



A straightforward double intramolecular cyclization of dibenzyl dichalcogenols into a triple bond[☆]

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ABSTRACT

The intramolecular cyclizations of four types of dibenzyl chalcogenols, which contained one or two ethynyl groups, were carried out. Either the double 5-*exo* or 6-*endo-dig* mode ring closure reaction regio- and stereoselectively proceeded to give the corresponding symmetrical bis(benzo[*c*]chalcogenophene) or bis(isochromene) derivatives from the dibenzyl chalcogenols having a diyne moiety. In contrast, the regioselective tandem 5-*exo-dig* mode intramolecular ring closure reactions of dibenzyl thiol and selenol having a mono-yne into a triple bond gave the *trans*-biisobenzothiophene and selenophene as the sole product. However, the similar cyclization of dibenzyl tellurol proceeded in both tandem 5-*exo* and 6-*endo-dig* modes to afford the *trans*-biisobenzotellurophene and ditellurachrysene in good yields with the ratio of 1:1. The X-ray structural analysis of these novel compounds is also presented.

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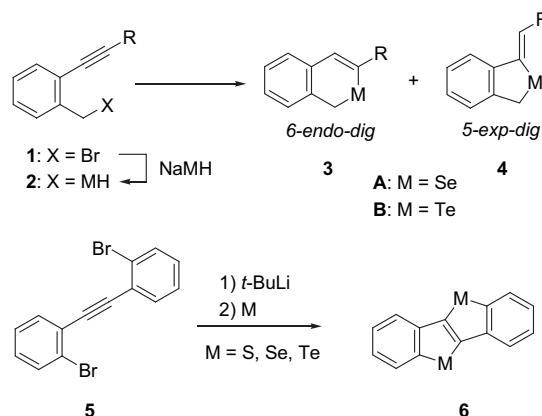
1. Introduction

Styrylthiophenes (phenylthienylethenes)² having a donor or an acceptor substituent on the benzene and thiophene ring are known to behave as good nonlinear optical (NLO) chromophores. Symmetrical and unsymmetrical bridged diarylethenes³ with heterocyclic aryl groups, such as thiophene and benzothiophene, display attractive chemical properties for use in molecular switches and molecular motors.

Tobe and co-workers⁴ recently determined that the flash vacuum pyrolysis of 1,6-diphenyl-1,5-hexadien-3-yne yielded the chrysene^{4a} through the tandem 6-*endo* cyclization, and the bridged phenylthienylethenes and dithienylethenes^{4b} were regio- and stereoselectively produced by the Pd-catalyzed 5-*exo* cyclization of the 1,5-hexadien-3-yne.⁵ To the best of our knowledge, there is no report on the preparation of the bridged heteroarylethene derivatives containing a chalcogen element except for sulfur and the heterochrysenes.

On the other hand, we have also reported the general method for the preparation⁶ of the isoselenochromenes **3A** and isotellurochromenes **3B** together with the (*Z*)-1-methylidene-2-indanes **4** containing selenium and tellurium atoms via an intramolecular cyclization reaction of the benzy selenols **2A** and

tellurols **2B** into a triple bond. The 6-*endo-dig* mode cyclization was the preferential reaction during the intramolecular *trans*-addition of the selenols or tellurols to an acetylenic moiety having an alkyl group, while the 5-*exo-dig* mode benzo[*c*]chalcogenophenes **4** were the main product in the case of the existence of a phenyl group at the triple bond. Moreover, the lithiation of 2,2'-dibromodiphenylacetylene **5** followed by chalcogen insertion resulted in tandem intramolecular ring closure to give the [1]benzochalcogeno[3,2-*b*][1]benzochalcogenophenes **6** (Scheme 1).⁷



Scheme 1.

[☆] See Ref. 1.

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As an extension of our ongoing work⁸ in which we succeeded in preparing the various types of five- to nine-membered heterocycles containing a chalcogen element using the intramolecular cyclization reaction of the chalcogenols into a triple bond, we decided to develop a procedure for the double or tandem intramolecular cyclizations of dibenzyl chalcogenols into an ethynyl moiety. In this cyclization reaction, there are three possible types of ring-closure modes: (i) double 6-*endo* mode; (ii) double 5-*exo* mode; and (iii) 6-*endo* and 5-*exo* mode. This finding led us to examine the possible intramolecular ring closure of the dibenzyl chalcogenols into a triple bond for synthesizing the novel heterocyclic systems.

2. Results and discussion

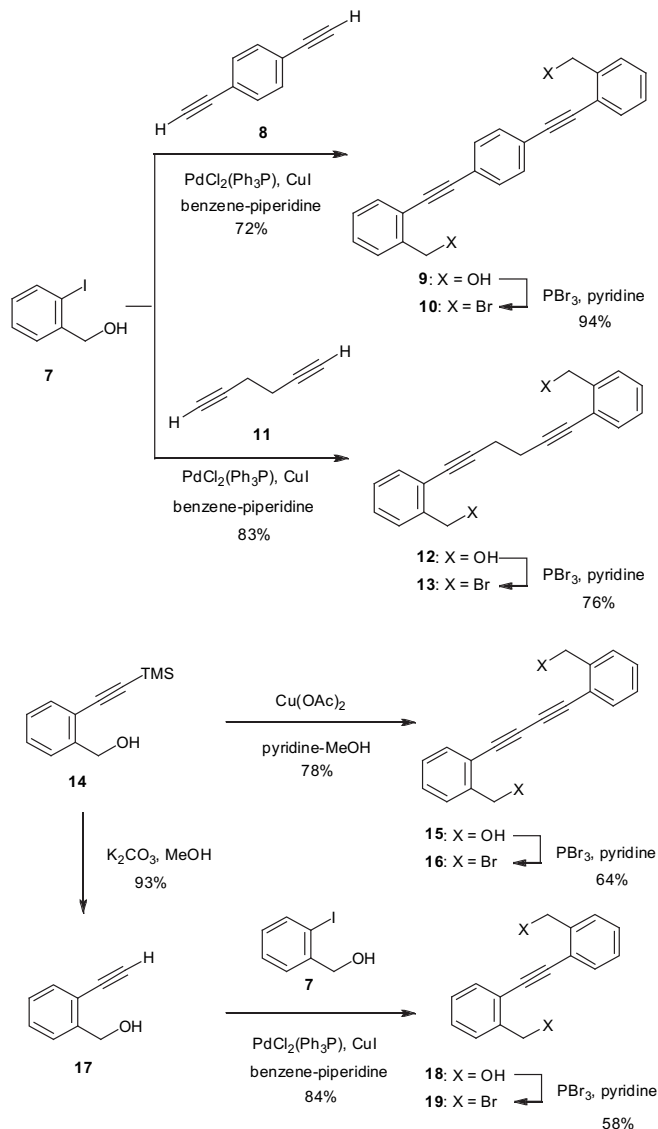
2.1. Synthesis of *o*-ethynyldibenzyl dibromides

The preparation of the starting key *o*-ethynyldibenzyl bromides **10**, **13**, **16**, **19** is shown in Scheme 2. The Sonogashira Pd-catalyzed coupling reaction⁹ of *o*-iodobenzyl alcohol **7** and 1,4-diethynylbenzene **8**¹⁰ with the appropriate modification gave the desired dibenzyl alcohol **9** in 72% yield. The benzyl alcohol **9** was readily brominated with PBr₃/pyridine to give the key compound **10** in 94% yield. Compound **12** was also synthesized by the reaction

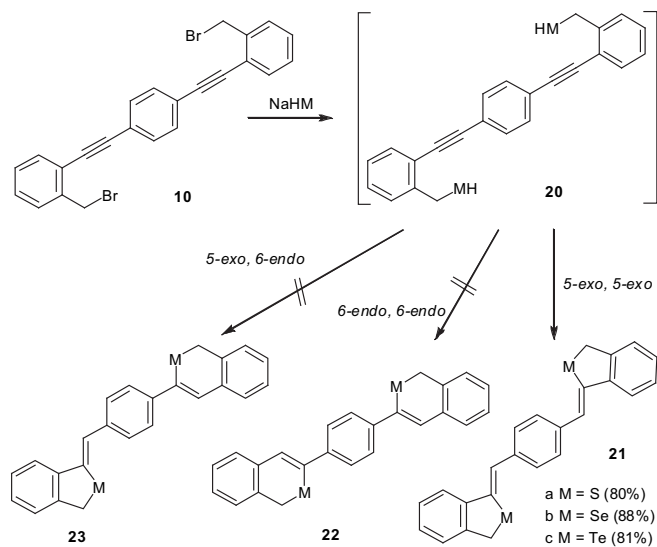
of **7** and 1,5-hexadiyne **11** in 83% yield using the Sonogashira protocol, followed by bromination to give **13**. After several unsuccessful attempts¹⁰ at the coupling reactions of the *o*-iodobenzyl alcohol **7** with the 1,3-butadiyne derivatives¹¹ for the synthesis of **15**, we were successful by employing the self-coupling reaction of the *o*-trimethylsilyl(TMS)ethynylbenzyl alcohol **14**. Compound **14**, when subjected to a reaction with Cu(OAc)₂ monohydrate in pyridine/MeOH¹² as a solvent at 100 °C, directly led to the diyne **15** along with removal of the TMS group in 78% yield. The reaction of the *o*-iodobenzyl alcohol **7** with *o*-ethynylbenzyl alcohol **17**, which was easily prepared by treatment of the TMS-ethynyl derivative **14**⁶ with K₂CO₃ in MeOH, gave the desired dibenzyl alcohol **18** under the Sonogashira coupling reaction conditions in 84% yield. **15** and **18** were then readily brominated to give the corresponding bromides **16** and **19** in 64% and 58% yields, respectively.

2.2. Cyclization of dibenzyl dichalcogenols

First, in order to prepare the dibenzyl chalcogenols **20**, precursors for the cyclization reaction, we examined the reaction of the dibenzyl bromide **10**, having a benzene ring between two triple bonds, with the sodium hydrogen chalcogenides (NaHM). The treatment of the dibromide **10** with 1.5 equiv of the commercially



Scheme 2.



Scheme 3.

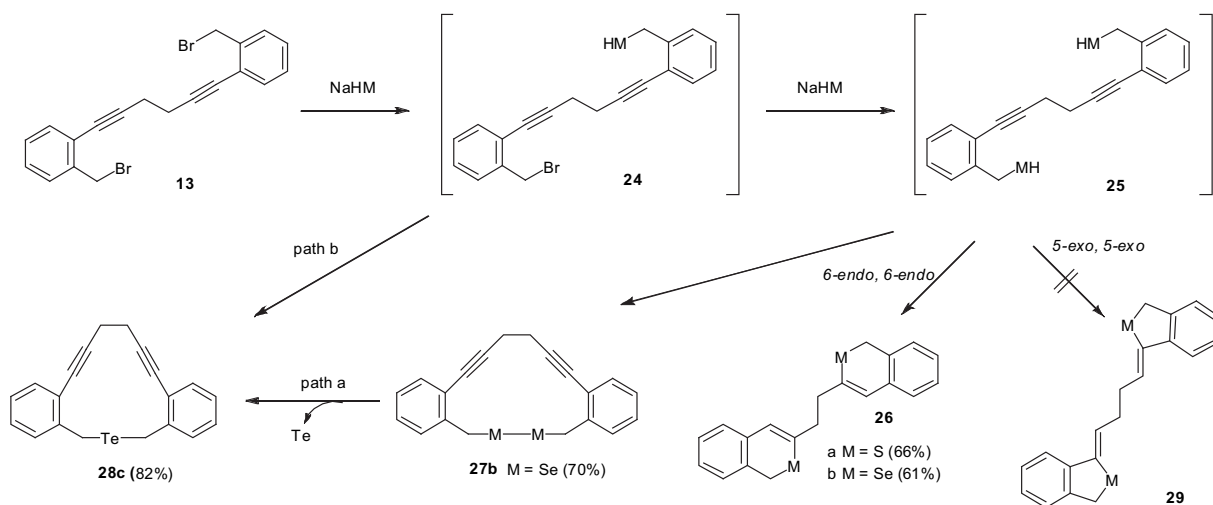
available NaHS hydrate in DMF at room temperature resulted in the direct ring closure to give the benzo[c]thiophene derivative **21a** in 80% yield without any characterized products. Compound **21a** can be produced by the tandem 5-exo mode cyclization of the specific benzyl thiol intermediate **20a** at the sp. carbon atom of the triple bond with excellent regio- and stereoselectivity. However, the reaction of **10** with 1.5 equiv of NaHSe,¹³ which was freshly prepared from selenium dust and NaBH₄ in dry DMF, gave a complex mixture including the desired benzo[c]selenophene **21b** in poor yield. When the dibromide **10** was treated with NaHSe, followed by addition of ethanol as a proton source after the disappearance of the starting dibromide, **21b** was formed in 88% yield as the sole product. In the case of the formation of the benzo[c]thiophene **21a**, the commercially available NaHS was hydrate. Thus, this cyclization reaction requires the addition of a proton source, such as water or ethanol. When we performed the reaction of compound **10** with NaHTe¹³ under similar conditions, this reaction also directly led to the benzo[c]tellurophenes **21c** in 81% yield. In these cases, neither the 6-endo, 6-endo mode **22** nor 5-exo, 6-endo mode compound **23** was obtained. Thus, the benzo[c]chalcogenophene derivatives containing two chalcogenophene rings linked by a 1,4-distyryl moiety were conveniently obtained.

Next, the reactions of the bis-benzyl bromide **13**, in which two ethynyl groups are linked by the ethylene moiety, with NaHS, NaHSe, and NaHTe were carried out. Compound **13** regioselectively reacted with NaHS in DMF to afford the bis(isothiochromenyl) ethane **26a**, which was the 6-endo, 6-endo mode cyclization product, in 66% yield as the sole product. The treatment of **13** with NaHSe under similar conditions at room temperature gave the fourteen-membered diselenide **27b** in 70% yield. When we similarly examined the reaction of compound **13** with NaHTe, this reaction directly led to the thirteen-membered telluride **28c** in 82% yield. The formation of **27b** and **28c** may proceed via the dibenzyl chalcogenol intermediates **25**, which might undergo intramolecular oxidative coupling to produce the diselenide **27b**, and then **28c** is generated by eliminating one tellurium atom from the ditelluride **27c** (path a). Alternatively, compound **28c** was directly obtained by the intramolecular coupling of the initial mono-telluride **24c** via path b. When the reaction of **13** with NaHSe was carried out at 110–115 °C, the 6-endo, 6-endo mode cyclization reaction was found to proceed giving the isoselenochromene derivative **26b** in 61% yield. However, the similar reaction of **13** with NaHTe produced a complex mixture without affording the corresponding 6-endo mode ring closure product **26c**, probably because of its thermal instability.

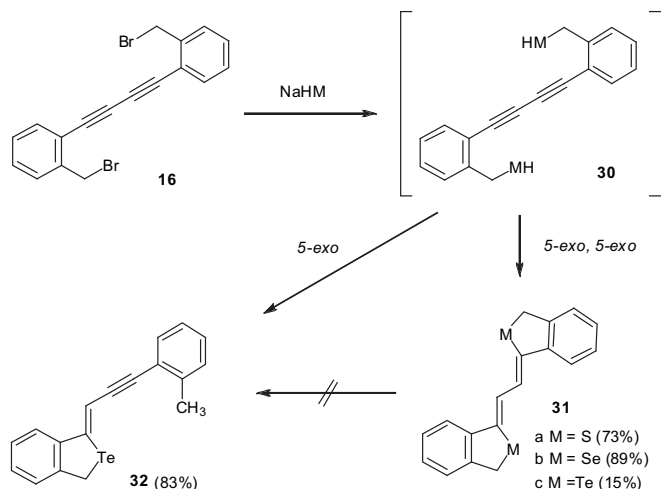
The behavior of these cyclization reactions of the benzyl chalcogenols shown in Schemes 3 and 4 were found to be dependent upon substitution on the triple bond, and is essentially similar to that of the mono benzyl chalcogenols Scheme 5.⁶

The 5-exo mode ring closure reaction is predominant in the intramolecular addition of the dibenzyl chalcogenols to an acetylenic moiety having a phenyl ring. On the contrary, the 6-exo mode cyclization compounds were the main product for the case of an ethylene moiety present at the triple bond.

Moreover, the dibenzyl bromide **16** having a conjugated diyne reacted with NaHS and NaHSe under the conditions described above to give the 5-exo mode cyclization products, the benzo[c]thiophene **31a** and benzo[c]selenophene **31b**, via the certain chalcogenol intermediates **30** in 73 and 89% yields, respectively. The desired tellurophene **31c** was obtained in this cyclization reaction in only 15% yield together with the mono 5-exo cyclized product **32** in 83% yield, while the 6-endo mode cyclization reaction did not proceed. The unexpected formation of **32**, in which one benzyl telluride (or bromide) may be reduced to a methyl group without cyclization, cannot be clearly explained in detail, while **31c** was not converted to **32** under the cyclization conditions. The (Z)-regiochemistry of the olefin moiety of **31** was determined by X-ray single crystallography using



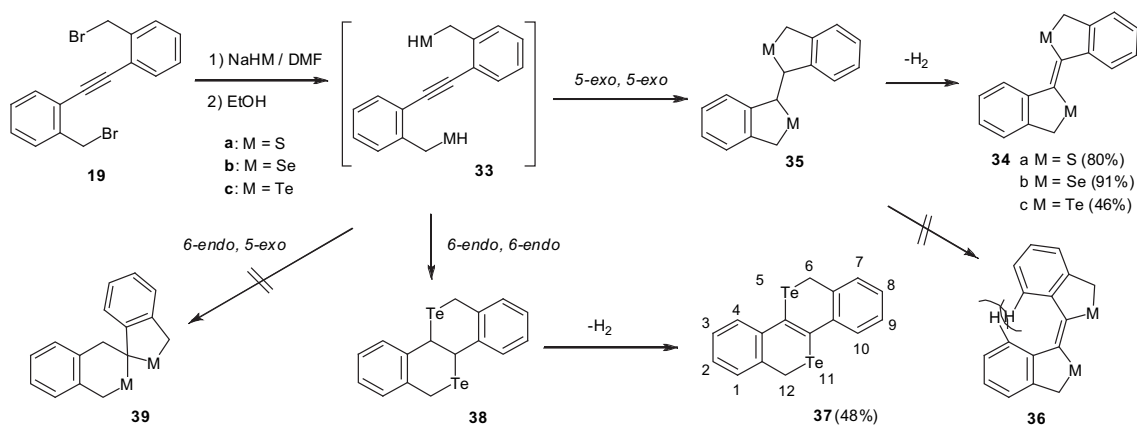
Scheme 4.



Scheme 5.

the selenium derivative **31b**.¹⁴ A convenient preparation of the bimethylenedibenzo[*c*]chalcogenophenes, directly linked to the 2,2' positions by a single carbon–carbon bond, was achieved.

Finally, the cyclization reactions of the dibenzyl chalcogenols **33** having one triple bond were examined. The bromide **19** was similarly treated with NaHS hydrate to afford the *trans*-biisobenzo[*c*]thiophene **34a** in 80% yield without any characterized products. Compound **34a** will be produced by the dehydrogenation of the essential cyclization product **35a**, which is generated by the tandem 5-*exo* mode cyclization of the benzyl thiol intermediate **33a** into the triple bond with excellent regio- and stereoselectivity. The treatment of **19** with freshly prepared NaHSe, and then the addition of ethanol gave the 5-*exo* mode *trans*-biisobenzo[*c*]selenophene **34b** in 91% yield as the sole product. In contrast, the reaction of the dibenzyl bromide **19** with NaHTe followed by the addition of ethanol resulted in both the tandem 5-*exo* and 6-*endo* mode ring closures to yield the *trans*-biisobenzo[*c*]tellurophene **34c** and the 5,11-dihydrotellurachrysene **37** in 46 and 48% yields, respectively. The pure *trans*-**34a** and **37** could be isolated by fractional recrystallization from CHCl₃. The formation of the tellurachrysene **37** would also be accomplished by the dehydrogenation from the essential 6-*endo* mode cyclization product **38**. The formation of *trans*-**34** by the dehydrogenation of **35** is more favored than that of *cis*-**36** due to the steric hindrance between the two inner *peri* hydrogens of the benzene rings. In these reactions, neither the essential cyclization products **35**, **38**, **39** nor alternative dehydrogenated *cis*-products **36** were obtained Scheme 6.



Scheme 6.

In all cases of the reaction of **19** with NaHS, NaHSe or NaHTe, the 6-*endo* and 5-*exo*-mode cyclizations did not proceed to give the corresponding products **39**.

2.3. Structure of 5-*exo* and 6-*endo* mode cyclization products

All the obtained compounds are new except for *trans*-biisothiophene **34a** were mainly characterized on the basis of the spectral analyses. The *trans*-3,3'-bibenzo[*c*]thienylidene **34a** was already synthesized by the NaBH₄ reduction of the *trans*-3,3'-bibenzo[*c*]thienylidene-1,1'-dione.¹⁵ The structure of **37** and regiochemistry of **34c** were finally determined by X-ray single crystallography. Figures 1 and 2 show the structures of **34c** and **37**, respectively. Tables 1 and 2 list the selected interatomic distances, angles, and torsional angles of **34c** and **37**.

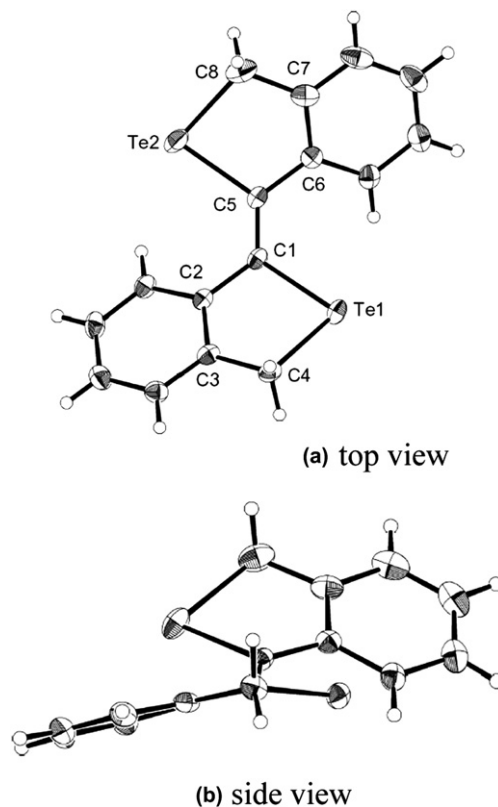


Figure 1. ORTEP drawing of **34c** with atomic numbering scheme for selected atoms (50% probability thermal level).

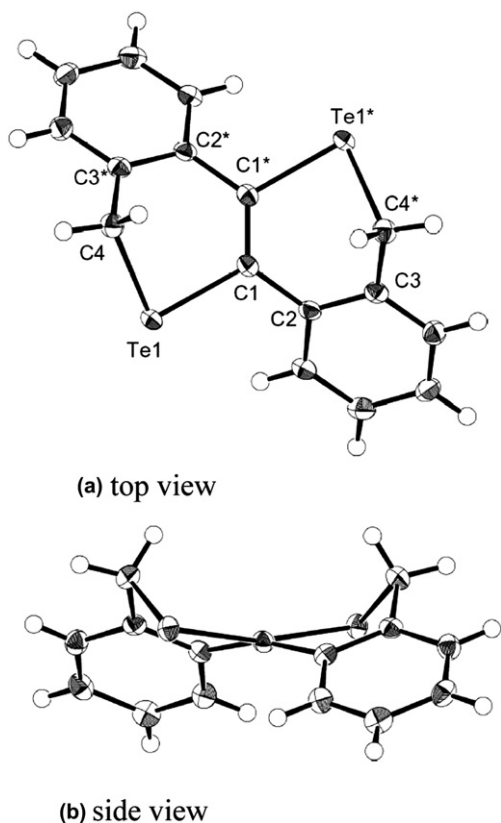


Figure 2. ORTEP drawing of **37** with atomic numbering scheme for selected atoms (50% probability thermal level).

Table 1
Selected bond lengths (Å) and bond angles (deg) of **34c**

Te1–C1	2.130(3)	Te2–C5	2.134(4)
Te1–C4	2.143(4)	Te2–C8	2.146(6)
C1–C2	1.475(5)	C5–C6	1.468(5)
C2–C3	1.408(5)	C6–C7	1.407(6)
C3–C4	1.385(6)	C7–C8	1.509(7)
C1–C5	1.347(5)		
C1–Te1–C4	83.4(1)	C5–Te2–C8	83.0(2)
C2–C1–Te1	126.7(3)	C6–C5–Te2	108.4(3)
C5–C1–C2	126.5(3)	C5–C1–Te1	124.9(3)
		C1–C5–Te2	124.6(3)

Table 2
Selected bond lengths (Å) and bond angles (deg) of **37**

C1–C1*	1.352(4)	C1–Te1	2.141(2)
C4*–Te1	2.168(2)	C1*–C2*	1.490(3)
C2*–C3*	1.412(3)	C3*–C4	1.498(3)
C1–Te1–C4	87.55(8)	C1–C1*–C2*	125.2(2)
C1*–C1–Te1	119.3(1)	C2–C1–Te1	115.4(1)
C3*–C2*–C1*	122.0(2)	C2*–C3*–C4	120.0(2)
C3*–C4–Te1	108.2(2)		

Although the benzo[*c*]tellurophenylidene skeleton found in **34c** has never been reported, the benzo[*c*]telluropene derivatives have been structurally characterized.¹⁶ The tellurium containing rings in **34c** have envelope structures. The bond angle of C–Te–C (82.6°) and the bond lengths of Te–C (2.130 and 2.143 Å) are normal within the expected values for the neutral Te^{II} compounds.

Compound **37** crystallizes from toluene to yield single crystals. Its X-ray structure was solved in chiral space group *C2* resulting from

the self-resolution of the two enantiomers of **37**, which may be caused by the axial chirality on the twisted central double bond, where the sign of the chirality is *S_a* for the single crystal. The tellurium-containing six-membered rings assume the twisted conformation of a two-fold axis of symmetry on the central double bond with the axial chirality. For the crystallographic structure of **37**, the tellurium-containing six-membered ring is a novel ring system not only as isotellurochromene, but also as saturated isotellurochroman skeletons. The bond lengths (C–Te, 2.141 and 2.168 Å) and angle (87.6°) around the tellurium are comparable to those observed in the telluracyclohexane skeletons in which the corresponding averaged bond length and angle are 2.157 Å and 89.3°, respectively.¹⁷

Both the 5-*exo* and 6-*endo* mode cyclizations are favored in Baldwin's rules,¹⁸ which may be helpful to expect the selectivity for ring-forming by the closure of the acyclic precursors. However, a heteroatom or anion, which attacks a tetrahedral, trigonal or diagonal carbon atom to make a new ring, must be the second periodic row one; i.e., C, N, O, etc. based on the rules. There are no systematic studies on the selectivity and stereochemical nature of the third period and behavior elements, especially the chalcogen elements, toward a triple bond.

Three chalcogenols **33**, the precursors for the intramolecular cyclizations are symmetrical compounds, which have no localized electrovalencies. Therefore, the ring-closure mode of **33** may be controlled by the distances between the chalcogen elements and the reactant sp. carbons in the triple bond. In order to explain the significant differences in the cyclization mode of the essential intermediates dithiol **33a**, diselenol **33b**, and ditelluro **33c**, the 3D-structures of **33** have been calculated by a density functional theory method (PCM/B3LYP/DZ, DZ=Lan12DZdp for S, Se, and Te; 6-31G* for C and H; PCM solvent=ethanol) using the Gaussian 03 program. Table 3 lists the distances between the chalcogen atoms (M1, M2) of the benzyl chalcogenol moieties and the C1 or C2 sp. carbons in the triple bond for the optimized structures of **33**.

Table 3
Distances (Å) of between chalcogen atoms and sp. carbons for **33a–c**

Compd.	M	M1–C1	M1–C2	M2–C1	M2–C2
33a	S	3.71	4.22	4.35	3.78
33b	Se	3.89	4.42	4.48	3.90
33c	Te	3.98	4.48	4.59	4.04

The S1...C1 and S1...C2 distances for the dithiol **33a** are 3.71 and 4.22 Å, respectively. The S2...C2 and S2...C1 have almost similar values (3.78 and 4.35 Å). It is presumed that the 5-*exo*, 5-*exo* mode ring closure reaction is more favored than the 6-*endo*, 6-*endo* mode one because the S1...C1 (S2...C2) distance is much shorter than the S1...C2 (S2...C1) one. Thus, the *trans*-biisobenzo[*c*]thiophene **34a** was formed through the dehydrogenation of the essential 5-*exo*, 5-*exo* mode cyclization product **35a**. No 6-*endo* mode heterocycles are detected in this tandem cyclization of the dithiol **33a**. The Se1...C1 distance of 3.89 Å is also clearly shorter than that of the Se1...C2 (4.42 Å) for **33b**. The distances to the C1 and C2 from the Se2 are similar. Thus, the essentially similar results are also obtained in this case. In the case of **33c**, both of the Te1...C1 (Te2...C2) and Te2...C1 (Te1...C2) distances were elongated compared with S and Se analogues. Therefore, both tandem 5-*exo* and 6-*endo*

mode ring closure reactions proceeded to afford the corresponding five- and six-membered tellurium heterocycles in the ratio of 1:1, respectively. Although these cyclization reactions are obviously multi steps and the exact mechanisms are still unclear, the experimental fact that compounds **34a,b** only are obtained during the cyclization of **33a,b** and both compounds **34c** and **37** are produced from **33c** in approximately equal yields could be explained by the calculated values of the distances between the chalcogen atoms and the sp. carbons of the triple bond of **33**.

3. Conclusion

In conclusion, we have shown that the dibenzyl dibromides **10**, **13**, **16**, **19** react with NaHM in DMF to give the corresponding dichalcogenols **20**, **25**, **30**, **33**, which fundamentally produce the bisbenzo[c]chalcogenophene or isochromene derivatives by either the regioselective double 5-*exo* or 6-*endo* mode intramolecular cyclization into a triple bond in almost good yields. These simple ring closure reactions offer a convenient access to the symmetrical five- or six-membered ring assembled heterocycles containing a chalcogen element and also ditellurachrysene.

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. ^1H 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 and *J* values are given in hertz. ^{13}C NMR spectra were measured on a JEOL ECA-400 (100 MHz) or JEOL ECP-500 (125 MHz) spectrometer.

4.1.1. 1,4-Bis[2-(hydroxymethyl)phenylethynyl]benzene 9. To a mixture of 1,4-diethynylbenzene **8**¹⁰ (3.15 g, 25 mmol) and *o*-iodobenzyl alcohol **7** (11.7 g, 50 mmol) in benzene (100 mL) and piperidine (50 mL) were added $\text{PdCl}_2(\text{Ph}_3\text{P})_2$ (260 mg, 0.37 mmol) and CuI (145 mg, 0.76 mmol). The mixture was stirred at room temperature under argon for 16 h. Cold water (100 mL) was added to the mixture, and the resulting aqueous mixture was extracted with benzene (100 mL \times 3). The combined organic extract was washed with water (150 mL \times 3), 5% H_2SO_4 (100 mL \times 3), satd NaHCO_3 (100 mL \times 2) and brine (200 mL \times 2), and then dried (MgSO_4). The benzene was removed in vacuo to give the crude **9**. Yield: 6.08 g (72%). Yellow prisms, mp 195–197 °C (from acetone/hexane). IR (KBr): 3352 (OH). ^1H NMR (500 MHz, CD_3OD): 4.86 (4H, s, $\text{PhCH}_2\times 2$), 7.29, 7.40, 7.51, 7.54–7.60 (2H, ddd, *J*=7.7, 7.5, 1.4 Hz, 2H, ddd, *J*=7.7, 7.6, 1.3 Hz, 2H, dd, *J*=7.5, 1.4 Hz, 6H, m, Ph–H). ^{13}C NMR (125 MHz, CD_3OD): 63.4 (t), 89.7 (s), 94.4 (s), 124.6 (s), 127.9 (s), 128.2 (d), 130.0 (d), 132.6 (d), 133.0 (d), 138.8 (d), 144.4 (s). EIMS: *m/z* (relative intensity, %) 338 (M^+ , 100), 289 (22), 178 (18). HRMS *m/z* M^+ calcd for $\text{C}_{24}\text{H}_{18}\text{O}_2$: 338.1307. Found: 338.1306.

4.1.2. 1,4-Bis[2-(bromomethyl)phenylethynyl]benzene 10. To a stirred solution of benzyl alcohol **9** (3.38 g, 10 mol) and pyridine (1.03 g, 13 mol) in dry CHCl_3 (10 mL) at 0 °C was slowly added PBr_3 (2.98 g, 11 mol). The mixture was stirred at same conditions for 15 h, and then poured into ice-water. The resulting aqueous mixture was extracted with CH_2Cl_2 (75 mL \times 3). The combined organic extract was washed with 5% H_2SO_4 (50 mL \times 2), satd NaHCO_3 (50 mL \times 2) and brine (100 mL \times 3), and then dried (MgSO_4). After removal of the organic solvent in vacuo, the residual oil was

purified by silica gel chromatography using *n*-hexane/ CH_2Cl_2 (10:1) as eluent to give pure **10**. Yield: 4.38 g (94%). Yellow needles, mp 164–166 °C (from CH_2Cl_2 /hexane). ^1H NMR (500 MHz, CDCl_3): 4.74 (4H, s, $\text{PhCH}_2\times 2$), 7.29–7.36, 7.46, 7.56 (4H, m, 2H, dd, *J*=7.2, 1.9 Hz, 2H, dd, *J*=7.0, 2.0 Hz, Ph–H), 7.59 (4H, s, 1,4-disubstituted Ph–H). ^{13}C NMR (125 MHz, CDCl_3): 32.0 (t), 88.5 (s), 94.9 (s), 123.0 (s), 123.2 (s), 128.6 (d), 129.0 (d), 129.8 (d), 131.6 (d), 132.6 (d), 139.3 (s). EIMS: *m/z* (relative intensity, %) 466, 464, 462 (M^+ , 50, 100, 50), 385, 383 (56, 55), 302 (80). HRMS *m/z* M^+ calcd for $\text{C}_{24}\text{H}_{16}^{81}\text{Br}_2$: 465.9584. Found: 465.9569.

4.1.3. 1,6-Bis[2-(hydroxymethyl)phenyl]hexa-1,5-diyne 12. *o*-Iodobenzyl alcohol **7** (23.4 g, 100 mol) was treated with hexa-1,5-diyne **11** (50 mol, 50% in hexane solution) instead of 1,4-diethynylbenzene **8** and worked up as described for the preparation of **9** to give **12**. Yield: 12.04 g (83%). Colorless prisms, mp 164–165 °C (from EtOH/benzene). IR (KBr): 3350 (OH). ^1H NMR (500 MHz, CD_3OD): 2.78 (4H, s, $\text{C}\equiv\text{CCH}_2\times 2$), 4.77 (4H, s, $\text{PhCH}_2\times 2$), 7.20, 7.31, 7.37, 7.47 (2H, ddd, *J*=7.6, 7.5, 1.3 Hz, 2H, ddd, *J*=7.7, 7.5, 1.4 Hz, 2H, dd, *J*=7.6, 1.4 Hz, 2H, dd, *J*=7.7, 1.3 Hz, Ph–H). ^{13}C NMR (125 MHz, CD_3OD): 20.7 (t), 63.5 (t), 80.0 (s), 94.3 (s), 122.7 (s), 127.6 (d), 128.0 (d), 129.1 (d), 133.0 (d), 144.3 (s). EIMS: *m/z* (relative intensity, %) 290 (M^+ , 3), 272 (86), 253 (60), 145 (72), 115 (100). HRMS *m/z* M^+ calcd for $\text{C}_{20}\text{H}_{18}\text{O}_2$: 290.1307. Found: 290.1301.

4.1.4. 1,6-Bis[2-(bromomethyl)phenyl]hexa-1,5-diyne 13. *o*-Benzyl alcohol **12** (3.38 g, 10 mmol) was treated with PBr_3 and worked up as described for the preparation of **10** to give **13**. Yield: 3.16 g (76%). Colorless needles, mp 124–126 °C (from CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3): 2.85 (4H, s, $\text{C}\equiv\text{CCH}_2\times 2$), 4.67 (4H, s, $\text{PhCH}_2\times 2$), 7.22–7.32, 7.39, 7.43 (4H, m, 2H, dd, *J*=7.6, 1.4 Hz, 2H, dd, *J*=7.4, 1.5 Hz, Ph–H). ^{13}C NMR (125 MHz, CDCl_3): 20.0 (t), 32.2 (t), 78.9 (s), 94.3 (s), 123.5 (s), 128.3 (d), 128.4 (d), 130.0 (d), 132.5 (d), 139.2 (s). EIMS: *m/z* (relative intensity, %) 418, 416, 414 (M^+ , 1, 3, 1), 335, 333 (9, 6), 256, 255 (37, 100), 128 (52). HRMS *m/z* M^+ calcd for $\text{C}_{20}\text{H}_{16}^{81}\text{Br}_2$: 417.9582. Found: 417.9603.

4.1.5. 1,4-Bis[2-(hydroxymethyl)phenyl]buta-1,3-diyne 15. To a stirred solution of $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$ (16.0 g, 80 mmol) in pyridine (150 mL) and MeOH (150 mL) was added at room temperature, trimethylsilylethynylbenzyl alcohol **14**⁶ (8.16 g, 40 mmol). The reaction mixture was heated for 2 h with stirring, the mixture was quenched with a saturated NH_4Cl solution (200 mL) and extracted with CH_2Cl_2 (150 mL \times 3). The organic extracts were washed with 5% H_2SO_4 (100 mL \times 2), satd NaHCO_3 (100 mL \times 2) and brine (150 mL \times 3), and then dried (MgSO_4). After removal of the organic solvent in vacuo, the residual oil was purified by silica gel chromatography using *n*-hexane/ CH_2Cl_2 (10:1) as eluent to give pure **15**. Yield: 7.90 g (78%). Pale yellow prisms, mp 174–176 °C (from EtOH). Lit.¹⁹ mp 176 °C.

4.1.6. 1,4-Bis[2-(bromomethyl)phenyl]buta-1,3-diyne 16. *o*-Benzyl alcohol **15** (2.62 g, 10 mmol) was treated with PBr_3 and worked up as described for the preparation of **10** to give **16**. Yield: 2.48 g (64%). Colorless needles, mp 139–140 °C (from CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3): 4.70 (4H, s, $\text{PhCH}_2\times 2$), 7.30, 7.37, 7.46, 7.57 (2H, ddd, *J*=7.6, 7.5, 1.0 Hz, 2H, ddd, *J*=7.7, 7.5, 1.2 Hz, 2H, dd, 7.6, 1.2 Hz, 2H, dd, *J*=7.7, 1.0 Hz, Ph–H). ^{13}C NMR (125 MHz, CDCl_3): 31.3 (t), 79.0 (s), 80.0 (s), 121.5 (s), 128.5 (d), 129.8 (d), 130.0 (d), 133.7 (d), 140.7 (s). EIMS: *m/z* (relative intensity, %) 390, 388, 386 (M^+ , 20, 40, 20), 309, 307 (28, 28), 228, 226 (100, 85). HRMS *m/z* M^+ calcd for $\text{C}_{18}\text{H}_{12}^{81}\text{Br}_2$: 389.9268. Found: 389.9276.

4.1.7. 2-Ethynylbenzyl alcohol 17. To a stirred solution of trimethylsilylethynylbenzyl alcohol **14**⁶ (14.28 g, 70 mmol) in methanol (70 mL) at room temperature was added K_2CO_3 (700 mg). After the

reaction mixture had been stirred for 1 h, it was poured into ice-water. The resulting aqueous mixture was extracted with CH_2Cl_2 (100 mL \times 3), and the combined organic extract was washed with brine (100 mL \times 3), and then dried (MgSO_4). The organic solvent was evaporated in vacuo to give almost pure **17**. Yield: 8.59 g (93%). Colorless prisms, mp 62–64 °C (from EtOAc/*n*-hexane). Lit.,²⁰ mp 61–62 °C.

4.1.8. 1,2-Bis[2-(hydroxymethyl)phenyl]ethyne 18. *o*-Iodobenzyl alcohol **7** (14.04 g, 60 mmol) was treated with *o*-ethynylbenzyl alcohol **17** (7.92 g, 60 mmol) instead of hexa-1,5-diyne **2** and worked up as described for the preparation of **9** to give **18**. Yield: 12.00 g (84%), colorless prisms, mp 130–133 °C (from EtOH/EtOAc). Lit.,²¹ mp 122–125 °C.

4.1.9. 1,2-Bis[2-(bromomethyl)phenyl]ethyne 19. *o*-Benzyl alcohol **18** (2.38 g, 10 mmol) was treated with PBr_3 and worked up as described for the preparation of **10** to give **19**. Yield: 2.11 g (58%). Colorless needles, mp 122–124 °C (from CH_2Cl_2 /hexane). Lit.,²² mp 127–128 °C.

4.2. General procedure for the reaction of dibenzyl dibromide **10**, **13**, **16**, **19** with NaHM

A solution of dibenzyl dibromide (1 mmol) in DMF (2 mL) was slowly added to a solution of NaHS hydrate (70%, 2.4 mmol) in DMF (5 mL) at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature for 12 h. In the case of NaHSe and NaHTe, EtOH (1 mL) was added, and the reaction mixture was stirred for 1 h. After addition of water (30 mL), the aqueous mixture was extracted with benzene (50 mL \times 3). The organic extract was washed with water (30 mL \times 3), brine (30 mL \times 3), dried (MgSO_4), and concentrated in vacuo. The resulting residue was purified by silica gel chromatography using *n*-hexane/ CH_2Cl_2 (30:1) as eluent to give pure product.

4.2.1. (Z,Z)-1,4-Bis(benzo[*c*]thiophene-1-methylidenyl)benzene 21a. Yield: 296 mg (80%). Reddish brown prisms, mp 195–197 °C, decomp., (from CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3): 4.53 (4H, s, $\text{PhCH}_2\text{S}\times 2$), 7.14 (2H, s, olefinic–H), 7.29–7.40, 7.66, 7.75 (6H, m, 4H, s, 2H, d, $J=7.8$ Hz, Ph–H). ^{13}C NMR (125 MHz, CDCl_3): 38.3 (t), 114.9 (d), 120.8 (d), 125.3 (d), 127.3 (d), 128.1 (d), 128.4 (d), 135.2 (s), 140.3 (s), 140.4 (s), 140.8 (s). EIMS: m/z (relative intensity, %) 370 (M^+ , 100), 337 (10). HRMS m/z M^+ calcd for $\text{C}_{24}\text{H}_{18}\text{S}_2$: 370.0850. Found: 370.0851.

4.2.2. (Z,Z)-1,4-Bis(benzo[*c*]selenophene-1-methylidenyl)benzene 21b. Yield: 410 mg (88%). Reddish brown prisms, mp 215–216 °C (from CHCl_3). ^1H NMR (500 MHz, CDCl_3): 4.53 (4H, s, $\text{PhCH}_2\text{Se}\times 2$), 7.26–7.33, 7.36, 7.59, 7.78 (4H, m, 2H, d, $J=5.7$ Hz, 4H, s, 2H, d, $J=7.3$ Hz, Ph–H), 7.52 (2H, s, olefinic–H). ^{13}C NMR (125 MHz, CDCl_3): 30.9 (t), 119.4 (d), 121.3 (d), 126.6 (d), 127.0 (d), 128.0 (d), 128.1 (d), 136.2 (s), 138.7 (s), 141.6 (s), 142.3 (s). EIMS: m/z (relative intensity, %) 466 (M^+ , 100), 464 (90), 462 (53). HRMS m/z M^+ calcd for $\text{C}_{24}\text{H}_{18}\text{Se}_2$: 465.9744. Found: 465.9743.

4.2.3. (Z,Z)-1,4-Bis(benzo[*c*]tellurophene-1-methylidenyl)benzene 21c. Yield: 410 mg (81%). Yellow prisms, mp 193–195 °C (from CHCl_3 /hexane). ^1H NMR (500 MHz, CDCl_3): 4.70 (4H, s, $\text{PhCH}_2\text{Te}\times 2$), 7.15–7.24, 7.26, 7.45, 7.80–7.89 (4H, m, 2H, s, 4H, s, 4H, m, olefinic- and Ph–H). ^{13}C NMR (125 MHz, CDCl_3): 11.9 (t), 122.2 (d), 126.4 (s), 126.8 (d), 127.5 (d), 127.6 (d), 128.0 (d), 128.5 (d), 138.4 (s), 143.7 (s), 146.5 (s). EIMS: m/z (relative intensity, %) 566, 564, 562, 560 (M^+ , 37, 70, 75, 51), 306 (100). HRMS m/z M^+ calcd for $\text{C}_{24}\text{H}_{18}\text{Te}_2$: 566.9536. Found: 566.9639.

4.2.4. 1,2-Bis(1*H*-isothiochromen-3-yl)ethane 26a. Yield: 251 mg (66%). Reddish brown oil. ^1H NMR (400 MHz, CDCl_3): 2.68 (4H, s,

CH_2CH_2), 3.85 (4H, s, $\text{PhCH}_2\text{S}\times 2$), 6.59 (2H, s, olefinic–H $\times 2$), 6.97–7.27 (8H, m, Ph–H). ^{13}C NMR (100 MHz, CDCl_3): 31.6 (t), 37.0 (t), 122.3 (d), 124.1 (d), 126.4 (d), 127.1 (s), 127.5 (d), 134.0 (s), 138.4 (s). EIMS: m/z (relative intensity, %) 322 (M^+ , 86), 161 (100), 160 (83), 128 (44). HRMS m/z M^+ calcd for $\text{C}_{20}\text{H}_{18}\text{S}_2$: 322.0850. Found: 322.0853.

4.2.5. Dibenzo[*d,l*]-1,2-diselenacyclotetradeca-6,10-diyne 27b. Yield: 291 mg (70%). Yellow prisms, mp 130–134 °C (from CH_2Cl_2 /hexane). IR (KBr): 2229 ($\text{C}\equiv\text{C}$). ^1H NMR (400 MHz, CDCl_3): 2.78 (4H, s, $\text{C}\equiv\text{CCH}_2\text{CH}_2\text{C}\equiv\text{C}$), 4.51 (4H, s, $\text{PhCH}_2\text{Se}\times 2$), 7.15, 7.23, 7.33, 7.38 (2H, ddd, $J=7.6$, 7.4, 1.3 Hz, 2H, ddd, $J=7.7$, 7.4, 1.5 Hz, 2H, dd, $J=7.7$, 1.3 Hz, 2H, dd, $J=7.7$, 1.5 Hz, Ph–H). ^{13}C NMR (100 MHz, CDCl_3): 19.9 (t), 31.5 (t), 80.2 (s), 92.5 (s), 123.0 (s), 126.7 (d), 128.3 (d), 129.7 (d), 131.9 (d), 141.3 (s). EIMS: m/z (relative intensity, %) 416 (M^+ , 90), 414 (82), 255 (78), 254 (73), 253 (100), 241 (57), 240 (53), 239 (75), 128 (95). HRMS m/z M^+ calcd for $\text{C}_{20}\text{H}_{16}\text{Se}_2$: 415.9586. Found: 415.9574. Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{Se}_2$: C, 57.99; H, 3.89. Found: C, 56.57; H, 3.98.

4.2.6. Dibenzo[*c,k*]telluracyclotrideca-5,9-diyne 28c. Yield: 317 mg (82%). Yellow prisms, mp 134–136 °C (from CH_2Cl_2 /hexane). IR (KBr): 2225 ($\text{C}\equiv\text{C}$). ^1H NMR (500 MHz, CDCl_3): 2.81 (4H, s, $\text{C}\equiv\text{CCH}_2\text{CH}_2\text{C}\equiv\text{C}$), 4.51 (4H, s, $\text{PhCH}_2\text{Te}\times 2$), 7.06, 7.16, 7.23, 7.34 (2H, ddd, $J=7.7$, 7.5, 1.4 Hz, 2H, ddd, $J=7.7$, 7.5, 1.4 Hz, 2H, dd, $J=7.7$, 1.4 Hz, 2H, dd, $J=7.7$, 1.4 Hz, Ph–H). ^{13}C NMR (125 MHz, CDCl_3): 6.3 (t), 20.0 (t), 80.6 (s), 93.8 (s), 122.1 (s), 125.8 (d), 128.2 (d), 128.4 (d), 131.9 (d), 143.0 (s). EIMS: m/z (relative intensity, %) 386 (M^+ , 63), 384 (58), 256 (60), 255 (100), 241 (72), 239 (58), 128 (90). HRMS m/z M^+ calcd for $\text{C}_{20}\text{H}_{16}\text{Te}$: 386.0315. Found: 386.0314. Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{Te}$: C, 62.57; H, 4.20. Found: C, 62.93; H, 4.37.

4.2.7. (Z,Z)-3*H*,3'*H*-1,1'-Bis(benzo[*c*]thiophenylidene)ethane 31a. Yield: 215 mg (73%). Brown prisms, mp 171–173 °C (from CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3): 4.47 (4H, s, $\text{PhCH}_2\text{Se}\times 2$), 6.81 (2H, s, olefinic–H $\times 2$), 7.24–7.33, 7.68 (6H, m, 2H, d, $J=7.7$ Hz, Ph–H). ^{13}C NMR (100 MHz, CDCl_3): 37.5 (t), 112.5 (d), 120.9 (d), 125.3 (d), 127.3 (d), 127.9 (d), 139.3 (s), 141.3 (s), 142.1 (s). EIMS: m/z (relative intensity, %) 294 (M^+ , 100), 259 (18). HRMS m/z M^+ calcd for $\text{C}_{18}\text{H}_{14}\text{S}_2$: 294.0537. Found: 294.0538.

4.2.8. (Z,Z)-3*H*,3'*H*-1,1'-Bis(benzo[*c*]selenophenylidene)ethane 31b. Yield: 347 mg (89%). Red prisms, mp 213–216 °C (from CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3): 4.51 (4H, s, $\text{PhCH}_2\text{Se}\times 2$), 6.97 (2H, s, olefinic–H $\times 2$), 7.21–7.25, 7.28–7.33, 7.70 (3H, m, 3H, m, 2H, d, $J=7.0$ Hz, Ph–H). ^{13}C NMR (125 MHz, CDCl_3): 30.3 (t), 118.2 (d), 121.5 (d), 126.6 (d), 127.0 (d), 127.9 (d), 141.2 (s), 141.7 (s), 142.6 (s). EIMS: m/z (relative intensity, %) 390 (M^+ , 96), 388 (86), 229 (97), 228 (100). HRMS m/z M^+ calcd for $\text{C}_{18}\text{H}_{14}\text{Se}_2$: 389.9426. Found: 389.9427.

4.2.9. (Z,Z)-3*H*,3'*H*-1,1'-Bis(benzo[*c*]tellurophenylidene)ethane 31c. Yield: 73 mg (15%). Red prisms, mp 136–138 °C (from CHCl_3 /hexane). ^1H NMR (400 MHz, CDCl_3): 4.47 (4H, s, $\text{PhCH}_2\text{Te}\times 2$), 7.00 (2H, s, olefinic–H $\times 2$), 7.17–7.18, 7.19–7.21, 7.73 (4H, m, 2H, m, 2H, d, $J=7.9$ Hz, Ph–H). ^{13}C NMR (100 MHz, CDCl_3): 11.7 (t), 122.2 (d), 126.8 (d), 128.1 (d), 128.6 (d), 129.0 (d), 131.4 (s), 144.7 (s), 145.4 (s). EIMS: m/z (relative intensity, %) 490, 488, 486 (M^+ , 40, 73, 78), 360 (45), 229 (99), 228 (100). HRMS m/z M^+ calcd for $\text{C}_{18}\text{H}_{14}\text{Te}_2$: 489.9222. Found: 489.9229.

4.2.10. (Z)-1-(3-*o*-Tolylprop-2-nylidene)-1,3-dihydrobenzo[*c*]tellurophene 32. Yield: 299 mg (83%). Yellow oil. IR (neat) cm^{-1} : 2181 ($\text{C}\equiv\text{C}$). ^1H NMR (400 MHz, CDCl_3): 2.43 (3H, s, Me), 4.03 (2H, s, PhCH_2Te), 7.11–7.28 (8H, m, Ph–H), 7.37 (1H, s, olefinic–H). ^{13}C NMR (100 MHz, CDCl_3): 6.1 (t), 21.4 (q), 113.9 (s), 125.9 (d), 127.1 (d),

127.7 (d), 127.8 (d), 128.0 (d), 130.2 (d), 130.7 (d), 131.7 (s), 132.2 (d), 134.9 (s), 139.2 (s), 139.8 (s), 140.1 (s), 143.6 (d), 146.4 (s). EIMS: m/z (relative intensity, %) 360, 358, 356 (M^+ , 47, 43, 37), 229 (100), 228 (95). HRMS m/z M^+ calcd for $C_{18}H_{14}^{130}Te$: 360.0159. Found: 360.0162.

4.2.11. *trans*-3*H*,3'*H*-1,1'-Bi(benzo[*c*]thiophenylidene) **34a.** Yield: 214 mg (80%). Yellow prisms (from CH_2Cl_2/n -hexane), mp 136–138 °C. 15 (Lit.,¹⁵ mp 138–140 °C. This compound was identical with the authentic sample. 1H NMR (500 MHz, $CDCl_3$): 4.53 (4H, s, $PhCH_2S \times 2$), 7.27, 7.35–7.43, 8.24 (2H, dd, $J=7.2$, 7.0 Hz, 4H, m, 2H, d, $J=8.1$ Hz, Ph–H). ^{13}C NMR (125 MHz, $CDCl_3$): 38.1 (t), 125.1 (d), 125.3 (d), 127.0 (d, two carbons), 127.5 (s), 140.5 (s), 141.7 (s). EIMS: m/z (relative intensity, %) 268 (M^+ , 100), 235 (42).

4.2.12. *trans*-3*H*,3'*H*-1,1'-Bi(benzo[*c*]selenophenylidene) **34b.** Yield: 331 mg (91%). Yellow prisms (from CH_2Cl_2/n -hexane), mp 126–127 °C. 1H NMR (500 MHz) 4.48 (4H, s, $PhCH_2Se \times 2$), 7.23 (2H, dd, $J=7.5$, 7.2 Hz), 7.33 (2H, dd, $J=7.3$, 7.2 Hz), 7.34 (2H, d, $J=7.3$ Hz), 7.81 (2H, d, $J=7.5$ Hz). ^{13}C NMR (125 MHz) 30.7 (t), 124.7 (d), 126.2 (s), 126.5 (d), 126.6 (d), 127.3 (d), 143.0 (s), 143.4 (s). EIMS: m/z (relative intensity, %) 364, 362 (M^+ , 100, 90), 283 (30), 202 (97). HRMS m/z M^+ calcd for $C_{16}H_{12}^{80}Se_2$: 363.9272. Found: 363.9269.

4.2.13. *trans*-3*H*,3'*H*-1,1'-Bi(benzo[*c*]tellurophenylidene) **34c.** Yield: 211 mg (46%). Red prisms (from $CHCl_3$), mp 177–179 °C (dec). 1H NMR (500 MHz) 4.73 (4H, s, $PhCH_2Te \times 2 \times 2$), 7.17–7.25, and 7.34 (6H, m and 2H, d, $J=6.6$ Hz, Ph–H). ^{13}C NMR (125 MHz) 11.9 (t), 118.2 (s), 123.0 (d), 126.6 (d), 128.2 (d), 128.3 (d), 145.2 (s), 150.7 (s). EIMS m/z (relative intensity): 464, 462, 460, 458 (M^+ , 18, 35, 37, 25), 203 (100). HRMS m/z M^+ calcd for $C_{16}H_{12}^{130}Te_2$: 463.9065. Found: 463.9022.

4.2.14. 6,12-Dihydro-5,11-ditellurachrysene **37.** Yield: 221 mg (48%). Yellow needles (from $CHCl_3$), mp 192–194 °C (dec). 1H NMR (500 MHz) 3.98 (4H, s, 6- and 12- H_2), Ph–H [7.13 (2H, ddd, $J=7.8$, 7.3, 1.4 Hz), 7.21 (2H, ddd, $J=7.6$, 7.3, 1.2 Hz), 7.27 (2H, dd, $J=7.6$, 1.4 Hz), 7.30 (2H, dd, $J=7.8$, 1.2 Hz)]. ^{13}C NMR (125 MHz) 8.04 (t), 126.18 (d), 127.34 (d), 128.32 (d), 128.41 (d), 133.10 (s), 144.64 (s). EIMS m/z (relative intensity): 464, 462, 460, 458 (M^+ , 15, 26, 30, 20), 203 (100). HRMS m/z M^+ calcd for $C_{16}H_{12}^{130}Te_2$: 463.9065. Found: 463.9091.

4.2.15. 1,2-Bis(1*H*-isoselechromen-3-yl)ethane **26b.** A solution of dibenzyl dibromide (1 mmol) in DMF (2 mL) was slowly added to a solution of freshly prepared NaHSe (2 mmol)¹³ in DMF (5 mL) at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature for 1 h. After addition of EtOH (1 mL), the mixture was heated at 110–115 °C for 20 h and worked up as described for the preparation of **21a** to give **26b**. Yield: 255 mg (61%). Yellow prisms, mp 155–156 °C (from $CHCl_3$ /hexane). 1H NMR (400 MHz, $CDCl_3$): 2.79 (4H, s, CH_2CH_2), 3.83 (4H, s, $PhCH_2Se \times 2$), 6.72 (2H, s, olefinic–H $\times 2$), 7.10–7.24 (8H, m, Ph–H). ^{13}C NMR (100 MHz, $CDCl_3$): 24.3 (t), 39.0 (t), 125.1 (d), 126.7 (d), 127.4 (d), 127.59 (d), 127.63 (d), 128.2 (s), 135.2 (s), 136.4 (s). EIMS: m/z (relative intensity, %) 418 (M^+ , 65), 416 (47), 209 (85), 207 (44), 128 (100). HRMS m/z M^+ calcd for $C_{20}H_{18}^{80}Se_2$: 417.9739. Found: 417.9741.

4.3. X-ray structure determination

Single crystals of **34c** were obtained from solutions of toluene after slow evaporation of the solvent at room temperature, **37** from solutions of hexane/ CH_2Cl_2 . Diffraction data were collected on a Bruker Apex-II CCD diffractometer equipped with a graphite

monochromated Mo K α radiation source ($\lambda=0.71073$ Å). The structures were solved by direct methods (SHELXS-97),²³ and refined by full-matrix least-square methods on F^2 for all reflections (SHELXL-97)²⁴ with all non-hydrogen atoms anisotropic and all hydrogen atoms isotropic.

For **34c**, the structure analysis is based on 2822 observed reflections with $I>2.00$ $\sigma(I)$ and 163 variable parameters; colorless prisms, 196 K, monoclinic, space group $P2_1/c$, $a=8.8295(6)$ Å, $b=11.1127(8)$ Å, $c=14.2605(10)$ Å, $\beta=92.925(1)^\circ$, $V=1397.41(17)$ Å³, $Z=4$, $R=0.0290$, $R_w=0.0701$, GOF=1.067.

For **37**, the structure analysis is based on 1520 observed reflections with $I>2.00$ $\sigma(I)$ and 83 variable parameters; colorless prisms, 196 K, triclinic, space group $C2$, $a=17.287(2)$ Å, $b=4.5844(6)$ Å, $c=8.6728(11)$ Å, $\beta=91.121(1)^\circ$, $V=687.18(15)$ Å³, $Z=2$, $R=0.0116$, $R_w=0.0308$, Flack Param=0.04(2), GOF=1.081.

CCDC-726522 for **34c** and CCDC-726523 for **37** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supplementary data

Supplementary data associated with this article (calculated 3D-structures of the chalcogenols **33**, and the ORTEP drawing and, X-ray data of **31b**) can be found in the online version. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.04.101. These data include MOL files and InChIKeys of the most important compounds described in this article.

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14. The ORTEP drawing and X-ray data of **31b** are available as [Supplementary data](#) of this article.
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