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Regio- and Stereoselective One-Pot Synthesis of New Heterocyclic Compounds with Two Selenium Atoms Based on 2-Bromomethyl-1,3-thiaselenole Using Phase Transfer Catalysis

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Abstract: To date, not a single representative of 2,3-dihydro-1,4-thiaselenin-2-yl selenides has been described in the literature. The reaction of 2-bromomethyl-1,3-thiaselenole with potassium selenocyanate at low temperature was accompanied by a rearrangement with ring expansion leading to six-membered 2,3-dihydro-1,4-thiaselenin-2-yl selenocyanate, which was used for the generation of sodium dihydro-1,4-thiaselenin-2-yl selenolate. The latter intermediate was involved in situ in the nucleophilic substitution and addition reactions under phase transfer catalysis conditions. The nucleophilic substitution reactions with alkyl halides gave alkyl, allyl and propargyl 2,3-dihydro-1,4-thiaselenin-2-yl selenides in 93–98% yields. The addition reactions of dihydro-1,4-thiaselenin-2-yl selenolate anion to alkyl acrylates, acrylonitrile and alkyl propiolates proceeded in a regio- and stereoselective fashion affording corresponding functionalized 2,3-dihydro-1,4-thiaselenin-2-yl selenides in 93–98% yields. Thus, the regio- and stereoselective one-pot synthesis of a novel family of 2,3-dihydro-1,4-thiaselenin-2-yl selenides has been developed based 2-bromomethyl-1,3-thiaselenole, potassium selenocyanate, alkyl halides and compound with activated double and triple bonds.

Keywords: 2,3-dihydro-1,4-thiaselenin-2-yl selenides; nucleophilic addition; activated alkenes; phase transfer catalysis; alkyl propiolates

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1. Introduction

The development of synthetic approaches to novel classes of organoselenium compounds continues to be a very active area of research driven by their promising biological properties. In fact, a diverse variety of organoselenium compounds and especially selenium-containing heterocycles are well-known for their antitumor, antibacterial, antiviral, antifungal, anti-inflammatory, anti-HIV, antioxidant and glutathione peroxidase-like activities [1–19].

Perhaps the most famous selenium-containing heterocyclic compound is ebselen, a novel anti-inflammatory drug, which also exhibit neuroprotective and glutathione peroxidase-like properties [6–8]. These valuable properties combined with low toxicity of ebselen have led to therapeutic application of this compound, which has undergone evaluation in clinical trials. This compound has been also used for the treatment and prevention of cardiovascular diseases and ischemic stroke [6–8]. It has been recently shown that ebselen inhibits CoV2 activity and viral replication [7].

The application of organoselenium compounds as electron donors for the preparation of organic metals, superconductors, semiconductors, ferromagnets and organic Dirac materials is another area of current interest [20–29]. Examples of six-membered selenium heterocycles of practical importance **1–7** are shown in Figure 1 [13–19].

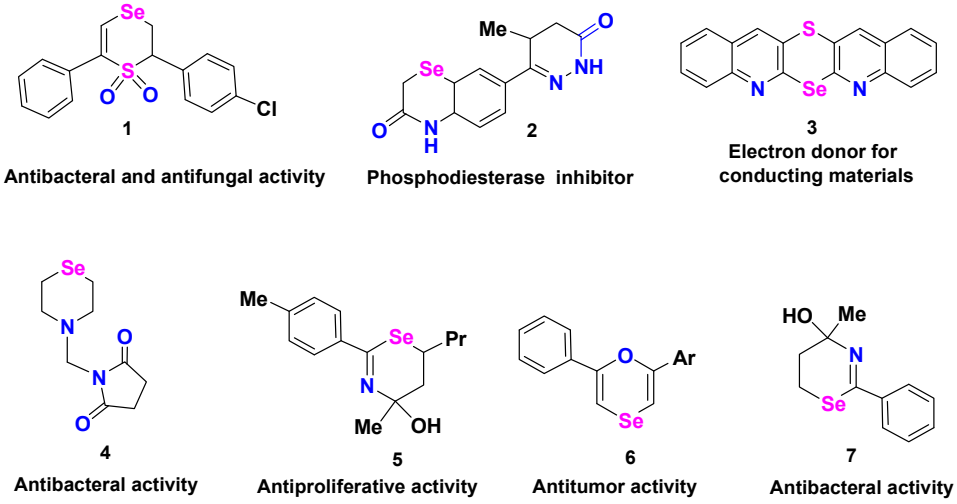


Figure 1. Examples of six-membered selenium heterocycles of practical importance: 2-(4-chlorophenyl)-6-phenyl-2,3-dihydro-1,4-oxaselenine-1,4-dione (**1**), 7-(4-methyl-6-oxo-1,4,5,6-tetrahydro-3-pyridazinyl)-2*H*-1,4-benzoselenazin-3(4*H*)-one (**2**), quino[2′,3′:5,6][1,4]thiaselenino[3,2-*b*]quinoline (**3**), 1-(1,4-selenazinan-4-ymethyl)-dihydro-1*H*-pyrrole-2,5-dione (**4**), 4-methyl-2-(4-methylphenyl)-6-propyl-5,6-dihydro-4*H*-1,3-selenazin-4-ol (**5**), 2-aryl-6-phenyl-1,4-oxaselenines (**6**), and 4-methyl-2-phenyl-5,6-dihydro-4*H*-1,3-selenazin-4-ol (**7**) [13–19].

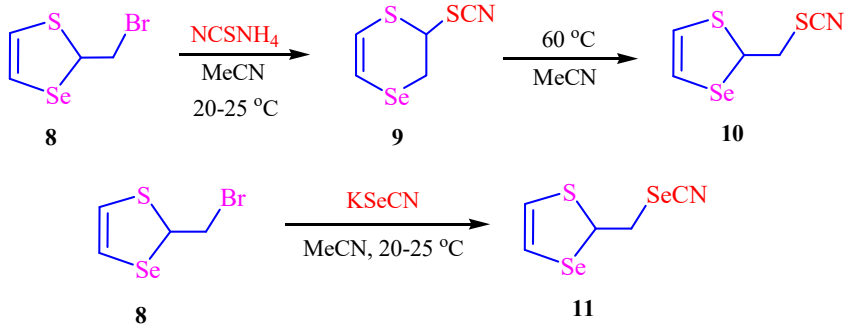
The synthetic organoselenium chemistry has been changed over the last two decades resulting in the development of easily accessible and efficient reagents, thus enabling the easy access to various classes of novel organoselenium compounds [30–54]. Novel electrophilic reagents, selenium dihalides, have been involved in the synthesis of organoselenium compounds. The application of selenium dihalides has opened up new possibilities for the development of synthetic approaches to novel classes of organoselenium compounds. Efficient approaches to selenium-containing heterocycles based on cyclization, annulation, annulation–functionalization, and selenocyclofunctionalization reactions have been developed [30–46].

2-Bromomethyl-1,3-thiaselenole (**8**) is a new unsaturated sulfur/selenium-containing heterocycle, a unique reagent with unexpected behavior in nucleophilic substitution reactions due to high anchimeric assistance effect of the selenium atom [54]. Thiaselenole **8** was obtained based on the reaction of selenium dibromide with divinyl sulfide [50].

We assume that thiaselenole **8** occurs in equilibrium with corresponding seleniranium cation, which considerably determines its chemical behavior in nucleophilic substitution reactions. Efficient regio- and stereoselective approaches to novel heterocyclic organochalcogen compounds by reactions of thiaselenole **8** with a variety of nucleophilic reagents have been developed [47–53].

The reaction of thiaselenole **8** with ammonium thiocyanate (acetonitrile, room temperature, 3 h) was accompanied by a rearrangement with ring expansion affording 2,3-dihydro-1,4-thiaselenin-2-yl thiocyanate (**9**) in 95% yield (Scheme 1) [55]. However, when the reaction was carried out at 60 °C for 25 h, five-membered 1,3-thiaselenol-2-ylmethyl thiocyanate (**10**) was obtained in 40% yield as a result of rearrangement of six-membered thiocyanate **9** [55]. The compound **10** was believed to be a more stable thermodynamic product, while six-membered thiocyanate **9** was considered a kinetic product.

The reaction of thiaselenole **8** with potassium selenocyanate in acetonitrile at room temperature for five minutes afforded 1,3-thiaselenol-2-ylmethyl selenocyanate (**11**) in 97% yield (Scheme 1) [56].

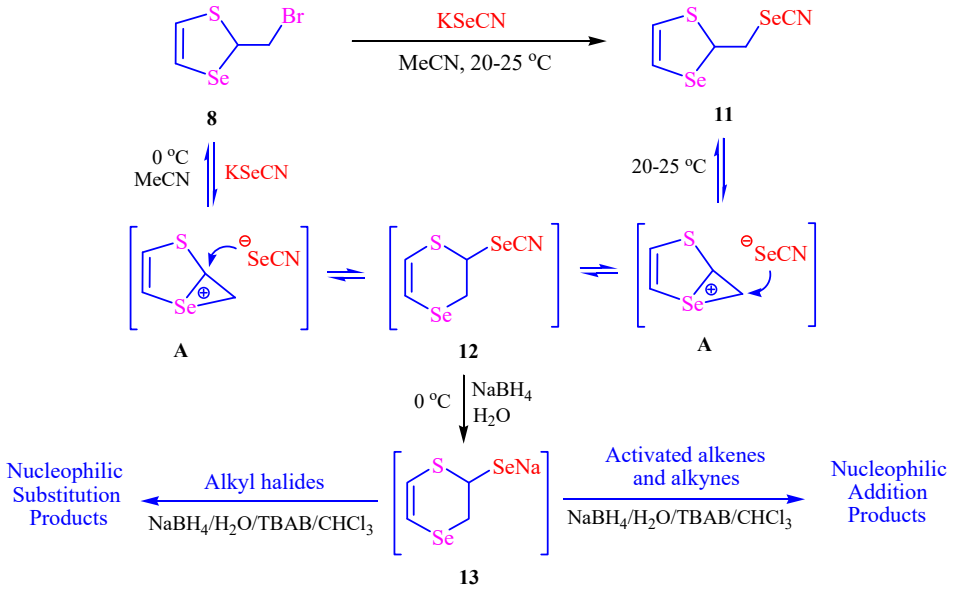


Scheme 1. The reactions of 2-bromomethyl-1,3-thiaselenole with thiocyanate and selenocyanate nucleophiles.

2. Results and Discussion

The aim of this research is the development of a regio- and stereoselective one-pot synthesis of a novel family of 2,3-dihydro-1,4-thiaselenin-2-yl selenides, containing various functions including carboxyl and vinyl groups. In fact, dihydro-1,4-thiaselenines are a very rare class of compounds. Only two representatives of dihydro-1,4-thiaselenines have been described in the literature prior to our research [57]. It is worth noting that a dihydro-1,4-thiaselenine derivative (2-(4-chlorophenyl)-6-phenyl-2,3-dihydro-1*H*-1,4-thiaselenine-1,1-dione, Figure 1) exhibits antibacterial and antifungal activities [19]. To date, not a single representative of 2,3-dihydro-1,4-thiaselenin-2-yl selenides has been described in the literature.

We assumed that the reaction of thiaselenole **8** with potassium selenocyanate initially led to the kinetic product, an intermediate six-membered selenocyanate, similarly to the reaction of thiaselenole **8** with ammonium thiocyanate (Scheme 1). Indeed, when the reaction thiaselenole **8** with potassium selenocyanate was monitored by NMR at low temperature (0 °C), the formation of intermediate 2,3-dihydro-1,4-thiaselenin-2-yl selenocyanate (**12**) was observed followed by its rearrangement to five-membered selenocyanate (**11**) (Scheme 2).



Scheme 2. The generation of sodium 2,3-dihydro-1,4-thiaselenin-2-yl selenolate **13** from intermediate 2,3-dihydro-1,4-thiaselenin-2-yl selenocyanate **12** at low temperature (0 °C).

Thus, like the formation of 1,3-thiaselenol-2-ylmethyl thiocyanate **10** by rearrangement of 2,3-dihydro-1,4-thiaselenin-2-yl thiocyanate **9** (Scheme 1), the reaction of thiaselenole **8** with potassium selenocyanate initially led to the six-membered thiaselenine **12** (the kinetic

product), which underwent a rearrangement to a five-membered selenocyanate **11** (the thermodynamic product). These rearrangements occur by nucleophilic attack of the selenocyanate anion at two different carbon atoms of the seleniranium intermediate **A** (Scheme 2).

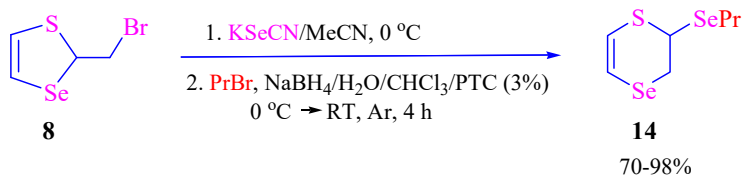
The reaction of thiaselenole **8** with potassium selenocyanate proceeded smoothly in acetonitrile at low temperature (0 °C) affording selenocyanate **12**. Reduction of organic selenocyanates to corresponding sodium organylselenolate by the action of sodium borohydride can be carried out in alcohol or in aqueous solutions since sodium borohydride is soluble in these media but exhibits negligible solubility in most common organic solvents. However, the use of alcohols (methanol, ethanol) as solvents for this reaction led to the formation of by-products as a result of nucleophilic substitution of bromine by methoxy or ethoxy groups. Previously we reported that the bromine atom in thiaselenole **8** can be easily substituted by the alkoxy group [58].

We succeeded in trapping intermediate dihydro-1,4-thiaselenin-2-yl selenocyanate **12** at low temperature (0 °C) and its conversion to sodium dihydro-1,4-thiaselenin-2-yl selenolate **13** by the action of sodium borohydride in an aqueous solution (Scheme 2). The intermediate selenolate **13** was involved in nucleophilic substitution reactions as well as in addition reactions to double and triple bonds affording corresponding dihydro-1,4-thiaselenin-2-yl selenides in high yields.

The intermediate sodium dihydro-1,4-thiaselenin-2-ylselenolate **13** was able to oxidize by air. However, we found that this undesirable transformation can be prevented by carrying out the reaction under an argon atmosphere and using an excess of sodium borohydride compared to stoichiometric amounts.

The relative efficiency of a number of catalysts: tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB), triethylbenzylammonium chloride (TEBAC), triethylbenzylammonium bromide (TEBAB) and Aliquat 336 TG was evaluated in the reaction of sodium dihydro-1,4-thiaselenin-2-ylselenolate **13** with propyl bromide under the same conditions (equimolar amounts of potassium selenocyanate and thiaselenole **8** (1.5 mmol), propyl bromide (1.7 mmol), the catalyst (3% mol), sodium borohydride/water/chloroform, 4 h, room temperature, under an argon atmosphere).

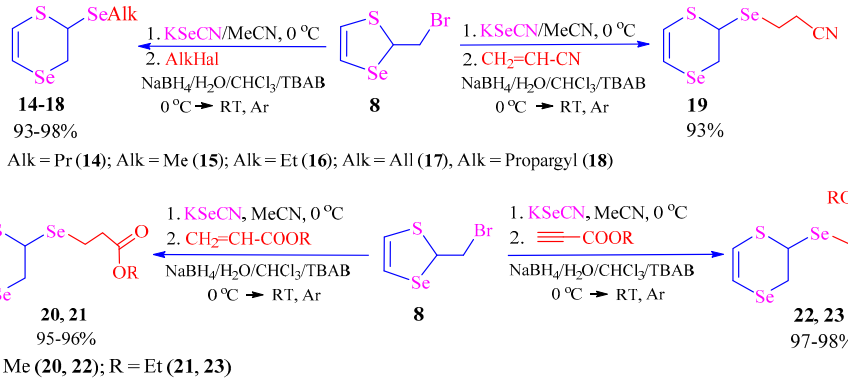
Based on the obtained product yields, it was concluded that TBAB showed the best result (the 98% yield of the product **14**, Scheme 3). The product **14** was obtained in 88–90% yield using TBAC and Aliquat 336 TG as catalysts. TEBAC and TEBAB were found to be less effective (74% and 70% yields of the product **14**, Scheme 3). Only 5% yield of the product **14** was obtained in the control experiment without the phase transfer catalyst under the same conditions.



Scheme 3. The synthesis of dihydro-1,4-thiaselenin-2-yl propyl selenide **14** from thiaselenole **8** under phase transfer catalysis conditions.

Since TBAB proved to be the best catalyst for the reaction of sodium dihydro-1,4-thiaselenin-2-ylselenolate **6,** subsequent experiments were carried out using TBAB. Along with propyl bromide, alkyl halides such as methyl iodide and ethyl bromides were involved in the reaction under the same conditions affording methyl and ethyl 2,3-dihydro-1,4-thiaselenin-2-yl selenides **15** and **16** in 93% and 96% yields, respectively (Table 1).

Table 1. The synthesis of the products **14–23** based on thiaselenole **1**, potassium selenocyanate and electrophilic reagents under phase transfer catalysis conditions.



Runs	Starting Compound	Duration (h)	TBAB (mol%)	Product	Yield (%)
1	Propyl bromide	4	3	**14**	98%
2	Methyl iodide	4	3	**15**	93%
3	Ethyl bromide	4	3	**16**	96%
4	Allyl bromide	3	3	**17**	98%
5	Propargyl bromide	3	3	**18**	97%
6	Acrylonitrile	6	6	**19**	93%
7	Methyl acrylate	5	6	**20**	95%
8	Ethyl acrylate	5	6	**21**	96%
9	Methyl propiolate	4	6	**22**	98%
10	Ethyl propiolate	4	6	**23**	97%

The reaction was carried out as a one-pot procedure. Potassium selenocyanate was added to a cooled to 0 °C (an ice bath) solution of thiaselenole **8** in acetonitrile and the mixture was stirred for 1 h at ~0 °C followed by solvent removing under reduced pressure at ~0 °C to give selenocyanate **12** as a residue. A cooled to ~0 °C solution of alkyl halides in chloroform and TBAB as a catalyst (3% mol) were added to the residue followed by the dropwise addition of a cooled to ~0 °C aqueous solution of sodium borohydride in degassed water under an argon atmosphere. The mixture was stirred for 2.5 h at ~0 °C on the ice bath, then the ice bath was removed and the mixture was stirred for 30 min while warming to room temperature. The products **14–16** were obtained in 93–98% yields after extraction with methylene chloride followed by removing the solvent under reduced pressure. This methodology allowed obtaining the target products in high yields and with good purity.

In the case of highly reactive methyl iodide, the slightly reduced yield of the product **15** (93%) was attributed to the possibility of alkylation at the selenium atoms of compound **15** to form water-soluble selenonium salts of the $R_3Se^-Hal^+$ type, which remain in the aqueous phase.

The intermediate sodium dihydro-1,4-thiaselenin-2-ylselenolate **13**, as well as sodium borohydride, are soluble in water, but not in organic phase. We suppose that TBAB can catalyze not only the nucleophilic reaction of the intermediate sodium selenate **13**, but also the reduction of selenocyanate **12** with sodium borohydride.

Unsaturated halogen-containing reagents, allyl and propargyl bromides, were involved in the nucleophilic substitution reaction with sodium dihydro-1,4-thiaselenin-2-yl selenolate **13** generated in situ from selenocyanate **12** (Table 1). The reactions with allyl and propargyl bromides proceeded faster than with alkyl bromides. It was found that stirring the mixture for 90 min at ~0 °C and for 30 min after removing on the ice bath is sufficient to obtain allyl and propargyl selenides **17** and **18** in near quantitative yields (97–98%) (total duration of the experiment was 3 h, Table 1).

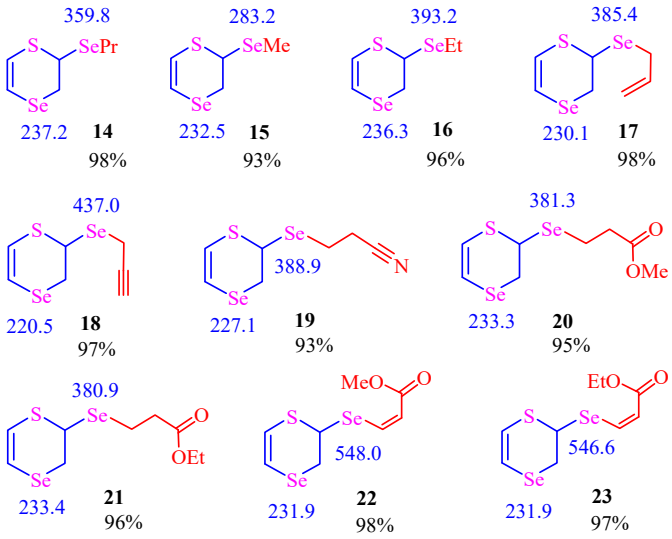
The nucleophilic addition of sodium thiaselenin-2-yl selenolate **13** to the activated double bond of alkyl acrylates and acrylonitrile was found to proceed slower compared to the nucleophilic substitution reaction with alkyl halides (Table 1). However, we found that doubling the amount of catalyst (from 3% mol to 6% mol) and increasing the duration of the reaction makes it possible to effectively carried out the nucleophilic addition reaction and to obtain 3-(1,2-dihydro-1,4-thiaselenin-2-ylselanyl)propanenitrile **19** and alkyl 3-(2,3-dihydro-1,4-thiaselenin-2-ylselanyl)-2-propanoates **20** and **21** in 93–96% yields (Table 1). It should be emphasized that the reactions with alkyl acrylates and acrylonitrile proceeded with high regioselectivity.

The regio- and stereoselective synthesis of alkyl (*Z*)-3-(2,3-dihydro-1,4-thiaselenin-2-ylselanyl)acrylates **22** and **23** in 97–98% yields was developed based on nucleophilic addition of selenolate **13** to alkyl propiolates (Table 1).

Selenium-centered anions are strong nucleophiles, which are superior to analogous sulfur-centered anions in nucleophilicity. It is known that reactions of selenium-centered nucleophiles with acetylenes often occurs stereoselectively as *anti*-addition to the triple bond giving vinyl selenides with (*Z*)-configuration [59,60]. The nucleophilic addition of sodium selenolate **13** to alkyl propiolates occurs in a regio- and stereoselective fashion affording products with (*Z*)-stereochemistry. The carbonyl group stabilizes the negative charge on the adjacent carbon atom in the intermediate derived from addition of sodium selenolate **13** to the activated triple bond of alkyl propiolates and determines the regioselectivity of the reaction.

The results obtained are summarized in Table 1. The reactions with allyl and propargyl bromides took less time and proceeded faster than with alkyl bromides (Table 1, runs 1–5). The addition reactions to acrylonitrile and alkyl acrylates required increasing the duration of the reaction and the content of the catalyst in comparison with the alkylation reactions in order to effectively carry out the process (Table 1, runs 1–8). The nucleophilic addition of sodium selenolate **13** to the activated triple bond of alkyl propiolates proceeded faster than to the activated double bond of alkyl acrylates (Table 1, runs 7–10). The reaction with alkyl propiolates took less time (4 h instead of 5 h) to obtain the products **22** and **23** in near quantitative yields.

The structural assignment of the synthesized compounds was made based on ^{1}H-, ^{13}C-, and ^{77}Se [61] NMR spectroscopy and mass spectrometry. The composition of the compounds was confirmed by elemental analysis. The obtained (2,3-dihydro-1,4-thiaselenin-2-yl) selenides **14–23** and the ^{77}Se-NMR data (ppm) are shown in Scheme 4.



Scheme 4. The obtained (1,2-dihydro-1,4-thiaselenin-2-yl) selenides **14–23** and the ^{77}Se-NMR data (colored in blue, ppm).

The selenium atom in the 2,3-dihydro-1,4-thiaselenine cycle of selenides **14–23** resonates in the region of 220.5–236.3 ppm. The same region was observed by us earlier in the ^{77}Se-NMR spectra of other 2,3-dihydro-1,4-thiaselenine derivatives including 2-(organylsulfanyl)-2,3-dihydro-1,4-thiaselenines [48,52]. It is worthy to note that the selenium atom in isomeric five-membered 2-substituted methyl-1,3-thiaselenole derivatives including compound **8** resonates in the downfield region of 513–528 ppm [51].

The signals of the selenium atom in the side chain are observed in a wider range of chemical shifts (359.8–548 ppm, Scheme 4), which depend on the nature of the adjacent functional group. The unshared electron pair of the selenium atom in the side chain is in conjugation with a double bond as well as with an electron-withdrawing carbonyl group in vinylic selenides **22** and **23**, and highest downfield shift of the selenium signals (546.6–548 ppm) are observed for compounds **22** and **23**.

In the ^{1}H-NMR spectra of vinyl selenides **22** and **23**, two doublets of olefinic protons of the SeCH=CHCOOAlk group are observed with a spin-spin coupling constant $^{3}J_{H,H}$ = 9.5 Hz, the value of which indicates (*Z*)-configuration of these compounds.

Molecular ions were detected in the mass spectra of synthesized compounds.

3. Materials and Methods

3.1. General Information

The ^{1}H (400.1 MHz), ^{13}C (100.6 MHz), and ^{77}Se (76.3 MHz) NMR spectra (the spectra can be found in Supplementary Materials) were recorded on a Bruker DPX-400 spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany) in $CDCl_3$ solutions and referred to the residual solvent peaks ($CDCl_3$, δ = 7.27 and 77.0 ppm for ^{1}H- and ^{13}C-NMR, respectively), and dimethyl selenide (^{77}Se-NMR).

Mass spectra were recorded on a Shimadzu GCMS-QP5050A (Shimadzu Corporation, Kyoto, Japan) with electron impact (EI) ionization (70 eV). Elemental analysis was performed on a Thermo Scientific Flash 2000 Elemental Analyzer (Thermo Fisher Scientific Inc., Milan, Italy). The distilled organic solvents and degassed water were used in syntheses.

3.2. Modified Procedure for the Preparation of Starting 2-Bromomethyl-1,3-thiaselenole

2-Bromomethyl-1,3-thiaselenole (**8**). A solution of bromine (1.6 g, 10 mmol) in carbon tetrachloride (5 mL) was added dropwise to a mixture of powdered selenium (0.79 g, 10 mmol) in carbon tetrachloride (5 mL) and the mixture was stirred until the solid dissolved. The obtained solution of selenium dibromide in carbon tetrachloride and a solution of divinyl sulfide (0.86 g, 10 mmol) in carbon tetrachloride (10 mL) were simultaneously added dropwise over 1 h to a flask containing carbon tetrachloride (10 mL) so that the molar ratio of both reagents in the mixture was approximately 1:1. The reaction mixture was stirred for 4 h and a solution of pyridine (0.95 g, 12 mmol) in carbon tetrachloride (10 mL) was added over 15 min, and the mixture was stirred overnight. The reaction mixture was filtered, and most of the solvent was removed by rotary evaporation. The residue (approximately 10 mL) was filtered and the solvent and the remaining pyridine were removed from the filtrate in vacuo to give pure thiaselenole **8** (1.95 g, 80% yield) as a brown oil.

3.3. Synthesis of Selenocyanates **11** *and* **12**

1,3-Thiaselenol-2-ylmethyl selenocyanate (**11**). Powdered selenium (158 mg, 2 mmol) was added to a solution of KCN (130 mg, 2 mmol) in MeOH (10 mL). The mixture was stirred at room temperature until the solid disappeared (usually ~0.5 h). The solvent was removed by rotary evaporator and a solution of thiaselenole **8** (488 mg, 2.00 mmol) in MeCN (10 mL) was added to the residue and the mixture was stirred at room temperature for 1 h and filtered. The solvent was removed in vacuum giving product **11** as a light yellow oil. Yield: 533 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 6.67 (d, $^{3}J_{H,H}$ = 6.3 Hz, $^{2}J_{Se,H}$ = 48.5 Hz, 1H, SeC<u>H</u>=CHS), 6.43 (d, $^{3}J_{H,H}$ = 6.3 Hz, 2H, SCHSe), 5.08 (dd, $^{3}J_{H,H}$ = 7.1 Hz, $^{3}J_{H,H}$ = 8.2Hz,

$^{2}J_{Se,H}$ = 20.0 Hz, 1H, SCHSe), 3.48 (dd, $^{3}J_{H,H}$ = 7.1 Hz, $^{2}J_{H,H}$ = 12.2 Hz, 1H, C$\underline{H}_b$SeCN), 3.41 (dd, $^{2}J_{H,H}$ = 12.2 Hz, $^{3}J_{H,H}$ = 8.2 Hz, 1H, C$\underline{H}_a$SeCN).

^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 119.26 (SeCH=$\underline{C}$HS), 113.75 ($^{1}J_{Se,C}$ = 106 Hz, Se$\underline{C}$H=CHS), 101.07 (SeCN), 46.48 ($^{1}J_{Se,C}$ = 70 Hz, SCHSe), 37.97 ($^{1}J_{Se,C}$ = 52 Hz, $\underline{C}H_2$SeCN).

^{77}Se NMR (76.3 MHz, $CDCl_3$), δ (ppm): 539.6 (SCHSe), 228.4 (CH_2SeCN).

MS (EI): *m*/*z* (%) = 271 (50, M^+), 165 (39), 151 (100), 107 (23), 85 (93), 84 (86), 71 (64), 59 (66), 58 (87), 45 (71).

Anal. Calcd for $C_5H_5NSSe_2$: C 22.32; H 1.87; N 5.21; S 11.92: Se, 58.69. Found: C 21.98; H 1.69; N 4.94; S 12.27: Se, 59.01.

2,3-Dihydro-1,4-thiaselenin-2-yl selenocyanate (**12**). A cooled to 0 °C solution of potassium selenocyanate (72 mg, 0.50 mmol) in MeCN (0.25 mL) was added to a cooled to 0 °C solution of thiaselenole **8** (122 mg, 0.50 mmol) in MeCN (0.25 mL) with stirring. The mixture was stirred on the ice bath at ~0 °C for 0.5 h under an argon atmosphere and the solvent was removed in vacuum giving a light yellow oil, which was analyzed by ^{1}H- and ^{13}C-NMR. The mixture contained selenocyanate **12** and thiaselenole **8**. The following spectral characteristics of selenocyanate **12** were detected. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 6.53 (dd, $^{3}J_{H,H}$ = 9.9 Hz, 1H, SeC$\underline{H}$=CHS), 6.37 (d, $^{3}J_{H,H}$ = 9.9 Hz, 1H, SeCH=C$\underline{H}$S), 5.21 (dd, $^{3}J_{H,H}$ = 2.1 Hz, $^{3}J_{H,H}$ = 6.6 Hz, 1H, SCHSe), 3.79 (dd, $^{2}J_{H,H}$ = 12.4 Hz, $^{3}J_{H,H}$ = 2.1 Hz, 1H, =CHSeC$\underline{H}_a$), 3.33 (dd, $^{2}J_{H,H}$ = 12.4 Hz, $^{3}J_{H,H}$ = 6.6 Hz, 1H, =CHSeC$\underline{H}_b$).

^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 116.76 (SeCH=$\underline{C}$HS), 110.66 (Se$\underline{C}$H=CHS), 101.88 (SeCN), 43.07 (SCHSe), 26.07 (=$\underline{C}$HSeCH$_2$).

3.4. Synthesis of 2,3-Dihydro-1,4-thiaselenin-2-yl Alkyl Selenides

*General procedure for the synthesis of compounds **14–16.*** Potassium selenocyanate (216 mg, 1.5 mmol) was added to a cooled to 0 °C (an ice bath) solution of thiaselenole **8** (366 mg, 1.5 mmol) in MeCN (1 mL) with stirring. The mixture was stirred at ~0 °C for 1 h and the solvent was removed under reduced pressure at ~0 °C. A cooled to ~0 °C solution of alkyl halides (1.7 mmol) in chloroform (1 mL) and tetrabutylammonium bromide (15 mg, 3% mol) were added to the residue followed by the dropwise addition of a cooled to ~0 °C (an ice bath) solution of $NaBH_4$ (0.086 g, 2.26 mmol) in degassed water (0.8 mL) under an argon atmosphere. The mixture was stirred for 2.5 h at ~0 °C on the ice bath, then the ice bath was removed and the mixture was stirred for 30 min while warming to room temperature. Degassed water (3 mL) was added and the reaction mixture was extracted with methylene chloride (3 × 8 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed by a rotary evaporator. The residue was dried in vacuum giving products **14–16** in 93–98% yields.

2,3-Dihydro-1,4-thiaselenin-2-yl propyl selenide (**14**). Yield: 420 mg (98%), a light-yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ: 1.03 (3H, t, ^{3}J = 7.4 Hz, CH_3), 1.74–1.82 (2H, m, $CH_3C\underline{H}_2$), 2.78–2.86 (2H, m, SeC$\underline{H}_2CH_2CH_3$), 3.34 (1H, dd, ^{2}J = 11.7 Hz, ^{3}J = 10.3 Hz, CH_2Se in cycle), 3.49 (1H, dd, ^{2}J = 11.7 Hz, ^{3}J = 2.8 Hz, CH_2Se in cycle), 4.50 (1H, dd, ^{3}J = 10.3 Hz, ^{3}J = 2.8 Hz, SCHSe), 6.42 (1H, d, ^{3}J = 9.7 Hz, =CHS), 6.51 (1H, d, ^{3}J = 9.7 Hz, =CHSe).

^{13}C-NMR (100 MHz, $CDCl_3$): 14.39 (CH_3), 23.84 ($\underline{C}H_2CH_3$), 25.54 ($^{1}J_{SeC}$ = 62.1 Hz, $SeCH_2$ in cycle), 26.88 ($^{1}J_{SeC}$ = 62.6 Hz, Se$\underline{C}H_2CH_2CH_3$), 34.82 ($^{1}J_{SeC}$ = 78.1 Hz, SCHSe), 108.74 ($^{1}J_{SeC}$ = 115.8 Hz, =CHSe), 120.66 (=CHS).

^{77}Se NMR (100 MHz, $CDCl_3$): δ 237.2 (cycle), 359.8.

MS: *m*/*z* (%): 288 (11) $[M]^+$, 165 (54), 151 (26), 85 (100).

Anal. Calcd for $C_7H_{12}SSe_2$: C 29.38; H 4.23; S 11.21; Se 55.19%. Found: C 29.54; H 4.18; S 11.10; Se 54.83%.

2,3-Dihydro-1,4-thiaselenin-2-yl methyl selenide (**15**). Yield: 360 mg (93%), a light-yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ: 2.17 (3H, s, CH_3), 3.28 (1H, dd, ^{2}J = 12.0 Hz, ^{3}J = 10.3 Hz, CH_2Se), 3.47 (1H, dd, ^{2}J = 12.0 Hz, ^{3}J = 2.6 Hz, CH_2Se), 4.46 (1H, dd, ^{3}J = 10.3 Hz, ^{3}J = 2.6 Hz, SCHSe), 6.40 (1H, d, ^{3}J = 9.9 Hz, =CHS), 6.48 (1H, d, ^{3}J = 9.9 Hz, =CHSe).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 3.68 ($^{1}J_{SeC}$ = 64.6 Hz, $SeCH_3$), 25.02 ($^{1}J_{SeC}$ = 60.6 Hz, $SeCH_2$), 35.10 ($^{1}J_{SeC}$ = 76.6 Hz, SCHSe), 108.69 ($^{1}J_{SeC}$ = 115.5 Hz, =CHSe), 120.64 (=CHS).

^{77}Se NMR (100 MHz, $CDCl_3$): δ 232.5 (cycle), 283.2.

MS: *m*/*z* (%): 260 (29) $[M]^+$, 165 (3), 151 (100), 107 (9), 107(12), 85 (45).

Anal. Calcd for $C_5H_8SSe_2$: C 23.27; H 3.12; S 12.42; Se 61.18%. Found: C 22.92; H 3.18; S 12.67; Se 60.89%.

2,3-Dihydro-1,4-thiaselenin-2-yl ethyl selenide (**16**). Yield: 392 mg (96%), a light-yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ: 1.50 (3H, t, ^3J = 7.4 Hz, $C\underline{H}_3CH_2$), 2.83 (2H, m, $SeC\underline{H}_2CH_3$), 3.32 (1H, dd, ^2J = 11.6 Hz, ^3J = 10.2 Hz, CH_2Se in cycle), 3.44 (1H, dd, ^2J = 11.6 Hz, ^3J = 2.8 Hz, CH_2Se in cycle), 4.45 (1H, dd, ^3J = 10.2 Hz, ^3J = 2.8 Hz, SCHSe), 6.36 (1H, d, ^3J = 9.8 Hz, =CHS), 6.42 (1H, d, ^3J = 9.8 Hz, =CHSe).

^{13}C-NMR (100 MHz, $CDCl_3$): 15.87 (CH_3), 18.33 ($^1J_{SeC}$ = 61.5 Hz, $Se\underline{C}H_2CH_3$), 25.58 ($^1J_{SeC}$ = 62.2 Hz, $SeCH_2$ in cycle), 34.70 ($^1J_{SeC}$ = 78.2 Hz, SCHSe), 108.84 ($^1J_{SeC}$ = 115.7 Hz, =CHSe), 120.64 (=CHS).

^{77}Se NMR (100 MHz, $CDCl_3$): δ 236.3 (cycle), 393.2.

MS: *m*/*z* (%): 272 (41) $[M]^+$, 165 (100), 151 (38), 108 (21), 85 (97).

Anal. Calcd for $C_6H_{10}SSe_2$: C 26.48; H 3.70; S 11.78; Se 58.03%. Found: C 26.92; H 3.55; S 12.01; Se 57.70%.

3.5. Synthesis of 2,3-Dihydro-1,4-thiaselenin-2-yl Allyl and 2-Propynyl Selenides **17** *and* **18**

*General procedure for synthesis of compounds **17** and **18**.* Potassium selenocyanate (260 mg, 1.8 mmol) was added to a cooled to 0 °C (an ice bath) solution of thiaselenole **8** (440 mg, 1.8 mmol) in MeCN (1.2 mL) with stirring. The mixture was stirred at ~0 °C for 1 h and the solvent was removed under reduced pressure at ~0 °C. A cooled to ~0 °C solution of allyl or 2-propynyl halides (2 mmol) in chloroform (1.5 mL) and tetrabutylammonium bromide (18 mg, 3% mol) were added to the residue followed by the dropwise addition of a cooled to ~0 °C (an ice bath) solution of $NaBH_4$ (0.104 g, 2.7 mmol) in degassed water (1 mL) under an argon atmosphere. The mixture was stirred for 90 min at ~0 °C on the ice bath, then the ice bath was removed and the mixture was stirred for 30 min while warming to room temperature. Degassed water (3 mL) was added and the reaction mixture was extracted with methylene chloride (3 × 10 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed by a rotary evaporator. The residue was dried in vacuum giving the products **17** and **18**.

Allyl 2,3-dihydro-1,4-thiaselenin-2-yl selenide (**17**). Yield: 500 mg (98%), a light-yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.22 (1H, dd, ^2J = 12.0 Hz, ^3J = 10.0 Hz, CH_2Se in cycle), 3.32 (1H, dd, ^2J = 13.6 Hz, ^3J = 8.1 Hz, CH_2Se), 3.42 (1H, dd, ^2J = 13.6 Hz, ^3J = 6.1 Hz, CH_2Se), 3.47 (1H, dd, ^2J = 12.0 Hz, ^3J = 2.6 Hz, CH_2Se in cycle), 4.33 (1H, dd, ^3J = 10.0 Hz, ^3J = 2.6 Hz, SCHSe), 5.16 (1H, dd, $^3J_{cis}$ = 10.2 Hz, ^4J = 1.3 Hz, $=CH_2$), 5.20 (1H, dd, $^3J_{trans}$ = 17.3 Hz, ^4J = 1.3 Hz, $=CH_2$), 5.84 (1H, m, $C\underline{H}=CH_2$), 6.41 (1H, d, ^3J = 9.8 Hz, =CHS), 6.51 (1H, d, ^3J = 9.8 Hz, =CHSe).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 25.56 ($^1J_{SeC}$ = 61.1 Hz, $SeCH_2$ in cycle), 27.19 ($^1J_{SeC}$ = 63.0 Hz, $SeCH_2$), 35.00 ($^1J_{SeC}$ = 76.1 Hz, SCHSe), 109.29 ($^1J_{SeC}$ = 116.2 Hz, =CHSe), 116.99 ($=CH_2$), 120.07 (=CHS), 134.41 (=CH).

^{77}Se NMR (100 MHz, $CDCl_3$): δ 230.1 (cycle), 385.4.

MS: *m*/*z* (%): 284 (12) $[M]^+$, 245(8) 165 (60), 151 (20), 119 (28), 85 (100).

Anal. Calcd for $C_7H_{10}SSe_2$: C 29.59; H 3.55; S 11.29; Se 55.58%. Found: C 22.92; H 3.18; S 12.67; Se 61.02%.

2,3-Dihydro-1,4-thiaselenin-2-yl 2-propynyl selenide (**18**). Yield: 493 mg (97%), a light-yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.31 (1H, t, ^3J = 2.6 Hz, ≡CH), 3.25 (1H, dd, ^2J = 11.7 Hz, ^3J = 9.2 Hz, CH_2Se in cycle), 3.43 (1H, dd, ^2J = 15.7 Hz, ^4J = 2.6 Hz, CH_2Se), 3.60 (1H, dd, ^2J = 11.7 Hz, ^3J = 2.2 Hz, CH_2Se in cycle), 3.64 (1H, dd, ^2J = 15.7 Hz, ^4J = 2.6 Hz, CH_2Se), 4.67 (1H, dd, ^3J = 9.2 Hz, ^3J = 2.1 Hz, SCHSe), 6.43 (1H, d, ^3J = 9.8 Hz, =CHS), 6.55 (1H, d, ^3J = 9.8 Hz, =CHSe).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 8.25 ($^1J_{SeC}$ = 62.3 Hz, $\underline{C}H_2C\equiv$), 25.58 ($^1J_{SeC}$ = 63.4 Hz, $SeCH_2$ in cycle), 36.23 ($^1J_{SeC}$ = 77.2 Hz, SCHSe), 72.03 (-C≡), 80.48 (≡CH), 109.67 ($^1J_{SeC}$ = 116.2 Hz, =CHSe), 119.44 (=CHS).

^{77}Se NMR (100 MHz, $CDCl_3$): δ 220.5 (cycle), 437.0.

MS: *m*/*z* (%): 284 (18) $[M]^+$, 218 (4), 165 (100), 151 (18), 85 (100).

Anal. Calcd for $C_7H_8SSe_2$: C 29.80; H 2.86; S 11.37; Se 55.98%. Found: C 29.90; H 3.05; S 11.11; Se 56.40%.

3.6. Synthesis of the Products **19**–**21**

General procedure for synthesis of the products **19**–**21**. Potassium selenocyanate (144 mg, 1 mmol) was added to a cooled to 0 °C (an ice bath) solution of thiaselenole **8** (244 mg, 1 mmol) in MeCN (0.7 mL) with stirring. The mixture was stirred at ~0 °C for 1 h and the solvent was removed under reduced pressure at ~0 °C. A cooled to ~0 °C solution of alkyl acrylates or acrylonitrile (1.2 mmol) in chloroform (0.5 mL) and tetrabutylammonium bromide (19 mg, 6% mol) were added to the residue followed by the dropwise addition of a cooled to ~0 °C (an ice bath) solution of $NaBH_4$ (0.057 g, 1.5 mmol) in degassed water (0.5 mL). The mixture was stirred for 3.5 h at ~0 °C on the ice bath, then the ice bath was removed and the mixture was stirred for 30 min while warming to room temperature. Degassed water (2 mL) was added and the reaction mixture was extracted with methylene chloride (3 × 8 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed by a rotary evaporator. The residue was dried in vacuum giving the products **19–21**.

3-(2,3-Dihydro-1,4-thiaselenin-2-ylselanyl)propanenitrile (**19**). Yield: 276 mg (93%), light-yellow oil. The total reaction time was 6 h.

^{1}H NMR (400 MHz, $CDCl_3$): 2.87 (2H, m, C$\underline{H}_2$CN), 2.98–3.12 (1H, m, $CH_2C\underline{H}_2$Se), 3.32 (1H, dd, ^2J = 12.0 Hz, ^3J = 9.3 Hz, CH_2Se in cycle), 3.59 (1H, dd, ^2J = 12.0 Hz, ^3J = 2.6 Hz, CH_2Se in cycle), 4.64 (1H, dd, ^3J = 9.3 Hz, ^3J = 2.6 Hz, SCHSe), 6.40 (1H, d, ^3J = 9.8 Hz, =CHS), 6.54 (1H, d, ^3J = 9.8 Hz, =CHSe).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 18.15 ($^1J_{SeC}$ = 66.6 Hz, $SeCH_2$ in cycle), 19.81 ($\underline{C}H_2CN$), 25.56 ($^1J_{SeC}$ = 63.2 Hz, CHSe$\underline{C}H_2CH_2$), 35.98 ($^1J_{SeC}$ = 77.1 Hz, SCHSe), 109.88 ($^1J_{SeC}$ = 116.2 Hz, =CHSe), 118.43 (CN), 119.31 (=CHS).

^{77}Se NMR (100 MHz, $CDCl_3$): δ 227.1 (cycle), 388.9.

MS: *m*/*z* (%): 299 (7) $[M]^+$, 165 (5), 151 (100), 107 (5), 85 (25).

Anal. Calcd for $C_7H_9NSSe_2$: C 28.29; H 3.05; N 4.71; S 10.79; Se 53.15. Found: C 28.07; H 2.93; N 4.58; S 10.56; Se 52.92.

Methyl 3-(2,3-dihydro-1,4-thiaselenin-2-ylselanyl)propanoate (**20**). Yield: 314 mg (95%), a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.77 (2H, t, ^3J = 7.2 Hz, C$\underline{H}_2$C=O), 2.97 (2H, t, ^3J = 6.9 Hz, CH_2Se), 3.29 (1H, dd, ^2J = 11.5 Hz, ^3J = 10.5 Hz, CH_2Se in cycle), 3.46 (1H, dd, ^2J = 11.5 Hz, ^3J = 2.8 Hz, CH_2Se in cycle), 3.66 (3H, s, CH_3), 4.50 (1H, dd, ^3J = 10.5 Hz, ^3J = 2.8 Hz, SCHSe), 6.35 (1H, d, ^3J = 9.7 Hz, =CHS), 6.43 (1H, d, ^3J = 9.7 Hz, =CHSe).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 18.29 ($^1J_{SeC}$ = 66.6 Hz, $SeCH_2$ in cycle), 25.47 ($^1J_{SeC}$ = 62.5 Hz, CHSe$\underline{C}H_2CH_2$), 35.48 ($\underline{C}H_2C$=O), 35.49 ($^1J_{SeC}$ = 77.4 Hz, SCHSe), 51.69 (CH_3), 109.15 ($^1J_{SeC}$ = 116.0 Hz, =CHSe), 120.21 (=CHS), 172.12 ($CH_2\underline{C}$=O).

^{77}Se NMR (100 MHz, $CDCl_3$): δ 233.3 (in cycle), 381.3.

MS: *m*/*z* (%): 330 (25) $[M]^+$, 165 (100), 151 (23), 107 (14), 85 (97).

Anal. Calcd for $C_8H_{12}O_2SSe_2$: C 29.10; H 3.66; S 9.71, Se 47.83%. Found: C 29.22; H 3.38; S 9.67, Se 48.11%.

Ethyl 3-(2,3-dihydro-1,4-thiaselenin-2-ylselanyl)propanoate (**21**). Yield: 330 mg (96%), a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (3H, t, ^3J = 7.2 Hz, C$\underline{H}_3CH_2$), 2.82 (2H, t, ^3J = 7.2 Hz, C$\underline{H}_2$C=O), 3.04 (2H, m, CH_2Se), 3.36 (1H, dd, ^2J = 11.7 Hz, ^3J = 9.9 Hz, CH_2Se in cycle), 3.53 (1H, dd, ^2J = 11.7 Hz, ^3J = 2.5 Hz, CH_2Se in cycle), 4.19 (2H, q, ^2J = 7.2 Hz, $C\underline{H}_2CH_3$), 4.57 (1H, д.д, ^3J = 9.9 Hz, SCHSe), 6.42 (1H, d, ^3J = 9.7 Hz, =CHS), 6.49 (1H, d, ^3J = 9.7 Hz, =CHSe).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 14.18 (CH_3), 18.51 ($^1J_{SeC}$ = 66.0 Hz, CHSe$\underline{C}H_2CH_2$), 25.59 ($^1J_{SeC}$ = 62.9 Hz, $SeCH_2$), 35.61 ($\underline{C}H_2C$=O), 35.86 (SCHSe), 60.79 (O$\underline{C}H_2CH_3$), 109.22 ($^1J_{SeC}$ = 115.5 Hz, =CHSe), 120.42 (=CHS), 171.87 ($CH_2\underline{C}$=O).

^{77}Se NMR (100 MHz, $CDCl_3$): δ 233.4 (in cycle), 380.9.

MS: *m*/*z* (%): 346 (24) $[M]^+$, 165 (100), 151 (50), 125 (1), 85 (76).

Anal. Calcd for $C_9H_{14}O_2SSe_2$: C 31.41; H 4.10; S 9.32, Se 45.88%. Found: C 31.33; H 4.08; S 9.25, Se 46.12%.

3.7. Synthesis of Alkyl (Z)-3-(2,3-Dihydro-1,4-thiaselenin-2-ylselanyl)acrylates

*General procedure for the synthesis of the products **22** and **23**.* Potassium selenocyanate (173 mg, 1.2 mmol) was added to a cooled to 0 °C (an ice bath) solution of thiaselenole **8** (293 mg, 1.2 mmol) in MeCN (1 mL) with stirring. The mixture was stirred at ~0 °C for 1 h and the solvent was removed under reduced pressure at ~0 °C. A cooled to ~0 °C solution of alkyl propiolates (1.5 mmol) in chloroform (1 mL) and tetrabutylammonium bromide (24 mg, 6% mol) were added to the residue followed by the dropwise addition of a cooled to ~0 °C (an ice bath) solution of $NaBH_4$ (0.07 g, 1.84 mmol) in degassed water (0.7 mL). The mixture was stirred for 2.5 h at ~0 °C on the ice bath, then the ice bath was removed and the mixture was stirred for 30 min while warming to room temperature. Degassed water (2 mL) was added and the reaction mixture was extracted with methylene chloride (3 × 10 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed by a rotary evaporator. The residue was dried in vacuum giving the products **22** and **23**.

Methyl (Z)-3-(2,3-dihydro-1,4-thiaselenin-2-ylselanyl)acrylate (**22**). Yield: 386 mg (98%), a light-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.32 (1H, dd, ^2J = 11.9 Hz, ^3J = 9.7 Hz, CH_2Se), 3.48 (1H, dd, ^2J = 11.9 Hz, ^3J = 2.6 Hz, CH_2Se), 3.71 (3H, s, CH_3), 4.48 (1H, dd, ^2J = 9.7 Hz, ^3J = 2.6 Hz, SCHSe), 6.35 (1H, d, ^3J = 9.5 Hz, SeCH=C<u>H</u>C=O), 6.37 (1H, d, ^3J = 9.8, =CHS), 6.46 (1H, d, ^3J = 9.8 Hz, =CHSe), 7.76 (1H, d, ^3J = 9.5 Hz, SeC<u>H</u>=CHC=O).

^{13}C NMR (100 MHz, $CDCl_3$): δ, ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.00 ($^1J_{SeC}$ = 62.1 Hz, $SeCH_2$), 37.67 ($^1J_{SeC}$ = 71.1 Hz, SCHSe), 51.63 (CH_3), 109.66 ($^1J_{SeC}$ = 116.8 Hz, =CHSe), 117.54 SeCH=<u>C</u>HC=O, 119.86 (=CHS), 144.18 ($^1J_{SeC}$ = 137.1 Hz, Se<u>C</u>H=CHC=O), 167.62 (CH_2<u>C</u>=O).

^{77}Se NMR (76 MHz, $CDCl_3$): δ 231.9 (in cycle), 548.0.

MS (EI), *m/z* (%): 330 (11) $[M]^+$, 251(6), 191(5), 165 (100), 151 (6), 85 (74).

Anal. Calcd for $C_8H_{10}O_2SSe_2$: C 29.38; H 3.07; S 9.77; Se 48.12%. Found: C 29.64; H 2.95; S 9.48; Se 47.83%.

Ethyl (Z)-3-(2,3-dihydro-1,4-thiaselenin-2-ylselanyl)acrylate (**23**). Yield: 399 mg (97%), a light-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 1.30 (3H, t, ^3J = 7.2 Hz, C<u>H</u>$_3CH_2$), 3.34 (1H, dd, ^2J = 11.9 Hz, ^3J = 9.7 Hz, CH_2Se), 3.48 (1H, dd, ^2J = 11.9 Hz, ^3J = 2.6 Hz, CH_2Se), 4.18 (2H, q, ^2J = 7.2 Hz, C<u>H</u>$_2CH_3$), 4.47 (1H, dd, ^2J = 9.7 Hz, ^3J = 2.6 Hz, SCHSe), 6.35 (1H, d, ^3J = 9.5 Hz, SeCH=C<u>H</u>C=O), 6.36 (1H, d, ^3J = 9.8 Hz, =CHS), 6.47 (1H, d, ^3J = 9.8 Hz, =CHSe), 7.75 (1H, d, ^3J = 9.5 Hz, SeC<u>H</u>=CHC=O).

^{13}C NMR (100 MHz, $CDCl_3$): δ, ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.97 (CH_3), 24.80 ($^1J_{SeC}$ = 71.9 Hz, $SeCH_2$), 37.43 ($^1J_{SeC}$ = 70.0 Hz, SCHSe), 60.41 (O<u>C</u>H_2CH_3), 109.48 ($^1J_{SeC}$ = 116.8 Hz, =CHSe), 117.59 (SeCH=C<u>H</u>C=O), 119.47 (=CHS), 143.86 Se<u>C</u>H=CHC=O), 167.06 (C=O).

^{77}Se NMR (76 MHz, $CDCl_3$): δ 231.9 (in cycle), 546.6.

MS (EI), *m/z* (%): 343 (24) $[M]^+$, 165 (100), 151 (50), 125 (1), 85 (76).

Anal. Calcd for $C_9H_{12}O_2SSe_2$: C 31.59; H 3.53; S 9.37; Se 46.15%. Found: C 31.74; H 3.71; S 9.28; Se 44.79%.

4. Conclusions

The regio- and stereoselective one-pot synthesis of a novel family of 2,3-dihydro-1,4-thiaselenin-2-yl selenides has been developed based on trapping intermediate dihydro-1,4-thiaselenin-2-yl selenolate anion at low temperature. The latter was generated from dihydro-1,4-thiaselenin-2-yl selenocyanate by the action of sodium borohydride and involved in nucleophilic substitution and addition reactions to activated double and triple bond under phase transfer catalysis conditions. The nucleophilic substitution reactions with alkyl halides give alkyl, allyl and propargyl 2,3-dihydro-1,4-thiaselenin-2-yl selenides in

93–98% yields. The addition reactions of dihydro-1,4-thiaselenin-2-yl selenolate anion to alkyl acrylates, acrylonitrile and alkyl propiolates proceed in a regio- and stereoselective fashion to afford 2,3-dihydro-1,4-thiaselenin-2-yl selenides, containing alkyl propanoates, cyanoethyl and alkyl propenoate groups, in high yields. It should be emphasized that not a single representative of 2,3-dihydro-1,4-thiaselenin-2-yl selenides has been previously described in the literature.

The obtained products are valuable intermediates for organic synthesis and compounds with putative biological activity. It is known that the 1,4-thiaselenine derivatives exhibit antibacterial and antifungal activities [18].

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12101236/s1, ^{1}H, ^{13}C, and ^{77}Se NMR spectra of the products.

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