

## Synthesis of alkenyl selenides and tellurides using PEG-400

Eder J. Lenardão, Márcio S. Silva, Maraisa Sachini, Renata G. Lara,  
Raquel G. Jacob, and Gelson Perin\*

*Instituto de Química e Geociências, LASOL, Universidade Federal de Pelotas, UFPel, P.O. Box  
354, 96010-900 Pelotas, RS, Brazil  
E-mail: [gelson\\_perin@ufpel.edu.br](mailto:gelson_perin@ufpel.edu.br)*

---

### Abstract

PEG-400 and glycerin were successfully used as recyclable solvents for the synthesis of several alkenyl selenides and tellurides, in good yields and with high selectivity by the hydrochalcogenation of terminal alkynes. The nucleophilic species of selenium and tellurium were generated *in situ* from the reaction of the respective diphenyl dichalcogenide with NaBH<sub>4</sub> at 60 °C. This easy, general and improved method furnishes the corresponding alkenyl chalcogenides preferentially with *Z* configuration. The PEG-400 can be reused up to 4 times without previous treatment with comparable yields and selectivity.

**Keywords:** PEG-400, hydrochalcogenation, alkenyl selenides, alkenyl tellurides

---

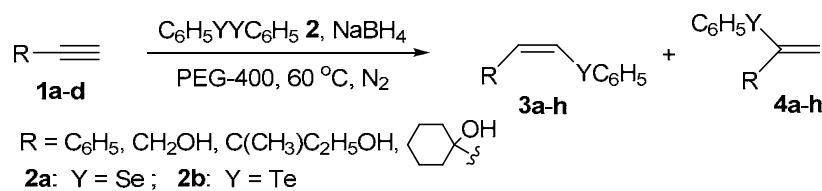
### Introduction

Alkenyl selenides and tellurides have been found to be very useful tools in organic synthesis, since they are very versatile intermediates for the selective construction of isolated or conjugated olefins,<sup>1</sup> such as the natural occurring montiporic acids A and B,<sup>2</sup> macrolactin A<sup>3</sup> and (-)-gymnodimine.<sup>4</sup> Besides, organoselenium and organotellurium compounds have attracted increased interest because of their unique biological and pharmacological properties.<sup>5</sup> In this way, various methods are mentioned for the preparation of alkenyl selenides and tellurides and the most common ones involve the addition of organo chalcogenols, or the respective chalcogenolate anions, to terminal or internal alkynes.<sup>1,6</sup> On the other hand, the development of environmentally benign and clean synthetic methods, including those involving solvent-free or the use of alternative solvents, such as water, ionic liquids and polyethylene glycol (PEG), has increased in recent years.<sup>7</sup> Despite several advantages, the solvent-free methods are restricted to systems where at least one of the reagents is liquid at room temperature, whereas the use of ionic liquids, especially imidazolium systems with PF<sub>6</sub> and BF<sub>4</sub> anions, have some drawbacks, such as the high cost and liberation of hazardous HF during recycling. Thus, the use of PEG and other alternative non-volatile solvents has been shown as an attractive way to cleaner organic synthesis. As a continuation of our studies toward the development of new and cleaner methods for the synthesis of alkenyl chalcogenides,<sup>8</sup> we report herein the results of the hydrochalcogenation of alkynes using NaBH<sub>4</sub>/PEG-400 (Scheme 1).

### Results and Discussion

Phenylacetylene **1a** and diphenyl diselenide **2a** were selected to establish the best conditions for the hydroselenation reaction. The amounts of PEG, NaBH<sub>4</sub>, the temperature and the use of N<sub>2</sub>

atmosphere were evaluated. The best condition involves stirring a mixture of **1a** (1 mmol), **2a** (0.5 mmol) and NaBH<sub>4</sub> (1.2 mmol) in PEG (1.0g) at 60 °C and under N<sub>2</sub> atmosphere for 30 min, affording, selectively, (*Z*)- $\beta$ -phenylselenostyrene **3a** in 85% yield (Table 1, entry 1). No increase in yields was observed using 2 equiv. of acetylene or a larger amount of PEG (2.0g). When the reaction was performed at room temperature, the yield of **3a** was only 50%. This protocol was extended to the reaction of alkynols **1b-d** with both diphenyl diselenide **2a** and diphenyl ditelluride **2b** (Scheme 1, Table 1). For the propargyl alcohols, a mixture of *anti*-Markovnikov **3** and Markovnikov adducts **4** was obtained in good yields, with predominance of the adduct (*Z*)-**3** (Scheme 1, Table 1, entries 2-4 and 6-8). It was observed that steric factors are important, because both the (**3**:**4**) ratio and the reaction time increase with the size of the group R (compare entries 2-4 and 6-8, Table 1). The formation of a mixture of isomers is described also for the methods which use volatile organic solvents.<sup>1c,6</sup> However, using this new PEG-based hydrochalcogenation protocol, the products are simply extracted with ether (5  $\times$  3 mL) and the PEG-400 is reused without significant loss in yields. Besides, the reaction time was significantly reduced compared to the classical methods under gently heating (60 °C)<sup>6c</sup> or under solvent-free conditions, with similar or improved yields.<sup>8a</sup> Thus, for example, under solvent-free conditions, **3c** and **4c**, were obtained in 65% yield after 48 hours by hydroselenation of alkynol **1c**,<sup>8a</sup> while using the new PEG-400 protocol, the same products were obtained in 80% yield after 1.5 h (Table 1, entry 3).



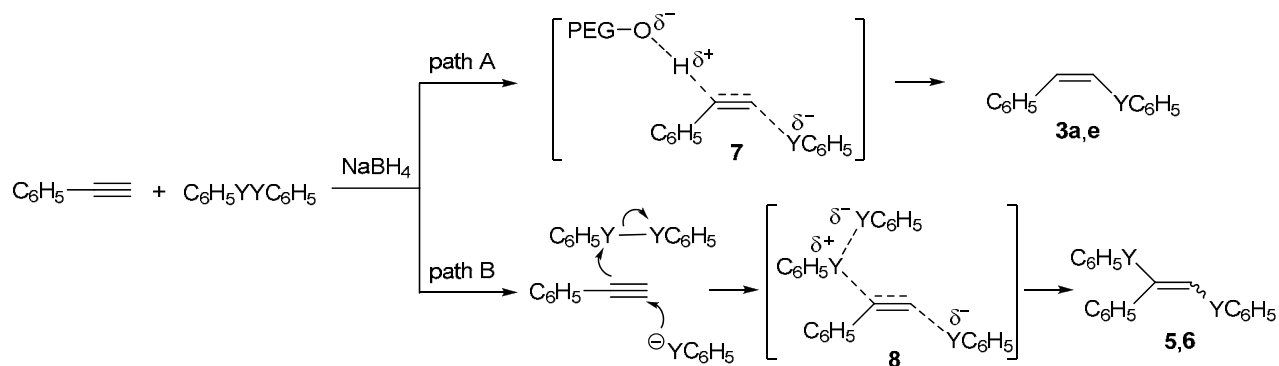
Scheme 1

The PEG-400 was reused up to 4 times without additional treatment, resulting in comparable yields and selectivity, simply by adding more reagents. Thus, for example, the hydroselenation of phenylacetylene **1a** was performed using pre-washed PEG-400 (after extraction with ether), giving (*Z*)-**3a** in 76, 73 and 71% yields, after the second, third and fourth cycles, respectively.

Because our interest in new uses for glycerin,<sup>9</sup> a renewable feed-stock easily available as a co-product in biodiesel production, we decide also to study the hydroselenation of phenylacetylene **1a** using this solvent. In contrast to the observed products when PEG-400 was the solvent, the formation of a mixture of (*E*)- and (*Z*)- 1,2-bis-phenylseleno styrenes **5a** and **6a** (Table 1, entry 9) occurred. The same result was obtained with diphenyl ditelluride **2b**, but in lower yield (Table 1, entry 10). When the alkynols **1b-d** were subjected to the hydrochalcogenation using glycerin alone as solvent, no alkenyl selenides were detected in all the tested conditions. However, when a 1:1 mixture of glycerin/PEG (1.0g) was used, the formation of alkenyl selenides was observed, although in modest yields. Thus, for example, diphenyl diselenide **2a** and alkynol **1c** reacted in presence of NaBH<sub>4</sub> to afford the desired products **3c** and **4c** in 58% yield after stirring for 2 hours.

A plausible mechanism for the reactions of phenyl acetylene with diphenyl dichalcogenides using PEG-400 or glycerin as solvent for formation of mono- and bis-phenylchalcogen alkenes respectively, is depicted on Scheme 2. When PEG-400 is used (path A) the mechanism is similar to the reaction using ethanol and the intermediate **7** could be involved in the formation of **3a** and **3e**.<sup>5c</sup> On the other hand, the formation of bis-phenylchalcogen alkenes **5** and **6** can be attributed probably

to the low solubility of the starting reagents in glycerin, which makes the reaction behavior like a solvent-free one, with formation of an intermediate analogous to **8** (Scheme 2, path B).<sup>8a</sup>



**Scheme 2**

**Table 1.** Hydrochalcogenation of alkynes using PEG-400 or glycerin as recyclable solvent

Entry	Alkyne <b>1</b>	Y <b>2</b>	Products <b>3 + 4 or 5 + 6</b>	Solvent	Time (h)	Yield <sup>a</sup> (%)	Ratio <sup>b</sup> <b>3:4 or 5:6</b>
1		Se		PEG	0.5	85	100 : 0
2		Se	 + 	PEG	1	50	79 : 21
3		Se	 + 	PEG	1.5	80	81 : 19
4		Se	 + 	PEG	2.5	65	86 : 14
5	<b>1a</b>	Te		PEG	1.5	83	100 : 0
6	<b>1b</b>	Te	 + 	PEG	1	95	73 : 27
7	<b>1c</b>	Te	 + 	PEG	2	70	97 : 03
8	<b>1d</b>	Te	 + 	PEG	3	60	94 : 06
9	<b>1a</b>	Se	 + 	Gly	1.0	75	77 : 23
10	<b>1a</b>	Te	 + 	Gly	3	45	82 : 18

<sup>a</sup>Yields of pure products isolated by column chromatography (hexanes/AcOEt). <sup>b</sup>Determined by GC of the crude reaction mixture and confirmed after isolation of the individual isomers.

## Conclusions

In conclusion, we have presented here a new methodology for the addition of nucleophilic species of selenium and tellurium to alkynyl alcohols and phenylacetylene, under mild conditions and with non-aqueous work-up. This improved, simple, fast and clean protocol uses recyclable PEG-400 or glycerin as solvent in addition to affording selectively mono- and bis-organochalcogenium alkenes.

## Experimental Section

**General Procedures.** The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{CDCl}_3$  solutions were recorded with a 200 MHz or a 400 MHz spectrometer (Bruker DPX), as noted. Chemical shifts are expressed as parts per million (ppm) downfield from tetramethylsilane as an internal standard. Low Resolution Mass Spectra (LRMS, EI) were obtained at 70 eV with a Hewlett Packard EM/CG HP-5988A spectrometer and elemental analyses were performed with a Perkin-Elmer CHN 2400 analyser.

### General procedure for the synthesis of alkenyl selenides and tellurides using PEG-400

To a pre-stirred mixture of alkynes **1** (1 mmol) and diphenyl dichalcogenide **2** (0.5 mmol) in PEG (1.0g) under  $\text{N}_2$  atmosphere,  $\text{NaBH}_4$  (0.046g; 1.2 mmol) was added at room temperature. Then, the temperature was slowly raised to 60  $^\circ\text{C}$  with stirring. The reaction progress was followed by TLC and after the time indicated in Table 1, the reaction mixture was extracted using ether (5 x 3 mL). The solvent was evaporated under reduced pressure and the residue was purified by column chromatography over silica gel eluting with hexanes or hexanes/ethyl acetate (99:1), yielding the products. The PEG was recovered and recycled without affecting the yields of the products. The spectral data are in perfect agreement with those reported in the literature and are listed below.

**(Z)-Phenyl(styryl)selane (3a).**<sup>6a,10a,b</sup> light yellow oil;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 6.77 (d,  $J = 10.2$ , 1H); 6.97 (d,  $J = 10.2$ , 1H); 7.20-7.35 (m, 4H); 7.36-7.40 (m, 4H); 7.54-7.60 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  137.0, 132.5, 131.4, 130.0, 129.2, 128.2, 128.1, 127.4, 127.2, 123.7. MS  $m/z$  (rel. int.) 260 ( $\text{M}^+$ , 5), 179 (52), 77 (100).

**(Z)-3-(Phenylselanyl)prop-2-en-1-ol (3b).**<sup>6d</sup> light yellow oil;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.43-7.54 (m, 2H); 7.22-7.27 (m, 3H); 6.58 (dt,  $J = 9.4$  and 1.4 Hz, 1H); 6.19 (dt,  $J = 9.4$  and 6.0 Hz, 1H); 4.24 (dd,  $J = 6.0$  and 1.0 Hz, 2H); 3.02 (broad s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  134.6, 132.6, 131.9, 129.3, 127.2, 122.9, 61.4. MS  $m/z$  (rel. int.) 214 ( $\text{M}^+$ , 46), 158 (89), 78 (100). 2-(Phenylselanyl)prop-2-en-1-ol (**4b**): light yellow oil;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.43-7.54 (m, 2H); 7.22-7.27 (m, 3H); 5.86 (s, 1H); 5.40 (s, 1H); 4.15 (s, 2H); 3.02 (broad s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  141.5, 133.9, 129.3, 128.3, 127.9, 118.3, 66.4. MS  $m/z$  (rel. int.) 214 ( $\text{M}^+$ , 49), 158 (31), 78 (100).

**(Z)-3-Methyl-1-(phenylselanyl)pent-1-en-3-ol (3c).**<sup>8b</sup> light yellow oil;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.51-7.54 (m, 2H); 7.25-7.28 (m, 3H); 6.47 (d,  $J = 10.0$  Hz, 1H); 5.93 (d,  $J = 10.0$  Hz, 1H); 2.05 (broad s, 1H); 1.66 (q,  $J = 7.6$  Hz, 2H); 1.36 (s, 3H); 0.96 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  135.6, 133.0, 132.5, 129.0, 127.1, 121.4, 75.5, 35.1, 27.3, 8.3. MS  $m/z$  (rel. int.) 256 ( $\text{M}^+$ , 43), 227 (100), 157 (65), 77 (82). 3-Methyl-2-(phenylselanyl)pent-1-en-3-ol (**4c**):<sup>8b</sup> light yellow oil;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.79-7.81 (m, 2H); 7.40-7.43 (m, 3H); 5.65 (s, 1H); 4.92 (s, 1H); 1.89 (broad s, 1H); 1.78 (q,  $J = 7.4$  Hz, 2H); 1.44 (s, 3H); 0.92 (t,  $J = 7.4$  Hz, 3H).

**(Z)-1-[2-(Phenylselanyl)vinyl]cyclohexanol (3d).** light yellow oil;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.52-7.57 (m, 2H); 7.26-7.31 (m, 3H); 6.47 (d,  $J = 9.8$ , 1H); 6.04 (d,  $J = 9.8$ , 1H); 1.51-1.68

(m, 10H); 1.83 (broad s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  136.3, 133.0, 132.6, 129.1, 127.2, 121.2, 73.9, 37.4, 25.3, 22.0. MS  $m/z$  (rel. int.) 282 ( $\text{M}^+$ , 59), 158 (23), 55 (100). Anal. Calcd. for  $\text{C}_{14}\text{H}_{18}\text{OSe}$ : C, 59.79; H, 6.45. Found: C, 59.85; H, 6.31. 1-[1-(Phenylselanyl)vinyl]cyclohexanol (**4d**):<sup>6i</sup> light yellow oil;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.52-7.57 (m, 2H); 7.26-7.31 (m, 3H); 5.75 (d,  $J = 1.0$ , 1H); 4.97 (d,  $J = 1.0$ , 1H); 1.51-1.68 (m, 10H); 1.82 (broad s, 1H). MS  $m/z$  (rel. int.) 282 ( $\text{M}^+$ , 55), 158 (17), 183 (100).

(**Z**)-Phenyl(styryl)tellane(**3e**).<sup>10a-c</sup> yellow oil;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.76-7.81 (m, 2H); 7.49 (d,  $J = 10.6$ , 1H); 7.22-7.45 (m, 8H); 7.10 (d,  $J = 10.6$ , 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  139.0, 138.0, 136.8, 129.4, 128.5, 128.1, 127.5, 127.3, 115.4, 109.3. MS  $m/z$  (rel. int.) 309 ( $\text{M}^+$  -1, 8), 181 (42), 77 (100).

(**Z**)-3-(Phenyltellanyl)prop-2-en-1-ol (**3f**).<sup>10d</sup> yellow oil;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.69-7.74 (m, 2H); 7.25-7.28 (m, 3H); 7.10 (dt,  $J = 9.8$  and 1.2 Hz, 1H); 6.50 (dt,  $J = 9.8$  and 6.0 Hz, 1H); 4.62 (dd,  $J = 5.8$  and 1.2 Hz, 2H); 2.01 (broad s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  139.0, 137.5, 137.0, 129.2, 127.6, 107.5, 64.2. MS  $m/z$  (rel. int.) 264 ( $\text{M}^+$ , 46), 207 (38), 77 (100). 2-(Phenyltellanyl)prop-2-en-1-ol (**4f**): yellow oil;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.74-7.79 (m, 2H); 7.25-7.28 (m, 3H); 6.25 (t,  $J = 1.2$  Hz, 1H); 5.68 (t,  $J = 1.2$  Hz, 1H); 4.72 (s, 2H); 2.04 (broad s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  139.0, 130.0, 129.4, 128.0, 123.5, 112.2, 69.3. MS  $m/z$  (rel. int.) 264 ( $\text{M}^+$ , 42), 207 (14), 77 (100).

(**Z**)-3-Methyl-1-(phenyltellanyl)pent-1-en-3-ol (**3g**).<sup>8a</sup> yellow oil;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.74-7.79 (m, 2H); 7.17-7.25 (m, 3H); 6.72 (d,  $J = 10.0$ , 1H); 6.37 (d,  $J = 10.0$ , 1H); 2.02 (broad s, 1H); 1.61 (q,  $J = 7.2$ , 2H); 1.30 (s, 3H); 0.95 (t,  $J = 7.2$ , 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  140.5, 140.0, 137.7, 129.0, 127.3, 105.2, 75.6, 34.7, 26.9, 8.0. MS  $m/z$  (rel. int.) 306 ( $\text{M}^+$ , 24), 199 (41), 77 (100). 3-Methyl-2-(phenyltellanyl)pent-1-en-3-ol (**4g**): yellow oil;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 5.89 (d,  $J = 1.4$ , 1H); 5.05 (d,  $J = 1.4$ , 1H); (Other peaks were overlapped with those of *Z*-isomer **3g**).

(**Z**)-1-[2-(Phenyltellanyl)vinyl]cyclohexanol (**3h**). yellow oil;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.74-7.79 (m, 2H); 7.16-7.28 (m, 3H); 6.69 (d,  $J = 9.9$ , 1H); 6.47 (d,  $J = 9.9$ , 1H); 1.25-1.67 (m, 10H); 1.87 (broad s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  140.9, 137.8, 129.0, 127.4, 118.8, 104.9, 74.4, 36.8, 25.2, 21.8. MS  $m/z$  (rel. int.) 332 ( $\text{M}^+$ , 31), 207 (15), 55 (100). Anal. Calcd. for  $\text{C}_{14}\text{H}_{18}\text{OTe}$ : C, 50.97; H, 5.50. Found: C, 50.99; H, 5.31. 1-[1-(Phenyltellanyl)vinyl]cyclohexanol (**4h**):<sup>10e</sup> yellow oil;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.79-7.81 (m, 2H); 7.28-7.39 (m, 3H); 5.99 (d,  $J = 1.4$ , 1H); 5.06 (d,  $J = 1.4$ , 1H); 1.93 (broad s, 1H); 1.25-1.67 (m, 10H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  146.0, 140.4, 129.4, 128.2, 117.9, 114.3, 76.2, 37.4, 25.5, 22.0. MS  $m/z$  (rel. int.) 332 ( $\text{M}^+$ , 32), 224 (100), 207 (12).

### General procedure for the synthesis of bis-organochalcogen alkenes **5** and **6** using glycerin

To a pre-stirred mixture of phenyl acetylene **1a** (0.102g; 1 mmol) and diphenyl dichalcogenide **2** (1 mmol) in glycerin (1.0g) under  $\text{N}_2$  atmosphere,  $\text{NaBH}_4$  (0.046g; 1.2 mmol) was added at room temperature. Then, the temperature was slowly raised to 60 °C with stirring. The reaction progress was followed by TLC and after the time indicated in Table 1, the reaction mixture was extracted and the products purified as described for the PEG procedure. The spectral data are in perfect agreement with those reported in the literature and are listed below.

(*E*)-1-[1-Phenyl-2-(phenylselanyl)vinylselanyl]benzene (**5a**).<sup>10f,g</sup> light yellow solid;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.36-7.48 (m, 6H); 7.10-7.29 (m, 9H); 7.07 (s, 1H). NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  139.5, 133.0, 132.1, 131.1, 130.6, 130.4, 129.2, 129.3, 128.6, 128.3, 128.4, 127.4, 127.3, 126.0. MS  $m/z$  (rel. int.) 416 ( $\text{M}^+$ , 13), 182 (64), 77 (100). (*Z*)-1-[1-Phenyl-2-(phenylselanyl)vinylselanyl]

benzene (**6a**):  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.60 (s, 1H); (other peaks were overlapped with those of *E*-isomer).

(*E*)-1-[1-Phenyl-2-(phenyltellanyl)vinyltellanyl]benzene (**5b**).<sup>10h</sup> yellow solid;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.73 (d,  $J = 6.8$ , 2H); 7.56 (d,  $J = 6.8$ , 2H); 7.37 (s, 1H); 7.17-7.33 (m, 11H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  144.6, 139.0, 137.6, 129.6, 129.4, 128.7, 128.3, 128.2, 127.9, 127.6, 120.9, 116.0, 115.7, 115.0. (*Z*)-1-[1-Phenyl-2-(phenyltellanyl)vinyltellanyl]benzene (**6b**):  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.36 (s, 1H); (other peaks were overlapped with those of *E*-isomer).

## Acknowledgements

This project is funded by CNPq, CAPES and FAPERGS.

## References

1. For the preparation and synthetic utility of vinyl selenides and tellurides see, for example: (a) Beletskaya, I.; Moberg, C. *Chem. Rev.* **2006**, *106*, 2320. (b) Zeni, G.; Lüdtke, D. S.; Panatieri, R. B.; Braga, A. L. *Chem. Rev.* **2006**, *106*, 1032. (c) Comasseto, J. V.; Ling, L. W.; Petragnani, N.; Stefani, H. A. *Synthesis* **1997**, 373. (d) Beletskaya, I. P.; Ananikov, V. P. *Eur. J. Org. Chem.* **2007**, 3431. (e) *Organoselenium Chemistry. A Practical Approach*; Back, T. G. Ed.; Oxford: New York, 2000. (f) *Organoselenium Chemistry - Modern Developments in Organic Synthesis*; Topics in Current Chemistry 208; Wirth, T. Ed.; Springer-Verlag: Heidelberg, 2000. (g) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S.; Rappoport, Z. Eds.; Wiley: New York, 1986; Vol. 1; 1987; Vol. 2. (h) Gusarova, N. K.; Chernysheva, N. A.; Yas'ko, S. V.; Kazantseva, T. I.; Ushakov, I. A.; Trofimov, B. A. *Synthesis* **2008**, 2743. (i) Trofimov, B. A.; Gusarova, N. K.; Malysheva, S. F.; Ivanova, N. I.; Sukhov, B. G.; Belogorlova, N. A.; Kuimov, V. A. *Synthesis* **2002**, 2207. (j) Perin, G.; Lenardão, E. J.; Jacob, R. G.; Panatieri, R. B. *Chem. Rev.* **2009**, *109*, 1277.
2. Zeni, G.; Panatieri, R. B.; Lissner, E.; Menezes, P. H.; Braga, A. L.; Stefani, H. A. *Org. Lett.* **2001**, *6*, 819.
3. Marino, J. P.; McClure, M. S.; Holub, D. P.; Comasseto, J. V.; Tucci, F. C. *J. Am. Chem. Soc.* **2002**, *124*, 1664.
4. Stewart, M.; Blunt, J. W.; Munro, M. H. G.; Robinson, W. T.; Hannah, D. J. *Tetrahedron Lett.* **1997**, *38*, 4889.
5. (a) Nogueira, C. W.; Zeni, G.; Rocha, J. B. T. *Chem. Rev.* **2004**, *104*, 6255. (b) Mugesh, G.; du Mont, W.-W.; Sies, H. *Chem. Rev.* **2001**, *101*, 2125.
6. (a) Wang, Z.; Tang, R.; Luo, P.; Deng, C.; Zhong, P.; Li, J. *Tetrahedron* **2008**, *64*, 10670. (b) Zeni, G.; Stracke, M. P.; Nogueira, C. W.; Braga, A. L.; Menezes, P. H.; Stefani, H. A. *Org. Lett.* **2004**, *6*, 1135. (c) Dabdoub, M. J.; Baroni, A. C. M.; Lenardão, E. J.; Gianeti, T. R.; Hurtado, G. R. *Tetrahedron* **2001**, *57*, 4271. (d) Barros, O. S. D.; Lang, E. S.; de Oliveira, C. A. F.; Peppe, C.; Zeni, G. *Tetrahedron Lett.* **2002**, *43*, 7921. (e) Comasseto, J. V. *J. Organomet. Chem.* **1983**, *253*, 131. (f) Dabdoub, M. J.; Cassol, T. M.; Batista, A. C. F. *Tetrahedron Lett.* **1996**, *37*, 9005. (g) Trofimov, B. A.; Amosova, S. V.; Gusarova, N. K.; Musorin, G. K. *Tetrahedron* **1982**, *38*, 713. (h) Trofimov, B. A.; Gusarova, N. K.; Tatarinova, A. A.; Potapov, V. A.; Sinegovskaya, L. M.; Amosova, S. V.; Voronkov, M. G. *Tetrahedron* **1988**, *44*, 6739. (i) Ananikov, V. P.; Malyshev, D. A.; Beletskaya, I. P.; Aleksandrov, G. G.; Eremenko, I. L. *J. Organomet. Chem.* **2003**, *679*, 162.

7. See, for instance: (a) Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. *Tetrahedron* **2005**, *61*, 1015. (b) Dupont, J.; Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667; (c) Dupont, J.; Consorti, C. S.; Spencer, J. J. *Braz. Chem. Soc.* **2000**, *11*, 337. (d) Consorti, C. S.; Souza, R. F.; Dupont, J.; Suarez, P. A. Z. *Quím. Nova* **2001**, *24*, 830. (e) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH Verlag: New York, 2002. (f) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. (g) Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772. (h) Davis Jr, J. H.; Fox, P. A. *Chem. Commun.* **2003**, 1209.
8. (a) Perin, G.; Jacob, R. G.; Dutra, L. G.; Azambuja, F.; Santos, G. F. F.; Lenardão, E. J. *Tetrahedron Lett.* **2006**, *47*, 935; (b) Lenardão, E. J.; Dutra, L. G.; Saraiva, M. T.; Jacob, R. G.; Perin, G. *Tetrahedron Lett.* **2007**, *48*, 8011. (c) Perin, G.; Jacob, R. G.; Azambuja, F.; Botteselle, G. V.; Siqueira, G. M.; Freitag, R. A.; Lenardão, E. J. *Tetrahedron Lett.* **2005**, *46*, 1679. (d) Perin, G.; Jacob, R. G.; Botteselle, G. V.; Kublik, E. L.; Lenardão, E. J.; Cella, R.; Santos, P. C. S. *J. Braz. Chem. Soc.* **2005**, *16*, 857. (e) Lenardão, E. J.; Silva, M. S.; Mendes, S. R.; Azambuja, F.; Jacob, R. G.; Santos, P. C. S.; Perin, G. *J. Braz. Chem. Soc.* **2007**, *18*, 943.
9. Lenardão, E. J.; Trecha, D. O.; Ferreira, P. C.; Jacob, R. G.; Perin, G.; *J. Braz. Chem. Soc.* **2009**, *20*, 93.
10. (a) Silveira, C. C.; Begnini, M. L.; Boeck, P.; Braga, A. L. *Synthesis* **1997**, 221. (b) Silveira, C. C.; Santos, P. C. S.; Mendes, S. R.; Braga, A. L. *J. Organomet. Chem.* **2008**, *693*, 3787. (c) Silveira, C. C.; Perin, G.; Braga, A. L.; Petragani, N. *Synlett* **1995**, 58; (d) Uemura, S.; Fukuzawa, S.; Patil, S. R. *J. Organomet. Chem.* **1983**, *243*, 9. (e) Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *J. Org. Chem.* **1987**, *52*, 4859. (f) Ananikov, V. P.; Beletskaya, I. P. *Russ. Chem. Bull., Int. Ed.* **2003**, *52*, 811. (g) Peppe, C.; Lang, E. S.; Ledesma, G. N.; Castro, L. B.; Barros, O. S. R.; Mello, P. A. *Synlett* **2005**, 3091. (h) Ogawa, A.; Yokoyama, K.; Obayashi, R.; Han, L.-B.; Kambe, N.; Sonoda, N. *Tetrahedron* **1993**, *49*, 1177.