Studies on tellurium-containing heterocycles. Part 18.¹ Preparation and structure of 2-benzotelluropyrylium salts and 2-benzoselenopyrylium salts

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The regioselective and stereospecific intramolecular ring closure reactions of *o*-ethynylbenzyl tellurols **5A** and *o*-ethynylbenzyl selenols **5B**, which were readily generated by the reaction of the *o*-ethynylbenzyl bromides **4** with sodium hydrogen telluride (NaHTe) or sodium hydrogen selenide (NaHSe), produced the isotellurochromenes **6A** and isoselenochromenes **6B** together with (*Z*)-1-methylidene-2-telluraindans **7A** and (*Z*)-1-methylidene-2-selenaindans **7B**, respectively. The obtained isochromenes **6A** and **6B** were transformed into the corresponding 2-benzotelluropyrylium tetrafluoroborates **9A** and 2-benzoselenopyrylium tetrafluoroborates **9B** by treatment with triphenylcarbenium tetrafluoroborate ($Ph_3C^+BF_4^-$) in excellent yields, respectively. An X-ray structural analysis of the *tert*-butyl derivatives **9Ac** and **9Bc** is also described.

Introduction

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The chemistry (syntheses, structure, physical properties, and reactions) of six-membered sulfur-containing heterocycles, thiopyrans,² thiopyrylium salts³ and their benzo derivatives has been widely investigated and well established. Recently, extensive synthetic work on their tellurium²⁻⁴ and selenium^{2,3} analogs has been undertaken. The monocyclic pyrylium salts and 1-benzo derivatives containing a selenium² or tellurium atom^{2,4} are known. However, no 2-benzotelluropyrylium salts,^{5a} a theoretically possible structural isomer of the latter, have been prepared until now. With regard to the 2-benzoselenopyrylium salts, the synthesis of only the unsubstituted derivative was reported by Renson and Pirson more than 35 years ago.⁶ Recently, we focused on the synthesis of various tellurium- or selenium-containing heterocycles⁷ based on the successive intramolecular addition of the tellurols or selenols to an ethynyl group. We have previously succeeded in the general and facile two-step synthesis of the 1-benzotelluropyrylium salts⁸ and 1-benzoselenopyrylium salts⁹ from the corresponding telluroor seleno-chromen-4-ones^{7e} and also examined their reactions¹⁰ with nucleophiles. As part of our continuing studies, we describe herein an extension of our synthetic strategy for the novel synthesis of the isotellurochromenes 6A and isoselenochromenes 6B, and their transformation into the corresponding title pyrylium salts 9.

Results and discussion

Preparation of 2-benzotelluropyrylium and 2-benzoselenopyrylium salts

There are two possible routes for the preparation of the key starting *o*-ethynylbenzyl bromides **4** from *o*-iodobenzyl alcohol **1** as shown in Scheme 1. Route A through the *o*-iodobenzyl bromide **2** is more effective than route B due to the use of **2** as a mutual starting material for ethynylation. However, this

ii Route A 2 $C \equiv C - R$ ii c = cRoute B OН a: R = Me $\mathbf{b}: \mathbf{R} = \mathbf{B}\mathbf{u}'$ 3 $\mathbf{c}: \mathbf{R} = \mathbf{B}\mathbf{u}^{t}$ d: R = Phe: R = TMSiii **f**: R = H

Scheme 1 Reagents and conditions: i, PBr₃, pyridine, CHCl₃, 0 °C to room temp., 6-10 h; ii, alkyne, PdCl₂(Ph₃P)₂, CuI, benzene–piperidine, room temp., 5-10 h; iii, K₂CO₃, MeOH, room temp., 1 h.

path was eliminated because the ethynylation of 2 did not occur and only the homo-coupling products of the alkynes were obtained. *o*-Ethynylbenzyl alcohols **3** were easily prepared by Sonogashira's procedure.¹¹ The palladium-catalyzed coupling reaction of *o*-iodobenzyl alcohol **1** with 1-substituted alkynes in a mixed solvent of benzene and piperidine gave the desired ethynyl derivatives **3**, which were readily brominated with phosphorus tribromide to give the corresponding benzyl bromides **4** in good yields. The trimethylsilyl (TMS) group on

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Scheme 2 Reagents and conditions: i, NaHTe or NaHSe (1.2 equiv.), DMF, 0 °C room temp., 1 h; ii, EtOH, 90 °C, 1–3 h; iii, $K_3Fe(CN)_6$, H_2O , room temp., 10 min; iv, NaBH₄, EtOH, room temp., 1 h; v, $Ph_3C^+BF_4^-$ (1.05 equiv.), MeNO₂, room temp., 30 min.

the triple bond of the benzyl bromide **4e** was easily removed to give the *o*-ethynylbenzyl bromide **4f** by treatment with potassium carbonate in methanol at room temperature.

The syntheses of the 2-benzotelluropyrylium salts 9A and 2-benzoselenopyrylium salts 9B are shown in Scheme 2. In order to obtain the isochromenes 6A and 6B, precursors for the preparation of the title compounds, we examined the conversion of the o-ethynylbenzyl bromides 4 into the o-ethynylbenzyl tellurols 5A or o-ethynylbenzyl selenols 5B. The treatment of the benzyl bromides 4 with sodium hydrogen telluride (NaHTe),¹² which was freshly prepared from tellurium dust and sodium borohydride in DMF, followed by the addition of ethanol, and then heating at 90 °C, resulted in the direct ring closure to afford the desired isotellurochromenes 6A, together with the five-membered compounds, the (Z)-1-methylidene-2-telluraindans 7A, via the specific tellurol intermediates 5A. The isotellurochromenes 6A were produced by the 6-endo-dig ring closure of 5A at the sp carbon atom of the ethynyl group. The 2-telluraindans 7A are the products of the 5-exo-dig reaction. The formation of compounds 5A was characterized by the isolation of the bis(o-ethynylbenzyl) ditellurides 8A, which were obtained by the potassium ferricyanide oxidation¹³ of 5A before heating in ethanol. The ditellurides 8A reverted back to the tellurols 5A by treatment with sodium borohydride in ethanol with reductive fission of the Te-Te bond. The trimethylsilylethynylbenzyl tellurol 5Ae also gave the 3-unsubstituted isotellurochromene 6Af directly with reductive removal of the TMS group under the reaction conditions, but in poor yield. The cyclization of ethynylbenzyl tellurol 5Af proceeds to afford 6Af in a higher, good yield. In this case, the 1-methylidene-2telluraindan 7Af was not obtained. It is well known and established that both intermolecular 7a,14 and intramolecular $^{7b-g}$ trans-additions of tellurols to a triple bond proceed stereospecifically to provide the anti Markovnikov-type products. The phenyl derivative 5Ad gave the isotellurochromene 6Ad and the telluraindans 7Ad in 19 and 71% yields, respectively. In the ¹H NMR (400 MHz) spectra of the telluraindans 7A, a nuclear Overhauser enhancement (NOE) was observed between the exocyclic methyne proton (1'-H) and the aromatic 7-H. Thus, the stereochemistry of the olefin moiety of 7A was found to be the (Z)-form.

The isoselenochromenes 6B and the (*Z*)-1-methylidene-2-selenaindans 7B were similarly obtained using sodium hydrogen selenide (NaHSe). *o*-Ethynylbenzyl selenol **5Bf** regioselectively cyclized to afford isoselenochromene **6Bf** without producing the 2-selenaindan **7Bf**. In contrast, in the case of the phenyl derivative **5Bd**, only the 5-*exo-dig* reaction proceeded to form the benzylidene-2-selenaindan **7Bd** in 66% yield. Overall, the 6-*endo-dig* ring closure was the preferential reaction during the present intramolecular *trans*-addition of the tellurols or the selenols to an acetylenic moiety except for the phenyl derivative **5d**. These results are summarized in Table 1, and the ¹H NMR and MS spectral data for **6** and **7** are collected in Tables 2 and 3, respectively. All the isotellurochromenes **6A** and the isoselenochromenes **6B** except for the 3-unsubstituted isochromene **6Bf**⁶ are hitherto unknown compounds.

Next, the transformation into the 2-benzotelluropyrylium salts 9A and the 2-benzoselenopyrylium salts 9B was carried out from the corresponding isochromenes 6A, 6B using the substrates obtained, except for the phenyl derivative 6Bd. The 3-tert-butyl derivatives 6Ac, 6Bc and the 3-unsubstituted isochromenes 6Af, 6Bf were treated with triphenylcarbenium tetrafluoroborate $(Ph_3C^+BF_4^-)$ in nitromethane at room temperature to give the desired corresponding 2-benzotelluropyrylium tetrafluoroborates 9Ac, 9Af and 2-benzoselenopyrylium tetrafluoroborates 9Bc, 9Bf as yellow or pale green prisms in high yields, respectively. These salts are quite stable and can be stored for several months even at room temperature under an argon atmosphere. However, they are instantaneously decomposed upon contact with water or a protic solvent such as an alcohol. In contrast, the 2-benzotelluropyrylium salts 9Aa, 9Ab and 2-benzoselenopyrylium salts 9Ba, 9Bb having another alkyl substituted group (methyl and n-butyl) on the C-3 position could not be obtained in a stable crystalline state from the corresponding isochromenes under the same conditions. They are too unstable to be isolated, and decompose even in solution in ca. 10-20 minutes. The reason why these pyrylium salts are not stable compared to the 3-tert-butyl and 3unsubstituted derivatives might be the reaction shown in Scheme 3. A β -hydrogen from the heteroatom of the pyrylium salts 9 would be attacked and eliminated by the strong base, the tetrafluoroborate (BF_4^{-}) anion, to form the *o*-quinonoid compounds 10, which would be unstable due to the destruction of the aromaticity of the benzene ring.

Similar β -hydrogen elimination behavior was observed in the case of the 1-benzyl-2-benzotelluropyrylium salt; the (*Z*)-1-benzylideneisotellurochromene^{5a} was isolated. 3-Phenyl-2benzotelluropyrylium salt **9Ad** was also moisture-sensitive

		6			7				
М	R	Yield (%) ^a	Appearance	Mp/°C	Yield (%) ^a	Appearance	Mp/°C		
Te	Me	66	Yellow prisms ^b	59	25	Yellow prisms ^b	73–74		
Te	\mathbf{Bu}^n	66	Yellow oil	_	20	Pale yellow oil			
Te	$\mathbf{B}\mathbf{u}^{t}$	84	Yellow prisms ^b	63	0				
Te	Ph	19	Yellow prisms ^d	51-52	71	Yellow prisms ^c	98–99		
Te	Н	64	Yellow prisms ^d	66-67	0				
Se	Me	48	Pale yellow prisms ^b	43	33	Pale yellow prisms ^b	61-63		
Se	\mathbf{Bu}^n	49	Yellow oil		22	Yellow oil			
Se	\mathbf{Bu}^{t}	60	Yellow prisms ^b	69-71	14	Yellow oil			
Se	Ph	0		_	66	Colorless prisms ^c	77-80		
Se	Н	56	Yellow oil		0				

Table 2 Spectral data for the isotellurochromenes 6A and the isoselenochromenes 6B										
		М	Formula	HRMS calcd (found)	$\delta_{\rm H}$ (90 MHz, CDCl ₃)					
Compd. no.	R				1-H ₂	4-H	Ph-H	R-H		
6Aa	Me	Te	C ₁₀ H ₁₀ Te	259.9845 (259.9845)	3.90 (s)	6.59 (q, J 1.7)	7.01–7.26 (4H, m)	2.40 (3H, d, J 1.7, Me)		
6Ab	Bu ⁿ	Te	$C_{13}H_{13}$ Te	302.0315 (302.0313)	3.86 (s)	6.59 (br s)	7.02–7.23 (4H, m)	0.93, 1.19–1.62, 2.59 (3H, t, <i>J</i> 6.2, 4H, m, 2H, br t, <i>J</i> 7.0, Bu ⁿ)		
6Ac	$\mathbf{B}\mathbf{u}^{t}$	Te	C ₁₃ H ₁₆ Te	302.0315 (302.0313)	3.79 (s)	6.64 (s)	7.10–7.26 (4H, m)	1.29 (9H, s, Bu ^t)		
6Ad	Ph	Te	$C_{15}H_{12}Te$	322.0002 (321.9996)	3.98 (s)	7.09 (s)		7.17–7.64 (9H, m, Ph)		
6Af	Н	Te	C ₉ H ₈ Te	245.9689 (245.9693)	3.86 (s)	7.02 (d, J 10.3)	7.10–7.25 (4H, m)	7.22 (d, J 10.3, H)		
6Ba	Me	Se	$C_{10}H_{10}Se$	209.9948 (209.9943)	3.85 (s)	6.63 (q, J 1.6)	6.92–7.30 (4H, m)	2.24 (3H, d, J 1.6, Me)		
6Bb	\mathbf{Bu}^n	Se	C ₁₃ H ₁₆ Se	252.0418 (252.0425)	3.85 (s)	6.71 (t, J 1.8)	6.97–7.34 (4H, m)	0.95, 1.22-1.83, 2.52 (3H, t, J 6.0,		
								4H, m, 2H, dt, <i>J</i> 1.8, 7.0, Bu ⁿ)		
6Bc	$\mathbf{B}\mathbf{u}^{t}$	Se	C ₁₃ H ₁₆ Se	252.0418 (252.0414)	3.76 (s)	6.70 (s)	7.12–7.26 (4H, m)	1.29 (9H, s, Bu ^t)		
6Bf	Н	Se	C ₉ H ₈ Se	195.9791 (195.9791)	3.84 (s)	6.79 (d, J 9.9)	7.09–7.25 (4H, m)	6.95 (d, J 9.9, H)		

Table 3 Spectral data for (Z)-1-methylidene-2-telluraindans 7A and (Z)-1-methylidene-2-selenaindans 7B

					$\delta_{\rm H}$ (90 MHz, CI	DCl ₃)		
Compd. no.	R	М	Formula	HRMS calcd (found)	1'-H	3-H ₂	Ph-H	R-H
7Aa	Me	Te	C ₁₀ H ₁₀ Te	259.9845 (259.9850)	6.76 (q, J 6.2)	4.65 (s)	7.05–7.76 (4H, m)	1.85 (3H, d, J 6.2, Me)
7Ab	Bu ⁿ	Te	$C_{13}H_{16}Te$	302.0315 (302.0312)	6.67 (t, J 6.6)	4.62 (s)	7.05–7.71 (4H, m)	0.93, 1.26–1.62, 2.09 (3H, t, <i>J</i> 6.6, 4H, m, 2H, dt, <i>J</i> 6.6, 7.0, Bu ⁿ)
7Ad	Ph	Te	C ₁₅ H ₁₂ Te	322.0002 (322.0005)	7.86 (s)	4.66 (s)		7.15–7.84 (9H, m, Ph)
7Ba	Me	Se	$C_{10}H_{10}Se$	209.9948 (209.9946)	6.44 (q, J 7.0)	4.38 (s)	7.03–7.70 (4H, m)	1.84 (3H, d, J 7.0, Me)
7Bb	\mathbf{Bu}^n	Se	C ₁₃ H ₁₆ Se	252.0418 (252.0428)	6.36 (t, J 7.0)	4.38 (s)	7.03–7.69 (4H, m)	0.94, 1.17–1.78, 2.16 (3H, t, <i>J</i> 6.6,
7Bc	\mathbf{Ru}^t	Se	C. H. Se	252 0418 (252 0417)	6.58(s)	4 38 (s)	7 12_7 71 (4H m)	4H, m, 2H, dt, J 6.6, 7.0, Bu'') 1 26 (9H s Bu')
7Bd	Ph	Se	$C_{15}H_{12}Se$	272.0105 (272.0104)	7.51 (s)	4.50 (s)	7.12 7.71 (411, m)	7.23–7.79 (9H, m, Ph)

and immediately decomposed upon contact with air. Thus, the deprotonation of these isochromenes by $Ph_3C^+BF_4^-$ to form the corresponding pyrylium salts was carried out in CD₃CN as a solvent, and the formation of **9Aa**, **9Ab**, **9Ad**, **9Ba** and **9Bb** was then monitored by ¹H NMR spectroscopy. The ¹H NMR spectral data of all the pyrylium salts **9A** and **9B** that have been prepared in the present study are listed in Table 4. The structures of these pyrylium salts **9** were elucidated from their ¹H and ¹³C NMR spectra and elemental analyses and also from single-crystal X-ray studies in the case of the *tert*-butyl derivatives **9Ac** and **9Bc**.

The ¹H NMR spectral data for the monocyclic unsubstituted thiopyrylium,15 selenopyrylium15 and telluropyrylium cations¹⁶ have been reported. However, no ¹H NMR data for the unsubstituted 2-benzothiopyrylium¹⁷ and 2-benzoselenopyrylium salts⁶ have been recorded in the literature, although they have been prepared; the 2-benzotelluropyrylium ring system was first constructed in this study. These ¹H NMR data (Table 4) and those of the 3-benzoyl-2-benzothiopyrylium cation reported by Shimizu and co-workers¹⁸ indicate a remarkable fact about their chemical shifts. The chemical shifts of the aromatic protons of the pyrylium salts 9A and 9B appear at lower fields, in particular, both the proton signals of 1-H (δ 12.05–13.31) and those of 4-H (δ 8.75–9.30) resonate at much lower fields compared to the 2-benzothiopyrylium salts.¹⁸ The chemical shift values of 1-H in these three pyrylium nuclei decrease in the order 9A (Te) > **9B** (Se) > thiopyrylium salt (S, δ 11.29).¹⁸ A similar tendency is observed for the 2-H protons of the five-membered heterocycles, the benzo[b]chalcogenophenes.^{7d} In contrast, the proton signals of 4-H of 9A and 9B appear at almost the same chemical shifts (δ 8.75–9.30); that of the thiopyrylium salt is

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 Table 4
 ¹H NMR spectral data for 2-benzotelluropyrylium 9A salts and 2-benzoselenopyrylium salts 9B

			$\frac{\partial_{\mathrm{H}}}{\partial_{\mathrm{H}}}$ (400 MHz, CD ₃ 0	CN)				
Compd. no.	R	М	1-H	4-H	Ph-H	R-H		
9Aa ^a	Me	Te	12.68 (br s)	8.75 (br s)	7.80–8.43 (4H, m)	3.14 (3H, br s, Me)		
9Ab ^a	\mathbf{Bu}^n	Te	12.96 (s)	8.85 (br s)	7.85-8.50 (4H, m)	0.98, 1.20–2.01, 3.54 (3H, t, J 7.6, 4H, m, 2H, t, J 7.9, Bu ⁿ)		
9Ac	$\mathbf{B}\mathbf{u}^{t}$	Te	13.25 (s)	9.12 (s)	7.81-8.53 (4H, m)	1.68 (9H, s, Bu')		
9Ad ^a	Ph	Te	13.11 (s)	9.20 (s)		7.77–8.55 (9H, m, Ph)		
9Af	Н	Te	13.31 (br d, J 2.9)	9.30 (d, J 11.0)	7.88–8.57 (4H, m)	10.48 (dd, <i>J</i> 11.0, 2.9, H)		
9Ba ^{<i>a</i>}	Me	Se	11.82 (br s)	8.82 (br s)	7.94–8.53 (4H, m)	3.14 (3H, br s, Me)		
9Bb ^{<i>a</i>}	Bu ⁿ	Se	11.86 (s)	8.85 (br s)	7.98–8.55 (4H, m)	0.99, 1.20–2.07, 3.47 (3H, t, <i>J</i> 8.2, 4H, m, 2H, br t, <i>J</i> 8.6, Bu ⁿ)		
9Bc	$\mathbf{B}\mathbf{u}^{t}$	Se	11.96 (s)	9.06 (s)	8.11-8.54 (4H, m)	1.70 (9H, s, Bu ^t)		
9Bf	Н	Se	12.05 (d, J 2.9)	9.15 (br s)	8.08-8.64 (4H, m)	9.87 (dd, J 9.5, 2.9, H)		
^a Not isolated	1.							

Table 5 Selected b	oond lengths (Å)	and angles (°) of 9Ac	Table 6 Selected bond lengths (Å) and angles (°) of 9Bc				
Te(1)-C(1)	2.003(7)	Te(1)-C(2)	2.042(5)	Se(1)–C(1)	1.806(5)	Se(1)–C(2)	1.853(4)
C(1) - C(9)	1.392(7)	C(2) - C(3)	1.374(8)	C(1) - C(9)	1.394(7)	C(2) - C(3)	1.363(6)
C(3) - C(8)	1.429(7)	C(8)–C(9)	1.439(8)	C(3) - C(8)	1.425(6)	C(8)–C(9)	1.418(7)
C(1)-Te(1)-C(2)	95.4(3)	Te(1)-C(1)-C(9)	125.2(4)	C(1)-Se(1)-C(2)	101.0(2)	Se(1)-C(1)-C(9)	124.8(3)
Te(1)-C(2)-C(3)	120.5(5)	C(2) - C(3) - C(8)	129.9(5)	Se(1)-C(2)-C(3)	120.3(3)	C(2) - C(3) - C(8)	128.2(4)
C(3) - C(8) - C(9)	124.6(5)	C(1)-C(9)-C(8)	124.4(5)	C(3)–C(8)–(9)	122.4(4)	C(1)–C(9)–C(8)	123.2(4)
				-			

observed somewhat more downfield (δ 9.50) because it has a benzoyl group as an electron-withdrawing substituent at the C-3 position.

X-Ray analysis

The structure of the 2-benzotelluropyrylium salt **9A**, which is a previously unknown heterocyclic ring system, was characterized by X-ray crystallographic analysis of a single crystal obtained by recrystallization from dichloromethane.

Fig. 1 shows the molecular structure of the 3-tert-butyl



Fig. 1 ORTEP drawing of 9Ac with 50% probability level.

derivative **9Ac**, and selected bond lengths and angles of **9Ac** are listed in Table 5. To our knowledge, this is the first crystal structure of benzotelluropyrylium, although the structure of one monocyclic telluropyrylium has been reported.¹⁹ The benzopyrylium ring system in **9Ac** is planar and the cation and anion lie on mirror planes. The tellurium atom has no significant interaction with the counter anion. The closest

distance from tellurium to the nearest fluorine in the borate is 3.790(3) Å, which is longer than the sum of the van der Waals radii (3.55 Å).²⁰ It is noteworthy that the carbon (C-1)–tellurium bond length (2.003 Å) in the telluropyrylium ring is significantly shorter than the typical covalent bond length of Te–C (2.12 Å). The shortness of the carbon–tellurium bond in **9Ac** is rather comparable to the values of the carbon (sp²)–tellurium double bond lengths that have been reported in the range of 1.987–2.298 Å with an average of 2.06 Å.²¹ Although the precise details of the resonance structures in the telluropyrylium are not clear, it is likely that the localized double bond that forms around the tellurium provides an important contribution to the overall description.

The structure of the corresponding 2-benzoselenopyrylium **9Bc** was determined for comparison. The molecular structure of **9Bc** and selected bond lengths and angles are given in Fig. 2 and Table 6, respectively.



Fig. 2 ORTEP drawing of 9Bc with 50% probability level.

The selenopyrylium **9Bc** showed an isomorphous structure to that of **9Ac** and also has mirror planes through the cation and anion. The C(1)–Se bond length [1.806(5) Å] is noticeably shorter than those usually observed for carbon–selenium single bond lengths (average 1.970 Å),²² being close to the C=Se double bond lengths that have been observed in selenoketones (1.774,^{23a} and 1.790 Å^{23b}).

Conclusion

In the present work, general preparations have been achieved for the isotellurochromenes and isoselenochromenes together with the (Z)-1-methylidene-2-indanes containing tellurium and selenium atoms by an intramolecular cyclization reaction with a triple bond. The isochromenes were transformed into the corresponding novel 2-benzotelluropyrylium and 2-benzoselenopyrylium salts. The structure of these pyrylium salts has been found to be quite flat based on the X-ray analyses of the *tert*-butyl derivatives. Examination of the reactivities of these pyrylium salts is in progress and will be reported in the near future.

Experimental

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were recorded on a Hitachi 270-30 spectrometer. Mass spectra (MS) and HRMS were recorded on a JEOL JMS-DX300 instrument. ¹H NMR spectra were recorded on a JEOL PMX-60 SI (60 MHz), a JEOL EX-90A (90 MHz) or a JEOL JNM-GSX 400 (400 MHz) spectrometer in CDCl₃ or CD₃CN using tetramethylsilane as the internal standard; *J* values are given in Hz. ¹³C NMR spectra and NOE spectra were measured on a JEOL JNM-GSX 400 spectrometer. ¹²⁵Te NMR spectra were recorded on a JEOL EX-400 spectrometer at 126.1 MHz, and samples were referenced to ¹²⁵TeMe₂ as an external standard. ⁷⁷Se NMR spectra were recorded on a JEOL EX-400 spectrometer at 76.2 MHz, and samples were referenced to Me₂Se as an external standard.

General procedure for the preparation of *o*-ethynylbenzyl alcohols 3a–e

To a mixture of alkyne (b: hex-1-yne, c: *tert*-butylacetylene, d: phenylacetylene, e: trimethylsilylacetylene, 0.11 mol) and o-iodobenzyl alcohol 1 (23.4 g, 0.1 mol)[†] in benzene (200 mL) and piperidine (200 mL) were added PdCl₂(Ph₃P)₂ (702 mg, 1 mmol) and CuI (400 mg, 2.1 mmol). The mixture was stirred at room temperature under argon for 6–10 h. Cold water (300 mL) was added to the mixture, and the resulting aqueous mixture was extracted with benzene (200 mL × 3). The combined organic extract was washed with water (200 mL × 4), 5% H₂SO₄ (200 mL × 3), sat. NaHCO₃ (200 mL × 2) and brine (200 mL × 2), and then dried (MgSO₄).

The benzene was removed *in vacuo*. The red residual oil was purified by silica gel chromatography using *n*-hexane– CH_2Cl_2 (1 : 1) as eluent to give pure **3**. In the case of **3a**, a slow stream of methylacetylene, which was prepared from 1,2-dibromopropane and KOH in refluxing *n*-BuOH, was immediately passed through the reaction mixture without isolation.

o-Prop-1-ynylbenzyl alcohol 3a. Yield 88%, pale yellow prisms, mp 71–72 °C (from benzene–*n*-hexane); v_{max} (KBr)/cm⁻¹ 3332 (OH), 2240 (C≡C); $\delta_{\rm H}$ (CDCl₃, 60 MHz) 2.08 (3H, s, Me), 2.35 (1H, s, OH), 4.80 (2H, s, Ph-CH₂-OH), 7.2–7.5 (4H, m, Ph-H) (HRMS *m*/*z*: M⁺ calcd for C₁₀H₁₀O: 146.0732; found: 146.0741).

o-n-Hex-1-ynylbenzyl alcohol 3b. Yield 92%, yellow oil; $ν_{max}$ (neat)/cm⁻¹ 3360 (OH), 2228 (C≡C); $δ_{\rm H}$ (CDCl₃, 60 MHz): 0.96, 1.3–1.8, 2.46 (3H, t, *J* 6, 4H, m, 2H, t, *J* 7, Bu^{*n*}), 2.25 (1H, s, OH), 4.82 (2H, s, Ph-CH₂-OH), 7.2–7.6 (4H, m, Ph-H) (HRMS *m*/*z*: M⁺ calcd for C₁₃H₁₆O: 188.1201; found: 188.1197).

o-(3,3-Dimethylbut-1-ynyl)benzyl alcohol 3c. Yield 88%, yellow oil; v_{max} (neat)/cm⁻¹ 3368 (OH), 2236 (C=C); δ_{H} (CDCl₃,

60 MHz) 1.36 (9H, s, Bu'), 2.47 (1H, s, OH), 4.80 (2H, s, Ph-C H_2 -OH), 7.2–7.5 (4H, m, Ph-H) (HRMS m/z: M⁺ calcd for C₁₃H₁₆O: 188.1201; found: 188.1197).

o-Phenylethynylbenzyl alcohol 3d. Yield 90%, pale yellow prisms, mp 70–72 °C (from benzene–*n*-hexane); v_{max} (KBr)/cm⁻¹ 3264 (OH), 2240 (C≡C); $\delta_{\rm H}$ (CDCl₃, 60 MHz) 2.38 (1H, s, OH), 4.93 (2H, s, Ph-CH₂-OH), 7.2–7.7 (9H, m, Ph-H) (HRMS *m*/*z*: M⁺ calcd for C₁₅H₁₂O: 208.0888; found: 208.0888).

o-Trimethysilylethynylbenzyl alcohol 3e. Yield 92%, yellow oil; v_{max} (neat)/cm⁻¹ 3352 (OH), 2156 (C≡C); $\delta_{\rm H}$ (CDCl₃, 60 MHz) 0.28 (9H, s, TMS), 2.45 (1H, s, OH), 4.85 (2H, s, Ph-CH₂-OH), 7.2–7.6 (4H, m, Ph-H) (HRMS *m*/*z*: M⁺ calcd for C₁₂H₁₆OSi: 204.0970; found: 204.0975).

General procedure for the preparation of *o*-ethynylbenzyl bromides 4a-e

To a stirred solution of *o*-ethynylbenzyl alcohol **3** (50 mmol) and pyridine (5.14 g, 65 mmol) in chloroform (50 mL) at 0 °C was slowly added phosphorus tribromide (14.9 g, 55 mmol). The mixture was stirred at room temperature for 6–12 h, and then poured into ice–water. The resulting aqueous mixture was extracted with CH_2Cl_2 (200 mL × 3), and the combined organic extract was washed with 5% H_2SO_4 (200 mL × 2), sat. NaHCO₃ (200 mL × 2) and brine (200 mL × 2), and then dried (MgSO₄). After removal of the organic solvent *in vacuo*, the residual oil was purified by silica gel chromatography using *n*-hexane as eluent to give the pure benzyl bromide **4**. The following compounds were thus prepared.

o-Prop-1-ynylbenzyl bromide 4a. Yield 85%, colorless oil; v_{max} (neat)/cm⁻¹ 2252, 2220 (C≡C); $\delta_{\rm H}$ (CDCl₃, 60 MHz) 2.12 (3H, s, Me), 4.67 (2H, s, Ph-CH₂-Br), 7.2–7.5 (4H, m, Ph-H) (HRMS *m*/*z*: M⁺ calcd for C₁₀H₉Br: 207.9888, 209.9868; found: 207.9881, 209.9866).

o-n-Hex-1-ynylbenzyl bromide 4b. Yield 78%, colorless oil; v_{max} (neat)/cm⁻¹ 2228 (C≡C); $\delta_{\rm H}$ (CDCl₃, 60 MHz) 0.97, 1.3–1.8, 2.49 (3H, t, *J* 6, 4H, m, 2H, t, *J* 7, Bu^{*n*}), 4.70 (2H, s, Ph-CH₂-Br), 7.2–7.6 (4H, m, Ph-H) (HRMS *m*/*z*: M⁺ calcd for C₁₃H₁₅Br: 250.0357, 252.0338; found: 250.0329, 252.0337).

o-(3,3-Dimethybut-1-ynyl)benzyl bromide 4c. Yield 80%, colorless oil; $ν_{max}$ (neat)/cm⁻¹ 2240 (C≡C); $δ_{\rm H}$ (CDCl₃, 60 MHz) 1.39 (9H, s, Bu'), 4.67 (2H, s, Ph-CH₂-Br), 7.2–7.5 (4H, m, Ph-H) (HRMS *m*/*z*: M⁺ calcd for C₁₃H₁₅Br: 250.0357, 252.0338; found: 250.0350, 252.0347).

o-Phenylethynylbenzyl bromide 4d. Yield 94%, colorless oil; ν_{max} (neat)/cm⁻¹ 2216 (C≡C); $\delta_{\rm H}$ (CDCl₃, 60 MHz) 4.72 (2H, s, Ph-CH₂-Br), 7.2–7.7 (9H, m, Ph-H) (HRMS *m*/*z*: M⁺ calcd for C₁₅H₁₁Br: 270.0044, 272.0025; found: 270.0038, 272.0021).

o-Trimethylsilylethynylbenzyl bromide 4e. Yield 76%, colorless oil; v_{max} (neat)/cm⁻¹ 2160 (C≡C); $\delta_{\rm H}$ (CDCl₃, 60 MHz) 0.30 (9H, s, TMS), 4.70 (2H, s, Ph-CH₂-Br), 7.2–7.7 (4H, m, Ph-H) (HRMS *m*/*z*: M⁺ calcd for C₁₂H₁₅BrSi: 266.0126, 268.0107; found: 266.0121, 268.0114).

o-Ethynylbenzyl bromide 4f. To a stirred solution of *o*-trimethylsilylethynylbenzyl bromide 4e (8.01 g, 30 mmol) in methanol (60 mL) at room temperature was added K_2CO_3 (0.35 g). After the reaction mixture had been stirred for 1 h, it was poured into ice–water. The resulting aqueous mixture was extracted with with CH_2Cl_2 (100 mL × 3), and the combined organic extract was washed with brine (100 mL × 2) and dried (MgSO₄). The organic solvent was evaporated *in vacuo* to give almost pure *o*-ethynylbenzyl bromide 4f (5.21 g, 89%) as a

[†] This compound **1** is commercially available, but easily obtained quantitatively by diborane reduction of *o*-iodobenzoic acid on a large scale.

colorless oil; v_{max} (neat)/cm⁻¹ 2108 (C=C); δ_{H} (CDCl₃, 60 MHz) 3.48 (1H, s, C=CH), 4.74 (2H, s, Ph-CH₂-Br), 7.3-7.7 (4H, m, Ph-H) (HRMS *m*/*z*: M⁺ calcd for C₉H₇Br: 193.9731, 195.9711; found: 193.9733, 195.9712).

General procedure for the treatment of the benzyl bromides 4 with NaHTe: formation of isotellurochromenes 6Aa-f and 1-methylidene-2-telluraindan 7Aa-f

A solution of o-ethynylbenzyl bromide 4 (10 mmol) in DMF (10 mL) was slowly added to a solution of NaHTe (12 mmol), which was freshly prepared from tellurium dust (1.53 g) and NaBH₄ (0.54 g) in DMF (40 mL) at 0 °C under an argon atmosphere. The reaction mixture was stirred under the conditions for 1 h. EtOH (40 mL) was added to the reaction mixture, and then the whole mixture was heated at 90 °C with stirring for 1-3 h. After addition of water (200 mL), the aqueous mixture was extracted with benzene ($100 \text{ mL} \times 3$). The organic extract was washed with water (200 mL \times 3) and brine (200 mL × 3), dried (MgSO₄), and concentrated in vacuo. The resulting residue was purified by silica gel chromatography using *n*-hexane as eluent to give pure 6A and 7A. The results and spectral data are given in Tables 1-3.

General procedure for the treatment of benzyl bromides 4 with NaHSe: formation of isoselenochromenes 6Ba-f and 1-methylidene-2-selenaindan 7Ba-f

A solution of 3 (10 mmol) in DMF (10 mL) was treated with sodium hydrogen selenide (12 mmol), prepared from selenium dust (0.96 g) and sodium borohydride (0.54 g), and worked up to give 6B and 7B. The results and spectral data are given in Tables 1-3.

General procedure for the preparation of 2-benzotelluropyrylium tetrafluoroborates 9A and 2-benzoselenopyrylium tetrafluoroborates 9B

 $Ph_3C^+BF_4^-$ (1.88 g, 5.5 mmol) was added to a stirred solution of the isochromenes 6 (1.51 g, 5 mmol) in dry MeNO₂ (10 mL) and the mixture was stirred at room temperature for 30 min. To the reaction mixture was added dry Et₂O to precipitate the pyrylium salts 9. The following compounds were thus obtained. (¹H NMR spectral data are listed in Table 4.)

3-tert-Butyl-2-benzotelluropyrylium tetrafluoroborate 9Ac. Yield 89%, pale green prisms (CH₂Cl₂-CHCl₃), mp 101 °C (decomp.); v_{max} (KBr)/cm⁻¹ 1054 (BF₄⁻); δ_{C} (CD₃CN, 100 MHz) 33.3 (q), 43.8 (s), 131.4 (d), 132.1 (d), 135.40 (d), 137.8 (d), 139.6 (d), 139.9 (s), 143.7 (s), 182.9 (s), 188.8 (d); $\delta_{\rm Te}$ (CD₃CN) 1257.5 (Anal. calcd for C₁₃H₁₅BF₄Te: C, 40.49; H, 3.92. Found: C, 40.35; H, 3.75%).

2-Benzotelluropyrylium tetrafluoroborate 9Af. Yield 89%, pale green prisms (CH₂Cl₂-CHCl₃); mp 109–113 °C (decomp.); v_{max} (KBr)/cm⁻¹ 1056 (BF₄⁻); δ_{C} (CD₃CN, 100 MHz) 132.0 (d), 132.5 (d), 135.3 (d), 139.5 (d), 141.0 (s), 142.3 (d), 142.4 (s), 146.7 (d), 193.2 (d) (Anal. calcd for C₉H₇BF₄Te: C, 32.80; H, 2.14. Found: C, 32.27; H, 2.20%).

3-tert-Butyl-2-benzoselenopyrylium tetrafluoroborate 9Bc. Yield 89%, pale green prisms (CH₂Cl₂-CHCl₃), mp 182-184 °C (decomp.); v_{max} (KBr)/cm⁻¹ 1056 (BF₄⁻); δ_{C} (CD₃CN, 100 MHz) 32.3 (q), 42.4 (s), 132.4 (d), 132.8 (d), 133.5 (d), 134.4 (d), 135.3 (s), 141.6 (d), 142.2 (s), 177.8 (s), 181.2 (d); δ_{se} (CD₃CN) 890.0 (Anal. calcd for C₁₃H₁₅BF₄Se: C, 46.33; H, 4.49. Found: C, 46.21; H, 4.46%).

2-Benzoselenopyrylium tetrafluoroborate 9Bf. Yield 85%, pale green prisms (CH₂Cl₂-CHCl₃), mp 127 °C (decomp.); v_{max} (KBr)/cm⁻¹ 1052 (BF₄⁻); $\delta_{\rm C}$ (CD₃CN, 100 MHz) 133.1 (d), 133.4 (d), 133.5 (d), 136.6 (s), 138.4 (d), 140.7 (s), 141.7 (d), 145.4 (d), 184.0 (d) (Anal. calcd for C₉H₇BF₄Se: C, 38.48; H, 2.51. Found: C, 38.53; H, 2.32%).

X-Ray data collection for 9Ac and 9Bc ±

Single crystals suitable for X-ray diffraction study of 9Ac and 9Bc were obtained from a dichloromethane solution of the compound at room temperature.

Crystal data for 9Ac. $C_{13}H_{15}BF_4Te$, M = 385.67, orthorhombic, *Pnma*, a = 14.2630(5), b = 6.7450(2), c = 14.3100(5) Å, V = 1376.68(7) Å³, Z = 4, $\rho_{calcd} = 1.861$ g cm⁻³. $R_w = 0.060$ (R = 0.100) and GOF = 1.356 for 1572 observed reflections [109 parameters, $I > 3.00\sigma(I)$].

Crystal data for 9Bc. $C_{13}H_{15}BF_4Se$, M = 337.03, orthorhombic, *Pnma*, a = 13.8420(4), b = 6.7860(1), c = 14.2960(5) Å, V = 1342.85(5) Å³, Z = 4, $\rho_{calcd} = 1.667$ g cm⁻³. R = 0.060 ($R_w =$ 0.108) and GOF = 1.475 for 1528 observed reflections [109 parameters, $I > 3.00\sigma(I)$]. All data were collected at 190 K on a MAC Science DIP2030 imaging plate with graphitemonochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The structure was solved using the teXsan (Rigaku) system and all nonhydrogen atoms were refined anisotropically. The hydrogen atoms were included at calculated positions but not refined. Atomic coordinates, bond lengths and angles, and other important parameters have been deposited at the Cambridge Crystallographic Data Centre. ‡

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[†]CCDC reference numbers 175478 and 175479. See http:// www.rsc.org/suppdata/p1/b1/b111045b/ for crystallographic files in .cif or other electronic format.

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