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Pd/Cu-Catalyzed Cross-Coupling of Bis(2-bromovinyl) Selenides with Terminal Acetylenes: Unusual Involvement of Selanyl Function in the Sonogashira Reaction

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Abstract: The Pd/Cu-catalyzed Sonogashira reaction of (*E*,*E*)-bis(2-bromovinyl) selenide and (*E*,*E*)-bis(1-bromo-1-hexen-2-yl) selenide with terminal alkynes was found to proceed at room temperature involving both bromine atoms and the selanyl function. As a result, new bis-(1,3-enynyl) selenides and enediyne hydrocarbons are formed with a complete retention of the stereoconfiguration of the initial selenides. Due to steric hindrances in the cross-coupling at the selenyl function in the case of (*E*,*E*)-bis(1-bromo-1-hexen-2-yl) selenide, the second process is realized to a lesser extent than with unsubstituted (*E*,*E*)-bis(2-bromovinyl) selenide.

Keywords: 2-bromovinyl selenides; cross-coupling; palladium catalyst; terminal acetylenes; endiynes; bis-(enynyl) selenides

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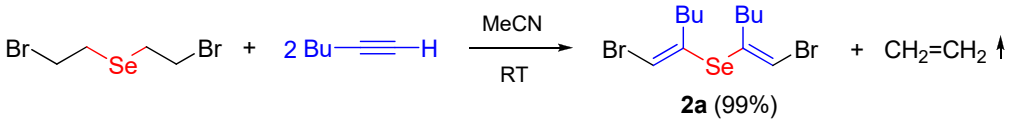
1. Introduction

Sonogashira cross-coupling of vinyl chlorides, bromides, iodides, and triflates with terminal acetylenes in a presence of Pd(0) or Pd(II)/CuI while using amine as a base is one of the effective methods for synthesis of enyne hydrocabons [1–5]. Recently, new Pd catalytic systems such as crystallized Pd/Cu nanoparticles on activated carbon [6] and a zeolite-supported Pd catalyst [7] were suggested and studied in Sonogashira cross-couplings of aryl halides with terminal acetylenes. At the same time, unsaturated chalcogenides could be convenient alternatives to halides as a source of electrophilic reagents in the Sonogashira reactions since the oxidative addition of organyl selenides at palladium proceeds faster than the addition of organic halides because the carbon-selenium bond is more labile than the carbon-halogen bond [8]. Nevertheless, so far in Sonogashira cross-coupling, only vinyl tellurides were introduced [9]. Thus, *Z*-vinyl tellurides afford corresponding enyne hydrocarbons with the retention of the *Z*-configuration in the reactions of cross-coupling with terminal acetylenes catalyzed with $PdCl_2$/CuI [10]. Similarly, *Z*,*Z*-bis(vinyl) tellurides react with terminal acetylenes at the same conditions affording endiyne hydrocarbons of the *Z*-configuration. However, divinyl selenides were completely inert in these reactions, and initial compounds usually were isolated unchanged no matter what palladium catalyst was taken [11]. In a case of *E*-1-bromovinyl selenides, in the cross-coupling reactions with terminal acetylenes catalyzed with $Pd(PPh_3)_4$, only one bromine atom was involved; the selanyl group did not participate in the reaction. As a result, only corresponding *Z*-2-organylseleno-1,3-enynes were isolated as the reaction products [12]. Similarly, affording *E*-1-arylselanyl substituted 1,3-enynes, which retain the configuration of the initial vinyl group; the reaction of *E*-1-iodo-2-arylseleno ethylenes with terminal acetylenes is realized [13]. In addition, in this case, the selanyl function does not participate in the reaction. To carry out cross-coupling of both tellanyl and selanyl functions in (*Z*,*Z*)- and (*E*,*E*)-bis(vinyl) chalcogenides

with terminal acetylenes, authors [14] managed using nickel catalyst Ni(dppe)Cl_2 combined with CuI. In addition, in this case, the reaction took place with the retention of the chalcogenides' initial configuration and formation of the corresponding enynes. Only in a case of acetylenic selenides using system $PdCl_2(PPh_3)_2$/$Cu(OAc)_2 \cdot H_2O$ in DMF, it was possible to realize the Sonogashira reaction with participation of the selanyl group. An interaction of aryl ethynyl butyl selenide with terminal acetylenes led here to the formation of diacetylenic hydrocarbons in high yields [15].

Previously, during an investigation of the electrophilic addition reaction to unsaturated compounds of selenium dibromide generated in situ from selenium and bromine, we synthesized (*E,E)*-bis(2-bromovinyl) selenide (**1**) which was prepared quantitatively by the stereoselective $SeBr_2$ addition to acetylene in CCl_4 at a 10-12 bar pressure in the autoclave [16]. The alkene-to-alkyne transfer reaction of bis(2-bromoethyl) selenide with 1-hexyne in acetonitrile [17] afforded (*E,E*)-bis(1-bromo-1-hexen-2-yl) selenide (**2a**), an analog of the selenide **1** in which α-protons are substituted with butyl groups (Scheme 1).

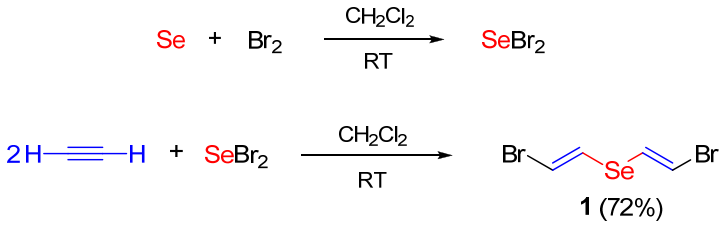


Scheme 1. Preparation of selenide **2a** by alkene-to-alkyne transfer reaction of bis(2-bromoethyl) selenide with 1-hexyne.

2. Results and Discussion

The aim of this work is to compare Sonogashira Pd-catalyzed cross-coupling of unsaturated (*E,E)*-bis(2-bromovinyl) selenide (**1**) and substituted at α-carbons (*E,E*)-bis(1-bromo-1-hexen-2-yl) selenide (**2a**) with terminal acetylenes.

In this work we prepared selenide **1** in 72% yield by the electrophilic addition of selenium dibromide to acetylene in dichlorometane at atmospheric pressure and room temperature (Scheme 2).



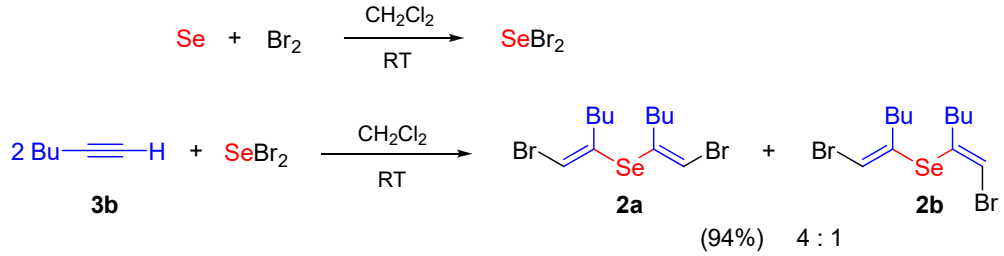
Scheme 2. Preparation of selenide **1** from acetylene and selenium dibromide at atmospheric pressure.

As compared to the synthesis of selenide **1** in an autoclave [16], the convenient method of compound **1** preparation at atmospheric pressure makes this reagent more available.

This approach was also used in the regio- and stereoselective synthesis of selenides **2a,b** in a high yield by the addition to 1-hexyne of selenium dibromide, similarly generated in situ from elemental selenium and bromine (Scheme 3). This "one pot" method allows you to exclude the intermediate stage of the bis(2-bromoethyl) selenide synthesis by the bubbling of ethylene through a $SeBr_2$ solution in $CHCl_3$ or CCl_4 and consequent isolation of the product [18]. Bis(2-bromoethyl) selenide used in the preparation method depicted in the Scheme 1 is, in fact, a substitute for $SeBr_2$, and, though the alkene-to-alkyne transfer reaction affords compound **2a** in a very high yield, the introduction of gaseous ethylene in the overall process makes it more complicated.

The reaction of thus-prepared $SeBr_2$ with 1-hexyne was carried out at room temperature in dichloromethane and afforded the product as a mixture of *E,E*-(**2a**) and *E,Z*-(**2b**) stereoisomers in a 4:1 ratio via the *anti*-Markovnikov *anti*- and *syn*-addition of selenium dibromide to 1-hexyne with a predominance of the *anti*-addition. Previously, we noticed a similar *anti*-Markovnikov addition with a predominance of the *anti*-addition for the

reaction of selenium dichloride and dibromide with propargyl bromide which was also realized in chloroform at room temperature [19].



Scheme 3. Preparation of selenides **2a** and **2b** by electrophilic addition of selenium dibromide to 1-hexyne (**3b**).

The structure of the selenides **2a** and **2b** that were prepared was confirmed by ^{1}H and ^{13}C NMR spectra. In particular, the ^{1}H NMR spectrum of the selenide **2a** is characterized by a singlet signal of the olefinic proton at δ 6.45 ppm and doublet satellite signals with a splitting constant $^{3}J_{SeH}$ 6.4 Hz due to the interaction with the selenium atom pointing to a *cis*-configuration of H and Se atoms in the molecule [19–21] and, correspondingly, to the *anti*-Markovnikov addition of $SeBr_2$ to 1-hexyne. In the selenide **2b,** two singlet signals of the olefinic protons at δ 6.30 and 6.62 ppm also show doublet satellite signals with the splitting constants $^{3}J_{SeH}$ 6.4 and 8.4 Hz, correspondingly, pointing here to *cis*- and *trans*-configurations of the appropriate fragments and hence to the *anti*-Markovnikov addition of $SeBr_2$ to both 1-hexyne molecules [19–21]. It is worthwhile to note that in the case of the Markovnikov addition, in the molecules **2a** and/or **2b**, geminal splitting constant $^{2}J_{SeH}$ 20.5 Hz was expected [21]. The *anti*-Markovnikov addition of $SeBr_2$ to 1-hexyne is evidenced also from direct splitting constant $^{1}J_{CSe}$ 110.4 Hz between ^{13}C and ^{77}Se atoms in the =*C*(Bu)-Se fragment and the splitting constant through two bonds $^{2}J_{SeC}$ 20.7 Hz between ^{13}C and ^{77}Se atoms in the =CH=C-Se fragment [22] in the ^{13}C NMR spectra of selenide **2a.**

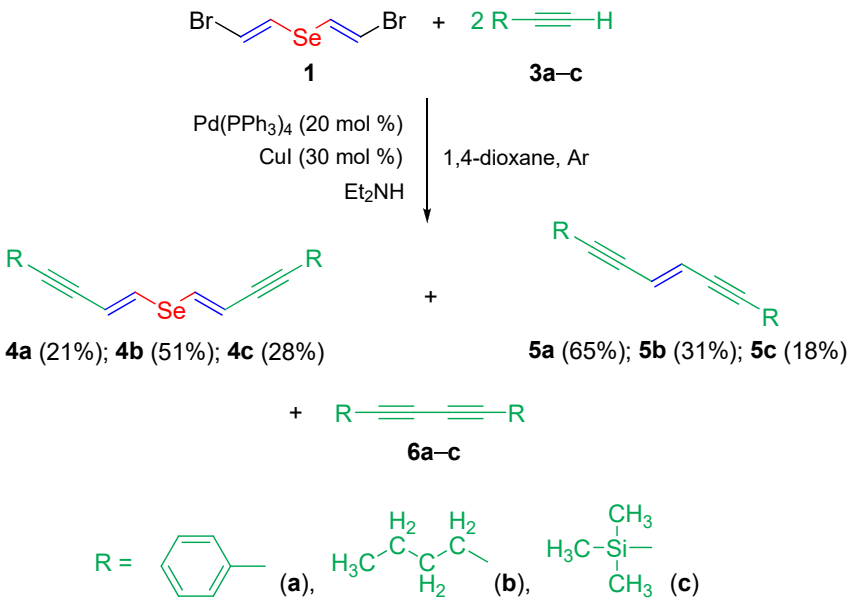
Presence in the selenides **1** and **2a** of the bromine atoms in the *trans*-position to the selenium atom makes them convenient starting compounds for the synthesis of bis-enynic selenides with the predetermined *E*-configuration via the Sonogashira reaction. Taking into account the results of the investigations [11–13], one would expect that the process should be chemoselective.

However, quite unexpectedly, cross-coupling of the selenide **1** with the terminal acetylenes such as phenylacetylene (**3a**), 1-hexyne (**3b**), and trimethyl ethynyl silane (**3c**) taken in three-fold excess, in a presence of $Pd(PPh_3)_4$ and CuI, and diethylamine as a base, resulted in formation both of expected bis-enynic selenides—bis[(*E*)-4-phenyl-1-buten-3-ynyl] selenide (**4a**), di[(*E*)-1-octen-3-ynyl] selenide (**4b**), and bis[(*E*)-4-(trimethylsilyl)-1-buten-3-ynyl] selenide (**4c**), correspondingly, in which configuration of the parent selenide **1** was retained, and endiynes—(*E*)-1,6-diphenyl-3-hexen-1,5-diyne (**5a**), (*E*)-7-tetradecen-5,9-diyne (**5b**), and trimethyl[(*E*)-6-(thimethylsilyl)-3-hexen-1,5-diynyl] silane (**5c**), which also retained the configuration of the parent selenide **1** (Scheme 4).

In accordance with the classical scheme of the cyclic catalytic reaction involving the formation of copper acetylides and diacetylenic Pd complexes which undergo further to the reductive elimination of acetylide-anions [4,5] the diacetylenes **6a-c** are formed in the reaction as the by-products. Their formation is confirmed both by the ^{1}H NMR spectra identical to the known ones and by the corresponding molecular ions in mass spectra of the compounds isolated.

According to the ^{1}H NMR spectra of the reaction mixtures efficiency of the selanyl function substitution as compared to the bromine atom substitution in the reaction, it depends greatly on the terminal acetylene nature. The ratio of selenide **4**:endiyne **5** is 1:3 for phenylacetylene (**3a**), 1:0.9 for 1-hexyne (**3b**), and 1:1.1 for trimethyl ethynyl silane (**3c**).

Yields of selenide **4**, at that, vary from 21% for compound **4a** to 51% for compound **4b**; yields of endiynes **5** vary from 18% for compound **5c** to 65% for compound **5a**.



Scheme 4. Sonogashira cross-coupling of selenide **1** with the terminal acetylenes **3** catalyzed by $Pd(PPh_3)_4$/CuI in dioxane.

The structures of the selenides **4a–c** are confirmed by ^{1}H and ^{13}C NMR data, GC-MS data, as well as elemental analyses. In the ^{1}H NMR spectra, two doublet proton signals with the splitting *trans*-constant (^3J 15.6–15.8 Hz) correspond to the ≡C-CH=CH-Se group of the *E*-configuration. The ^{13}C NMR spectra are characterized by low-field signals of the CH= carbons adjacent to the acetylenic bond (δ 114.60–115.53 ppm) and high-field carbon signals of the =CH-Se group (δ 128.4–132.22 ppm).

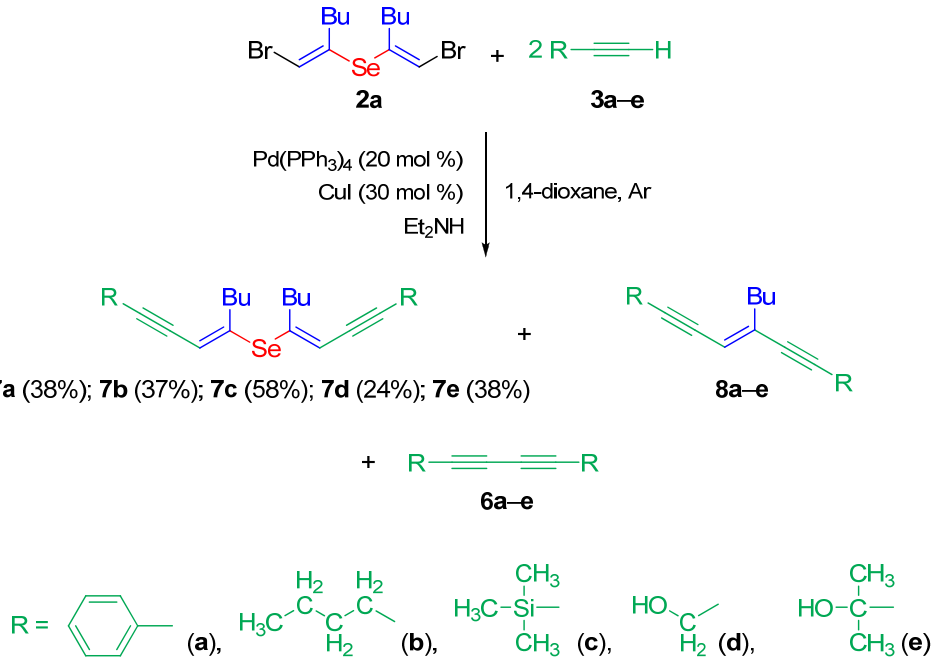
E-Enediynes **5a–c** formed in the reactions are known [17,19–21] and moreover are commercially available compounds. They are identified by a comparison of the ^{1}H NMR spectra with the known spectra of *E*- [23,24] and *Z*-isomers [23,25,26] of the corresponding enediynes as well as by mass- spectra demonstrating pronounced molecular ions.

In order to clear out the influence of the substituted bis(2-bromovinyl) selenide structure on chemoselectivity of the Sonogashira reaction, we carried out cross-coupling of the selenide **2a** with phenylacetylene (**3a**), 1-hexyne (**3b**), trimethyl ethynyl silane (**3c**), 2-propynol-1 (**3d**), 2-methyl-3-butyn-2-ol (**3e**) taken in three-fold excess as in a case of selenide **1.** The conditions of the reaction were the same as for selenide **1**, and, as a catalyst, $Pd(PPh_3)_4$ was used in a presence of CuI and diethylamine.

It was found that in this case the reaction mostly proceeded as a substitution of bromine atoms with the acetylenic function to give corresponding bis-4-substituted (*E*,*E*)-bis[1-butyl-1-buten-3-yn-yl] selenides **7a–e** which retain the configuration of the parent selenide **2a** (Scheme 5). Selenides **7a–e** were isolated from the reaction mixtures by column chromatography on silica gel.

Formation of these products was confirmed by the ^{1}H, ^{13}C NMR spectroscopy, and GC-MS data. The corresponding molecular ions are observed in the GC-MS spectra as well as fragment ions $[M - R]^+$ and the ions characteristic of the particular selenide with regard to the structure of the acetylenic moiety. In the ^{1}H NMR spectra, the singlet (in the case of the selenides **7a,c,e**) or triplet (in the case of the selenides **7b,d** due to the interaction through five bonds in the =CH-C≡C-CH_2 system) signals of olefinic protons were detected. In turn, these signals are accompanied by doublet satellite signals with the splitting constants $^3J_{SeH}$ 4.2–5.1 Hz due to the interaction with the selenium atom which confirm the *cis*-configuration of Se and H atoms in the molecule [19–21]. Presence in the ^{13}C

NMR spectra of the interaction between the ^{13}C and ^{77}Se atoms through one bond in the =C-Se moiety with the splitting constant $^{1}J_{CSe}$ 100.0–114.4 Hz and through two bonds in the CH=C-Se fragment with $^{2}J_{CSe}$ 14.2–15.1 Hz confirms the given structures of the selenides **7**. In the case of the selenide **7c**, the structure was unambiguously confirmed by 2D ^{1}H-^{13}C NMR spectroscopy hmbc ^{13}C.



Scheme 5. Sonogashira cross-coupling of the selenide **2a** with the terminal acetylenes **3** catalyzed by $Pd(PPh_3)_4$/CuI in dioxane.

Cross-coupling at the selanyl function, as in the case of selenide **1,** was also found for selenide **2a** (Scheme 5). Though we failed to isolate the corresponding enediynes **8a–e** in a pure form by column chromatography, they were unequivocally identified by the corresponding molecular and fragment ions on analyzing the GC-MS spectra of the product mixtures obtained. However, in contrast to the reaction of the selenide **1** with terminal acetylenes in which the ratio of the selenides **4** and enediynes **5** vary from 1:3 to 1:0.9, efficiency of cross-coupling at the selanyl function for selenide **2a** is significantly lower: enediynes **8a–e** are formed either in the insignificant (a ratio selenide **7**: enediyne **8** is 1:0.2 for acetylene **3a**, 1:0.18 for acetylene **3c**, 1:0.14 for acetylene **3e**, according to ^{1}H NMR data) or in the trace amounts. So, efficiency of cross-coupling at the selanyl function in the selenide **2a** is significantly influenced by reduced steric availability of selenium in the molecule.

As in the case of selenide **1**, in the reaction of selenide **2a**, the diacetylenes **6a–e**, which are the commercially available products, are formed as the by-products. Their formation was confirmed both by the ^{1}H NMR spectra identical to the known ones and by the corresponding molecular ions in the GC-MS spectra of the reaction mixtures.

3. Materials and Methods

3.1. General Information

The ^{1}H (400.13 MHz) and ^{13}C (100.61 MHz) spectra as well as ^{13}C-*J*mod were recorded on a Bruker Avance DPX 400 spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany) in 5–10% $CDCl_3$ solutions using the solvent proton (δ 7.27 ppm) and carbon (δ 77.16 ppm) signals as internal standards. Electron ionization-mass spectra (EI-MS) were determined on a Shimadzu QP-5050A (Shimadzu Corporation, Kyoto, Japan) at 70 eV. Elemental analyses were performed on a Thermo Scientific Flash 2000 Elemental Analyzer (Thermo Fisher Scientific Inc., Milan, Italy). Melting points were determined on a Kofler Hot-Stage

Microscope PolyTherm A apparatus (Wagner & Munz GmbH, München, Germany). Dry 1,4-dioxane was used as a solvent. $Pd(PPh_3)_4$, CuI, and terminal acetylenes were purchased from Alfa-Aesar.

*3.2. Synthesis of Starting Selenide **1***

*(E,E)-Bis(2-bromovinyl) selenide (**1**).* A methylene chloride solution saturated with acetylene was obtained by bubbling acetylene into methylene chloride (40 mL) for 1 h at room temperature. A mixture of selenium powder (0.79 g, 10 mmol) and bromine (1.6 g, 10 mmol) in methylene chloride (5 mL) was stirred at ambient temperature until the solid disappeared. The obtained solution of selenium dibromide was added dropwise for 20 min to the methylene chloride solution saturated with acetylene (40 mmol) at room temperature. During the addition, bubbling of acetylene was continued. After addition, acetylene was bubbled into the reaction mixture for 3 h at room temperature. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel (eluent: hexane → hexane/chloroform 9:1) to give selenide **1** (2.09 g, 72% yield) as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.43 (d, ^3J = 13.7 Hz, 2H, 2CHBr=), 6.91 (d, ^3J = 13.7 Hz, 2H, 2SeCH=). Lit. [16]. ^{1}H NMR ($CDCl_3$): δ 6.43 (d, 2H, ^3J = 13.3 Hz, 2H, 2CHBr=), 6.91 (d, ^3J = 13.3 Hz, 2H, 2SeCH=).

*3.3. Synthesis of Selenides **2a,b***

A mixture of selenium powder (0.16 g, 2 mmol) and bromine (0.32 g, 4 mmol) in methylene chloride (1 mL) was stirred 2 h at ambient temperature until the solid disappeared. The solution of $SeBr_2$ thus prepared was slowly added dropwise at ambient temperature to a solution of 1-hexyne (0.35 g, 4.2 mmol) in methylene chloride (20 mL), and the reaction mixture was stirred for 12 h. Evaporation of the solvent in a vacuum gave selenide **2** (0.755 g, 94%) as a mixture of *E,E*- and *E,Z*-isomers in a 4:1 ratio according to the ^{1}H NMR data. Selenide **2a** was isolated from the mixture by column chromatography on silica gel (eluent: hexane → hexane/chloroform (9:1)).

*(E,E)-Bis(1-bromo-1-hexen-2-yl) selenide (**2a**).*

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, ^3J = 7.3 Hz, 6H, $2CH_3$), 1.37 (sextet, ^3J = 7.4 Hz, 4H, $2CH_2$), 1.52 (quintet, ^3J = 7.6 Hz, 4H, $2CH_2$), 2.44 (t, ^3J = 7.6 Hz, 4H, $2CH_2$,), 6.45 (s, $^3J_{SeH(cis)}$ = 6.4 Hz, 2H, 2=CH). Lit. [17]: 0.96–0.93 (m, 6H), 1.41–1.32 (m, 4H), 1.56–1.48 (m, 4H), 2.46–2.42 (m, 4H), 6.45 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 14.03 (C^6), 22.25 (C^5), 29.81 (C^4), 34.90 (C^3), 107.53 (d, $^2J_{SeC}$ = 20.7 Hz, =CH), 135.12 ($^1J_{CSe}$ = 110.4 Hz, C-Se). Lit. [17]: 13.90, 22.12, 29.68, 34.77, 107.40, 134.97.

MS (EI), *m/z* (%): 404 (5) $[M]^+$, 362 (1) $[M - C_3H_6]^+$, 323 (6), 281 (3), 269 (2), 244 (9) $[M - BrC{\equiv}CC_4H_9]^+$, 202 (26), 187 (3), 173 (2), 163 (12), 145 (7), 133 (8), 119 (27), 107 (5), 93 (12), 79 (64), 67 (21), 57 (53), 41 (100) $[C_3H_5]^+$.

Anal. calcd for $C_{12}H_{20}Br_2Se$ (403.06): C, 35.76; H, 5.00; Br, 39.65; Se, 19.60%. Found: C, 35.62; H, 4.95; Br, 39.45; Se, 19.74%.

*(E,Z)-Bis(1-bromo-1-hexen-2-yl) selenide (**2b**).*

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, ^3J = 7.3 Hz, 3H, CH_3), 0.95 (t, ^3J = 7.6 Hz, 3H, CH_3), 1.36 (sextet, ^3J = 7.4 Hz, 4H, $2CH_2$), 1.53 (quintet, ^3J = 7.5 Hz, 2H, CH_2), 1.56 (quintet, ^3J = 7.5 Hz, 2H, CH_2), 2.48 (t, ^3J = 7.5 Hz, 2H, CH_2), 2.59 (t, ^3J = 7.2 Hz, 2H, CH_2), 6.30 (s, $^3J_{SeH(cis)}$ = 6.4 Hz, 1H, =CH), 6.62 (s, $^3J_{SeH(trans)}$ = 8.4 Hz, 1H, =CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 14.03(C^6), 21.77(C^5), 30.10(C^4), 35.23(C^3), 38.38(C^3), 104.47 (=CH), 116.31 (=CH), 135.11 (C-Se).

The ^{1}H and ^{13}C NMR spectra of the selenides **2a** and **2b** see in Supplementary Materials.

*3.4. Cross-Coupling of (E,E)-bis(2-bromovinyl) selenide (**1**) with Terminal Acetylenes **3***

*Cross-coupling of selenide **1** with phenylacetylene (**3a**).* A mixture of CuI (0.029 g, 0.15 mmol,), $Pd(PPh_3)_4$ (0.116 g, 0.1 mmol), and diethyl amine (0.29 g, 4 mmol) in 1,4-dioxane (2.5 mL) was stirred in an argon atmosphere at ambient temperature for 15 min; selenide **1** (0.145 g, 0.5 mL)

in 1,4-dioxane (0.5 mL) was added to the resulting solution; stirring was continued for 1 h, and then, into the reaction mixture, acetylene **3a** was introduced in 1,4-dioxane (1 mL). After additional stirring for 24 h in an argon atmosphere at room temperature, the resulting mixture was diluted with water (25 mL) and extracted with chloroform (3 × 15 mL); the chloroform extract was dried over $CaCl_2$. After removal of the solvent and excess of the reagents in a vacuum, a residue was rinsed with hexane. From the obtained reaction mixture (0.255 g) containing, according to the ^{1}H NMR data, selenide **4a** and endiyne **5a** in a ratio 1:3 as well as diphenyl diacetylene (**6a**), the products **4a** and **5a** were isolated by column chromatography on silica gel (eluent: hexane → hexane/chloroform (9:1) → chloroform).

*Bis[(E)-4-phenyl-1-buten-3-ynyl] selenide (**4a**)*, 0.035 g (21%), brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14 (d, ^3J 15.8 Hz, 1H, =CH-C≡,), 7.09 (d, ^3J 15.8, 1H, SeCH=), 7.29–7.33 (m, $6H_{arom}$), 7.43–7.46 (m, $4H_{arom}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 87.58 (≡C), 91.09 (≡C), 114.72 (=C<u>H</u>-C≡), 123.15 (C_{arom}), 128.51 (C_{arom}H), 130.83 (C_{arom}H), 131.59 (=CHSe), 131.64 (C_{arom}H).

MS (EI), *m/z* (%): $[M]^+$ 334 (16), 276 (9), $[M - H_2Se]^+$ 252 (100), 239 (10), 226 (11), 176 (4), 152 (12), 139 (7), 126 (58), 115 (24), 101 (10), 77 (25).

Anal. calcd for $C_{20}H_{14}Se$ (333.28): C, 72.07; H, 4.23; Se, 23.69%. Found: C, 72.15; H, 4.47; Se, 23.89%.

*(E)-1,6-Diphenyl-3-hexen-1,5-diyne (**5a**)*, 0.074 g (65%), light-brown needles, mp 110 °C. Lit. [23]: mp. 110–112 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.27 (s, 2H, =CH), 7.29–7.33 (m, $6H_{arom}$), 7.43–7.46 (m, $4H_{arom}$). Lit. *E*-isomer [23]: 6.29 (s, 2H, =CH), 7.26–7.36 (m, $6H_{arom}$), 7.45–7.49 (m, $4H_{arom}$); *Z*-isomer [23]: 6.10 (s, 2H, =CH), 7.33–7.36 (m, $6H_{arom}$), 7.50–7.54 (m, $4H_{arom}$).

MS (EI), *m/z* (%): $[M]^+$ 228 (100), $[M\text{-}C_2H_2]^+$ 202 (14), 150 (5), 126 (20), 113 (26), 100 (9), 77 (3).

*Cross-coupling of selenide **1** with 1-hexyne (**3b**).* Similarly, a mixture of CuI (0.035 g, 0.18 mmol), $Pd(PPh_3)_4$ (0.114 g, 0.1 mmol), diethyl amine (0.29 g, 4 mmol), selenide **1** (0.148 g, 0.51 mmol), acetylene **3b** (0.255 g, 3.1 mmol) in 1,4-dioxane (6 mL) was afforded after 20 h stirring, a mixture of products (0.392 g) containing, according to the ^{1}H NMR data, selenide **4b** and endiyne **5b** in a ratio 1:0.9 as well as dodeca-5,7-diyne (**6b**). The products were isolated by the column chromatography on silica gel (eluent: hexane → hexane/chloroform (9:1) → chloroform).

*Di[(E)-1-octen-3-ynyl] selenide (**4b**)*, 0. 075 g (51%), brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, ^3J = 7.2 Hz, 6H, $2CH_3$), 1.42 (sextet, ^3J = 7.3 Hz, 4H, $2CH_2$), 1.52 (quintet, ^3J = 7.2 Hz, 4H, $2CH_2$), 2.31 (t d, ^3J = 6.9 Hz, ^5J = 2.2 Hz, 4H, 2 =CH-C≡C-C<u>H</u>$_2$), 5.89 (d t, ^3J = 15.8 Hz, ^5J = 2.2 Hz, 2H, 2 =C<u>H</u>-C≡C-CH_2), 6.84 (d, ^3J 15.8 Hz, 2H, 2SeCH=).

^{13}C NMR (100 MHz, $CDCl_3$): δ 13.71 (CH_3) 19.29 (<u>C</u>H$_2$-CH_3), 22.10 (<u>C</u>H$_2$-C≡), 30.82 (CH_2), 78.86 (C≡), 92.28 (C≡), 115.50 (=<u>C</u>H-C≡), 128.91 (=<u>C</u>HSe).

MS (EI), *m/z* (%): $[M]^+$ 294 (30), $[M - C_3H_7]^+$ 251 (18), 209 (28), 195 (55), 183 (6), 169 (9), 155 (24), 141 (48), 128 (100), 115 (57), 105 (11), 91 (45), 77 (30), 65 (36).

Anal. calcd for $C_{16}H_{22}Se$ (293.31): C, 65.51; H, 7.56; Se, 26.93%. Found: C, 65.87; H, 7.35; Se, 26.74%.

*(E)-7-Tetradec-5,9-diyne (**5b**)*, 0.030 g (31%), brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, ^3J = 7.2 Hz, 6H, $2CH_3$), 1.39–1.44 (sextet, ^3J = 7.3 Hz, 4H, $2CH_2$), 1.48–1.55 (quintet, ^3J = 7.2 Hz, 4H, $2CH_2$), 2.25 (t, ^3J = 7.0 Hz, 4H, $2CH_2$), 5.88 (s, 2H, CH=CH). Lit. *Z*-isomer [25]: 0.90 (t, 6H, ^3J = 7.2 Hz, $2CH_3$), 1.48 (m, 8H, $4CH_2$), 2.37 (t, ^3J = 6.8 Hz, 4H, $2CH_2$), 5.70 (s, 2H, CH=CH).

MS (EI), *m/z* (%): $[M]^+$ 188 (57), $[M - CH_3]^+$ 173 (3), $[M - C_3H_7]^+$ 145 (22), $[M - C_4H_9]^+$ 131 (78), 117 (88), 115 (77), 105 (38), 91 (100), 77 (55), 63 (27), 51 (31).

*Cross-coupling of selenide **1** with trimethyl ethynyl silane (**3c**).* Similarly, a mixture of CuI (0.030 g, 0.16 mmol), $Pd(PPh_3)_4$ (0.116 g, 0.1 mmol), diethyl amine (0.298 g, 4.1 mmol), selenide **1** (0.149 g, 0.51 mmol), acetylene **3c** (0.301 g, 3.1 mmol) in 1,4-dioxane (6 mL) was afforded after 24 h stirring, a mixture of products (0.278 g) containing, according to the

^{1}H NMR data, selenide **4c** and endiyne **5c** in a ratio 1:1.1 as well as 1,4-bis(trimethylsilyl) butadiyne (**6c**). The products were isolated by the column chromatography on silica gel (eluent: hexane → hexane/chloroform (4:1) → chloroform).

*Bis[(E)-4-(trimethylsilyl)-1-buten-3-ynyl] selenide (**4c**)*, 0.046 g (28%), light-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.20 (s, 18H, $2Si(CH_3)_3$), 5.93 (d, ^3J = 15.6 Hz, 2H, 2=CH-C≡), 7.04 (d, ^3J = 15.6 Hz, 2H, 2=CHSe).

^{13}C NMR (100 MHz, $CDCl_3$): δ -0.05 [$(CH_3)_3Si$], 96.41 (≡C-Si), 102.75 (≡C-C=), 114.60 (=CH-C≡), 132.23 (=CH-Se).

MS (EI), *m/z* (%): $[M]^+$ 326 (5), $[M - CH_3]^+$ 311 (4), 295 (3), 223 (2), 173 (10), 155 (2), 145 (10), 123 (2), 108 (10), $[(CH_3)_3Si]^+$ 73 (100).

Anal. calcd for $C_{14}H_{22}Si_2Se$ (325.46): C, 51.67; H, 6.81; Se, 24.26%. Found: C, 51.23; H, 6.35; Se, 23.95%.

*Trimethyl [(E)-6-(trimethylsilyl)-3-hexen-1,5-diynyl] silane (**5c**)*, 0.039 g (18%), light-yellow crystals, mp 75 °C. Lit. [27]: 75–76 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.18 (s, 18H, $2(CH_3)_3Si$), 5.99 (s, 2H, CH=CH). Lit. *E*-isomer [24]: 0.17 (s, 18H, $2Si(CH_3)_3$), 5.99 (s, 2H, CH=CH). *Z*-isomer [26]: 0.20 (s, 18H, $2Si(CH_3)_3$), 5.88 (s, 2H, CH=CH).

MS (EI), *m/z* (%): $[M]^+$ 220 (16), $[M - CH_3]^+$ 205 (100), [M - $(CH_3)_3Si]^+$ 147 (2), 145(6), 107 (2), 95 (24), $[(CH_3)_3Si]^+$ 73 (54).

The ^{1}H and ^{13}C NMR spectra of the selenides **4b,c** see in Supplementary Materials.

*3.5. Cross-Coupling of (E,E)-Bis(1-bromo-1-hexen-2-yl) selenide (**2a**) with Terminal Acetylenes **3***

*Cross-coupling of selenide **2a** with phenylacetylene (**3a**).* A mixture of CuI (0.029 g, 0.15 mmol,) $Pd(PPh_3)_4$ (0.116 g, 0.1 mmol), and diethyl amine (0.29 g, 4 mmol) in 1,4-dioxane (2.5 mL) was stirred in an argon atmosphere at ambient temperature for 15 min; selenide **2a** (0.202 g, 0.5 mL) in 1,4-dioxane (0.5 mL) was added to the resulting solution; stirring was continued for 1 h, and then, into the reaction mixture, acetylene **3a** was introduced in 1,4-dioxane (1 mL). After additional stirring for 20 h in an argon atmosphere at room temperature, the resulting mixture was diluted with water (25 mL) and extracted with chloroform (3 × 15 mL); the chloroform extract was dried over $CaCl_2$. After removal of the solvent and excess of the reagents in a vacuum, a residue was dissolved in chloroform and filtered through silica gel. From the obtained product mixture containing, according to the ^{1}H NMR data, selenide **7a** and endiyne **8a** in a ratio 1:0.2 as well as diacetylene **6a**, the compound **7a** was isolated by column chromatography on silica gel (eluent: hexane → hexane/chloroform (1:1) → chloroform). Endiyne **8a** was identified in a mixture with selenide **7a** and diacetylene **6a** by GC-MS.

*(E,E)-Bis[1-butyl-4-phenyl-1-buten-3-yn-1-yl] selenide (**7a**)*, 0.083 g (38%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (t, ^3J = 7.4 Hz, 6H, CH_3), 1.44 (sextet, ^3J = 7.4 Hz, 4H, CH_2), 1.63 (quintet, ^3J = 7.4 Hz, 4H, CH_2), 2.70 (t, ^3J = 7.4 Hz, 4H, CH_2), 6.06 (s, $^3J_{SeH}$ 5.0 Hz, 2H, =CH), 7.33–7.36 (m, $6H_{arom}$), 7.44–7.47 (m, $4H_{arom}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 14.10 (C^8), 22.34 (C^7), 31.27 (C^6), 35.67 (C^5), 86.68 (≡C), 94.37 (≡C), 114.57 ($^2J_{CSe}$ = 15.1 Hz, =CH), 123.59 (C_{arom}), 128.34 (C_{arom}), 128.52 (C_{arom}), 131.50 (C_{arom}), 148.97 ($^1J_{CSe}$ = 100.0 Hz, C-Se).

MS (EI), *m/z* (%): 446 (4) $[M]^+$, 417 (2) $[M - C_2H_5]^+$, 403 (12) $[M - C_3H_7]^+$, 389 (4) $[M - C_4H_9]^+$, 369 (2) $[M - C_6H_5]^+$, 359 (4), 347 (12), 343 (4), 332 (4), 323 (3), 309 (3), 293 (4), 279 (13), 265 (27), 253 (9), 241 (5), 229 (3), 219 (9), 202 (11), 165 (28), 152 (26), 191 (8), 141 (47), 128 (27), 115 (100), 102 (12), 91 (43), 77 (26) $[C_6H_5]^+$, 67 (18), 55 (25), 43 (19), 41 (56).

Anal. calcd for $C_{28}H_{30}Se$ (445.50): C, 75.49; H, 6.79; Se, 17.72%. Found: C, 75.67; H, 6.90; Se, 17.50%.

*(E)-3-Butyl-1,6-diphenyl-3-hexen-1,5-diyne (**8a**).*

MS (EI), *m/z* (%): 284 (100) $[M]^+$, 269 (2) $[M - CH_3]^+$, 253 (18), 241 (93) [M -$C_3H_7]^+$, 226 (28), 215 (17), 202 (10), 191 (11), 178 (12), 165 (25), 152 (7), 139 (16), 127 (28), 115 (78), 106 (6), 91 (18), 77 (23) $[C_6H_5]^+$, 63 (20), 51 (15) $[C_4H_3]^+$, 39 (17) $[C_3H_3]^+$.

*Cross-coupling of selenide **2a** with hexyne (**3b**).* Similarly, stirring for 20 h a mixture of CuI (0.021 g, 0.11 mmol), $Pd(PPh_3)_4$ (0.081 g, 0.07 mmol), diethyl amine (0.205 g, 2.8 mmol), selenide **2a** (0.14 g, 0.35 mmol), and acetylene **3b** (0.173 g, 2.1 mmol) in 1,4-dioxane (3.5 mL) afforded, after filtration through a layer of silica gel, a product mixture containing, according to the ^{1}H NMR data, selenide **7b** and a trace of endiyne **8b** as well as diyne **6b.** Selenide **7b** was isolated from the mixture by column chromatography on silica gel (eluent: hexane → hexane/chloroform (9:1) → chloroform). Endiyne **8b** was identified in the product mixture by GC-MS.

*(E,E)-Bis[1-butyl-1-octen-3-yn-1-yl] selenide (**7b**)*, 0.053 g (37%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, ^3J = 7.2 Hz, 6H, $2CH_3$), 0.92 (t, ^3J = 7.2 Hz, 6H, $2CH_3$), 1.34 (sextet, ^3J = 7.3 Hz, 4H, $2CH_2$), 1.44 (quintet, ^3J = 7.3 Hz, 4H, $2CH_2$), 1.47–1.55 (m, 8H, $2CH_2CH_2$), 2.35 (d t, ^3J = 6.7 Hz, ^5J = 1.8 Hz, 4H, $2CH_2$-C≡), 2.52 (t, ^3J = 7.5 Hz, 4H, $2CH_2$-C=), 5.76 (t, ^5J = 1.8 Hz, $^3J_{SeH}$ = 4.5 Hz, 2H, 2=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 13.70 (C^{12}), 14.04 (C^1), 19.43 (C^{11}), 22.08 (C^9), 22.30 (C^2), 30.98 (C^{10}), 31.12 (C^3), 35.27 (C^4), 88.33 (≡C), 95.40 (≡C), 115.05 ($^2J_{SeC}$ = 14.9 Hz, =C), 146.71 ($^1J_{CSe}$ = 108.4 Hz, C-Se).

MS (EI), *m/z* (%): 406 (4) $[M]^+$, 363 (11) $[M - C_3H_7]^+$, 349 (4) $[M - C_4H_9]^+$, 321 (4), 307 (15), 293 (3), 277 (3), 265 (7), 251 (8), 239 (3), 227 (3), 211 (3), 197 (8), 183 (7), 169 (8), 155 (10), 143 (9), 129 (10), 117 (11), 105 (17), 91 (41), 77 (38), 67 (28), 55 (44), 41 (100) $[C_3H_5]^+$.

Anal. calcd for $C_{24}H_{38}Se$ (405.52): C, 71.08; H, 9.45; Se, 19.47%. Found: C, 71.32; H, 9.70; Se, 19.54%.

*(E)-7-Butyl-7-tetradecen-5,9-diyne (**8b**).*

MS (EI), *m/z* (%): 244 (49) $[M]^+$, 201 (6) $[M - CH_3]^+$, 187 (17) $[M - C_4H_9]^+$, 173 (10), 159 (41), 145 (92), 131 (75), 117 (79), 105 (42), 91 (73), 77 (37), 65 (29), 57 (23), 55 (42), 41 (100) $[C_3H_5]^+$, 39 (32) $[C_3H_3]^+$.

*Cross-coupling of selenide **2a** with trimethyl ethynyl silane (**3c**).* Similarly, stirring for 20 h a mixture of CuI (0.044 g, 0.23 mmol), $Pd(PPh_3)_4$ (0.174 g, 0.15 mmol), diethyl amine (0.435 g, 6.0 mmol), selenide **2a** (0.303 g, 0.75 mmol), and acetylene **3c** (0.443 g, 4.5 mmol) in 1,4-dioxane (6 mL) afforded, after filtration through a layer of silica gel, a product mixture containing, according to the ^{1}H NMR and GC-MS data, selenide **7c** and endiyne **8c** in a ratio 1:0.18 as well as diyne **6c.** Selenide **7c** was isolated from the mixture by column chromatography on silica gel (eluent: hexane → hexane/chloroform (4:1) → chloroform). Endiyne **8c** was identified in the product mixture by GC-MS.

*(E,E)-Bis[1-butyl-4-(trimethylsilyl)-1-buten-3-ynyl] selenide (**7c**)*, 0.192 g (58%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.20 (s, 18H, $2Si(CH_3)_3$), 0.94 (t, ^3J = 7.3 Hz, 6H, $2CH_3$), 1.35 (sextet, ^3J = 7.4 Hz, 4H, $2CH_2$), 1.54 (quintet, ^3J = 7.5 Hz, 4H, $2CH_2$), 2.57 (t, ^3J = 7.5 Hz, 4H, $2CH_2$), 5.78 (s, $^3J_{SeH}$ = 4.5 Hz, 2H, 2=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 0.04 ($SiCH_3$), 14.00 (C^8), 22.14 (C^7), 31.04 (C^6), 35.58 (C^5), 99.69 (≡C-Si), 101.95 (≡C-C=,) 114.53 ($^2J_{SeC}$ = 14.4 Hz, =CH), 150.52 ($^1J_{CSe}$ = 111.7 Hz, C-Se).

MS (EI), *m/z* (%): 438 (2) $[M]^+$, 396 (3) $[M - C_3H_6]^+$, 365 (2) $[M - (CH_3)_3Si]^+$, 307 (2), 293 (2), 245 (4), 227 (1), 183 (2), 155 (2), 145 (2), 135 (2), 121 (6), 105 (3), 83 (6), 73 (100) $[(CH_3)_3Si]^+$, 59 (18) $[(CH_3)_2SiH]^+$, 45 (8) $[CH_3SiH_2]^+$.

Anal. calcd for $C_{22}H_{38}Si_2Se$ (437.67): C, 60.37; H, 8.75; Se, 18.04%. Found: C, 60.61; H, 8.95; Se, 17.94%.

*[(E)-4-Butyl-6-(trimethylsilyl)-3-hexen-1,5-diynyl] trimethyl silane (**8c**).*

MS (EI), *m/z* (%): 276 (30) $[M]^+$, 261 (36) $[M - CH_3]^+$, 245 (25), 229 (3), 219 (15) $[M - C_4H_9]^+$, 203 (4) $[M - (CH_3)_3Si]^+$, 189(10), 173 (7), 159 (9), 145 (10), 131 (7), 123 (11), 121 (3), 109 (3), 97 (8), 83 (8), 73 (100) $[(CH_3)_3Si]^+$, 59 (26) $[(CH_3)_2SiH]^+$, 45 (19) $[CH_3SiH_2]^+$.

*Cross-coupling of selenide **2a** with 2-propyn-1-ol (**3d**).* Similarly, stirring for 72 h a mixture of CuI (0.029 g, 0.15 mmol), $Pd(PPh_3)_4$ (0.116 g, 0.1 mmol), diethyl amine (0.29 g, 4.0 mmol), selenide **2a** (0.202 g, 0.5 mmol), and acetylene **3d** (0.336 g, 6.0 mmol) in 1,4-dioxane (6 mL) afforded, after extraction with hexane and diethyl ether, a product mixture containing, according to the ^{1}H NMR data, selenide **7d** and endiyne **8d** as a trace as well as 2,4-hexadiyn-

1,5-diol (**6d**). Selenide **7d** was isolated from the mixture by column chromatography on silica gel (eluent: hexane → hexane/chloroform (4:1) → chloroform). Endiyne **8d** was identified in the product mixture by GC-MS.

*(E)-5-[(E)-1-Butyl-5-hydroxy-1-penten-3-ynyl] selanyl-4-nonen-2-yn-1-ol (**7d**)*, 0.042 g (24%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, ^3J = 7.2 Hz, 6H, $2CH_3$), 1.34 (sextet, ^3J = 7.5 Hz, 4H, $2CH_2$), 1.52 (quintet, ^3J = 7.6 Hz, 4H, $2CH_2$), 1.66 (br s, 2H, 2OH), 2.55 (t, ^3J = 7.4 Hz, 4H, $2CH_2$), 4.43 (d, ^5J = 2.1 Hz, 4H, 2≡C-CH_2), 5.80 (t, ^5J = 2.1 Hz, $^3J_{SeH}$ = 4.2 Hz, 2H, 2=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 13.51 (C^9), 22.24(C^8), 31.13(C^7), 35.44(C^6), 51.85 (CH_2-OH), 82.63 (≡C), 92.12 (≡C), 113.83 ($^2J_{SeC}$ = 16.0 Hz, =CH), 149.50 ($^1J_{CSe}$ = 100.2 Hz, =C-Se).

MS (EI), *m/z* (%): 354 (5) $[M]^+$, 337 (4) [M - OH]$^+$, 323 (1) $[M - CH_2OH]^+$, 307 (5), 297 (1) $[M - C_4H_9]^+$, 293 (4), 279 (2), 265 (3), 251 (4), 237 (4), 223 (5), 209 (4), 197 (4), 183 (6), 171 (4), 157 (6), 143 (10), 117 (10), 105 (9), 91 (31), 77 (30), 67 (40), 41 (100).

Anal. calcd for $C_{18}H_{26}O_2Se$ (353.36): C, 61.18; H, 7.42; Se, 22.35%. Found: C, 61.06; H, 7.25; Se, 22.37%.

*(E)-4-Butyl-4-octen-2,6-diyn-1,8-diol (**8d**).*

MS (EI), *m/z* (%): 192 (51) $[M]^+$, 145 (10), 131 (37), 115 (47), 103 (53), 91 (85), 77 (100) $[C_6H_5]^+$, 63 (42) $[C_5H_3]^+$, 55 (47) $[HOCH_2C{\equiv}C]^+$, 51 (50) $[C_4H_3]^+$, 43 (30) $[C_3H_7]^+$, 41 (76) $[C_3H_5]^+$, 39 (83) $[C_3H_3]^+$.

*Cross-coupling of selenide **2a** with 2-methyl-3-butyn-2-ol (**3e**).* Similarly, stirring for 20 h a mixture of CuI (0.019 g, 0.10 mmol), $Pd(PPh_3)_4$ (0.087 g, 0.07 mmol), diethyl amine (0.193 g, 2.6 mmol), selenide **2a** (0.135 g, 0.33 mmol), and acetylene **3e** (0.167 g, 2.0 mmol) in 1,4-dioxane (3.5 mL) afforded a product mixture containing, according to the ^{1}H NMR data, selenide **7e** and endiyne **8e** in a ratio 1:0.14 as well as 2,7-dimethyl-3,5-octadiyn-2,7-diol (**6e**). Selenide **7e** was isolated from the mixture by column chromatography on silica gel (eluent: hexane → hexane/chloroform (4:1) → chloroform). Endiyne **8e** was identified in the product mixture by GC-MS.

*(E)-6-[(E)-1-Butyl-5-hydroxy-5-methyl-1-hexen-3-ynyl]selanyl-2-methyl-5-decen-3-yn-2-ol (**7e**)*, 0.051 g (38%).

^{1}H NMR (400 MHz, $CDCl_3$): 0.93 (t, ^3J = 7.3 Hz, 6H, $2CH_3$), 1.35 (sextet, ^3J = 7.3 Hz, 4H, $2CH_2$), 1.52 (quintet, ^3J = 7.1 Hz, 4H, $2CH_2$), 1.53 (s, 12H, $4CH_3$), 2.53 (t, ^3J = 7.4 Hz, 4H, CH_2), 5.77 (s, $^3J_{SeH}$ = 5.1 Hz, 2H, 2=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 14.03 (C^{10}), 22.24 (C^9), 31.03 (C^8), 31.58 ($\underline{C}H_3$-C-OH), 35.40 (C^7), 65.87 (C-OH), 79.19 (≡C), 98.73 (≡C), 113.93 ($^2J_{CSe}$ = 14.2 Hz, =C), 148.76 ($^1J_{CSe}$ = 114.4 Hz, =C-Se).

MS (EI), *m/z* (%): 410 (1) $[M]^+$, 377 (2), 363 (2), 351 (1) $[M - C(CH_3)_2OH]^+$, 349 (2), 335 (2), 293 (1), 277 (2), 269 (1), 251 (2), 235 (2), 225 (1), 211 (2), 197 (2), 185 (3), 69 (2), 155 (2), 143 (3), 129 (2), 105 (6), 91 (11), 77 (12), 67 (10), 59 (19) $[(CH_3)_2COH]^+$, 43 (100) $[C_3H_7]^+$, 41 (24) $[C_3H_5]^+$.

Anal. calcd for $C_{22}H_{34}O_2Se$ (409.46): C, 64.53; H, 8.37; Se, 19.28%. Found: C, 64.42; H, 8.20; Se, 19.14%.

*(E)-5-Butyl-2,9-dimethyl-5-decen-3,7-diyn-2,9-diol (**8e**).*

MS (EI), *m/z* (%): 248 (6) $[M]^+$, 233 (6) $[M - CH_3]^+$, 215 (5), 187 (4), 173 (5), 157 (3), 145 (9), 129 (6), 115 (6), 105 (7), 91 (11), 65 (6), 59 (7), 55 (7), 43 (100) $[C_3H_7]^+$, 39 (7) $[C_3H_3]^+$.

The ^{1}H and ^{13}C NMR spectra of the selenides **7a**–**e** see in Supplementary Materials.

4. Conclusions

(*E*,*E*)-Bis(2-bromovinyl) selenides were subjected to a cross-coupling reaction with terminal acetylenes in a presence of Pd/CuI catalysts at room temperature involving both the bromine atom and selanyl function and affording substituted bis(enynyl) selenides and endiyne hydrocarbons with complete retention of the initial selenide configuration. Due to a steric hindrance in a case of (*E*,*E*)-bis(1-bromo-1-hexen-2-yl) selenide, cross-coupling at selanyl function was realized to a lesser extent compared to unsubstituted (*E*,*E*)-bis(2-bromovinyl) selenide.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12121589/s1, ^{1}H and ^{13}C NMR spectra of the products.

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