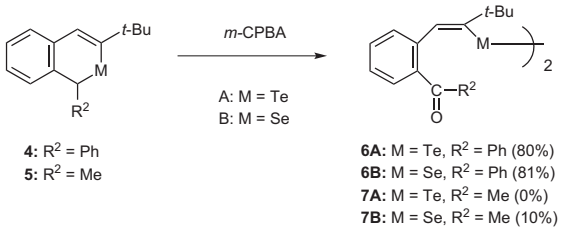
also produced the corresponding ditellurides **3Ab** in 43% yield, and the 3-alkyl **1Ac**–**f**, 3-alkenyl **1Ag**, and the 3-phenylisotellurochromenes **1Ah** were oxidized in moderate to good yields to give the corresponding ditellurides **3Ac**–**h** via the presumable telluroxide **2A** (entries 2–8).

Based on this isotellurochromene oxidation result, we have become significantly interested in the similar *m*-CPBA oxidation of selenium analogues, i.e., the isoselenochromenes **1B** comparing the highly substituted isoselenochromenes reported by Okuma.[16]

When the isoselenochromenes **1B** bearing a primary, secondary or tertiary alkyl group at the C-3 position and unsubstituted derivatives were oxidized by *m*-CPBA under the same conditions, the corresponding ring-opening bis(*o*-formylstyryl) diselenides **3Ba**–**g** were obtained in one-pot from **1B** in yields ranging from 55% to 88% without any ring contraction products(entries 9–15). The obtained results are quite similar to the *m*-CPBA oxidation of the isotellurochromenes.

2.2. *m*-CPBA oxidation of 1-methyl and 1-phenylisotellurochromenes and isoselenochromenes

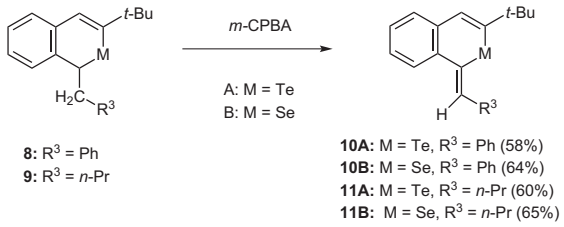
Next, a similar *m*-CPBA oxidation of the 1-substituted 3-*tert*-butylisochromenes was carried out (Scheme 3). These compounds are readily obtained from 3-*tert*-butyl-1*H*-isotellurochromene **1Aa** and -1*H*-isoselenochromene **1Ba**, which are superior substrates in stability and synthetic easiness via the corresponding 2-benzopyrylium salts. 3-*tert*-Butyl-1-phenyl-1*H*-isotellurochromene **4A**[6c] and -1*H*-isoselenochromene **4B**[6b] were similarly oxidized to produce the bis(*o*-benzoylstyryl) ditelluride **6A** and diselenide **6B** by *m*-CPBA under the same conditions in 80% and 81% yields, respectively. While the oxidation of 1-methylisotellurochromene **5A**[6c] with *m*-CPBA gave a complex mixture without the desired bis(*o*-acetylstyryl) ditelluride **7A** under the same conditions, the bis(*o*-acetylstyryl) diselenide **7B** was determined to form by the *m*-CPBA oxidation of 1-methylisoselenochromene **5B**[6b] in only 10% yield along with many uncharacterized compounds.



Scheme 3.

2.3. *m*-CPBA oxidation of 1-benzyl and 1-butylisotellurochromenes and isoselenochromenes

In contrast, when the 1-benzyl **8**[6b] and 1-*n*-butylisochromenes **9**,[6c] which had a methylene moiety at the C-1 position of the isochromene ring, were oxidized with *m*-CPBA, the (*Z*)-methylidene compounds **10**, **11** were produced in range of 58–65% yields as shown in Scheme 4. The structures of the benzylidene derivatives **10A**, **B** were identical to the authentic samples,[5a,6b] which were reported in our previous paper. The butylidene compounds **11**, which were produced from the corresponding isochromenes **9**, were characterized by spectral comparison with **10**.

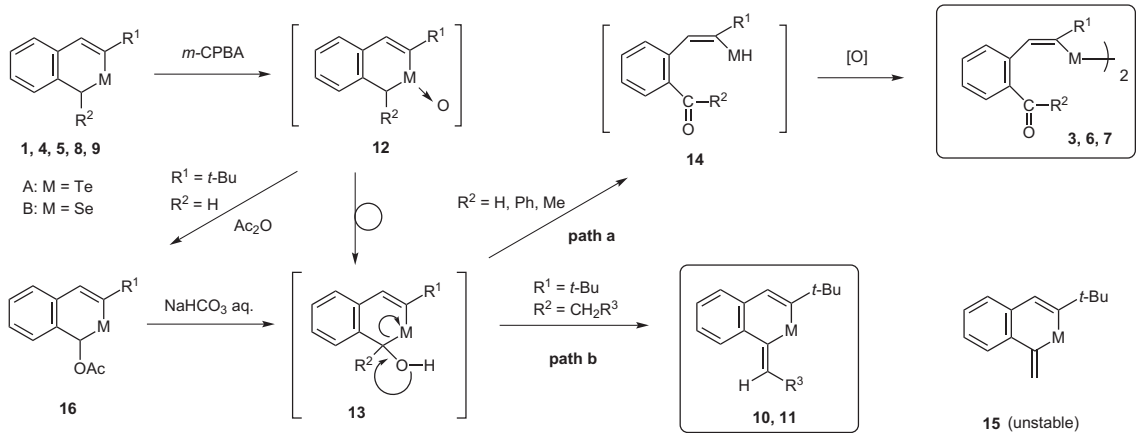


Scheme 4.

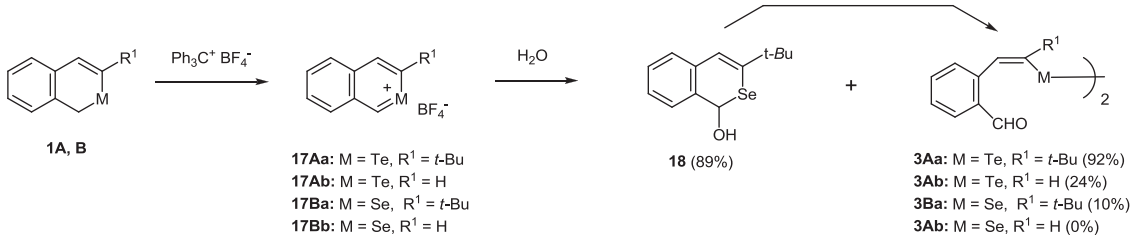
A plausible mechanism for the formation of both the benzoyl **6** and acetyl derivatives **7** from **4** and **5** may be similar to the formyl derivatives **3** from the isochromenes **1** (Scheme 5). The essential telluroxides **12A** or selenoxides **12B** generated by the oxidation of the corresponding isochromenes **1**, **4**, **5**, **8**, and **9** rearranged to afford the 1-hydroxyisochromenes **13** by a Pummerer-type rearrangement. The intermediate **13** undergoes ring-opening with migration of the hydroxy proton to form the vinyltellurol **14A** or selenol **14B** (path a). The resulting **14** may be oxidized by *m*-CPBA or air to give the distyryl derivatives **3**, **6**, and **7**. The 1-methylidene compounds **10** and **11** would be formed by the dehydration of the intermediate **13** (path b). In these cases, the corresponding distyryl ditellurides and diselenides were not obtained. The significant differences in the formation of products according to whether or not the 1-substituent is a primary alkyl group could be clearly explained; path b is suggested to be predominant because of the following point. There are two possible paths for the formations of the dichalcogenides (path a) and 1-methylideneisochromenes (path b) from the 1-benzylisochromenes **8** and the 1-*n*-butylisochromenes **9** having a methylene moiety at the C-1 position of the isochromene ring including the 1-methyl derivatives **5**. However, the *m*-CPBA oxidation of **8** and **9** gave only methylene compounds **10** and **11**, and no bis(*o*-acylstyryl) ditelluride and diselenide. For the *m*-CPBA oxidation of the 1-methylisochromenes **5**, the dehydration reaction of the intermediate **13** may mainly proceeded to produce the *exo*-methylene compounds **15**, which are probably too unstable to isolate. Therefore, the products decomposed, and a small amount of **7B** was obtained from **5**. All of the telluroxides **12A**, selenoxides **12B**, and 1-hydroxyisochromenes **13** could not be isolated due to their unstabilities. Fortunately, the oxidation of the *tert*-butyl derivative **1Aa** with *m*-CPBA, followed by treatment with Ac_2O at room temperature resulted in a Pummerer rearrangement to afford the expected 1-acetoxyisotellurochromene **16** together with a small amount of the ditelluride **3Aa**. The hydrolysis of the isolated acetoxy derivative **16** with $NaHCO_3$ aq gave the ditelluride **3Aa** in almost quantitative yield. This finding on the *m*-CPBA oxidation of the isochromenes suggests that the essential oxidative products are clearly the 1-hydroxy derivatives **13**. In the case of only 1-substituted isochromenes **8** and **9** having at least a methylene moiety, including the 1-methylisochromenes **5**, the (*Z*)-methylidene compounds **10** and **11** were produced by the dehydration of **13** (path b); the *exo*-methylene compounds **15** could not be obtained because of their instability. When the dehydration of **13** is impossible such as **1** and **4**, the ring-opening reaction mainly proceeded to give the dichalcogenides **3** and **6** through further oxidation of the chalcogenols **14**, which are the tautomers of 1-hydroxyisochromenes **13** (path a). Thus, path a is predominant.

2.4. Hydrolysis of 2-benzopyrylium salts

In addition, the ditellurides **3A** and selenides **3B** could be obtained by the hydrolysis of the 2-benzotelluropyrylium **17A**[6a] and 2-benzoselenopyrylium tetrafluoroborates **17B**[6a] in high yields, which had previously been prepared by the treatment of the isochromenes **1** with triphenylcarbenium tetrafluoroborate ($Ph_3C^+BF_4^-$) in $MeNO_2$ in high yields (Scheme 6). We have reported[6b–e] the reaction of the 2-benzotelluropyrylium and 2-benzoselenopyrylium salts with several nucleophiles, such as hydrides, alkoxides, amines, and an active methylene compound to afford the corresponding 1-substituted isochromenes as the sole products in good to high yields.



Scheme 5.



Scheme 6.

When the 3-*tert*-butyltelluropyrylium salt **17Aa** was treated with cold water, the (*Z*)-bis(*o*-formylstyryl) ditelluride **3Aa** was isolated in 92% yield. However, the hydrolysis of the 3-unsubstituted telluropyrylium salt **17Ab** produced the distyryl ditelluride **3Ab** in only 24% yield. The 3-*tert*-butylselenopyrylium salt **17Ba** was hydrolyzed to give the 1-hydroxyisoselenochromene **18** and the diselenides **3Ba**, which were isolated in 89% and 10% yields, respectively; the former is probably the initial product, and was easily transformed to give **3Ba** in quantitative yield by storage for a few days on contact with air or oxidation with an appropriate oxidizing reagent such as *m*-CPBA. The initial **18** were produced by the nucleophilic attack of water at the C-1 position of the pyrylium cation **17Ba**, and then oxidized to give **3Ba**. Unfortunately, the treatment of the 3-unsubstituted selenopyrylium salt **17Bb** with H_2O gave a complex mixture without any products. Compounds **18** (**13Ba**) should be produced by the oxidation of the isoselenochromene **1Ba** with *m*-CPBA under the above conditions, but not isolated.

2.5. Structure of (*Z*)-bis(*o*-formylstyryl) ditelluride

The geometry of the double bond in products **3**, **6**, and **7** was proved to be (*Z*)-stereochemistry based on the vicinal coupling constant (J=10 Hz) in the ^{1}H NMR spectra of the nonsubstituted derivative **3Ab**. The molecular structure of **3** was finally established by an X-ray crystallographic analysis using the *tert*-butyl ditelluride **3Aa**. The ORTEP drawing is shown in Fig. 1. The Te–Te bond length of **3Aa** (2.715(1) Å) is close to the averaged value of the neutral diorgano ditellurides (2.705 Å), which was calculated based on the reported structure in Cambridge Structural Database.[19] The torsion angle of C–Te–Te–C in **3Aa** is 132.3° and has a *transoid* conformation. Although the intramolecular Te–O or –N interactions have been found in the organotellurium compounds containing oxygen or nitrogen atom(s) in their functional group,[20] no such significant interaction around the tellurium is observed in **3Aa** in which the shortest Te–O distance is 4.860 Å.

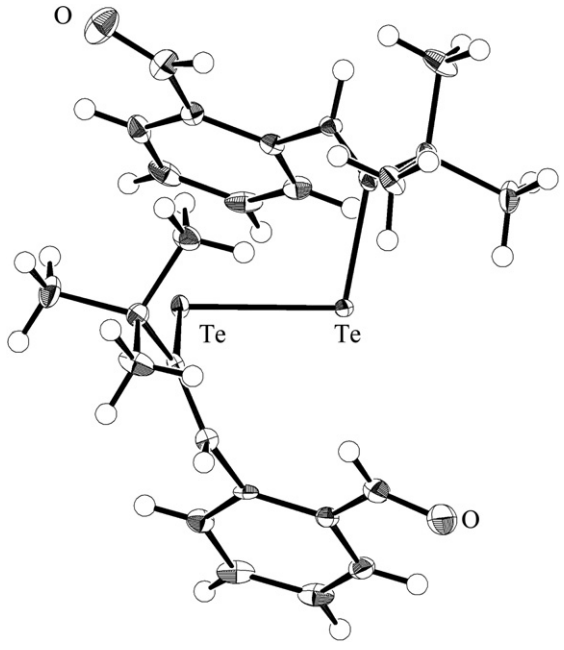
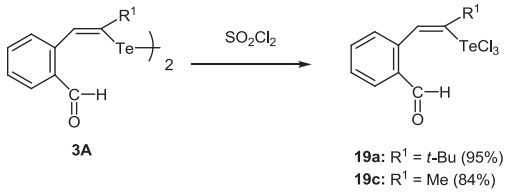


Fig. 1. An ORTEP drawing of **3Aa** with thermal ellipsoid plot (50% probability).

2.6. Chlorination of (*Z*)-bis(*o*-formylstyryl) ditelluride

Finally, the reactivities of the obtained ditellurides were examined. The *tert*-butyl ditelluride **3Aa** was easily converted to the tellurium trichloride **19** by means the fission of the Te–Te bond by treatment of sulfuryl chloride. The treatment of **3Aa** and **3Ac** with a small amount excess of sulfuryl chloride in CH_2Cl_2 at 0 °C produced the trichlorides **19a** and **19c** in 95% and 84% yields, respectively, as shown in Scheme 7.



Scheme 7.

3. Conclusion

In the present study, the *m*-CPBA oxidation of the isotellurochoromenes and isoselenochromenes having substituents at the C-1 and (or) C-3 position of the isochromene ring was examined. As a result, this novel ring-opening *m*-CPBA oxidation of the isotellurochoromenes and isoselenochromenes has provided the facile one-pot alternative preparation of the divinyl ditellurides and selenides.

4. Experimental section

4.1. General

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were recorded on a Horiba FT-720 spectrophotometer. MS and HRMS spectra were recorded on a JEOL JMS-DX300 instrument. ^{1}H NMR spectra were recorded on a PMX-60SI (60 MHz), JEOL EX-90A (90 MHz), JEOL ECA-400 (400 MHz) or JEOL ECP-500 (500 MHz) spectrometer using TMS as internal standard in $CDCl_3$ and J values are given in hertz. ^{13}C NMR spectra were recorded on a JEOL ECA-400 (100 Hz) or JEOL ECP-500 (125 Hz) spectrometer in $CDCl_3$.

^{77}Se and ^{125}Te NMR spectra were obtained on a Bruker AVANCE II 600 (76.3, 189 MHz) spectrometer in $CDCl_3$ with external standards.

4.2. Starting materials

4.2.1. Isotellurochromenes and isoselenochromenes. The starting materials, 3-*tert*-butyl-1*H*-isotellurochromene **1Aa**,[6a] 1*H*-isotellurochromene **1Ab**,[6a] 3-methyl-1*H*-isotellurochromene **1Ac**,[6a] 3-*n*-butyl-1*H*-isotellurochromene **1Ae**,[6a] 3-phenyl-1*H*-isotellurochromene **1Ah**,[6a] 3-*tert*-butyl-1-phenyl-1*H*-isotellurochromene **4A**,[6c] 3-*tert*-butyl-1-methyl-1*H*-isotellurochromene **5A**,[6c] 1-benzyl-3-*tert*-butyl-1*H*-isotellurochromene **8A**,[6b] 1-*n*-butyl-3-*tert*-butyl-1*H*-isotellurochromene **9A**,[6c] 3-*tert*-butyl-1*H*-isoselenochromene **1Ba**,[6a] 1*H*-isoselenochromene **1Bb**,[6a] 3-methyl-1*H*-isoselenochromene **1Bc**,[6a] 3-*n*-butyl-1*H*-isoselenochromene **1Be**,[6a] 3-*tert*-butyl-1-phenyl-1*H*-isoselenochromene **4B**,[6b] 3-*tert*-butyl-1-methyl-1*H*-isoselenochromene **5B**,[6b] 1-benzyl-3-*tert*-butyl-1*H*-isoselenochromene **8B**,[6b] and 1-*n*-butyl-3-*tert*-butyl-1*H*-isoselenochromene **9B**[6b] were prepared by the literature method. 3-*n*-Propyl-1*H*-isotellurochromene **1Ad**, 3-*n*-octyl-1*H*-isotellurochromene **1Af**, 3-cyclohexenyl-1*H*-isotellurochromene **1Ag**, 3-*n*-propyl-1*H*-isoselenochromene **1Bd**, 3-*n*-octyl-1*H*-isoselenochromene **1Bf**, and 3-cyclohexenyl-1*H*-isoselenochromene **1Bg** were also synthesized according to the literature method.[6]

*4.2.1.1. 3-n-Propyl-1H-isotellurochromene **1Ad**.* Yield 63%, yellow oil. ^{1}H NMR (90 MHz): 0.96, 1.3–1.7, 2.56 (3H, t, *J*=7 Hz, 2H, m, 2H, t, *J*=7 Hz, *n*-Pr), 3.88 (2H, s, 1-H_2), 6.61 (1H, s, 4-H), 7.0–7.3 (4H, m, Ph–H); MS *m*/*z* (relative intensity, %): 288 (M^+, 75), 286 (70), 129 (100); HRMS *m*/*z*: calcd for $C_{12}H_{14}Te$: 288.0158. Found: 288.0153.

*4.2.1.2. 3-n-Octyl-1H-isotellurochromene **1Af**.* Yield 80%, yellow oil. ^{1}H NMR (90 MHz): 0.88, 1.1–1.6, 2.57 (3H, t, *J*=7 Hz, 12H, m, 2H, t, *J*=7 Hz, *n*-Oct), 3.85 (2H, s, 1-H_2), 6.59 (1H, s, 4-H), 7.1–7.2 (4H, m, Ph–H); MS *m*/*z* (relative intensity, %): 358 (M^+, 100), 356 (92), 129 (65); HRMS *m*/*z*: calcd for $C_{17}H_{24}Te$: 358.0941. Found: 358.0940.

*4.2.1.3. 3-Cyclohexenyl-1H-isotellurochromene **1Ag**.* Yield 65%, yellow oil. ^{1}H NMR (90 MHz): 1.4–1.8, 2.0–2.6, 6.0 (4H, m, 4H, m, 1H, m, cyclohexenyl–H), 3.77 (2H, s, 1-H_2), 6.83 (1H, s, 4-H), 7.0–7.2 (4H, m, Ph–H); MS *m*/*z* (relative intensity, %): 326 (M^+, 100), 324 (90), 196 (43), 167 (55); HRMS *m*/*z*: M^+ calcd for $C_{15}H_{16}Te$: 326.0315. Found: 326.0317.

*4.2.1.4. 3-n-Propyl-1H-isoselenochromene **1Bd**.* Yield 63%, yellow oil. ^{1}H NMR (90 MHz): 0.97, 1.3–1.8, 2.46 (3H, t, *J*=7 Hz, 2H, m, 2H, t, *J*=7 Hz, *n*-Pr), 3.80 (2H, s, 1-H_2), 6.57 (1H, s, 4-H), 7.0–7.5 (4H, m, Ph–H); MS *m*/*z* (relative intensity, %): 238 (M^+, 100), 236 (48), 209 (35), 128 (61); HRMS *m*/*z*: M^+ calcd for $C_{12}H_{14}Se$: 238.0261. Found: 238.026.

*4.2.1.5. 3-n-Octyl-1H-isoselenochromene **1Bf**.* Yield 60%, yellow oil. ^{1}H NMR (90 MHz): 0.88, 1.1–1.7, 2.48 (3H, t, *J*=7 Hz, 12H, m, 2H, t, *J*=7 Hz, *n*-Oct), 3.83 (2H, s, 1-H_2), 6.64 (1H, s, 4-H), 7.1–7.3 (4H, m, Ph–H); MS *m*/*z* (relative intensity, %): 308 (M^+, 100), 306 (50), 209 (36), 128 (50); HRMS *m*/*z*: M^+ calcd for $C_{17}H_{24}Se$: 308.1044. Found: 308.1045.

*4.2.1.6. 3-Cyclohexenyl-1H-isoselenochromene **1Bg**.* Yield 68%, yellow oil. ^{1}H NMR (500 MHz): 1.61–1.67, 1.72–1.78, 2.22–2.28, 2.43–2.48, 3.80, 6.35 (2H, m, 2H, m, 2H, m, 2H, m, 3H, s, 1H, t, *J*=4.2 Hz, cyclohexenyl–H, 2H, s, 1-H_2), 6.91 (1H, s, 4-H), 7.12–7.21 (4H, m, Ph–H); MS *m*/*z* (relative intensity, %): 276 (M^+, 100), 274 (55), 209 (40), 128 (60); HRMS *m*/*z*: M^+ calcd for $C_{15}H_{16}Se$: 276.0418. Found: 276.0413.

4.2.2. 2-Benzotelluropyrylium salts and 2-benzoselenopyrylium salts. The starting 2-benzotelluropyrylium salts **17A** and 2-benzoselenopyrylium salts **17B** were easily prepared in good yields by the reported method.[6a]

4.3. Typical procedure for *m*-CPBA oxidation of 1*H*-isotellurochromenes 1A, 4A, 5A, 8A, 9A and 1*H*-isoselenochromenes 1B, 4B, 5B, 8B, 9B

m-CPBA (70%, 296 mg, 1.2 mmol) was added to a solution of 3-*tert*-butylisotellurochromene (**1Aa**, 302 mg, 1.0 mmol) in dry $CHCl_3$ (10 mL) at 0 °C and the mixture was stirred at room temperature for 1 h. After addition of satd $NaHCO_3$ aq (10 mL), aqueous mixture was extracted with CH_2Cl_2 (50 mL×3). The organic layers were washed with NH_4Cl aq, brine (30 mL×2), dried ($MgSO_4$), and evaporated. The resulting residue was chromatographed on silica gel using *n*-hexane/CH_2Cl_2 (2:1) as an eluent to give pure ditelluride.

*4.3.1. (Z)-Bis(α-tert-butyl-o-formylstyryl) ditelluride **3Aa**.* Yield: 263 mg (83%), dark red prisms, mp 140–143 °C (from acetone/hexane). IR (KBr, cm^{-1}): 1690 (C=O); ^{1}H NMR (500 MHz): 1.24 (18H, s, *t*-Bu×2), 6.88 (2H, s, Ph–C*H*=C–×2), 7.20, 7.36, 7.47, 7.80 (2H, d, *J*=7.6 Hz, 2H, dd, *J*=7.7, 7.7 Hz, 2H, ddd, *J*=7.7, 7.6, 1.4 Hz, 2H, dd, *J*=7.7, 1.4 Hz, Ph–H), 10.06 (2H, s, CHO×2); ^{13}C NMR (125 MHz): 30.7 (q), 41.3 (s) 127.5 (d), 128.3 (d), 131.6 (d), 133.5 (s), 133.6 (d), 134.6 (d), 138.0 (s), 144.4 (s), 191.5 (d); ^{125}Te NMR (189 MHz): 275.8; MS *m*/*z* (relative intensity, %): 634, 632, 630, 628 (M^+, 1, 2, 2, 1), 187 (100), 145 (33), 115 (22); HRMS *m*/*z* calcd for $C_{26}H_{30}O_2{}^{130}Te_2$: 634.0370. Found: 634.0352.

*4.3.2. (Z)-Bis(o-formylstyryl) ditelluride **3Ab**.* Yield: 112 mg (43%), orange prisms, mp 95–97 °C (from CH_2Cl_2/hexane). IR (KBr, cm^{-1}): 1694 (C=O); ^{1}H NMR (500 MHz): 7.28 (2H, d, *J*=10.3 Hz, Ph–C*H*=C–×2), 7.92 (2H, d, *J*=10.3 Hz, –CH=C*H*–Te×2), 7.26, 7.44, 7.55, 7.86 (2H, d, *J*=7.8 Hz, 2H, dd, *J*=7.6, 7.4 Hz, 2H, ddd, *J*=7.8, 7.4, 1.4 Hz, 2H, dd, *J*=7.6, 1.4 Hz, Ph–H), 10.21 (2H, s, CHO×2); ^{13}C NMR (125 MHz): 112.9 (d), 127.9 (d), 128.4 (d), 130.9 (d), 132.9 (s), 134.0 (d), 135.4 (d), 141.8 (s), 191.7 (d); MS *m*/*z* (relative intensity, %): 522, 520, 518, 516 (M^+, 2, 3, 3, 2), 131 (100), 103 (22), 77 (14); HRMS *m*/*z* calcd for $C_{18}H_{14}O_2{}^{130}Te_2$:521.9118. Found: 521.9088.

*4.3.3. (Z)-Bis(o-formyl-α-methylstyryl) ditelluride **3Ac**.* Yield: 156 mg (57%), orange oil. IR (neat, cm^{-1}): 1693 (C=O); ^{1}H NMR (500 MHz): 2.57 (6H, d, *J*=1.6 Hz, Me), 7.02 (2H, d, *J*=1.6 Hz, Ph–C*H*=C–×2), 7.28, 7.47, 7.59, 7.91 (2H, dd, *J*=7.6, 0.6 Hz, 2H, ddd, *J*=7.8, 7.4, 0.6 Hz, 2H, ddd, *J*=7.6, 7.4, 1.4 Hz, 2H, dd, *J*=7.8, 1.4 Hz, Ph–H), 10.19 (2H, s, CHO×2); ^{13}C NMR (125 MHz): 32.2 (q), 117.0 (s), 128.4 (d), 129.3 (d), 130.3 (d), 131.8 (d), 133.8 (s), 134.0 (d), 143.3 (s), 191.7 (d); MS *m*/*z* (relative intensity, %): 550, 548, 546, 544 (M^+, 1, 2, 2, 1), 145 (100), 115 (35); HRMS *m*/*z* calcd for $C_{20}H_{18}O_2{}^{130}Te_2$:549.9431. Found: 549.9440.

*4.3.4. (Z)-Bis(o-formyl-α-n-propylstyryl) ditelluride **3Ad**.* Yield: 181 mg (60%), orange oil. IR (neat, cm^{-1}): 1691 (C=O); ^{1}H NMR (500 MHz): 0.94, 1.47–1.58, 2.62 (6H, t, *J*=7.3 Hz, 4H, m, 4H, t, *J*=7.3 Hz, *n*-Pr), 6.97 (2H, s, Ph–C*H*=C–×2), 7.25, 7.46, 7.58, 7.90 (2H, d, *J*=7.5 Hz, 2H, dd, *J*=7.7, 7.5 Hz, 2H, ddd, *J*=7.5, 7.5, 1.2 Hz, 2H, dd, *J*=7.7, 1.2 Hz, Ph–H), 10.19 (2H, s, CHO×2); ^{13}C NMR (125 MHz): 13.1 (q), 23.0 (t), 45.2 (t), 124.1 (s), 128.3 (d), 129.1 (d), 130.5 (d), 131.4 (d), 133.6 (s), 133.9 (d), 143.5 (s), 191.5 (d); MS *m*/*z* (relative intensity, %): 606, 604, 602, 600 (M^+, 4, 7, 8, 5), 173 (100), 145 (10), 115 (14); HRMS *m*/*z* calcd for $C_{24}H_{26}O_2{}^{130}Te_2$: 606.0057. Found: 606.0057.

*4.3.5. (Z)-Bis(α-n-butyl-o-formylstyryl) ditelluride **3Ae**.* Yield: 221 mg (70%), orange oil. IR (neat, cm^{-1}): 1695 (C=O); ^{1}H NMR (500 MHz): 0.92, 1.32–1.40, 1.47–1.54, 2.65 (3H, t, *J*=7.3 Hz, 4H, m, 4H, m, 4H, t, *J*=7.4 Hz, *n*-Bu), 6.97 (2H, s, Ph–C*H*=C–×2), 7.25, 7.46,

7.57, 7.90 (2H, d, J=7.6 Hz, 2H, dd, J=7.7, 7.5 Hz, 2H, dd, J=7.6, 7.5 Hz, 2H, d, J=7.7 Hz, Ph–H), 10.17 (2H, s, CHO×2). ^{13}C NMR (125 MHz): 14.1 (q), 21.8 (t), 32.0 (t), 43.0 (t), 124.3 (s), 128.3 (d), 129.0 (d), 130.5 (d), 131.2 (d), 133.6 (s), 133.9 (d), 143.5 (s), 191.5 (d); MS m/z (relative intensity, %): 634, 632, 630, 628 (M^+, 1, 2, 2, 1), 187 (100), 145 (33), 115 (22); HRMS m/z calcd for $C_{26}H_{30}O_2^{130}Te_2$: 634.0370. Found: 634.0370.

4.3.6. (Z)-Bis(o-formylα-n-octylstyryl) ditelluride ***3Af***. Yield: 230 mg (62%), orange oil. IR (neat, cm^{-1}): 1697 (C=O); ^{1}H NMR (500 MHz): 0.90, 1.22–1.38, 1.46–1.56 2.63 (3H, t, J=7.0 Hz, 20H, m, 4H, 4H, t, J=7.5 Hz, *n*-Oct), 6.96 (2H, s, Ph–C*H*=C–×2), 7.24, 7.45, 7.57, 7.90 (2H, d, J=7.6 Hz, 2H, dd, J=7.7, 7.5 Hz, 2H, ddd, J=7.6, 7.5, 1.2 Hz, 2H, d, J=7.7, 1.2 Hz, Ph–H), 10.18 (2H, s, CHO×2); ^{13}C NMR (125 MHz): 14.2 (q), 22.7 (t), 28.7 (t), 29.3 (t), 29.5 (t), 29.9 (t), 31.9 (t), 43.3 (t), 124.4 (s), 128.3 (d), 130.0 (d), 130.5 (d), 131.1 (d), 133.6 (s), 133.9 (d), 143.5 (s), 191.5 (d); MS m/z (relative intensity, %): 746 (M^+, 1, 2, 2, 1), 243 (100), 145 (10), 129 (10); HRMS m/z calcd for $C_{34}H_{46}O_2^{130}Te_2$: 746.1622. Found: 746.1625.

4.3.7. (Z)-Bis(α-cyclohexenyl-o-formylstyryl) ditelluride ***3Ag***. Yield: 282 mg (83%), orange oil. IR (neat, cm^{-1}): 1691 (C=O); ^{1}H NMR (90 MHz): 1.15–2.50, 5.75 (16H, m, 2H, br s, cyclohexenyl–H), 6.95 (2H, s, Ph–C*H*=C–×2), 7.2–7.9 (8H, m, Ph–H), 10.12 (2H, s, CHO×2); MS m/z (relative intensity, %): 682 (M^+, 2, 3, 3, 2), 211 (100), 141 (13); HRMS m/z calcd for $C_{30}H_{30}O_2^{130}Te_2$: 682.0372. Found: 682.0374.

4.3.8. (Z)-Bis(o-formyl-α-phenylstyryl) ditelluride ***3Ah***. Yield: 262 mg (78%), orange needles, mp 40–45 °C (from $CHCl_3$/hexane). IR (neat, cm^{-1}): 1693 (C=O); ^{1}H NMR (500 MHz): 7.05 (2H, s, Ph–C*H*=C–×2), 7.08, 7.20–7.62, 7.84 (2H, d, J=7.4 Hz, 14H, m, 2H, dd, J=7.6, 1.2 Hz, Ph–H), 10.14 (2H, s, CHO×2); ^{13}C NMR (125 MHz): 123.1 (s), 127.9 (d), 128.0 (d), 128.3 (d), 129.4 (d), 130.0 (d), 130.1 (d), 133.4 (s), 133.7 (d), 135.0 (d), 142.7 (s), 144.4 (s), 191.7 (d); MS m/z (relative intensity, %): 674 (M^+, 2, 3, 3, 2), 207 (100), 178 (45); HRMS m/z calcd for $C_{30}H_{22}O_2^{130}Te_2$: 673.9744. Found: 673.9739.

4.3.9. (Z)-Bis(α-tert-butyl-o-formylstyryl) diselenide ***3Ba***. Yield: 234 mg (88%), orange prisms, mp 117–119 °C (from CH_2Cl_2/hexane). IR (KBr, cm^{-1}): 1690 (C=O); ^{1}H NMR (500 MHz): 1.17 (18H, s, *t*-Bu), 7.13 (2H, s, Ph–C*H*=C–×2), 7.26, 7.38, 7.50, 7.84 (2H, d, J=7.4 Hz, 2H, dd, J=7.7, 7.3 Hz, 2H, ddd, J=7.6, 7.4, 1.4 Hz, 2H, dd, J=7.7, 1.4 Hz, Ph–H), 10.07 (2H, s, CHO×2); ^{13}C NMR (125 MHz): 29.9 (q), 40.3 (s), 127.4 (d), 128.6 (d), 129.5 (d), 131.1 (d), 133.3 (d), 133.4 (s), 142.0 (s), 151.6 (s), 191.6 (d); ^{77}Se NMR (76.3 MHz): 396.7; MS m/z (relative intensity, %): 534, 532, 530, 528 (M^+, 2, 2), 187 (100); HRMS m/z calcd for $C_{26}H_{30}O_2^{80}Se_2$: 534.0576. Found: 534.0579.

4.3.10. (Z)-Bis(o-formylstyryl) diselenide ***3Bb***. Yield: 162 mg (77%), yellow prisms, mp 75–77 °C (from CH_2Cl_2/hexane). IR (KBr, cm^{-1}): 1696 (C=O); ^{1}H NMR (500 MHz): 7.20 (2H, d, J=10.0 Hz, Ph–C*H*=C–×2), 7.42 (2H, d, J=10.0 Hz, –CH=C*H*–Se×2), 7.39, 7.48, 7.60, 7.90 (2H, dd, J=7.7, 1.0 Hz, 2H, ddd, J=7.7, 7.5, 1.0 Hz, 2H, ddd, J=7.7, 7.5, 1.4 Hz, 2H, dd, J=7.7, 1.4 Hz, Ph–H), 10.20 (2H, s, CHO×2); ^{13}C NMR (125 MHz): 128.4 (d), 129.3 (d), 129.4 (d), 129.8 (d), 131.4 (d), 133.1 (s), 133.7 (d), 138.7 (s), 191.7 (d); MS m/z (relative intensity, %): 422, 420 (M^+, 2, 2), 183 (10), 131 (100), 102 (12); HRMS m/z calcd for $C_{18}H_{14}O_2^{80}Se_2$: 421.9324. Found: 421.9337.

4.3.11. (Z)-Bis(o-formyl-α-methylstyryl) diselenide ***3Bc***. Yield: 123 mg (55%), orange oil. IR (neat, cm^{-1}): 1692 (C=O); ^{1}H NMR (500 MHz): 2.31 (6H, s, Me), 7.07 (2H, br s, Ph–C*H*=C–×2), 7.28, 7.44, 7.57, 7.89 (2H, d, J=7.6 Hz, 2H, dd, J=7.7, 7.6 Hz, 2H, dd, J=7.6, 7.6 Hz, 2H, d, J=7.7 Hz, Ph–H), 10.16 (2H, s, CHO×2); ^{13}C NMR (125 MHz): 26.6 (q), 127.3 (d), 128.1 (d), 129.6 (d), 130.8 (d), 133.5 (s), 133.6 (d), 134.8 (s), 140.4 (s), 191.7 (d); MS m/z (relative intensity, %): 450, 448 (M^+, 1, 1), 145 (100), 115 (22); HRMS m/z calcd for $C_{20}H_{18}O_2^{80}Se_2$: 449.9637. Found: 449.9644.

4.3.12. (Z)-Bis(o-formyl-α-n-propylstyryl) diselenide ***3Bd***. Yield: 153 mg (61%), orange oil. IR (neat, cm^{-1}): 1693 (C=O); ^{1}H NMR (90 MHz): 0.88, 1.3–1.6, 2.51 (6H, t, J=7 Hz, 4H, m, 4H, t, J=7 Hz, *n*-Pr), 7.00 (2H, s, Ph–C*H*=C–×2), 7.1–7.9 (8H, m, Ph–H), 10.10 (2H, s, CHO×2); MS m/z (relative intensity, %): 506, 504 (M^+, 1, 1), 237 (10), 173 (100); HRMS m/z calcd for $C_{24}H_{26}O_2^{80}Se_2$: 506.0263.Found: 506.0266.

4.3.13. (Z)-Bis(α-n-butyl-o-formylstyryl) diselenide ***3Be***. Yield: 202 mg (76%), yellow oil. IR (neat, cm^{-1}): 1695 (C=O); ^{1}H NMR (500 MHz): 0.8, 1.24–1.35, 1.15–1.53, 2.49 (6H, t, J=7.3 Hz, 4H, m, 4H, m, 4H, t, J=7.2 Hz, *n*-Bu), 7.05 (2H, s, Ph–C*H*=C–×2), 7.25, 7.44, 7.56, 7.89 (2H, dd, J=7.5, 1.1 Hz, 2H, ddd, J=7.8, 7.5, 1.1 Hz, 2H, ddd, J=7.5, 7.5, 1.4 Hz, 2H, dd, J=7.8, 1.4 Hz, Ph–H), 10.16 (2H, s, CHO×2); ^{13}C NMR (125 MHz): 14.0 (q), 21.9 (t), 31.0 (t), 38.2 (t), 127.1 (d), 128.1 (d), 129.3 (d), 131.0 (d), 133.5 (d), 133.6 (s), 140.2 (s), 140.7 (s), 191.6 (d); MS m/z (relative intensity, %): 534, 532 (M^+, 1, 1), 267 (2), 187 (100); HRMS m/z calcd for $C_{26}H_{30}O_2^{80}Se_2$: 534.0576. Found: 534.0577.

4.3.14. (Z)-Bis(o-formyl-α-n-octylstyryl) diselenide ***3Bf***. Yield: 209 mg (65%), yellow oil. IR (neat, cm^{-1}): 1695 (C=O); ^{1}H NMR (90 MHz): 0.85, 1.1–1.7, 2.48 (3H, t, J=6 Hz, 24H, m, 4H, t, J=7 Hz, *n*-Oct), 7.23 (2H, s, Ph–C*H*=C–×2), 7.34, 7.41, 7.52, 7.83 (2H, ddd, J=7.9, 7.3, 0.6 Hz, 2H, dd, J=7.7, 0.6 Hz, 2H, ddd, J=7.7, 7.3, 1.3 Hz, 2H, dd, J=7.9, 1.3 Hz, Ph–H), 10.19 (2H, s, CHO×2); ^{13}C NMR (125 MHz): 13.5 (q), 22.0 (t), 22.27 (t), 22.31 (t), 22. 4 (t), 34.3 (t), 34.4 (t), 40.4 (t), 127.3 (s), 128.1 (d), 129.1 (d), 129.3 (d), 129.6 (d), 133.5 (s), 133.6 (d), 140.7 (s), 191.6 (s); MS m/z (relative intensity, %): 646, 644 (M^+, 1, 1), 307 (15), 243 (100); HRMS m/z calcd for $C_{34}H_{46}O_2^{80}Se_2$: 646.1828. Found: 646.1840.

4.3.15. (Z)-Bis(α-cyclohexenyl-o-formylstyryl) diselenide ***3Bg***. Yield: 211 mg (73%), yellow oil. IR (neat, cm^{-1}): 1691 (C=O); ^{1}H NMR (900 MHz): 1.38–1.43, 1.47–1.52, 2.03–2.11, 2.21–2.27, 6.00 (4H, m, 4H, m, 4H, m, 4H, m, 2H, t, J=3.9 Hz, cyclohexenyl–H), 6.98 (2H, s, Ph–C*H*=C–×2), 7.2–7.8 (8H, m, Ph–H), 10.15 (2H, s, CHO×2); MS m/z (relative intensity, %): 582, 580 (M^+, 1, 1), 391 (27), 149 (100); HRMS m/z calcd for $C_{30}H_{30}O_2^{80}Se_2$: 582.0576. Found: 582.0573.

4.3.16. (Z)-Bis(o-benzoyl-α-tert-butylstyryl) ditelluride ***6A***. Yield: 313 mg (80%), orange oil. IR (neat, cm^{-1}): 1660 (C=O); ^{1}H NMR (500 MHz): 1.46 (18H, s, *t*-Bu), 7.47 (2H, s, Ph–C*H*=), 6.89, 7.07, 7.41–7.52, 7.53–7.57, 8.06 (2H, ddd, J=8.4, 6.2, 06 Hz, 2H, ddd, J=8.5, 6.3, 0.9 Hz, 8H, m, 4H, m, 2H, d, J=9.3 Hz, Ph–H); ^{13}C NMR (125 MHz): 28.8 (q), 44.6 (s), 125.5 (d), 123.9 (d), 125.4 (d), 126.5 (d), 128.2 (d), 128.9 (d), 129.8 (d), 130.2 (d), 132.4 (s), 139.0 (s), 144.6 (s), 150.6 (s), 206.5 (s); MS m/z (relative intensity, %): 786, 784, 782, 780 (M^+, 12, 18, 20, 15), 263 (100), 207 (35), 105 (52); HRMS m/z: M^+ calcd for $C_{38}H_{38}O_2^{130}Te_2$: 786.0996. Found: 786.1004.

4.3.17. (Z)-Bis(o-benzoyl-α-tert-butylstyryl) diselenide ***6B***. Yield: 277 mg (81%), yellow oil. IR (neat, cm^{-1}): 1662 (C=O). ^{1}H NMR (500 MHz): 0.91 (18H, s, *t*-Bu), 6.94 (2H, s, Ph–C*H*=), 7.27–7.32, 7.70 (14H, m, 4H, dd J=8.3, 1.3 Hz, Ph–H); ^{13}C NMR (125 MHz): 29.8 (q), 40.2 (s), 126.5 (d), 128.2 (d), 129.4 (d), 130.08 (d), 130.09 (d), 130.8 (d), 132.54 (d), 132.56 (d), 138.0 (s), 138.1 (s), 138.3 (s), 148.1 (s), 197.5 (s); MS m/z (relative intensity, %): 686, 684 (M^+, 1, 1), 327 (53), 263 (100); HRMS m/z: M^+ calcd for $C_{38}H_{38}O_2^{80}Se_2$: 686.1202. Found: 686.1114.

4.3.18. (Z)-Bis(o-acetyl-α-tert-butylstyryl) diselenide ***7B***. Yield: 21%, yellow oil. IR (neat, cm^{-1}): 1679 (C=O); ^{1}H NMR (500 MHz): 1.40 (18H, s, *t*-Bu), 1.47 (6H, s, $COCH_3$), 7.18 (2H, s, Ph–C*H*=), 7.51, 7.54, 7.68, 8.17 (2H, ddd, J=8.0, 7.1, 1.3 Hz, 2H, dd, J=8.0, 1.3 Hz, 2H, ddd, J=8.0, 7.1, 1.3 Hz, 2H, dd, J=8.0, 1.3 Hz, Ph–H); ^{13}C NMR (125 MHz): 31.1 (q), 32.8 (q), 39.1 (s), 118.1 (d), 124.6 (d), 127.5 (s), 128.3 (d),

131.9 (d), 133.5 (d), 139.3 (s), 155.9 (s), 192.6 (s); MS *m*/*z* (relative intensity, %): 562, 560 (M^+, 1, 1), 266 (40), 251 (100), 249 (50); HRMS *m*/*z*: M^+ calcd for $C_{28}H_{34}O_2^{80}Se_2$: 562.0889. Found: 562.0891.

4.3.19. (Z)-1-Benzylidene-3-tert-butyl-1H-isotellurochromene ***10A***. Yield: 58%, pale yellow prisms, mp 104–106 °C (from $CHCl_3$/hexane). ^1H NMR (500 MHz): 1.24 (9H, s, *t*-Bu), 6.86 (1H, s, 4-H), 7.20, 7.24–7.31, 7.33–7.38, 7.40–7.45, 7.53 (1H, dd, *J*=8.0, 1.2 Hz, 3H, m, 2H, m, 2H, m, 1H, d, *J*=7.5 Hz, Ph–H), 7.49 (s, C*H*=Ph); ^{13}C NMR (125 MHz): 30.9 (q), 39.3 (s), 118.8 (s), 125.4 (d), 125.6 (d), 127.7 (d), 128.1 (d), 128.2 (d), 128.3 (d), 128.5 (d), 131.0 (d), 133.4 (s), 136.8 (s), 137.2 (d), 139.4 (s), 140.2 (s).

4.3.20. (Z)-1-Benzylidene-3-tert-butyl-1H-isoselenochromene ***10B***. Yield: 64%, pale yellow prisms, mp 127–128 °C (from $CHCl_3$/hexane). ^1H NMR (500 MHz): 1.25 (9H, s, *t*-Bu), 6.72 (1H, s, 4-H), 7.21 (1H, s, C*H*=Ph), 7.14, 7.22–7.30, 7.33–7.44, 7.55 (1H, dd, *J*=7.5 Hz, 3H, m, 4H, m, 1H, d, *J*=7.6 Hz, Ph–H); ^{13}C NMR (125 MHz): 30.2 (q), 38.0 (s), 119.1 (d), 125.0 (d), 127.1 (d), 128.0 (d), 128.1 (d), 128.3 (d), 129.0 (d), 129.1 (d), 129.3 (s), 129.6 (d), 131.0 (s), 134.2 (s), 137.2 (s), 147.6 (s).

4.3.21. (Z)-1-n-Butylidene-3-tert-butyl-1H-isotellurochromene ***11A***. Yield: 60%, orange oil. ^1H NMR (90 MHz): 1.27 (9H, s, *t*-Bu), 0.93, 1.30–1.70, 2.10–2.40 (3H, t, *J*=7.6 Hz, 2H, m, 2H, m, *n*-Pr), 6.19 (1H, t, *J*=7 Hz, C=C*H*–*n*-Pr), 6.75 (1H, s, Ph–C*H*=), 7.00–7.50 (4H, m, Ph–H); MS *m*/*z* (relative intensity, %): 356 (M^+, 100), 354 (85), 327 (45), 301 (60); HRMS *m*/*z*: M^+ calcd for $C_{17}H_{22}^{130}Te$: 356.0784. Found: 356.0786.

4.3.22. (Z)-3-tert-Butyl-1-n-butylidene-1H-isoselenochromene ***11B***. Yield: 65%, yellow oil. ^1H NMR (90 MHz): 1.30 (9H, s, *t*-Bu), 0.98, 1.48–1.00, 2.25 (3H, t, *J*=7 Hz, 2H, m, 2H, m, *n*-Pr), 6.12 (1H, t, *J*=7 Hz, C=C*H*–*n*-Pr), 6.67 (1H, s, Ph–C*H*=), 7.15–7.43 (4H, m, Ph–H); MS *m*/*z* (relative intensity, %): 306 (M^+, 90), 304 (60), 277 (100), 275 (81), 165 (36); HRMS *m*/*z*: M^+ calcd for $C_{17}H_{22}^{80}Se$: 306.0887. Found: 306.0883.

4.4. 1-Acetoxy-3-*tert*-butyl-1*H*-isotellurochromene 16

m-CPBA (70%, 296 mg, 1.2 mmol) was added to a solution of 3-*tert*-butylisotellurochromene (**1Aa**, 302 mg, 1.0 mmol) in dry $CHCl_3$ (10 mL) at 0 °C under argon atmosphere and the mixture was stirred under same conditions. After 30 min, Ac_2O (1.0 mL) was added to the reaction mixture and stirred for another 1 h. The reaction mixture was quenched with water (10 mL), the aqueous mixture was extracted with CH_2Cl_2 (50 mL×3). The organic layers were washed with brine (30 mL×2), dried ($MgSO_4$), and evaporated. The residue was triturated and extracted with hexane, and filtrated to remove *m*-chlorobenzoic acid. The filtrate was evaporated to provide 1-acetoxyisotellurochromene in an almost pure state. Yellow oil. IR (neat, cm^{-1}): 1697 (C=O); ^1H NMR (90 MHz): 1.51 (9H, s, *t*-Bu), 2.15 (3H, s, $COCH_3$), 4.94 (1H, s, 1-H), 7.33 (1H, s, 4-H), 7.22–7.93 (4H, m, Ph–H); MS *m*/*z* (relative intensity, %): 360 (M^+, 5), 301 (65), 187 (18), 156 (75), 139 (100); HRMS *m*/*z*: M^+ calcd for $C_{15}H_{18}O_2^{130}Te$: 360.0369. Found: 360.0368.

4.5. Hydrolysis of 1-acetoxy-3-*tert*-butyl-1*H*-isotellurochromene 16: formation of 3Aa

To the obtained crude 1-acetoxyisotellurochromene **16** in $CHCl_3$ (10 mL) was added satd aq $NaHCO_3$ (5 mL mL). The reaction mixture was vigorously stirred at room temperature, immediately became reddish orange color. The mixture was extracted with CH_2Cl_2 (10 mL×2), the combined organic layer was washed with brine (30 mL×2), dried ($MgSO_4$), and evaporated in vacuo. The residue was chromatographed on silica gel using *n*-hexane/CH_2Cl_2 (1:1) as eluent to give **3Aa** in almost quantitative yield.

4.6. Hydrolysis of telluropyrylium salts 17A and selenopyrylium salts 17B

H_2O (6 mL) was added to a suspended solution of the pyrylium salts **16** (0.3 mmol) in Et_2O (12 mL). The reaction mixture was vigorously stirred at room temperature for 30 min, and extracted with Et_2O (20 mL×3). The organic layer was washed with brine (30 mL×2), dried ($MgSO_4$), and evaporated in vacuo. The residue was chromatographed on silica gel using *n*-hexane/CH_2Cl_2 (1:1) as eluent to give **3** and **18**.

4.6.1. (Z)-Bis(α-tert-butyl-o-formylstyryl) ditelluride ***3Aa***. Yield: 92%.

4.6.2. (Z)-Bis(o-formylstyryl) ditelluride ***3Ab***. Yield: 24%.

4.6.3. (Z)-Bis(α-tert-butyl-o-formylstyryl) diselenide ***3Ba***. Yield: 10%. Yellow prisms, mp 117–119 °C (from $CHCl_3$/hexane).

4.6.4. 3-tert-Butyl-1-hydroxy-1H-isoselenochromene ***18***. Yield: 89%, yellow oil. IR (neat, cm^{-1}): 3388 (OH). ^1H NMR (90 MHz): 1.31 (9H, s, *t*-Bu), 2.37 (1H, d, *J*=8 Hz, OH), 6.02 (1H, d, *J*=8 Hz, 1-H), 6.90 (1H, s, 4-H), 7.3–7.4 (4H, m, Ph–H); MS *m*/*z* (relative intensity, %): 268 (M^+, 100), 187 (79), 131 (48), 115 (17); HRMS *m*/*z*: M^+ calcd for $C_{13}H_{16}OSe$: 268.0366. Found: 268.0372.

4.7. (*o*-Formylstyryl)tellurium(IV) trichloride 19

SO_2Cl_2 (five drops, 92 mg) was added to a solution of the *o*-formylstyryl ditelluride **3A** (0.5 mmol) in dry CH_2Cl_2 (2 mL) at 0 °C. The reaction mixture was vigorously stirred at room temperature for 30 min, and evaporated. The resulting residue was recrystallized from Et_2O or CH_2Cl_2/hexane.

4.7.1. α-tert-Butyl-o-formylstyryltellurium(IV) trichloride ***19a***. Yield: 95%, colorless prisms, mp 216–218 °C (decomp. from Et_2O). IR (KBr, cm^{-1}): 1681 (C=O); ^1H NMR (500 MHz): 1.69 (9H, s, *t*-Bu), 7.15–7.80, 7.94, 8.05 (2H, m, 1H, dd, *J*=6.1, 1.5 Hz, 1H, dd, *J*=6.7, 2.2 Hz, Ph–H), 8.08 (1H, s, Ph–C*H*=), 10.11 (1H, s, CHO); ^{13}C NMR (125 MHz): 30.3 (q), 45.4 (s), 131.0 (d), 131.8 (d), 132.1 (d), 133.0 (s), 133.3 (d), 134.3 (d), 135.5 (s), 164.7 (s), 190.4 (d); MS *m*/*z* (relative intensity, %): 389 (M^+–Cl, 5), 351 (3), 307 (25), 301 (30), 187 (100).

4.7.2. o-Formyl-α-methylstyryltellurium(IV) trichloride ***19c***. Yield: 84%, colorless prisms, mp 107–109 °C (decomp. from CH_2Cl_2/hexane); IR (KBr, cm^{-1}): 1704 (C=O); ^1H NMR (500 MHz): 2.95 (3H, s, Me), 7.41–7.82, 7.96–8.08 (2H, m, 2H, m, Ph–H), 8.19 (1H, s, Ph–C*H*=), 10.01 (1H, s, CHO); MS *m*/*z* (relative intensity, %): 347, 345, 343, 341 (M^+–Cl, 3, 8, 7, 3), 274 (11), 272 (10), 145 (100), 115 (45).

4.8. Crystal data for 3Aa

Single crystals of **3Aa** were obtained from solutions of acetone/hexane after slow evaporation of the solvents at room temperature. Diffraction data were collected on a Bruker Apex-II CCD diffractometer equipped with a graphite monochromated Mo Kα radiation source (λ=0.71073 Å). The structures were solved by direct methods (SHELXS-97), and refined by full-matrix least-square methods on F^2 for all reflections (SHELXL-97) with all non-hydrogen atoms anisotropic and all hydrogen atoms isotropic.

For **3Aa**, the structure analysis is based on 2511 observed reflections with $I>2.00\sigma(I)$ and 139 variable parameters; red prisms, $C_{26}H_{30}O_2Te_2$, FW=629.7, 113 K, *orthorhombic*, space group *Pbcn*,

a=11.027(4) Å, b=19.194(7) Å, c=11.662(5) Å, V=2468.3(2) Å^3, Z=4, R=0.0533, R_w=0.1365, GOF=1.163.

CCDC 881933 for **3Aa** contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/products/csd/request/.

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