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Short Report

Synthesis and Reactivity of α-Phenylseleno-β-substituted Styrenes. Preparation of (*Z*)-Allyl Alcohols, (*E*)-α-Phenyl-α,β-unsaturated Aldehydes and α-Aryl Acetophenones

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Foi desenvolvido um método simples e eficiente para a síntese de β-estirenos α-fenilseleno-substituídos, através da reação do α-(fenilselenobenzil)fosfonato de dietila e NaH na presença de aldeídos. A reação destes produtos com *n*-BuLi e posterior captura do ânion com aldeídos ou DMF levou à formação, exclusivamente, de álcoois de configuração *Z* e aldeídos α,β-insaturados de configuração *E*, respectivamente. Além disto, a hidrólise dos selenetos na presença de $TiCl_4$ levou à formação de α-arilacetofenonas em bons rendimentos.

A new and efficient method was developed to prepare α-phenylseleno-β-substituted styrenes by reaction of diethyl α-phenylseleno benzylphosphonate with NaH and aldehydes. Selenium-lithium exchange by reaction with *n*-BuLi yielded the vinyl lithium species, which were captured with several electrophiles, like aldehydes and DMF, affording exclusively (*Z*)-allyl alcohols, and (*E*)-α-phenyl-α-β-unsaturated aldehydes, respectively in good yields. The hydrolysis of the vinyl selenides in presence of $TiCl_4$ allowed the corresponding α-aryl acetophenones.

Keywords: Horner-Wittig reactions, vinyl selenides, transmetallation, α-β-unsaturated aldehydes, *Z*-allyl alcohols

Introduction

Organoselenium compounds constitute useful intermediates in organic synthesis and much attention has been devoted to their preparation and synthetic utilization.[1] Among the different classes of these compounds, vinyl selenides constitute a very useful intermediate, because of the versatile reactivity of the selanyl group and the presence of carbon-carbon double bond.[2] Considerable efforts have been directed to preparation of vinyl chalcogenides by the Wittig-type reaction, including the synthesis of vinyl selenides di- and trisubstituted by Wittig[3,4] and Horner-Wittig reaction.[5,6] An interesting aspect of this approach is the possibility to synthesize vinyl selenides with homologation of the carbon skeleton.[7]

To the best of our knowledge, the only methods reported for the preparation of α-phenylseleno-β-substituted styrenes involve the reaction of *Z*-α-(phenylseleno)vinyl *p*-toluensulfonates with $Ph_2Cu(CN)Li_2$ in presence of catalytic amounts of $Pd(PPh_3)_2Cl_2$ (only three examples)[8] and the hydroselenation of phenylacetylene using aluminum phenylselenolate anion (one example),[9] while the Wittig-type reaction have not been considered as a general synthetic strategy to date.

Recently, we have described practical and utile methodologies for the preparation of vinyl sulfides,[10] selenides,[10,11] tellurides,[10,12] ketene telluroacetals,[13,14] ketene (Te,S)-acetals[15] and α-phenyltelluro- and α-phenylseleno acrylonitriles[16] based on Wittig-type reactions. Due to our continuous interest on the synthesis and reactivity of new vinyl chalcogenides,[17] we report here the application of the Horner-Wittig reaction to the synthesis of α-phenylseleno-β-substituted styrenes **6** (Scheme 1, Table 1). The Se/Li exchange followed by capture of the intermediate vinyl lithium with electrophiles, and the hydrolysis of some obtained vinyl selenides are also described (Scheme 2, Table 2).

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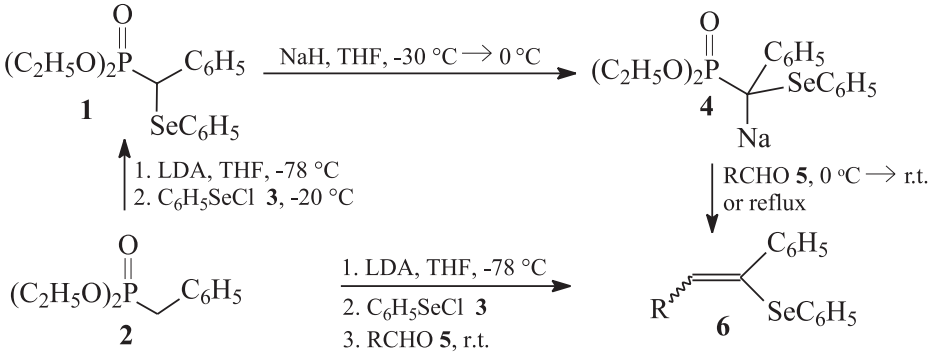
Results and Discussion

Phenylselenophosphonate **1** was selected as starting material for our new protocol to preparation of α-phenylseleno-β-substituted styrenes and **8** was obtained in good yield by the reaction of diethyl benzylphosphonate **2** with LDA, followed by addition of phenylselenenyl chloride **3** (Scheme 1).[5] The treatment of **1** with NaH would generated the intermediate anion **4** which, upon reaction with aldehydes **5**, afforded the desired product **6a**-**h**, as depicted in Scheme 1. When the reaction was performed using aromatic aldehydes (**5a**-**e**) and *n*-butyraldehyde (**5f**), the vinyl selenides **6a**-**e** and **6f** were obtained in moderate to good yields (entries 1-6, Table 1). However, with isobutyraldehyde (**5g**) and formaldehyde (**5h**), the yields obtained were lowers (entries 7-8, Table 1) and no reaction was observed with ketones (cyclohexanone, acetophenone and 3-pentanone). The lack of reactivity of ketones was previously reported when the Wittig reaction of selenophosphoranes with ketones was attempted.[24]

Alternatively, the vinyl selenides **6** can be obtained directly from **2**, by reaction with LDA, phenylselenyl chloride **3** and then with the carbonyl compound **5**, in a one-pot process (without isolation of intermediate **1**), as depicted in Scheme 1. However, it was observed that the reaction gave the product in a lower overall yield. For example, benzaldehyde **5a** reacts with 2 equiv. of phosphonate **2**, providing **6a** in 40% yield, while by using 1.0 equiv. of the phosphonate **2**, the yield drops down to 28%, compared to the 70% yield using 1.0 equiv. of the α-phenylselenophosphonate **1** (entry 1, Table 1).

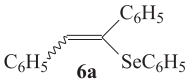
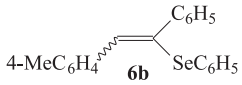
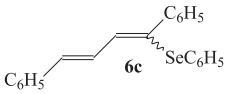
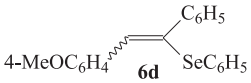
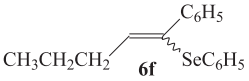
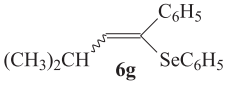
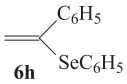
The method described here exhibits good generality and the yields are comparable with those described on literature,[8,9] being successful with several aromatic and aliphatic aldehydes, including cynamaldehyde **5c**. Moreover, the preparation of α-phenylseleno-β-substituted styrenes with chain elongation is not possible by using these methods, which obviously limits their application in organic synthesis. It is noteworthy that by our method it was also possible to prepare the simplest vinyl selenide **6h**, derived from formaldehyde, albeit in a modest 40% yield. Although most experiments were performed on a 1.0 mmol scale, these reactions can also be performed successfully on higher scale (up to 10 mmol) with comparable yields.

For all the substrates, the formation of a mixture of *Z* and *E* isomers was observed. The stereochemistry of the obtained olefins, **6b**-**d** and **6f**-**g,** was assigned by ^{1}H NMR. For example, for 1-phenyl-1-(phenylseleno)-1-pentene (**6f**), two triplets for the vinylic hydrogens, at δ 6.32 (*Z* isomer) and 6.13 (*E* isomer), with *J* 7.2 Hz, were observed, in a 73:27 ratio. Likewise, for 1-phenyl-1-(phenylseleno)-2-isopropylethene (**6g**), two doublets (*J* 10.0 Hz) were observed at δ 6.12 (*Z* isomer) and 5.96 (*E* isomer) in a 63:37 ratio. However, for **6a** and **6e** this ratio could not be determined directly by ^{1}H NMR, because the vinylic hydrogen signals overlapped with the aromatic one. Besides, the products were also not stable enough to perform GC analysis, even using different columns and conditions. To confirm the formation of the products as a *Z* + *E* mixture, a ^{77}Se NMR study was performed with **6a** as a selected example. The presence of isomers could be easily confirmed since two peaks were observed in the ^{77}Se NMR spectra at δ 400.2 and 522.4 ppm (60.5 MHz) in a 67:33 ratio. These results where also confirmed by the analysis of their ^{13}C NMR spectra and are comparable with results previously described.[15,16] The isomeric ratio of **6e** was determined by analogy with **6a**, based on the assumption of that the *Z*-isomer was also formed preferentially, according to the analysis of its ^{13}C NMR.



Scheme 1.

Table 1. Synthesis of α-phenylseleno-β-substituted styrenes **6** according to Scheme 1

Entry	R	Product **6**	Reaction time / (h)	Reaction Temp.	Yield[a] / (%)	Ratio (*Z* : *E*)
1	C_6H_5 **5a**	 **6a**	2	r.t.	70	67 : 33
2	4-MeC_6H_4 **5b**	 **6b**	2	r.t.	58	63 : 37
3	C_6H_5CH=CH **5c**	 **6c**	2	r.t.	67	80 : 20
4	4-MeOC_6H_4 **5d**	 **6d**	2	r.t.	83	86 : 14
5	4-ClC_6H_4 **5e**	 **6e**	2	r.t.	70	60 : 40
6	$CH_3CH_2CH_2$ **5f**	 **6f**	1.5	reflux	60	73 : 27
7	$(CH_3)_2CH$ **5g**	 **6g**	1.5	reflux	46	63 : 37
8	H **5h**	 **6h**	1.5	reflux	40	–

[a]Yields in pure products isolated by chromatography (hexanes) and identified by mass spectra, ^{1}H and ^{13}C NMR.

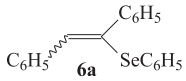
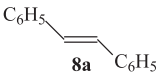
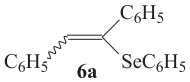
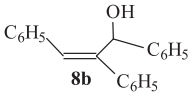
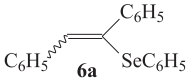
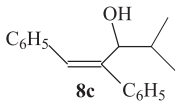
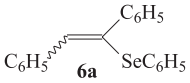
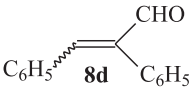
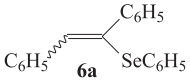
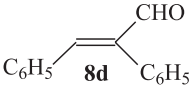
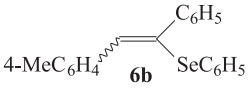
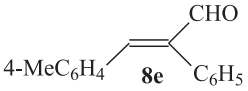
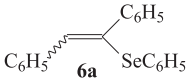
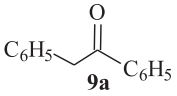
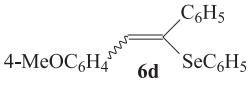
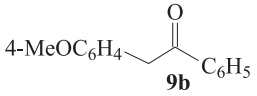
Selective Se/Li exchange and hydrolysis reaction of the vinyl selenides

The selenium moiety can be easily and selectively removed from vinyl selenides by treatment with different reagents.[2] For example, they can be coupled with Grignard reagents[2,25] or organozinc halides[26] by Ni-catalysis, and transmetallated with organyl lithium species.[27] In the present work we decided to study the selective removal of the Se moiety from α-phenyl vinyl selenides **6**. For this purpose, we treated some of the prepared products with *n*-BuLi at -78 °C and captured the intermediate vinyllithium with several electrophiles (Scheme 2).

The lithium-selenium exchange reaction on **6a** (67:33; *Z*:*E* ratio) with *n*-BuLi, followed by treatment with aqueous ammonium chloride furnished exclusively *E*-1,2-diphenylethene **8a** in 70% yield, as detected by the ^{1}H NMR (200 MHz) analysis of their vinylic hydrogens (δ 7.08 ppm, singlet, 2H). In addition to **8a**, $C_6H_5SeC_4H_9$ and $C_6H_5C{\equiv}CC_6H_5$ (by-product of *n*-BuLi acting as base by removing the vinylic hydrogen of **6a**) were isolated. The formation of **8a** (*E*-isomer) and $C_6H_5C{\equiv}CC_6H_5$ are an indication that the α-phenyllithium anion suffers fast isomerization to the most stable one. The intermediate **7** was also converted to the corresponding allyl alcohols **8b** and **8c** by reaction with benzaldehyde and isobutyraldehyde, respectively. The products were obtained in 61% (**8b**) and 65% (**8c**) yield, and exclusively with *Z*-configuration (entries 2 and 3, Table 2).

By changing the electrophile by DMF, **6a** was converted to *E*-2,3-diphenyl-2-propenal (**8d**) in 63% yield (entry 4, Table 2). In this reaction, DMF was added at –78 °C and the stirring was continued at this temperature for 1 hour. It was observed the formation of a mixture of *E* and *Z* isomers in a 71:29 ratio. The products were easily separable by column chromatography and the more polar

Table 2. Products from the Se/Li exchange reaction and hydrolysis on vinyl selenides **6**

Entry	Vinyl Selenide **6**	Electrophile	Product **8** or **9**	Yield[a] / (%)	Ratio (*E* : *Z*)
1	 **6a**	H_2O	 **8a**	70	100 : 0
2	 **6a**	C_6H_5CHO	 **8b**	61	0 : 100
3	 **6a**	$(CH_3)_2CHCHO$	 **8c**	65	0 : 100
4	 **6a**	DMF	 **8d**	63	71 : 29
5	 **6a**	DMF	 **8d**	55	100 : 0
6	 **6b**	DMF	 **8e**	68	100 : 0
7	 **6a**	–	 **9a**	73	–
8	 **6d**	–	 **9b**	65	–

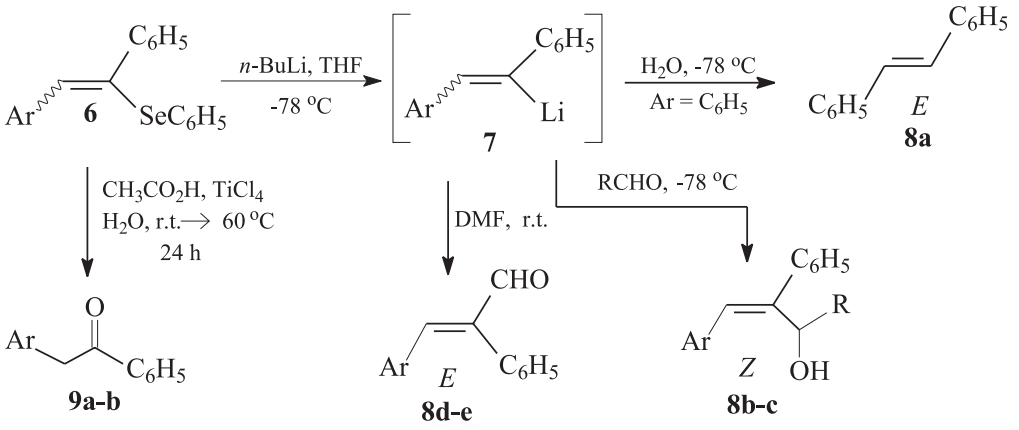
[a]Yields in pure products isolated by chromatography (AcOEt/hexanes) and identified by mass spectra, ^1H and ^{13}C NMR.

showed the *Z*-configuration by NOESY NMR (400 MHz). However, a very interesting feature was the fact that, warming up the solution slowly to room temperature and stirring to this temperature for 2h, followed by aqueous quenching, it was observed that, regardless of the geometry **6a**, the product exhibited exclusively the most stable *E*-configuration, as confirmed by NOESY NMR (entry 5, Table 2). The presence of only one isomer was confirmed by analysis of the ^{13}C NMR spectra, where single peaks for all individual carbons were observed. The same behavior was observed when a *Z*+*E* mixture of 1-phenyl-1-(phenylseleno)-2-(4-methylphenyl) ethene (**6b**) in a 63:37 ratio was used in the Se/Li exchange. By using the same procedure described above (2h at r.t.), *E*-2-phenyl-3-(4-methylphenyl)-2-propenal (**8e**) was obtained exclusively in 68% yield (entry 6, Table 2). In this way, even starting from a *Z*+*E* mixture of vinyl selenides, only the most stable *E* olefin was formed under the reaction conditions.

The synthesis of ketones by the hydrolysis of vinyl selenides in presence of trifluoracetic acid, Lewis acid and $HgCl_2$ is well documented.[1,2] However, to our knowledge no method was described for the preparation of aromatic ketones from vinyl selenides.

In the present work, we decided to study the hydrolysis[4] of some vinyl selenides prepared. The reaction of the vinyl selenide **6a** with $TiCl_4$ (2 mmol) in acetic acid, furnished the corresponding aromatic ketone **9a** in 73% yield, as depicted in Scheme 2 (entry 7, Table 2). The same reaction starting from **6d** gave the corresponding ketone **9b** in 65% yield (entry 8, Table 2). However, when **6a** was treated with $HgCl_2$ or $K_{10}/Fe(NO_3)_3$ did not react at all and the use of CF_3CO_2H furnished the product, albeit in low yield (30%).

In conclusion, we have developed a new and simple methodology for the synthesis of α-phenylseleno-β-substituted styrenes **6**. The prepared vinyl selenides were shown useful as precursors of functionalized trisubstituted olefins with high stereoselectivity affording exclusively *Z*-



Scheme 2.

allyl alcohols and *E*-α-phenyl-α,β-unsaturated aldehydes. We have also described the first synthesis of α-aryl acetophenones via acid hydrolysis of vinyl selenides.

Experimental

General

^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded with a 200 MHz, 300 MHz or a 400 MHz spectrometer as noted. Chemical shifts are expressed as parts *per* million (ppm) downfield from tetramethyl silane as an internal standard. For the ^{77}Se NMR analysis $(C_6H_5Se)_2$-$CDCl_3$ (δ 463.0 ppm) was used as external reference. Mass spectra (EI) were obtained at 70 eV with a Hewlett Packard EM/CG HP-5988A spectrometer, infra-red spectra were acquired on a Perkin-Elmer 1310 Spectrometer and elemental analyses were performed with a Vario EL Elementar Analysis System. Merck's silica gel (230-400 mesh) was used for flash chromatography. THF was distilled over sodium/benzophenone immediately before use.

Procedure for the synthesis of α*-phenylseleno benzylphosphonate (**1**)*

To a solution of LDA (10 mmol) in THF (10 mL) at -78 °C under nitrogen was added dropwise a solution of phosphonate **2** (1.140 g; 5 mmol) in THF (5 mL). After stirring for 20 min at this temperature, a solution of C_6H_5SeCl (0.960 g; 5 mmol) in THF (6 mL) was added. The temperature was raised to -20 °C and stirring was continued for 30 minutes; then, ethyl acetate (30 mL) was added and the mixture washed with water (3 × 20 mL). The organic layer was separated and dried with $MgSO_4$ and the solvent removed under vacuum. The residue was purified by column chromatography (SiO_2) using hexanes/ethyl acetate (50:50) to afford **1**, as a light yellow oil. Yield: 1.440g (75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (t, *J* 7.0 Hz, 3H), 1.26 (t, *J* 7.0 Hz, 3H), 3.75-4.00 (m, 2H), 4.12 (q, *J* 7.7 Hz, 2H), 4.27 (d, *J* 18.0 Hz, 1H), 7.13-7.26 (m, 6H), 7.32 (d, *J* 7.7 Hz, 2H), 7.42 (d, *J* 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.3, 16.4, 42.8 (d, *J* 147.7 Hz), 63.2, 63.3, 127.6, 128.3, 128.5, 129.0, 129.4, 129.5, 134.9, 136.3. MS *m/z* (rel. int.) 384 (M^+ + 1, 8.8), 227 (13.4), 157 (7.0), 91 (56.6), 77 (100.0).

General procedure for the synthesis of α*-phenylseleno-*β*-organyl styrenes (**6a-h**)*

To a solution of NaH (0.049g, 2.0 mmol) in THF (5 mL) at -30 °C under nitrogen was added, dropwise, a solution of selenophosphonate **1** (0.383g, 1 mmol) in THF (3 mL). The temperature was raised to 0 °C under stirring (30 minutes). Then, the aldehyde (1.1 mmol) was added and the stirring continued for 2 hours at room temperature or 1.5 hour at reflux temperature (see Table 1). The reaction mixture was treated with water (20 mL) and extracted with ethyl acetate (3 × 25 mL). The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure. The residue was purified by column chromatography (SiO_2) using hexanes as eluent. Spectral data of **6a-h** are listed below.

*(Z+E)-1-Phenyl-1-(phenylseleno)-2-phenylethene (**6a**).*[8] The aforementioned procedure was used, employing benzaldehyde, **5a**. Yield: 0.235g (70%); *Z*:*E* ratio = 67:33. *Z + E isomers*: ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.81-7.40 (m, 12H), 7.48-7.61 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 126.6, 126.8, 127.6, 127.7, 127.8, 127.9, 127.95, 128.0, 128.4, 128.6(3C), 128.8, 129.1, 129.2, 129.3, 129.6, 130.4, 131.1, 132.4, 134.6, 134.7, 135.0, 135.7, 136.8, 137.6, 139.4, 142.0. MS *m/z* (rel. int.) 336 (M^+, 9.1), 178 (45.9), 28 (100.0). Anal. Calc. for $C_{20}H_{16}Se$: C, 71.64; H, 4.81. Found: C, 71.77; H, 5.00.

(Z+E)-1-Phenyl-1-(phenylseleno)-2-(4-methylphenyl) ethene (***6b***). The aforementioned procedure was used, employing 4-methylbenzaldehyde, **5b**. Yield: 0.203g (58%); *Z*:*E* ratio = 63:37. *Z* + *E isomers*: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.19 (*E*) and 2.33 (*Z*) (2s, 3H), 6.83-6.97 (m, 2H), 7.00-7.04 (m, 2H), 7.13-7.24 (m, 7H), 7.48-7.52 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.1, 21.3, 126.4, 127.4, 127.6, 127.7, 127.9, 128.3, 128.6(2C), 128.7(3C), 129.0, 129.2, 129.3, 129.8, 130.6, 131.7, 132.2, 133.5, 133.9, 134.2, 134.4, 134.7, 135.2, 136.7, 137.5, 139.6, 142.2. MS *m*/*z* (rel. int.) 350 (M^+, 5.0), 193 (15.8), 178 (13.2), 28 (100.0).

(Z+E)-1-Phenyl-1-(phenylseleno)-4-phenyl-1,3-butadiene (***6c***). The aforementioned procedure was used, employing cinnamaldehyde, **5c**. Yield: 0.243g (67%); *Z*:*E* ratio = 80:20. *Z* + *E isomers*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (*E*) (d, *J* 15.4 Hz, 0.2H), 6.65 (*E*) (d, *J* 11.0 Hz, 0.2H), 6.78 (*E*) (dd, *J* 15.4 and 11.0 Hz, 0.2H), 6.76 (*Z*) (d, *J* 15.6 Hz, 0.8H), 7.55 (*Z*) (dd, *J* 15.6 and 10.5 Hz, 0.8H), 7.00-7.62 (*Z* + *E*) (m, 15H + 0.8H vinylic Z); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.5, 126.2, 126.4, 126.7, 127.5, 127.6, 127.8, 127.9, 128.0, 128.1, 128.2, 128.5, 128.6,128.7, 129.0, 129.1, 129.7, 130.7, 130.75, 131.4, 132.4, 133.1, 134.1, 134.2, 136.0, 136.8, 137.0, 141.2. MS *m*/*z* (rel. int.) 205 (M^+ -C_6H_5Se, 1.4) 77 (1.5), 28 (100.0). Anal. Calc. for $C_{22}H_{18}Se$: C, 73.13; H, 5.02. Found: C, 73.57; H, 5.03.

(Z+E)-1-Phenyl-1-(phenylseleno)-2-(4-metoxyphenyl) ethene (***6d***).[18] The aforementioned procedure was used, employing 4-methoxybenzaldehyde, **5d**. Yield: 0.304g (83%); *Z*:*E* ratio = 86:14. *Z* + *E isomers*: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.60 (*E*) and 3.71 (*Z*) (2s, 3H), 6.59-7.60 (m, 15H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 54.9, 55.1, 113.4, 114.0, 126.2, 126.3, 126.5, 127.1, 127.3, 127.5, 127.6, 127.9, 128.1, 128.3, 128.4, 128.5, 128.6, 128.9, 129.3, 130.0, 130.1, 130.7, 131.8, 131.9, 134.1, 135.2, 137.5, 142.4, 159.1, 159.2. MS *m*/*z* (rel. int.) 366 (M^+, 6.5) 209 (19.1), 28 (100.0).

(Z+E)-1-Phenyl-1-(phenylseleno)-2-(4-chlorophenyl) ethene (***6e***). The aforementioned procedure was used, employing 4-chlorobenzaldehyde, **5e**. Yield: 0.259g (70%); *Z*:*E* ratio = 60:40. *Z* + *E isomers*: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.00-7.33 (m, 11H), 7.48-7.54 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 126.6, 126.7, 127.7, 127.9, 128.0, 128.1, 128.2, 128.4, 128.5, 128.7, 129.0, 129.1, 129.9, 130.1, 130.5, 130.9, 132.2, 133.1, 133.5, 134.8, 135.0, 135.2, 135.5, 135.9, 137.0, 138.9, 141.7, 146.6. MS *m*/*z* (rel. int.) 370 (M^+, 6.2) 213 (16.3), 178 (24.0) 28 (100.0). Anal. Calc. for $C_{20}H_{15}ClSe$: C, 64.97; H, 4.09. Found: C, 64.95; H, 4.18.

(Z+E)-1-Phenyl-1-(phenylseleno)-1-pentene (***6f***). The aforementioned procedure was used, employing butyraldehyde, **5f**. Yield: 0.181g (60%); *Z*:*E* ratio = 73:27. *Z* + *E isomers*: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.84 (*E*) and 0.97 (*Z*) (2t, *J* 7.2 Hz, 3H), 1.38 (*E*) and 1.52 (*Z*) (2 sext, *J* 7.2 Hz, 2H), 2.05 (*E*) and 2.48 (*Z*) (2q, *J* 7.2 Hz, 2H), 6.13 (*E*) (t, *J* 7.2 Hz, 0.28H; vinylic), 6.32 (*Z*) (t, *J* 7.2 Hz, 0.72H; vinylic), (*Z* + *E*) 7.00-7.62 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.6, 13.8, 22.5, 22.7, 32.6, 35.1, 126.0, 127.0, 127.2, 127.6, 127.8, 127.9, 128.1, 128.8, 128.9, 129.1, 129.2, 130.9, 131.1, 131.3, 131.5, 132.8, 133.2, 137.1, 139.6, 141.9. MS *m*/*z* (rel. int.) 302 (M^+, 26.8), 145 (56.7), 91 (100.0), 77 (35.7). Anal. Calc. for $C_{17}H_{18}Se$: C, 67.77; H, 6.02. Found: C, 67.54; H, 5.95.

(Z+E)-1-Phenyl-1-(phenylseleno)-2-isopropylethene (***6g***). The aforementioned procedure was used, employing isobutyraldehyde, **5g**. Yield: 0.139g (46%); *Z*:*E* ratio = 63:37. *Z* + *E isomers*: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (*E*) and 1.08 (*Z*) (2d, *J* 6.6 Hz, 6H), 2.30-2.57 (*E*) and 3.00-3.25 (*Z*) (2m, 1H), 5.96 (*E*) (d, *J* 10.0 Hz, 0.37H; vinylic), 6.12 (*Z*) (d, *J* 10.0 Hz, 0.63H; vinylic), (*Z* + *E*) 7.04-7.60 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.6(2C), 22.9(2C), 29.8, 32.6, 126.0, 127.0, 127.1, 127.2, 127.8, 127.9, 128.1, 128.8, 128.9, 130.0, 130.9, 131.4, 133.1, 139.8, 141.7, 144.3, 146.7. MS *m*/*z* (rel. int.) 302 (M^+, 26.9), 145 (100.0), 117 (47.3), 91 (32.8). Anal. Calc. for $C_{17}H_{18}Se$: C, 67.77; H, 6.02. Found: C, 67.45; H, 5.98.

1-Phenyl-1-phenylselenoethene (***6h***).[9] The aforementioned procedure was used, employing formaldehyde, **5h**. Yield: 0.104g (40%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.37 (s, 1H), 5.88 (s, 1H), 7.17-7.35 (m, 6H), 7.47-7.62 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 117.8, 127.3, 127.6, 128.3, 128.5, 128.6, 129.1, 134.1, 140.0, 141.9. MS *m*/*z* (rel. int.) 178 (M^+ -3, -Se, 2.4), 157 (2.0), 105 (8.8), 77 (7.6), 28 (100.0).

General procedure for the Se/Li exchange preparation of ***8a-e***

To a solution of **6** (1 mmol) in THF (4 mL) at -78 °C under nitrogen was added, dropwise, a solution of *n*-BuLi (0.71 mL, 1.1 mmol, 1.54 mol L^{-1} solution in hexanes). After 20 minutes of stirring at this temperature, the electrophile (1.5 mmol) was added. The mixture was stirred for 1h at -78 °C, then diluted with ethyl acetate

(30 mL) and washed with water (3 × 20 mL). The organic layer was separated and dried with $MgSO_4$ and the solvent removed under reduced pressure. The residue was purified by column chromatography over silica gel using hexanes (for **8a**) or a mixture of hexanes/ethyl acetate (for **8b**-**e**) as eluent.

*Trans-stilbene (**8a**).*[19] The same procedure as above was followed using **6a** and water (0.5 mL) as electrophile. Yield: 0.126g (70%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.08 (s, 2H), 7.13-7.36 (m, 6H), 7.46-7.50 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 126.3, 126.5, 127.6, 128.6, 137.3.

*E-1,2,3-Triphenyl-2-propen-1-ol (**8b**).*[20] The same procedure as above was followed using **6a** and benzaldehyde, **5a** (0.159g, 1.5mmol) as electrophile. Yield: 0.175g (61%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.19 (br s, 1H), 6.16 (s, 1H); 6.99 (s, 1H), 7.20-7.43 (m, 15H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 71.1, 126.0, 127.0, 127.3, 127.4, 128.0, 128.2, 128.3, 128.4, 128.7, 131.8, 136.6, 139.3, 142.3, 142.6.

*E-1-Isopropyl-2,3-diphenyl-2-propen-1-ol (**8c**).*[20] The same procedure as above was followed using **6a** and isobutyraldehyde, **5g** (0.108g, 1.5mmol) as electrophile. Yield: 0.164g (65%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.68 (d, *J* 6.8 Hz, 3H), 0.96 (d, *J* 6.6 Hz, 3H), 1.60-1.90 (m, 1H), 2.00 (br s, 1H); 4.42 (d, *J* 10.0 Hz, 1H), 6.79 (s, 1H), 7.28-7.36 (m, 8H), 7.60-7.65 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.9, 19.2, 31.6, 76.1, 126.9, 127.1, 127.9, 128.2, 128.5, 128.9, 133.2, 137.1, 141.0, 143.8.

*(Z + E)-2,3-Diphenyl-2-propenal (**8d**).*[21] The same procedure as above was followed using **6a** and DMF (0.1mL, 1.29 mmol) as electrophile. Yield: 0.131g (63%). *Z isomer*: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.38-7.44 (m, 10H), 7.86 (s, 1H), 10.1 (s, 1H); *Z + E isomer*: ^{13}C NMR (50 MHz, $CDCl_3$) δ 128.2, 128.4, 128.8, 129.3, 130.1, 130.7, 133.3, 134.0, 141.7, 150.0, 193.7.

*E-2,3-Diphenyl-2-propenal (**8d**).*[21] The same procedure as above was followed. However, the reaction was stirred at -78 °C for 20 min and was allowed to reach room temperature (20 min) and stirred for additional 2 h at this temperature. Yield: 0.114g (55%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.16-7.26 (m, 7H), 7.35-7.41 (m, 4H), 9.76 (s, 1H).

*E-2-Phenyl-3-(4-methylphenyl)-2-propenal (**8e**).*[22] The same procedure as above was followed using **6b**. Yield: 0.151g (68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.30 (s, 3H), 7.02-7.11 (m, 4H), 7.17-7.20 (m, 2H), 7.35-7.44 (m, 4H), 9.74 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 128.2, 128.8, 129.3, 130.8, 131.3, 133.6, 140.9, 141.0, 150.4, 193.9.

*General procedure for hydrolysis of vinyl selenides **6a** and **6d**. Preparation of **9a** and **9b***

To a two-necked 25 mL round-bottomed flask under atmosphere of nitrogen containing acetic acid (5 mL), $TiCl_4$ (0.22 mL, 2 mmol) was added. After stirring the mixture for 5 minutes at room temperature, a solution of vinyl selenide (1mmol) in acetic acid (10 mL) was added. The reaction was stirred at this temperature for 20 minutes, then water (4.0 mL) was added and the stirring continued for 4 h at room temperature and for 16 h at 60 °C. The reaction mixture was treated with water and extracted with ethyl acetate (3 × 20 mL). The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure. The residue was purified by column chromatography using hexanes/ethyl acetate (98:2) as eluent.

*2-Phenylacetophenone (**9a**).*[23] Yield: 0.143g (73%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.06 (s, 2H), 6.90-7.15 (m, 5H), 7.10-7.36 (m, 3H), 7.77-7.81 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 45.5, 126.9, 128.6, 128.7, 129.4, 133.1, 134.5, 136.6, 197.6. IR (KBr) ν_{max}/cm^{-1}: 1684 (CO).

*2-(4-Methoxyphenyl)acetophenone (**9b**).*[23] Yield: 0.147g (65%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.74 (s, 3H), 4.10 (s, 2H), 6.72-6.77 (m, 2H), 7.06-7.11 (m, 2H), 7.34-7.46 (m, 3H), 7.90-7.94 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 46.8, 51.4, 125.9, 128.1, 128.3, 129.1, 129.5, 133.5, 134.8, 135.6, 198.5. IR (KBr) ν_{max}/cm^{-1}: 1575 (CO).

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