Synthesis and Reactivity of Divinylselenium Dichlorides and Dibromides

Samuel Braverman,* Tatiana Pechenick-Azizi, Hugo E. Gottlieb, Milon Sprecher

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel
Fax +972(3)7384053; E-mail: bravers@mail.biu.ac.il

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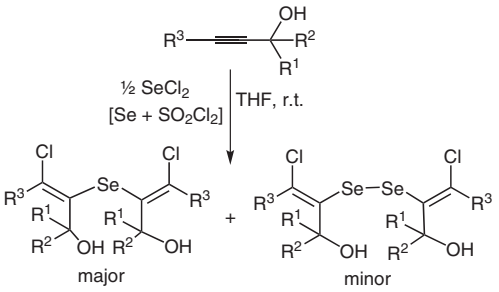
Abstract: Regio- and stereospecific electrophilic addition reactions of selenium tetrachloride and selenium tetrabromide to propargyl alcohols are reported. (*Z*,*Z*)-Bis(β-chlorovinyl)selenium dichlorides were isolated in high yields, and their reactivity was dependent on their substitution pattern. Products derived from unsubstituted, α-methyl-, or α,α-dimethylpropargyl alcohols readily underwent transfer of chlorine atoms to one of the two double bonds. (*Z*,*Z*)-Bis(β-chlorovinyl)selenium dichlorides derived from γ-phenyl- or γ-isopropenylpropargyl alcohols underwent cyclization to form benzoselenophene derivatives; this was accompanied by the formation of the corresponding dichloro-substituted allylic alcohols. In contrast, selenium tetrachloride reacts with γ-phenylpropargyl alcohol exclusively as a chlorinating agent, giving (3-chloroprop-1-yn-1-yl)benzene quantitatively. Products of regio- and stereospecific electrophilic addition of selenium tetrabromide are also described. Reaction mechanisms are proposed.

Key words: electrophilic additions, alkynes, alcohols, selenium, halides

Our past experience with reactions of propargyl alcohols with electrophilic sulfur reagents such as sulfur dichloride (SCl_2)[1] or disulfur dichloride (S_2Cl_2)[2] led us to examine the reactions of the corresponding selenium analogues. Selenium dichloride ($SeCl_2$) was prepared, according to a recently reported procedure, from elemental selenium and sulfuryl chloride (SO_2Cl_2) in tetrahydrofuran.[3] Its reactions with various propargyl alcohols showed some surprising results. Unlike sulfur dichloride, selenium dichloride readily undergoes 1,2-addition to the triple bond of propargyl alcohols, resulting in the formation of functionalized (*Z*,*Z*)-bis(β-chlorovinyl)selenides in high yields and with complete regio- and stereospecificity (Scheme 1).[4,5] In some cases, the selenide is accompanied by the corresponding diselenide. Furthermore, and contrary to expectations, the divinylselenides and diselenides are the products of *syn*-addition with anti-Markovnikov orientation. The hydroxy group of the reactants appears to be responsible for this behavior. We recently proposed a possible mechanism for electrophilic addition of selenium dichloride to the triple bond of a propargyl alcohol that involves selenirenium ion intermediates.[5] Prompted by these results, we decided to investigate the addition of selenium tetrachloride to propargyl alcohols with the hope of obtaining the corresponding divinylselenium dichlorides in a regio- and stereospecific manner. The expected



Scheme 1

product was likely to be of synthetic interest because of the presence of a reactive selenium dichloride moiety.

Addition reactions of tetravalent selenium reagents ($SeCl_4$, $SeBr_4$, $ArSeCl_3$, or $ArSeBr_3$) to alkenes have received some attention,[6–10] and they have been found to be generally nonregioselective.

Although, dialkyl- and diarylselenium dihalides have been known for many years,[11] and are employed as intermediates for the synthesis of other organoselenium compounds, isolated divinylselenium dichlorides are almost unknown. More than forty years ago, bis(2-chlorovinyl)selenium dichloride and bis(2-chloro-2-phenylvinyl)selenium dichloride were prepared in 9 and 73% yields, respectively, by treatment of acetylene or phenylacetylene, respectively, with $SeCl_4$, but the stereochemistry of the products was not reported.[12a]

Some three decades ago, it was reported that the reaction of phenylacetylene derivatives with $SeCl_4$ and $SeBr_4$ leads to the corresponding benzoselenophene derivatives.[12b–d]

Recently, a stereospecific synthesis of (*E*,*E*)-bis(2-chlorovinyl) selenide from selenium tetrachloride and acetylene has been reported,[13a,b] but no bis(2-chlorovinyl)selenium dichloride was isolated. Electrophilic additions of $SeBr_4$ and $SeCl_4$ to diorganyl(diethynyl)silanes[13c–g] and diorganyl(diethynyl)germanes[13g,h] have been reported to result in regio- and stereoselective formation of a new class of unsaturated five-membered heterocycles. It was proposed that, initially, $SeCl_4$ and $SeBr_4$ participate in the reaction as halogenation agents, leading to the formation of the intermediate ethynyl(1,2-dihalovinyl)silanes or -germanes and selenium dihalides. This is followed by Markovnikov *trans*-addition of the resulting selenium dihalide to the triple bond, followed by anti-Markovnikov addition of the selenenyl halide to the dihalovinyl moiety.

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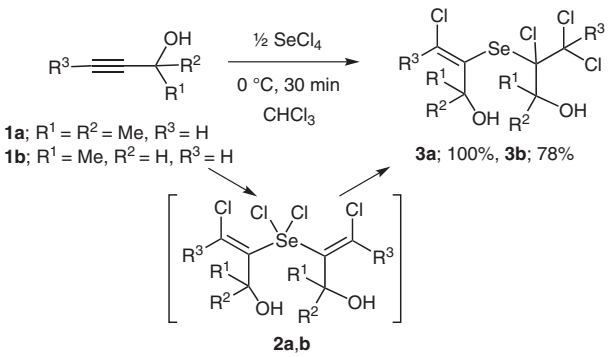
To the best of our knowledge, no addition of SeX_4 to propargyl alcohols has been reported. Because of the synthetic potential of divinylselenium dichlorides as intermediates in organoselenium chemistry, and the fact that the hydroxy group plays an important role in the regio- and stereospecific addition of $SeCl_2$,[4,5] we were interested in exploring the addition reactions of $SeCl_4$ and $SeBr_4$ with propargyl alcohols, and the stereochemistry of these reactions.

The reaction of 2-methylbut-3-yn-2-ol (α,α-dimethylpropargyl alcohol) with commercially available selenium tetrachloride in dry chloroform under argon at 0 °C for 30 minutes gave a product that was not the expected divinylselenium dichloride **2a** (Scheme 2). ^1H and ^{13}C NMR spectra showed two CH peaks, one olefinic (7.08, 128.87 ppm, respectively) and one aliphatic (6.36, 77.29 ppm, respectively), as well as four signals for different methyl groups. On the basis of the $^1J_{C-Se}$ values[14] (143.07 ppm, $^1J_{C-Se}$ = 124.2 Hz and 86.88 ppm, $^1J_{C-Se}$ = 113.9 Hz), the ^{13}C NMR spectrum shows that two quaternary carbons (one olefinic and one aliphatic) are attached to the selenium atom. Two CH carbons show corresponding $^2J_{C-Se}$ values (128.87 ppm, $^2J_{C-Se}$ = 28.2 Hz and 77.29 ppm, $^2J_{C-Se}$ = 13.0 Hz). The new product had an unsymmetrical structure with one chiral center and only one double bond. On the basis of the ^1H and ^{13}C NMR spectra and a high-resolution mass spectrometric elemental analysis, we conclude that this product is (3*Z*)-4-chloro-3-{[1-chloro-1-(dichloromethyl)-2-hydroxy-2-methylpropyl]selanyl}-2-methylbut-3-en-2-ol (**3a**; Scheme 2). The stereochemistry of the double bond was determined by a NOESY experiment in which a NOE interaction between methyl and olefinic hydrogen atoms was detected; their chemical shifts were assigned by heteronuclear multiple bond correlation (HMBC) and heteronuclear single quantum coherence (HMQC) experiments.

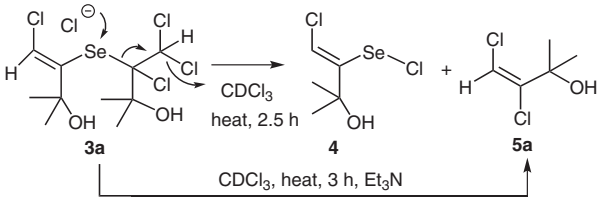


Scheme 2

The formation of the selenide **3a** can be explained in terms of spontaneous transfer of chlorines in the corresponding divinylselenium dichloride intermediate **2a** to one of the two double bonds. Selenide **3a** was unstable, especially in the crude mixture, and required immediate purification by column chromatography. After isolation, product **3a** could be stored at –18 °C for several days. The reaction conditions mentioned above were different from those used for the reaction of propargyl alcohols with $SeCl_2$. In the present case, for convenience, the alcohol was added to a suspension of $SeCl_4$ in dry chloroform, and the reaction proceeded at a lower temperature and in a shorter time. The use of chloroform as a solvent made it possible to determine the end point of the reaction from the complete disappearance of the solid $SeCl_4$. The reaction of but-3-yn-2-ol (α-methylpropargyl alcohol) with $SeCl_4$ led to a similar type of product **3b**, which was obtained as a mixture of four diastereomers because of the presence of two chiral centers. The diastereomers were separated by column chromatography and found to be stable even after refluxing in chloroform solution for three hours. To recapitulate, the addition of $SeCl_4$ to the triple bond of these propargyl alcohols was found to be *syn* with an anti-Markovnikov orientation.

In sharp contrast to the above, the electrophilic addition of $TeCl_4$ to propargyl alcohols led to the corresponding (chlorovinyl)tellurium trichlorides, which were obtained as mixtures of regio- and stereoisomers.[5]

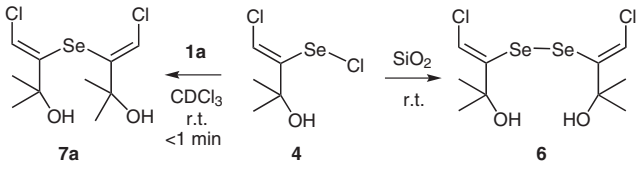
Interestingly, the unsymmetrical selenide **3a** underwent slow disproportionation upon heating for 2.5 hours in refluxing chloroform, or more slowly at room temperature, to give a mixture of (3*E*)-3,4-dichloro-2-methylbut-3-en-2-ol (**5a**) and, apparently, the vinylselenenyl chloride **4** (Scheme 3). When the reaction was performed in the presence of triethylamine for three hours at the reflux, alcohol **5a** was obtained as the sole organic product, accompanied by precipitation of selenium. We conclude that the two chlorine atoms in alcohol **5a** have an *anti* orientation, because no NOE interaction between the methyl and vinyl hydrogen atoms was observed.



Scheme 3

The formation of **4** and **5a** involves the 1,2-elimination of selenium and chlorine, and could be initiated by attack by a chloride ion on selenium (Scheme 3).

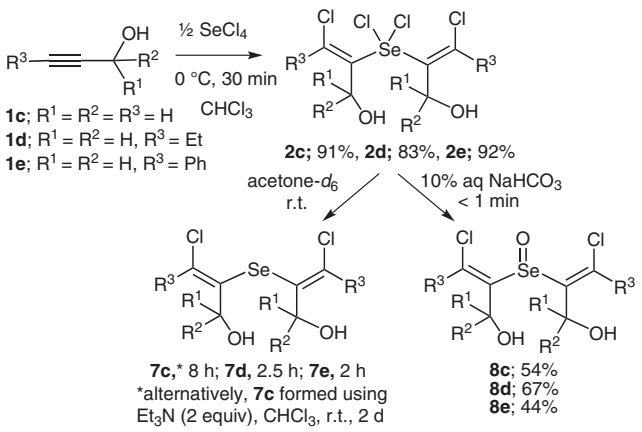
The vinylselenenyl chloride **4** was identified in the reaction mixture by using ^1H and ^{13}C NMR spectroscopy, and its presence was confirmed by two-dimensional NMR experiments, as well as by high-resolution mass spectroscopic analysis. Attempts at isolation by silica gel chromatography gave the (Z,Z)-divinyl diselenide **6** (Scheme 4).[4,5] On addition of α,α-dimethylpropargyl alcohol **1a** to the reaction mixture, the intermediate **4** was immediately converted into the corresponding (Z,Z)-divinyl selenide **7a**.[4,5]



Scheme 4

To study the scope and limitation of the reactivity of the putative divinylselenium dichlorides intermediates, we examined the reaction of $SeCl_4$ with unsubstituted and γ-substituted propargyl alcohols. Furthermore, the isolation of the divinylselenium dichloride intermediate would demonstrate that products of type **3** may indeed be formed as a result of transfer of chlorine from an intermediate **2** to one of the two double bonds. In principle, and like the recently reported electrophilic addition of selenium tetrahalides to diorganyldiethynylsilanes,[13] the formation of product **3** might be explained to result from direct chlorination of half the propargyl alcohol by $SeCl_4$ (0.5 equivalents), leading to 2,3-dichloroprop-2-en-1-ol and $SeCl_2$, followed by addition of the latter to the second half of the propargyl alcohol to form (2-chlorovinyl)selenenyl chloride, the electrophilic addition of which to 2,3-dichloroprop-2-en-1-ol should yield **3**.

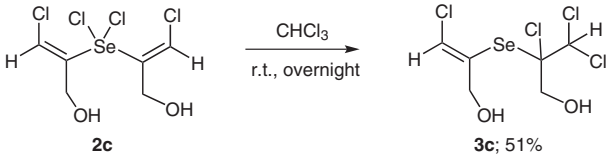
In the event, by careful low-temperature workup, we succeeded in isolating high yields of the divinylselenium dichlorides **2c–e** derived from unsubstituted, γ-ethyl- and γ-phenyl-substituted propargyl alcohols (Scheme 5), and we were able to characterize these products. These unstable products, upon standing in acetone-d_6 solution at room temperature for 2–8 hours underwent dechlorination to form the corresponding selenides **7c–e** with the same regio- and stereochemistry as the products obtained from the reaction of the corresponding propargyl alcohols with $SeCl_2$[4,5] (Scheme 5). Compound **7c** also formed from **2c** in the presence of triethylamine (two equivalents) in chloroform at room temperature for two days. A similar dechlorination reaction of saturated selenium dichloride in refluxing acetone has been reported.[15]



Scheme 5

In addition, during the workup, unsubstituted ethyl- and phenyldivinylselenium dichlorides were easily converted into the corresponding selenoxide **8c–e** by rapid hydrolysis with 10% aqueous sodium bicarbonate, followed by extraction with ethyl acetate (Scheme 5). The selenoxides were stable solids and were easily purified and identified spectroscopically. The characteristic NMR splitting pattern of diastereotopic methylene protons caused by the chirality of selenoxides, as well as the IR and high-resolution mass spectra support this structure. This reaction represents a simple method for preparing stable vinylic selenoxides in a regio- and stereospecific manner. An alternative preparation of divinylic selenoxides by oxidation of the selenides has been recently reported by us,[4,5] and their synthetic applications will be discussed separately.

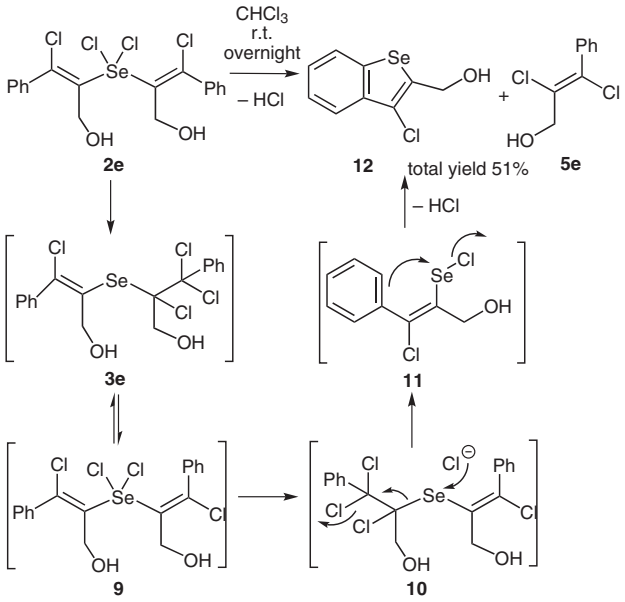
In keeping with the above, when a chloroform solution of divinylselenium dichloride **2c** was stirred overnight the unsymmetrical selenide **3c** (Scheme 6) was obtained; this was found to be stable, even on refluxing in chloroform for two hours.



Scheme 6

In the case of 3-phenylprop-2-yn-1-ol (γ-phenylpropargyl alcohol), the corresponding (Z,Z)-divinylselenium dichloride **2e** gave (3-chloro-1-benzoselenophen-2-yl)methanol (**12**) and (2*E*)-2,3-dichloro-3-phenylprop-2-en-1-ol (**5e**) (Scheme 7). In addition, during silica gel chromatography benzoselenophene **12** underwent partial substitution of the hydroxy group by chlorine to form 3-chloro-2-(chloromethyl)-1-benzoselenophene (**12a**), possibly because of to the presence of traces of hydrogen chloride. On the basis of an absence of a NOE interaction between the phenyl and methylene hydrogen atoms, we believe that the two chlorine atoms in alcohol **5e** have an *anti* orientation. Interestingly, the reaction of the same alcohol with $SeCl_2$ gave the corresponding divinyl selenide, and no cyclization product was observed.[4,5]

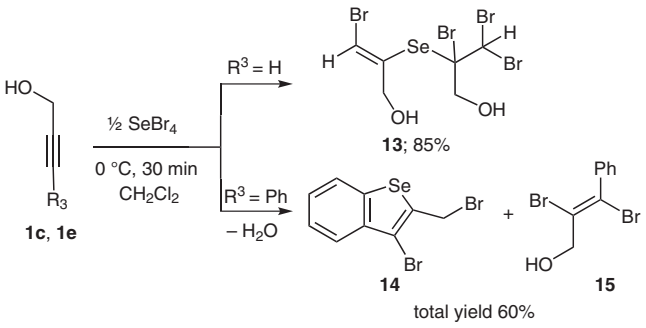
As mentioned above, the reaction of phenylacetylene derivatives with selenium tetrachloride or tetrabromide to give the corresponding benzoselenophenes has been reported before.[12] However, in these cases, benzoselenophenes were formed through cyclization of the corresponding (*E*)-β-chloro-vinylselenium trihalide intermediate, accompanied by release of HX and X_2. In contrast, in the present case the (*Z*,*Z*)-configuration of the divinyl selenium dichloride **2e** prevents the immediate direct ring closure form to the corresponding benzoselenophene. Conversion of **2e** into **12** and **5e** is a multistep reaction whose details are as yet undetermined, although the following mechanism might rationalize the formation of the thermodynamically desirable product **12** (Scheme 7).



Scheme 7

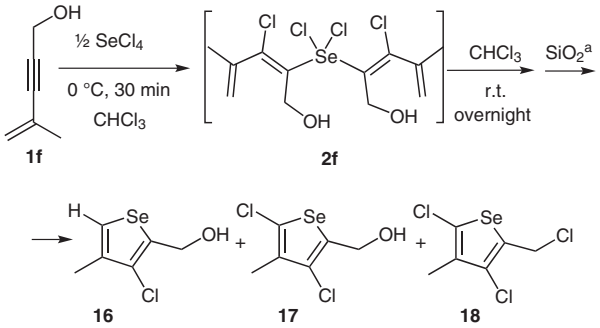
The research was then extended to $SeBr_4$. The reaction of unsubstituted propargyl alcohol with selenium tetrabromide in dry dichloromethane solution under argon at 0 °C for 30 min gave product **13**, which is presumably formed by spontaneous transfer of bromine atoms from selenium to one of the two double bonds of the corresponding divinylselenium dibromide intermediate (Scheme 8). In contrast to the analogous chloro-substituted product **3c**, which is stable even in refluxing chloroform, product **13** was found to be stable only at –18 °C. Because of this instability, our attempts to perform a NOESY experiment to determine the configuration of the double bond failed. However, on the basis of the strong similarity between the ^1H and ^{13}C NMR spectra of the product **13** and those of the chloro-substituted analogue **3c**, especially the chemical shifts of the allylic methylene groups, we conclude that *syn*-addition occurred. Reaction of 3-phenylprop-2-yn-1-ol (**1e**) with $SeBr_4$ under the above conditions led directly to the formation of 3-bromo-2-(bromomethyl)-1-benzoselenophene (**14**) and (2*E*)-2,3-dibromo-3-phenylprop-2-en-1-ol (**15**) (Scheme 8). An *anti* orientation of the two bromine atoms in the latter was assigned, because no NOE interaction was observed between the phenyl and methylene hydrogen atoms. In both cases, and in contrast with the chloro-substituted analogue, the corresponding divinylselenium dibromide intermediates could not be isolated, their reaction being much faster at lower temperatures (30 min at 0 °C) than was the case with **2c** and **2e** (overnight at room temperature).

Prompted by the results that we obtained with 3-phenylprop-2-yn-1-ol, we reacted 4-methylpent-4-en-2-yn-1-ol with $SeCl_4$. Although, the corresponding divinylselenium dichloride could not be isolated, the cyclization products (3-chloro-4-methylselenophen-2-yl)methanol (**16**), (3,5-dichloro-4-methylselenophen-2-yl)methanol (**17**), and



Scheme 8

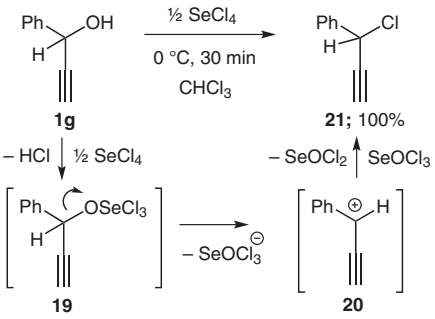
2,4-dichloro-5-(chloromethyl)-3-methylselenophene (**18**) were successfully purified and identified (Scheme 9). The formation of selenophene **16** is similar to the formation of benzoselenophene **12**, whereas the formation of selenophene **17** involves electrophilic aromatic substitution of the α-carbon atom by chlorinating species. Selenophene **18** may be the product of reaction of selenophene **17** with hydrogen chloride.



Scheme 9

The reaction of 1-phenylprop-2-yn-1-ol with $SeCl_4$ under the above conditions led to the formation of the corresponding α-phenylpropargyl chloride **21**[16] in quantitative yield without any acetylene–allene isomerization, and no product of $SeCl_4$ addition to the triple bond (Scheme 10). The reaction of the same alcohol with $SeCl_2$ led to the formation of the corresponding divinyl selenide.[4,5] It is known that $SeCl_4$ reacts with saturated α-phenylalkyl alcohols by an S_N1-like mechanism.[17] In this connection it may be noted that reaction of substituted 1-phenylprop-2-yn-1-ol with hydrogen bromide leads to the corresponding allenyl bromide by an S_N2' mechanism, exclusively.[18]

In conclusion, selenium tetrahalides were found to undergo electrophilic addition with propargyl alcohols in a regio- and stereospecific manner. A range of novel (*Z*,*Z*)-bis(β-chlorovinyl)selenium dichlorides and dibromides were prepared. *Syn*-addition and anti-Markovnikov orientation were shown to occur by means of NOESY experiments and from the values of $^1J_{C-Se}$ and $^2J_{C-Se}$, respectively. These compounds undergo halogen transfer



Scheme 10

to one of the two double bonds and fragmentation/cyclization to form benzoselenophene derivatives. Isolated (*Z*,*Z*)-bis(β-chlorovinyl)selenium dichlorides can be hydrolyzed to the corresponding selenoxides by aqueous sodium bicarbonate or reduced to the corresponding selenides in acetone.

$CHCl_3$ and CH_2Cl_2 were distilled from P_2O_5 and stored under argon. THF was distilled from Na by using benzophenone. $SeBr_4$ was prepared according to the known procedure.[13e] 4-methylpent-4-en-2-yn-1-ol (**1f**, 100%), which is commercially available, was prepared from the corresponding alkyne and paraformaldehyde by using TMEDA and BuLi in dry THF (30 min, –78 °C; 1.5 h, r.t.). All other solvents and reagents were commercially available and were used without further purification. Column chromatography was performed on silica gel 60 (230–400 mesh), and TLC was performed on precoated Merck 60 F_{254} silica gel plates (2.00 mm). Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. IR spectra were recorded on a Bruker Tensor 27 FTIR instrument. Mass spectra were recorded on an Auto flex TOF/TOF MALDI instrument (Bruker, Germany). HRMS were obtained on a VG-Fison Autospec instrument. NMR spectra were recorded at 298 K by using 300-, 600-, or 700-MHz spectrometers (^{13}C NMR frequencies of 75.5, 150.9, or 176.1 MHz, respectively) in $CDCl_3$ or other deuterated solvents with TMS as the internal standard. Chemical shifts are reported in ppm, and coupling constants in Hz. The Se–C coupling constants were measured from the ^{77}Se satellites in the ^{13}C NMR spectra. The Se–H coupling constants were measured from the ^{77}Se satellites in the ^1H NMR spectra. In some cases the structures were unambiguously determined with the aid of two-dimensional techniques, such as COSY, HMQC, or HMBC. The stereochemistry of the double bond was assigned by using the NOESY technique.

Reactions of $SeCl_4$ and $SeBr_4$ with Propargyl Alcohols; General Procedure

The appropriate propargyl alcohol (2 mmol) was added to a soln of $SeCl_4$ or $SeBr_4$ (1 mmol) in anhyd $CHCl_3$ or anhyd CH_2Cl_2 (12 mL) at 0 °C under argon, and the mixture was stirred at 0 °C for 30 min. This reaction taken to be complete when the insoluble $SeCl_4$ and $SeBr_4$ had disappeared. The solvent was then removed under reduced pressure. In the case of the addition reactions of $SeCl_4$ with alcohols **1c**, **1e**, or **1f**, the products were dissolved in $CDCl_3$ and allowed to stand at r.t. overnight.

(2*Z*,2′*Z*)-2,2′-(Dichloro-λ⁴-selanediyl)bis(3-chloroprop-2-en-1-ol) (2c)

White solid; yield: 91%. (Because of instability at r.t., the mp could not been measured).

IR (neat): 1026, 1072, 1455, 1594, 2935, 3331 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.26 (t, *J* = 1.5 Hz, 2 H), 4.95 (d, *J* = 1.5 Hz, 4 H), 2.95 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ =145.3 ($^1J_{C-Se}$ = 104.0 Hz, =C–), 132.7 ($^2J_{C-Se}$ = 17.8 Hz, =CH–), 59.7 ($-CH_2-$).

MS (CI/CH_4): *m/z* (%) = 334 (24) [M^+], 262 (40), 154 (45), 83 (100).

HRMS: *m/z* [M^+] calcd for $C_6H_8O_2{}^{35}Cl_2{}^{37}Cl_2{}^{78}Se$: 333.8392; found: 333.8391.

(2*Z*,2′*Z*)-2,2′-(Dichloro-λ⁴-selanediyl)bis(3-chloropent-2-en-1-ol) (2d)

Yellow viscous liquid; yield: 83%.

IR (neat): 1012, 1136, 1457, 1602, 2980, 3384 cm^{-1}

^1H NMR (300 MHz, $CDCl_3$): δ = 4.90 (s, 4 H), 4.02 (br s, 2 H), 2.88 (q, *J* = 7.2 Hz, 4 H), 1.36 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ =151.7 (=C–), 137.7 ($^1J_{C-Se}$ = 102.0 Hz, =C–), 63.2 ($-CH_2-$), 33.4 ($-CH_2-$), 12.0 ($-CH_3$).

MS: (Failed because of the instability of the compound.)

(2*Z*,2′*Z*)-2,2′-(Dichloro-λ⁴-selanediyl)bis(3-chloro-3-phenylprop-2-en-1-ol) (2e)

Light yellow sticky liquid; yield: 92%.

IR (neat): 1031, 1068, 1216, 1590, 1608, 3013, 3375 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.41 (m, 10 H), 4.99 (s, 4 H), 3.40 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.0 (=C–), 140.0 (=C–), 136.1 (=C–), 131.6 (=CH–), 128.9 [=CH– (×2)], 128.6 [=CH– (×2)], 63.02 ($-CH_2-$).

MS: (Failed because of the instability of the compound.)

(3*Z*)-4-Chloro-3-{[1-chloro-1-(dichloromethyl)-2-hydroxy-2-methylpropyl]selanyl}-2-methylbut-3-en-2-ol (3a)

The product was isolated by chromatography [silica gel, hexanes–EtOAc (4:1)] followed by washing with $CDCl_3$.

White solid; yield: quant (^1H NMR), 39% (isolated); mp 78.5 ± 0.5 °C.

IR (neat): 1142, 1177, 1365, 1459, 1559, 1708, 2983, 3345 cm^{-1}.

^1H NMR (700 MHz, $CDCl_3$): δ = 7.08 (s, 1 H), 6.36 (s, 1 H), 3.47 (br s, 2 H), 1.73 (s, 3 H), 1.64 (s, 3 H), 1.62 (s, 3 H), 1.60 (s, 3 H).

^{13}C NMR (176 MHz, $CDCl_3$): δ = 143.1 ($^1J_{C-Se}$ = 124.2 Hz, =C–), 128.9 ($^2J_{C-Se}$ = 28.2 Hz, =CH–), 86.9 ($^1J_{C-Se}$ = 113.9 Hz, –C–Cl), 78.8 (–C–C–Cl), 77.3 ($^2J_{C-Se}$ = 13.0 Hz, –CH–), 73.2 (–C–), 28.5 ($-CH_3$), 28.0 ($-CH_3$), 27.7 ($-CH_3$), 27.6 ($-CH_3$).

MS (CI/CH_4): *m/z* (%) = 388 (4) [M^+], 294 (34), 199 (22), 182 (24), 181 (26).

HRMS: *m/z* [M^+] calcd for $C_{10}H_{16}O_2{}^{35}Cl_4{}^{80}Se$: 387.9070; found: 387.9070.

(3*Z*)-4-Chloro-3-{[1-chloro-1-(dichloromethyl)-2-hydroxypropyl]selanyl}but-3-en-2-ol (3b)

The products were isolated by chromatography [silica gel, hexanes–EtOAc (5:1)] as a mixture of four stereoisomers in the ratio 6.6:4.6:2.1:1.0; total isolated yield: 78%.

First stereoisomer: colorless liquid.

IR (neat): 1064, 1126, 1172, 1287, 1373, 1449, 1587, 2982, 3358 cm^{-1}.

^1H NMR (700 MHz, $CDCl_3$): δ = 6.84 (d, *J* = 0.9 Hz, 1 H), 6.22 (s, 1 H), 5.09 (qd, *J* = 6.6, 0.9 Hz, 1 H), 4.25 (q, *J* = 6.3 Hz, 1 H), 4.14 (br s, 2 H), 1.51 (d, *J* = 6.6 Hz, 3 H), 1.31 (d, *J* = 6.3 Hz, 3 H).

^{13}C NMR (176 MHz, $CDCl_3$): δ = 136.2 ($^1J_{C-Se}$ = 123.0 Hz, =C−), 128.9 ($^2J_{C-Se}$ = 16.0 Hz, =CH–), 85.7 ($^1J_{C-Se}$ = 110.0 Hz, −C−), 75.9 ($^2J_{C-Se}$ = 29.5 Hz, −CH−), 73.2 (−CH−), 65.9 (−CH−), 22.4 (−CH_3), 18.9 (−CH_3).

MS (CI/CH_4): *m/z* (%) = 364 (9) [M^+], 307 (100), 271 (23), 253 (29).

HRMS: *m/z* [M^+] calcd for $C_8H_{12}O_2{}^{35}Cl_2{}^{37}Cl_2{}^{80}Se$: 363.8698; found: 363.8716.

Second stereoisomer: yellow liquid.

IR (neat): 1067, 1123, 1261, 1374, 1450, 1586, 2982, 3384 cm^{-1}.

^{1}H NMR (700 MHz, $CDCl_3$): δ = 6.90 (d, *J* = 0.9 Hz, 1 H), 6.32 (s, 1 H), 5.01 (qd, *J* = 6.3, 0.9 Hz, 1 H), 4.49 (q, *J* = 6.3 Hz, 1 H), 2.84 (br s, 2 H), 1.57 (d, *J* = 6.3 Hz, 3 H), 1.36 (d, *J* = 6.3 Hz, 3 H).

^{13}C NMR (176 MHz, $CDCl_3$): δ = 136.9 ($^1J_{C-Se}$ = 123.5 Hz, = C−), 129.2 ($^2J_{C-Se}$ = 19.0 Hz, =CH–), 83.5 ($^1J_{C-Se}$ = 110.0 Hz, −C−), 77.6 (−CH−), 73.6 ($^2J_{C-Se}$ = 13.5 Hz, −CH−), 66.6 ($^2J_{C-Se}$ = 25.5 Hz, −CH−), 22.1 (−CH_3), 20.2 (−CH_3).

MS (CI/CH_4): *m/z* (%) = 366 (8) [M – 2H]$^+$, 307 (100), 271 (20), 252 (34).

HRMS: *m/z* [M – 2H]$^+$ calcd for $C_8H_{10}O_2{}^{37}Cl_4{}^{80}Se$: 365.8482; found: 365.8489.

Third stereoisomer: from the mixture of the third and fourth stereoisomers (yellow liquid).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.13 (d, *J* = 1.2 Hz, 1 H), 6.20 (s, 1 H), 5.12 (qd, *J* = 6.3, 1.2 Hz, 1 H), 4.29 (q, *J* = 6.3 Hz, 1 H), 3.63 (br s, 2 H), 1.63 (d, *J* = 6.3 Hz, 3 H), 1.34 (d, *J* = 6.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.1 ($^1J_{C-Se}$ = 127.5 Hz, =C−), 130.1 ($^2J_{C-Se}$ = 16.0 Hz, =CH–), 83.9 (−C−), 77.5 (−CH−), 73.1 (−CH−), 66.4 (−CH−), 22.8 (−CH_3), 20.4 (−CH_3).

Fourth stereoisomer: from the mixture of the third and fourth stereoisomers (yellow liquid).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.90 (d, *J* = 1.2 Hz, 1 H), 6.15 (s, 1 H), 5.04 (qd, *J* = 6.6, 1.2 Hz, 1 H), 4.49 (q, *J* = 6.0 Hz, 1 H), 3.63 (br s, 2 H), 1.46 (d, *J* = 6.0 Hz, 3 H), 1.36 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.0 (=C–), 129.5 ($^2J_{C-Se}$ = 21.5 Hz, =CH–), 84.0 (−C−), 77.7 (−CH−), 74.1 (−CH−), 66.4 (−CH−), 22.0 (−CH_3), 19.1 (−CH_3).

Mixture of the third and fourth stereoisomers

IR (neat): 1065, 1126, 1374, 1451, 1581, 2981, 3284 cm^{-1}.

MS (CI/CH_4): *m/z* (%) = 358 (10%) [M^+], 307 (100), 271 (24), 253 (7).

HRMS: *m/z* [M^+] calcd for $C_8H_{12}O_2{}^{35}Cl_4{}^{78}Se$: 357.8764; found: 357.8766.

(2*Z*)-3-Chloro-2-{[1,2,2-trichloro-1-(hydroxymethyl)ethyl]selanyl}prop-2-en-1-ol (3c)

The product was isolated by chromatography [silica gel, hexanes–EtOAc (5:1)] as a light yellow liquid; yield: 51%.

IR (neat): 1075, 1230, 1364, 1455, 1593, 1704, 2933, 3338 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.96 (t, *J* = 1.5 Hz, 1 H), 6.36 (s, 1 H), AB system: 4.73 and 4.32 (dd, *J* = 13.8, 1.5 Hz, 1 H each), 4.52 (br s, 2 H), ABq: 3.98 and 3.86 (d, *J* = 12.9 Hz, 1 H each).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.6 ($^1J_{C-Se}$ = 119.1 Hz, =C–), 129.9 ($^2J_{C-Se}$ = 17.5 Hz, =CH–), 82.6 ($^1J_{C-Se}$ = 105.2 Hz, −C−), 75.8 ($^2J_{C-Se}$ = 26.9 Hz, −C−,), 66.9 (−CH_2−), 61.8 (−CH_2−).

MS (CI/CH_4): *m/z* (%) = 332 (38) [M^+], 279 (100), 154 (94).

HRMS: *m/z* [M^+] calcd for $C_6H_8O_2{}^{35}Cl_2{}^{37}Cl_2{}^{76}Se$: 331.8411; found: 331.8408.

(3*E*)-3,4-Dichloro-2-methylbut-3-en-2-ol (5a)

The product was isolated by chromatography [silica gel, hexanes–EtOAc (5:1)] as a yellow liquid; yield: quant (^{1}H NMR), 35% (isolated).

IR (neat): 1140, 1177, 1367, 1461, 1612, 2985, 3399 cm^{-1}.

^{1}H NMR (700 MHz, $CDCl_3$): δ = 6.60 (s, 1 H), 2.78 (br s, 1 H), 1.48 (s, 6 H).

^{13}C NMR (176 MHz, $CDCl_3$): 143.1 (=C–Cl), 115.0 (=CH–), 74.3 (−C−), 28.6 (−CH_3).

MS (CI/CH_4): *m/z* (%) = 154 (5) [M^+], 139 (64) [M – OH]$^+$, 137 (100) [M – OH]$^+$.

HRMS: *m/z* [M^+] calcd for $C_5H_8O^{35}Cl_2$ 153.9952; found: 153.9913.

(3-Chloro-1-benzoselenophen-2-yl)methanol (12) and (2*E*)-2,3-Dichloro-3-phenylprop-2-en-1-ol (5e)

The products were isolated by chromatography [silica gel, hexanes–EtOAc (5:1 to 4:1 to 2:1)] as a 1:1 mixture; total isolated yield for **12**, **12a**, and **5e**: 51%.

From the mixture of **12** and **5a** (yellow liquid):

12

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.824–7.813 (m, 1 H^7), 7.821–7.807 (m, 1 H^4), 7.45–7.43 (m, 1 H^5), 7.33–7.31 (m, 1 H^6), 5.01 (s, 2 H), 3.32 (br s, 1 H).

^{13}C NMR (176 MHz, $CDCl_3$): 141.8 ($^1J_{C-Se}$ = 110.5 Hz, =C–CH_2OH), 138.6 (=C–C−Cl), 137.4 ($^1J_{C-Se}$ = 102.3 Hz, =C–Se−C−CH_2OH), 125.5 ($^2J_{C-Se}$ = 14.7 Hz, =CH^7−), 125.2 (=CH^6−), 124.9 (=CH^5−), 123.5 (=CH^4−), 117.4 (=C–Cl), 60.0 ($^2J_{C-Se}$ = 13.5 Hz, −CH_2−).

MS (CI/CH_4): *m/z* (%) = 244 (55) [M^+], 229 (100).

HRMS: *m/z* [M^+] calcd for $C_9H_7O^{35}Cl^{78}Se$: 243.9358; found: 243.9374.

5e

^{1}H NMR (700 MHz, $CDCl_3$): δ = 7.51–7.50 (m, 2 H), 7.41–7.37 (m, 3 H), 4.66 (s, 2 H), 3.32 (br s, 1 H).

^{13}C NMR (176 MHz, $CDCl_3$): 136.2 (=C– *ipso*), 129.9 (=C–Ph), 129.1 (=CH– *para*), 128.8 (=CH– *ortho*), 128.6 (=C–CH_2OH), 128.0 (=CH– *meta*), 63.5 (−CH_2−).

MS (CI/CH_4): *m/z* (%) = 204 (16) [M^+], 187 (42), 185 (50).

HRMS: *m/z* [M^+] calcd for $C_9H_8O^{35}Cl^{37}Cl$ 203.9923; found: 203.9903.

Mixture of **12** and **5e**

IR (neat): 1032, 1115, 1252, 1445, 1631, 3385 cm^{-1}.

3-Chloro-2-(chloromethyl)-1-benzoselenophene (12a)

Isolated by using the conditions described above as a yellow liquid.

IR (neat): 1020, 1110, 1252, 1303, 1433, 1690, 3057 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79–7.74 (m, 2 H), 7.42–7.37 (m, 1 H), 7.33–7.27 (m, 1 H), 4.88 (s, 2 H, $^3J_{Se-H}$ = 9.0 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): 138.2 ($^1J_{C-Se}$ = 102.8 Hz, =C–), 138.0 (=C–), 136.5 ($^1J_{C-Se}$ = 110.5 Hz, =C–), 126.4 (=CH–), 125.6 ($^2J_{C-Se}$ = 15.0 Hz, =CH–), 125.4 (=CH–), 124.5 (=CH–), 122.0 (=C–), 43.3 (−CH_2−).

MS (CI/CH_4): *m/z* (%) = 264 (35) [M^+], 229 (100) [M – Cl]$^+$.

HRMS: *m/z* [M^+] calcd for $C_9H_6{}^{35}Cl_2{}^{78}Se$: 261.9020; found: 261.9037.

(2*Z*)-3-Bromo-2-{[1,2,2-tribromo-1-(hydroxymethyl)ethyl]selanyl}prop-2-en-1-ol (13)
The product was isolated by chromatography [silica gel, hexanes–EtOAc (3:1)] as a yellow liquid; yield: 85% (isolated).

IR (neat): 1060, 1129, 1242, 1450, 1582, 2992, 3384 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.26 (t, *J* = 1.5 Hz, 1 H), 6.34 (s, 1 H), 5.00 (br s, 2 H), AB system: 4.67 and 4.34 (dd, *J* = 14.1, 1.5 Hz, 1 H each), ABq: 4.12 and 3.99 (d, *J* = 13.2 Hz, 1 H each).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 133.1 ($^1J_{C–Se}$ = 121.6 Hz, =C–), 118.7 ($^2J_{C–Se}$ = 16.0 Hz, =CH–), 76.4 ($^1J_{C–Se}$ = 109.5 Hz, −C−), 68.4 (−CH_2−), 64.1 (−CH_2−), 50.0 ($^2J_{C–Se}$ = 24.9 Hz, −CH−).

MS (CI/CH_4): *m/z* (%) = 512 (1) [M^+], 494 (1), 432 (1), 413 (4).

HRMS: *m/z* [M^+] calcd for $C_6H_8O_2{}^{79}Br_2{}^{81}Br_2{}^{80}Se$: 511.6382; found: 511.6409.

3-Bromo-2-(bromomethyl)-1-benzoselenophene (14) and (2*E*)-2,3-Dibromo-3-phenylprop-2-en-1-ol (15)
The products were obtained as a 1:1 mixture; total isolated yield for **14** and **15**: 60%. The products were separated and isolated chromatography [silica gel, hexane (100%) then hexanes–EtOAc (10:1 to 5:1)].

(2*E*)-2,3-Dibromo-3-phenylprop-2-en-1-ol (14)
White solid; mp 106.5 ± 0.5 °C.

IR (neat): 1090, 1205, 1245, 1293, 1433, 3028 cm^{-1}.

^1H NMR (700 MHz, $CDCl_3$): δ = 7.84 (dm, *J* = 8.4 Hz, 1 H), 7.81 (dm, *J* = 8.4 Hz, 1 H), 7.47–7.44 (m, 1 H), 7.37–7.35 (m, 1 H), 4.86 (s, 2 H, $^3J_{Se–H}$ = 10.5 Hz).

^{13}C NMR (176 MHz, $CDCl_3$): δ = 139.5 (=C–), 139.0 ($^1J_{C–Se}$ = 102.7 Hz, =C–), 137.8 ($^1J_{C–Se}$ = 110.0 Hz, =C–), 126.4 ($^3J_{C–Se}$ = 9.0 Hz, =CH–), 126.0 (=CH–), 125.6 (=CH–), 125.5 ($^2J_{C–Se}$ = 15.6 Hz, =CH–), 111.7 (=C–), 28.3 ($^2J_{C–Se}$ = 20.8 Hz, −CH_2−).

MS (CI/CH_4): *m/z* (%) = 354 (12) [M^+], 273 (100).

HRMS: *m/z* [M^+] calcd for $C_9H_6{}^{81}Br_2{}^{78}Se$: 353.7968; found: 353.7967.

(2*E*)-2,3-Dibromo-3-phenylprop-2-en-1-ol (15)
Yellow liquid.

IR (neat): 1031, 1085, 1201, 1245, 1443, 2930, 3357 cm^{-1}.

^1H NMR (700 MHz, $CDCl_3$): δ = 7.39–7.31 (m, 5 H), 4.84 (br d, *J* = 3.9 Hz, 2 H), 2.82 (br t, *J* = 3.9 Hz, 1 H).

^{13}C NMR (176 MHz, $CDCl_3$): 140.0 (=C–), 129.1 (=CH–), 128.9 [=CH– (×2)], 128.4 [=CH– (×2)], 122.2 (=C–), 118.5 (=C–), 67.7 (−CH_2−).

MS (CI/CH_4): *m/z* (%) = 292 (49) [M^+], 275 (100), 273 (68), 213 (68), 211 (73), 131 (42).

HRMS: *m/z* [M^+] calcd for $C_9H_8O^{79}Br^{81}Br$ 291.8921; found: 291.8923.

(3-Chloro-4-methylselenophen-2-yl)methanol (16), (3,5-Dichloro-4-methylselenophen-2-yl)methanol (17), and 2,4-Dichloro-5-(chloromethyl)-3-methylselenophene (18)
The products, obtained in a total isolated yield of 52%, were separated and isolated by chromatography [silica gel, hexanes–EtOAc (10:1)].

(3-Chloro-4-methylselenophen-2-yl)methanol (16)
Yellow liquid.

IR (neat): 1000, 1048, 1139, 1341, 1435, 2920, 3333 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.50 (q, *J* = 1.0 Hz, 1 H, $^2J_{Se–H}$ = 47.7 Hz), 4.82 (s, 2 H, $^3J_{Se–H}$ = 7.7 Hz), 2.39 (br s, 1 H), 2.16 (d, *J* = 1.0 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.0 ($^1J_{C–Se}$ = 114.0 Hz, =C–), 137.5 (=C–), 123.5 (=C–), 123.0 ($^1J_{C–Se}$ = 109.7 Hz, =CH–), 60.2 ($^2J_{C–Se}$ = 15.5 Hz, −CH_2−), 17.0 (−CH_3).

MS (CI/CH_4): *m/z* (%) = 210 (32) [M^+], 193 (100).

HRMS: *m/z* [M^+] calcd for $C_6H_7O^{35}Cl^{80}Se$: 209.9351; found: 209.9349.

(3,5-Dichloro-4-methylselenophen-2-yl)methanol (17)
White solid; mp 73 ± 1 °C.

IR (neat): 1047, 1315, 1343, 1475, 2920, 3263 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 4.81 (d, *J* = 6.0 Hz, 2 H, $^3J_{Se–H}$ = 7.3 Hz), 2.11 (s, 3 H), 2.08 (t, *J* = 6.0 Hz, 1 H).

^{13}C NMR (75 MHz, CDCl3): δ = 139.8 ($^1J_{C–Se}$ = 112.5 Hz, =C–), 134. 8 (=C–), 126.1 ($^1J_{C–Se}$ = 123.2 Hz, =C–), 121.7 (=C–,), 60.1 ($^2J_{C–Se}$ = 14.0 Hz, −CH_2−), 14.2 (−CH_3).

MS (CI/CH_4): *m/z* (%) = 242 (25) [M^+], 227 (100).

HRMS: *m/z* [M^+] calcd for $C_6H_6O^{35}Cl_2{}^{78}Se$: 241.8969; found: 241.8980.

2,4-Dichloro-5-(chloromethyl)-3-methylselenophene (18)
Yellow liquid

IR (neat): 1021, 1041, 1259, 1325, 1481, 1561, 2923 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 4.76 (s, 2 H, $^3J_{Se–H}$ = 9.3 Hz), 2.13 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 135.1 ($^1J_{C–Se}$ = 112.3 Hz, =C–), 134.8 (=C–), 128.1 ($^1J_{C–Se}$ = 123.9 Hz, =C–), 125.7 (=C–), 40.0 ($^2J_{C–Se}$ = 17.9 Hz, −CH_2−), 14.4 (−CH_3).

MS (EI^+):(%) = 264 (9) [M^+], 227 (100).

HRMS: *m/z* [M^+] calcd for $C_6H_5{}^{35}Cl^{37}Cl_2{}^{78}Se$: 263.8571; found: 263.8576.

Preparation of Divinyl Selenoxides from Divinylselenium Dichlorides: General Procedure
EtOAc (70 mL) was added to the reaction mixture containing the freshly prepared divinylselenium dichloride (1 mmol), and the mixture was washed with 10% aq $NaHCO_3$ (15 mL). The organic phase was dried ($MgSO_4$) and the solvent was removed under reduced pressure.

(2*Z*,2′*Z*)-2,2′-Seleninylbis(3-chloroprop-2-en-1-ol) (8c)
The product was isolated by chromatography [silica gel, hexanes–EtOAc (3:1 to 2:1) and EtOAc–MeOH (1:1)], followed by crystallization ($CHCl_3$) as a white solid; yield: 54% (isolated); mp 70 ± 1 °C.

IR (neat): 798 (Se=O), 1031, 1054, 1421, 1454, 1618, 2920, 3242 cm^{-1}.

^1H NMR (300 MHz, CD_3OD): δ = 6.95 (t, *J* = 1.5 Hz, 2 H), 4.83 (br s, 2 H), AB system: 4.69 and 4.46 (dd, *J* = 14.4, 1.5 Hz, 2 H each).

^{13}C NMR (75 MHz, CD_3OD): δ = 145.7 ($^1J_{C–Se}$ = 118.3 Hz, −C=), 126.2 ($^2J_{C–Se}$ = 19.0 Hz, =CH–), 57.7 (−CH_2).

MS MALDI [DCTB(AN)]: [M^+] 278.918 ([MH^+], 1517.40).

(2*Z*,2′*Z*)-2,2′-Seleninylbis(3-chloropent-2-en-1-ol) (8d)
The product was isolated by chromatography [silica gel, hexanes–EtOAc (2:1 to 1:1) then EtOAc–MeOH (3:1)], followed by crystallization (pentane–$CHCl_3$) as a white solid; yield: 67% (isolated); mp 87.5 ± 0.5 °C.

IR (neat): 817 (Se=O), 1014, 1133, 1458, 1622, 2979, 3280 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): AB system: 4.81 (dd, J = 13.5, 6.6 Hz, 2 H) and 4.67 (dd, J = 13.5, 6.3 Hz, 2 H), 4.55 (dd, J = 6.6, 6.3 Hz, 2 H), AB system: 2.70 and 2.58 (dq, J = 14.5, 7.2 Hz, 2 H each), 1.26 (t, J = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.9 ($^2J_{C–Se}$ = 20.4 Hz, −C=), 136.6 ($^1J_{C–Se}$ = 120.2 Hz, =C–), 58.7 ($-CH_2-$), 31.5 ($-CH_2-$), 12.2 ($-CH_3$).

MS (CI/CH_4): *m/z* (%) = 335 (7) $[M + H]^+$, 318 (35) $[M – O]^+$, 299 (32), 283 (39), 265 (59), 247 (32).

HRMS: *m/z* $[M^+]$ calcd for $C_{10}H_{17}O_3{}^{35}Cl_2{}^{80}Se$: 334.9720; found: 334.9715.

(2*Z*,2′*Z*)-2,2′-Seleninylbis(3-chloro-3-phenylprop-2-en-1-ol) (8e)

The product was isolated by chromatography [silica gel, hexanes–EtOAc (1:1) then EtOAc–MeOH (4:1)] as a white solid; yield: 44% (isolated); mp 151.5 ± 0.5 °C.

IR (neat): 812 (Se=O), 1091, 1181, 1243, 1358, 1444, 1620, 2927, 3361 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.41–7.36 (m, 2 H), 7.30–7.25 (m, 4 H), 7.11–7.09 (m, 4 H), 5.24 (br s, 2 H), ABq: 4.97 and 4.77 (d, J = 13.8 Hz, 2 H each).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 142.3 ($^2J_{C–Se}$ = 23.4 Hz, −C=), 139.7 ($^1J_{C–Se}$ = 123.9 Hz, =C–), 135.5 (=C–), 130.6 (=CH–), 128.9 [=CH– (×2)], 128.7 [=CH– (×2)], 58.9 ($-CH_2-$).

MS MALDI (DHB(AN)): $[M^+]$ 430.972 ($[MH^+]$ 1367.75).

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