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Synthesis of (*Z*)-1-phenylseleno-1,4-diorganyl-1-buten-3-ynes: hydroselenation of symmetrical and unsymmetrical 1,4-diorganyl-1,3-butadiynes

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Abstract—The hydroselenation of 1-organyl-1,3-butadiynes and 1,4-diorganyl-1,3-butadiynes with the sodium phenylselenolate anion, which was generated in situ by reacting diphenyl diselenide with $NaBH_4$ in aqueous ethanol, results in the regio-, stereo- and chemoselective formation the 1-phenylseleno-4-organyl-1-buten-3-ynes and 1-phenylseleno-1,4-diorganyl-1-buten-3-ynes of *Z* configuration respectively. The lack of selectivity with the 2-hydroxy-2-methyl-3,5-dodecadiyne was observed and the obtained product structures were studied in detail.

Vinyl selenides are important reagents and intermediates in organic synthesis and among a large list of described transformations, the ability of these compounds to participate in the formation of carbon–carbon bonds by the Ni-catalyzed cross-coupling reactions with magnesium[1–5] or zinc[6] reagents is remarkably interesting. Only few synthetic approaches have been reported for 1,1-disubstituted vinylic selenides,[7–10] while a large number of methods for 1,2-disubstituted vinyl selenides of *E* or *Z* configuration are known.[11–13] The most common method involves the addition of organo selenols to terminal alkynes under different reaction conditions. It should be noted that the regio- and stereochemistry of the obtained products is very sensitive to the reaction conditions. For example, the addition of phenyl selenol to terminal acetylenes at 50°C provides the anti-Marcovnikov products of *Z* configuration as the major products,[14–18] but at 120°C a 1:1 mixture of *Z* and *E* vinyl selenides is formed.[18] The Pd-catalyzed hydroselenation[8] of alkyl mono-substituted acetylenes affords the 1-alkyl-1-phenylseleno ethenes as the main products among the 1,2-disubstituted isomers. The opposite regioselectivity is observed when an aryl group is linked to the triple bond of the starting material. The use of organo selenols as reagents is a remarkable disadvantage that cannot be disregarded in view of the difficulties in preparing and handling these very volatile, bad-smelling, toxic and air-sensitive compounds.

In our opinion, diphenyl diselenide, a commercially available, stable and odorless solid, could be a more convenient and an alternative reagent to be used to perform the hydroselenation of alkynes by the in situ generation of selenolate anions.[2,7] However, to the best of our knowledge, only the (*Z*)-styryl phenyl selenide was synthesized by the hydroselenation of phenylacetylene using the PhSeSePh/$NaBH_4$/EtOH system.[2] On the other hand, we have reported that using the diisobutylaluminum selenolate anion to perform the hydroselenation of terminal acetylenes, a complete inversion of the regiochemistry takes place, exclusively affording the 1,1-disubstituted vinyl selenides.[7]

We have previously demonstrated that the addition of sodium[19,20] or lithium[21] butyl tellurolate or aryl tellurolate anions to 1,4-diorganyl-1,3-butadiynes is a highly regio-, stereo- and chemoselective process. Although the selenoarsenation of alkynes using carboxylic diphenylarsinous anhydroselenides with complete regio- and stereoselectivity has been previously described,[22] studies on the prospects of such an approach in the case of organo selenolate anions and dimeric acetylenes have not been previously reported. Within the context of our interest in exploring a convenient access to chalcogeno enynes as useful synthetic intermediates for the synthesis of enediynes[23] or chalcogenoenones,[24] we were looking for an efficient entry into 1-phenylseleno-1-buten-3-ynes **2** and **8** through the addition of the phenylselenolate anion to 1,3-butadiynes **1** and **7**. We report here that, upon treatment with $NaBH_4$ in 95% ethanol and diphenyldiselenide, 1,4-diorganyl-1,3-butadiynes and related systems undergo a highly regio-, stereo- and chemoselective hydroselenation delivering the desired 1-phenylseleno enyne of *Z* configuration (Table 1; Schemes 1 and 3). All the obtained products are quite stable in pure form and

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Table 1. Symmetrical and unsymmetrical (*Z*)-1-phenylseleno-1-buten-3-ynes obtained

Entry	1,3-butadiyne[a]	Product	Reaction time (h)	Yield (%)[b,c]
1	H—≡—≡—C_6H_{13} **1a**	C_6H_5Se **2a** C_6H_{13}	3.0	75[d]
2	H—≡—≡—C_4H_9 **1b**	C_6H_5Se **2b** C_4H_9	3.0	66[d]
3	H—≡—≡—C_6H_5 **1c**	C_6H_5Se **2c** C_6H_5	3.0	65[d]
4	H—≡— (cyclohexene) **1d**	C_6H_5Se **2d**	3.0	68[d]
5	C_6H_5—≡—≡—C_6H_5 **7a**	C_6H_5, C_6H_5Se **8a** C_6H_5	4.5	68
6	HO—≡—≡—OH **7b**	HO, C_6H_5Se **8b** OH	5.0	54

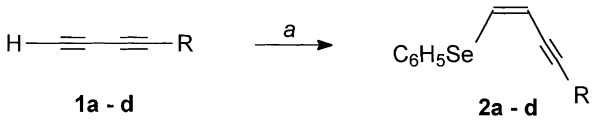
[a]Terminal butadiynes **1a**–**d** were prepared and used in situ.
[b]Isolated yields.
[c]Products purified by column chromatography.
[d]Overall yield (two steps from acetylenic alcohols **6**)

were identified by ^{1}H NMR (Z>98%), ^{13}C NMR, IR and HRMS spectroscopy.

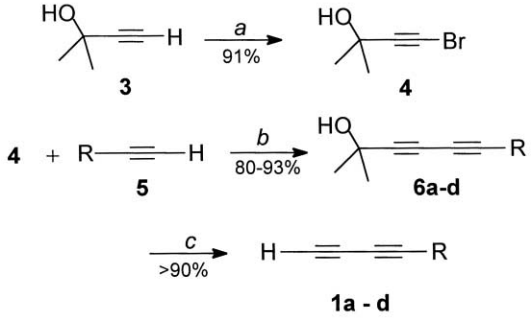
In the cases of compounds **1a**–**d**, attack to the terminal triple bond was clearly more favorable, leading to the formation of products **2a**–**d** in 65–75% yield (Table 1, entries 1–4). The *Z* stereochemistry (and consequently the regiochemistry) of the obtained products was easily determined by the coupling constants (J=9.6 Hz) of doublets attributed to the olefinic hydrogens, characteristic of *cis* vinyl coupling. The terminal monosubstituted butadiynes **1a**–**d** were prepared and used in situ from the diacetylenic alcohols of type **6** by treatment with NaOH (or NaH) in toluene or xylenes under reflux.[19,25] We prepared the required acetylenic alcohols **6** by the Cadiot-Chodkiewicz unsymmetrical cross-coupling reaction of the 4-bromo-2-methyl-3-butyn-2-ol[26] **4** with commercially available terminal alkynes **5** as illustrated in Scheme 2. This approach is more practical and convenient than the previous one used by us[19,23] in which the synthesis of several bromo acetylenes is necessary to be reacted with the 2-methyl-3-butyn-2-ol **3**.

Compounds **8a** and **8b** were obtained in 68 and 54% yield, respectively, by reaction of PhSeSePh (0.5 equiv.) with $NaBH_4$/EtOH in the presence of the symmetrically substituted butadiynes **7a** and **7b** (Scheme 3), refluxing the mixture for the time reported in Table 1 (entries 5 and 6). The corresponding olefinic hydrogens appear as singlets at 6.4 ppm for **8a** and 6.5 ppm for **8b**. Under the employed reaction conditions, the hydroselenation of only one triple bond always occurred. The formation of the di-hydroselenation product was no detected by ^{1}H or ^{13}C NMR (400 and 100 MHz respectively), however, no experiments using diphenyldiselenide excess were performed.

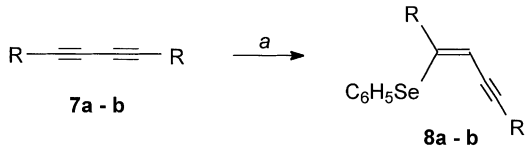
The symmetrically disubstituted butadiynes **7a** and **7b** were obtained, isolated and purified by the Glaser method, using the CuCl/TMEDA/O_2/acetone system.[27]



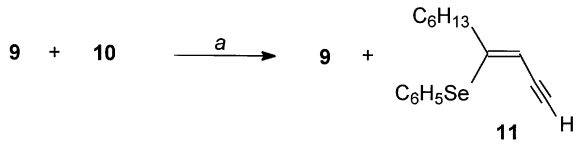
Scheme 1. *a.* 1/2 $C_6H_5Se)_2$, $NaBH_4$/EtOH, reflux, N_2.



Scheme 2. *a.* KOH/H_2O, Br_2, <4°C; *b.* CuCl, NH_2OH.HCl, 30% $BuNH_2$ (aq. sol.); *c.* NaOH (or NaH)/toluene, reflux for 10 min.



Scheme 3. *a*. 1/2 $C_6H_5Se)_2$, $NaBH_4$/EtOH, reflux, N_2.



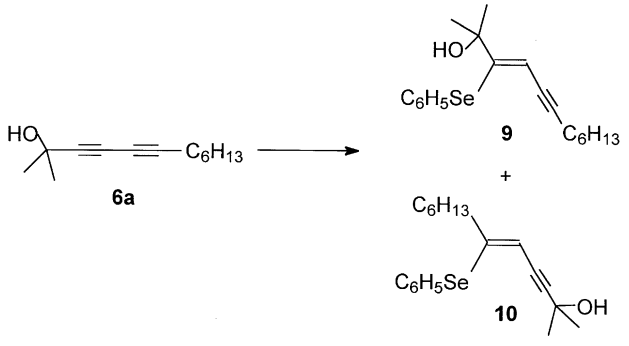
Scheme 5. *a*. NaOH, toluene, reflux, 15 min.

For di- and trisubstituted olefins containing different substituents, it is possible the existence of three and six different isomers respectively. On the other hand, from compounds **7a** and **7b**, the formation of four hydroselenated isomers could be expected, while from **1a**–**d** the formation of seven isomers should be possible. Consequently, it is noteworthy the fact that in all cases illustrated in Table 1, the hydroselenation reaction of 1,3-butadiynes **1a**–**d**, **7a** and **7b** was regio-, stereo- and chemo-selective affording only one compound (Table 1).

However, reacting the 2-hydroxy-2-methyl-3,5-dodecadiyne **6a** with 0.5 equiv. of PhSeSePh and $NaBH_4$ in ethanol, under reflux for 24 h, the appearance of two different signals in the olefinic region of the ^{1}H NMR spectrum (a triplet at 6.47 ppm and a singlet at 5.79 ppm) indicated the formation of two isomers which were identified as being compounds **9** and **10** (Scheme 4) on the basis of the observations described below. The **9**:**10** mixture was obtained at a 58:42 ratio as determined by the relative integrals of the olefinic hydrogens in the ^{1}H NMR spectrum.

The coupling constant for the signal at 6.47 ppm (a triplet when expanded) is quite small (≅2.4 Hz), then we considered the possibility of a propargylic or an allylic coupling between the olefinic hydrogen and the methylenic hydrogens of the alkyl chain attached to the triple bond (typically between 2 and 3 Hz[28]) in **9** or to the double bond (typically between 0 and 3 Hz[28]) in **10**.

To obtain additional evidences, the mixture of isomers was submitted to ^{1}H NOESY experiments. The two signals corresponding to the allylic and to the propargylic hydrogens of compounds **9** and **10** overlap in the ^{1}H NMR, appearing as a multiplet at 2.1–2.2 ppm. An enhancement of one triplet in this region was observed as the vinylic hydrogen (singlet at 5.79 ppm) was irradiated. It was possible to assign the irradiated singlet to compound **10** because the observation indicates a *cis* relation between the olefinic hydrogen and the allylic hydrogens. On the other hand, no NOE was observed for any signal at 2.1–2.2 ppm, irradiating the other olefinic hydrogen that appears as a triplet (J≅2.4 Hz) at 6.47 ppm. In addition, it was possible to conclude that the triplet at 6.47 ppm correspond to compound **9**. The results observed in the NOESY experiments are in accordance with the typical coupling constants range[28] (2.4 Hz observed in **9** and 0 Hz in **10**).



Scheme 4.

In order to support this observation more forcefully, it appeared desirable to find a reaction that would give reliable indication by its structural outcome that the assignment done for **9** and **10** was correct. In this way, an additional evidence for the proposed structures was obtained by reacting the mixture of **9** and **10** with powdered NaOH in toluene under reflux for 15 min (Scheme 5). After this time the initially yellow reaction mixture turned brown. Analysis of the crude reaction mixture by TLC and ^{1}H NMR, indicated the formation of a new compound, which was characterized as **11**. This compound was formed by the retro-Favorskii reaction[29] while the isomer **9** remained untouched as confirmed by TLC and by the presence of the triplet at 6.47 ppm. Compounds **9** and **11** were isolated by preparative TLC plates (Analtech, SiO_2-GF, 2000 microns) and fully characterized by HRMS, ^{1}H, ^{13}C NMR and IR.

In conclusion, we developed the first regio-, stereo- and chemoselective hydroselenation of 1,3-butadiynes employing the sodium phenylselenolate generated in situ by reaction of PhSeSePh and $NaBH_4$ in ethanol. Synthetic applications of (*Z*)-1-phenylseleno-1-buten-3-ynes obtained here are currently under study in our laboratory and results concerning this matter should be published in due course.

1. Experimental

1.1. General remarks

^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded with a 400 MHz spectrometer. Chemical shifts are expressed as parts per million (ppm) downfield from tetramethylsilane as an internal standard. Infra-red spectra were acquired on a Perkin-Elmer Spectrum BX Spectrometer. HRMS were obtained at Department of Chemistry, University of Michigan. Commercial 95% ethanol (Merck) was used without previous purification. THF was distilled over sodium/benzophenone immediately before use. All reactions were carried out under an atmosphere of dry nitrogen and monitored by TLC using prepared plates (silica gel 60 F254 on aluminium). Merck silica gel (230–400 mesh) was used for flash chromatography. Diphenyl diselenide was prepared by the method reported in the literature.[30]

1.1.1. 4-Bromo-2-methyl-3-butyn-2-ol (4).[26] To a two-neck

round bottomed flask equipped with an addition funnel, thermometer and cooled at 0°C under stirring, KOH (89.2 g) and water (349 mL were added to obtain an 88% KOH aqueous solution. Keeping the temperature inside the flask between −5 and −10°C, bromine (33.88 g; 11 mL; 200 mmol) was added dropwise. The dark red color discharged and the mixture was stirred for an additional 10 min. To the resulting solution, the 2-methyl-3-butyn-2-ol (19.6 mL; 23.16 g; 276 mmol) in hexanes (40 mL) was added through the addition funnel and the reaction mixture was stirred for 10 min. A white solid can be observed floating on the colorless solution. The reaction was diluted with ethyl ether (150–200 mL) washed with water (4×60 mL), the organic phase dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure. The residue was distilled using a Kugelrohr apparatus (b.p. 68°C/12 Torr.) to afford the pure compound **4**. Yield: 29.71 g (91%).

1.2. Typical procedure for the cross-coupling reaction of 4-bromo-2-methyl-3-butyn-2-ol (4) with terminal alkynes. Synthesis of unsymmetrical 1,4-diorganyl-1,3-butadiynes 6a–d

To a 250 mL round-bottomed flask containing a 30% n-butylamine aqueous solution (70 mL), cuprous chloride CuCl (0.11 g), hydroxylamine hydrochloride (0.325 g) and the appropriate terminal alkyne (60 mmol) were added at 0°C under magnetic stirring. A smoke is observed and after 5–10 min. the solution turned yellow. Then, the 1-bromo-3-methyl-1-butyn-3-ol was added (8.15 g; 50 mmol). When the addition was complete, the mixture became blue (after 5 min). After 10 min. more $NH_2OH.HCl$ was added to turn the mixture yellow. This last process was repeated several times during 5 h (always to turn the color solution from blue to yellow). The product was extracted with diethyl ether (3×40 mL) and the organic phase washed with brine (3×40 mL) and water (2×30 mL), dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel using hexane to remove the non-polar components and then a mixture of hexanes/ethylacetate (8/2) was used as mobile phase, to afford the pure compounds **6a**–**d** in a 71–89% yield range. Compounds **6a**–**d** obtained here were used to generated the 1-organyl-1,3-butadiynes **1a**–**d** as described in the following experimental procedures.

1.2.1. 1-Phenylseleno-1-undecen-3-yne (2a). Powdered NaOH (0.22 g; 5.5 mmol) was added to a two-neck round bottomed flask equipped with a reflux condenser, containing a solution of 2-hydroxy-2-methyl-3,5-dodecadiyne **6a** (5.0 mmol) in dry toluene (10 mL) under a nitrogen atmosphere. The white mixture was slowly heated to reach reflux temperature, at this time the reaction mixture became dark brown and was refluxed until (up to 1 h) all the starting material was transformed (followed by TLC). The solution of the 1,3-decadiyne **1a** obtained was cooled to room temperature and then a solution of diphenyldiselenide (0.78 g, 2.5 mmol) in 95% ethanol (50 mL) was added. $NaBH_4$ (0.472 g; 12.5 mmol) was added under vigorous stirring and gas evolution was observed during addition. The reaction mixture was stirred under reflux for 3 h, allowed to reach room temperature, diluted with ethyl acetate (60 mL) and washed with brine (3×30 mL) and water (3×30 mL). After drying the organic phase over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel using hexane as mobile phase, to give the pure phenylseleno enyne **2a** as a yellow oil. Yield: 1.093 g (75%). ^{1}H NMR (400 MHz) (δ in $CDCl_3$) 0.90 (t, J=7.2 Hz, 3H), 1.25–1.35(m, 4H), 1.45 (quint., J=7.2 Hz, 2H), 1.58 (quint., J=7.2 Hz, 2H), 2.38 (t, J=7.2 Hz, 2H), 5.97 (dt, J=9.6 Hz, $J\cong$2 Hz, 1H), 6.88 (d, J=9.6 Hz, 1H), 7.28 (m, 3H), 7.55 (m, 2H); ^{13}C NMR 14.0, 19.7, 22.5, 28.5, 28.6, 31.3, 77.8, 98.9, 110.5, 127.5, 129.2, 130.0, 132.8, 135.0; HRMS 292.0724 found. 292.0730 calcd.

1.2.2. 1-Phenylseleno-1-octen-3-yne (2b). The same procedure as for **2a** was followed, affording the pure compound **2b** as a yellow oil. (Yield: 0.869 g (66%). ^{1}H NMR (400 MHz) (δ in $CDCl_3$) 0.94 (t, J=7.2 Hz, 3H), 1.49 (sext., J=7.2 Hz, 2H), 1.57 (quint., J=7.2 Hz, 2H), 2.40 (t, J=7.2 Hz, 2H), 5.98(dt, J=9.6 Hz, $J\cong$2 Hz, 1H), 6.89 (d, J=9.6 Hz, 1H), 7.25 (m, 3H), 7.58 (m, 2H); ^{13}C NMR 13.6, 19.4, 21.6, 30.7, 77.7, 99.9, 110.6, 127.6, 129.3, 130.0, 132.9, 135.1; HRMS 264.0418 found. 264.0417 calcd.

1.2.3. 1-Phenylseleno-4-phenyl-1-buten-3-yne (2c). The same procedure as for **2a** was followed, affording the pure compound **2c** as a yellow oil. Yield: 0.92 g (65%). ^{1}H NMR (400 MHz) (δ in $CDCl_3$) 6.17 (d, J=9.6 Hz, 1H), 7.07 (d, J=9.6 Hz, 1H), 7.30 (m, 6H), 7.48 (m, 2H), 7.56 (m, 2H); ^{13}C NMR 86.5, 97.2, 109.8, 123.1, 127.7, 128.2, 128.3, 129.3, 129.8, 131.4, 132.9, 137.5; HRMS 284.0095 found. 284.0104 calcd.

1.2.4. 1-Phenylseleno-4-cyclohexenyl-1-buten-3-yne (2d). The same procedure as for **2a** was followed, affording the pure compound **2d** as yellow oil. Yield: 0.976 g (68%). ^{1}H NMR (400 MHz) (δ in $CDCl_3$) 1.52–1.68 (m, 4H), 2.12 (m, 2H), 2.21 (m, 2H), 6.09 (d, J=9.6 Hz, 1H), 6.19 (s, 1H), 6.94 (d, J=9.6 Hz, 1H), 7.28 (m, 3H), 7.55 (m, 2H); ^{13}C NMR 21.4, 22.2, 25.7, 29.0, 84.0, 99.3, 110.2, 120.6, 127.6, 129.2, 130.0, 132.8, 135.3, 135.8; HRMS 288.0411 found. 288.0417 calcd.

1.2.5. 1-Phenylseleno-1,4-diphenyl-1-buten-3-yne (8a). To a solution of the 1,4-diphenyl-1,3-butadiyne **7a** (1.797 g; 5.0 mmol) and diphenyldiselenide (0.78 g, 2.5 mmol) in 95% ethanol (50 mL) under a nitrogen atmosphere, $NaBH_4$ (0.472 g; 12.5 mmol) was added at room temperature, under vigorous stirring. Gas evolution was observed during addition. The reaction mixture was stirred under reflux for 4.5 h, allowed to reach room temperature, diluted with ethyl acetate (60 mL) and washed with brine (3×30 mL) and water (3×30 mL). After drying the organic phase over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel using hexane as mobile phase, to give the pure butylseleno enyne **8a** as a yellow solid. m.p.=67–68°C; Yield: 1.222 g (68%). ^{1}H NMR (400 MHz) (δ in $CDCl_3$) 6.40 (s, 1H), 7.07 (m, 3H), 7.19 (m, 3H), 7.22–7.38 (m, 5H), 7.40–7.50 (m, 4H); ^{13}C NMR 88.3, 97.6, 112.6, 123.2, 126.9, 127.9, 128.2, 128.3, 129.9,

131.4, 133.0, 133.2, 139.4, 147.1; HRMS 360.0410 found. 360.0417 calcd.

1.2.6. 2,7-Dihydroxy-2,7-dimethyl-3-phenylseleno-3-octen-5-yne (8b). To a solution of the 2,7-dihydroxy-2,7-dimethyl-3,5-octadiyne **7b** (1.616 g; 5.0 mmol) and diphenyldiselenide (0.78 g, 2.5 mmol) in 95% ethanol (50 mL) under a nitrogen atmosphere, $NaBH_4$ (0.472 g; 12.5 mmol) was added at room temperature under vigorous stirring. Gas evolution was observed during addition. The reaction mixture was stirred under reflux for 5.0 h and then allowed to reach room temperature. Work-up and purification as above (for **8a**) gave the pure butylseleno enyne **8b** as a yellow solid. m.p.=104–106°C; Yield: 0.873 g (54%). ^{1}H NMR (400 MHz) (δ in $CDCl_3$) 1.27 (s, 6H), 1.51 (s, 6H), 1.55 (br. s, 1H), 2.21 (br.s, 1H), 6.50 (s, 1H), 7.20 (t, J=8.4 Hz, 1H), 7.26 (t, J=8.4 Hz, 2H), 7.45 (d, J=8.4 Hz, 2H); ^{13}C NMR 29.2, 29.7, 30.7, 31.0, 65.3, 74.8, 80.1, 102.4, 114.4, 126.3, 129.0, 130.5, 131.9, 153.5; HRMS 324.0623 found. 324.0628 calcd.

1.3. Transformation of 6a into the mixture of compounds 9 and 10

To a solution of the 2-hydroxy-2-methyl-3,5-decadiyne **6a** (0.96 g; 5.0 mmol) and diphenyldiselenide (0.78 g, 2.5 mmol) in 95% ethanol (50 mL) under a nitrogen atmosphere, $NaBH_4$ (0.472 g; 12.5 mmol) was added at room temperature, under vigorous stirring. Gas evolution was observed during addition. The reaction mixture was stirred under reflux for 24 h, allowed to reach room temperature, diluted with ethyl acetate (60 mL) and washed with brine (3×30 mL) and water (3×30 mL). After drying the organic phase over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel using hexane as mobile phase, to give a 58:42 (ratio determined by ^{1}H NMR) mixture of butylseleno enynes **9** and **10** as a yellow solid.

1.3.1. 2-Hydroxy-2-methyl-6-phenylseleno-5-dodecen-3-yne (10). Compound **10** was not isolated from the mixture obtained above (**9**+**10**). ^{1}H NMR signals were assigned using data from mixture of **9**+**10**. ^{1}H NMR (400 MHz) (δ in $CDCl_3$) 0.84 (t, J=7.2 Hz, 3H), 1.09–1.11 (m, 2H), 1.10–1.38 (m, 6H), 1.55 (s, 6H), 2.14 (t, J=7.2 Hz, 2H), 2.27 (br. s, 1H), 5.79 (s, 1H), 7.25–7.35 (m, 3H), 7.58 (d, J=8.4 Hz, 2H); ^{13}C NMR 13.99, 19.2, 22.4, 28.3, 28.8, 31.1, 37.4, 65.7, 79.86, 100.0, 107.4, 127.9, 128.1, 129.0, 135.5, 150.5

1.3.2. 2-Hydroxy-2-methyl-3-phenylseleno-3-dodecen-5-yne (9). Compound **9** was isolated after transformation of **10** in compound **11** (see experimental procedure below). ^{1}H NMR (400 MHz) (δ in $CDCl_3$) 0.87 (t, J=7.2 Hz, 3H), 1.10–1.38 (m, 8H), 1.47 (s, 6H), 2.13 (t, J=7.2 Hz, 2H), 2.23 (br. s, 1H), 6.47 (t, $J\cong$2.4 Hz, 1H), 7.16–7.25 (m, 3H), 7.45 (d, J=8.4 Hz, 2H); ^{13}C NMR 14.0, 19.6, 22.5, 28.3, 28.4, 29.2, 31.3, 74.7, 78.6, 99.2, 116.5, 126.3, 128.8, 130.8, 131.5, 151.3; HRMS 350.1145 found. 350.1148 calcd.

1.3.3. 4-Phenylseleno-3-decen-1-yne (11). Powdered NaOH (0.22 g) was added to a two-neck round bottomed flask equipped with a reflux condenser, containing a solution compounds **9** and **10** (mixture obtained as above in a 5.0 mmol scale) in dry toluene (15 mL) under a nitrogen atmosphere. The yellow mixture was slowly heated to reach reflux temperature, at this time the reaction mixture became dark brown and was refluxed for 15 min. The formation of a new compound (less polar than the alcohols) was observed monitoring the reaction by TLC. The reaction mixture was allowed to reach room temperature, diluted with ethyl acetate (60 mL) and washed with brine (3×30 mL) and water (3×30 mL). After drying the organic phase over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel using hexane as mobile phase, to get the pure butylseleno enyne **11** as a yellow oil and then compound **9** in the pure form, by using hexane/ethyl acetate (7/3) as the mobile phase. ^{1}H NMR (400 MHz) (δ in $CDCl_3$) 0.82 (t, J=7.2 Hz, 3H), 1.07–1.40 (m, 8H), 2.13 (t, J=7.2 Hz, 2H), 3.32 (s, 1H), 5.79 (s, 1H), 7.22–7.40 (m, 3H), 7.61 (d, J=8.4 Hz, 2H); ^{13}C NMR 14.0, 22.4, 28.3, 28.7, 31.4, 37.2, 81.2, 83.1, 106.7, 127.4, 128.4, 129.1, 136.0, 152.5; HRMS 292.0734 found. 292.0730 calcd.

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