RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

ARTICLE

Stereoselective Synthesis of Alkyl Styryl Selenides in One-Pot: A Straightforward Approach by *in situ* Dialkyl Diselenide Formation under Transition Metal-Free Conditions

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Adrián A. Heredia[a] and Alicia B. Peñéñory[a*]

A simple procedure for the synthesis of alkyl styryl selenides was developed. This methodology involves the *in situ* generation of selenolate anions by a one-pot and three-step protocol where a nucleophilic substitution between KSeCN and alkyl halides affords the corresponding alkyl selenocyanate in the first step, giving dialkyl diselenide by a further K_3PO_4-assisted reaction. Subsequent reduction yields the alkyl selenolate anions which react with substituted (*E,Z*)-β-styryl halides to afford the corresponding vinyl selenides with retention of stereochemistry and from moderate to excellent yields. This procedure does not require catalyst, proceeds under air atmosphere and within short reaction time, and is free from diselenide and malodorous and air-sensitive alkyl selenols as starting materials.

Introduction

Selenium containing compounds have attracted considerable attention due to their versatility in organic synthetic procedures and their potential biological activities.[1] Among them, vinyl selenides are important synthetic intermediates in organic chemistry.[2,3] In these molecules, it is possible to combine known reactions of organoselenium compounds with the ability to form new C-C bonds involving the double bond of the vinyl selenides, since the selenium atom is able to stabilize both negative and positive charges. Due to the relevance of vinyl selenides, numerous synthetic methods have been reported for their synthesis such as Wittig-type reactions,[4] addition of nucleophilic and electrophilic selenium reagents to alkynes[5] and allenes,[6] use of acetylenic selenides and direct substitution of a halogen atom on the double bond by selenolate anions.[2,3,7] In many cases, the yield and stereoselectivity of the reactions are controlled by the use of transition-metal complexes such as Pd,[8] Cu,[9] Rh,[10] La[11] and Ni[12] among others.[13] Nevertheless, the requirement of specific ligands and the air sensitivity of some catalytic systems involve a common limitation to their industrial and large-scale application. Some few examples of the preparation of vinyl selenides from diaryldiselenide without using transition-metal catalyst have also been reported.[5a,14] However, this last methodology is restricted to the commercial and synthetic availability of diaryldiselenide reagent.

Recently we have reported a simple methodology for the stereoselective synthesis of alkyl styryl sulfides by a one-pot base-assisted procedure without transition metals. This reaction proceeds under mild conditions at short times, and is free from malodorous and air-sensitive alkyl thiols.[15]

Considering these previous results, we envisage the possibility of extending the methodology above described to the synthesis of alkyl styryl selenides, using potassium selenocyanate (KSeCN, **1**) as a selenium source. As in the case of KSCOMe, KSeCN, it is easy to handle, commercially available and widely used as a selenium source for the synthesis of organic seleno- and isoselenocyanates, whose moderated reactivity allows easy interconversion to other interesting functional groups.[16] We now report a simple and convenient synthetic procedure for the preparation of alkyl arylvinyl selenides, by employing KSeCN.

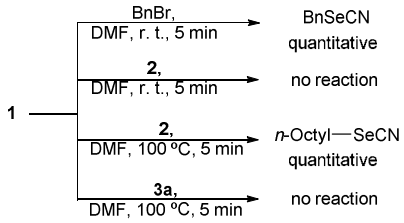
Results and discussion

First, we explored the reactivity of KSeCN (**1**) towards different organic halides, in DMF as a solvent (Scheme 1). After 5 min at room temperature, salt **1** reacted with benzyl bromide affording exclusively the substitution product benzyl selenocyanate. On the other hand, its reactivity was moderate towards primary alkyl halides, such as *n*-octyl bromide (**2**). Thus, there was no reaction at room temperature after 5 min, while the yield of *n*-octylselenocyanate was quantitative at 100 °C. Finally, (*E*)-β-bromostyrene (**3a**) did not react with **1** after 2 h at 100 °C.

[a] INFIQC, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, X5000HUA Córdoba, Argentina,* penenory@fcq.unc.edu.ar.

† Footnotes relating to the title and/or authors should appear here.

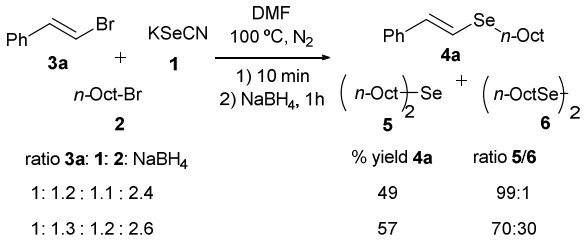
Electronic Supplementary Information (ESI) available: Spectra(^{1}H, ^{13}C and ^{77}Se NMR) for all the products (**4a-l** and **Z4a**).See DOI: 10.1039/x0xx00000x



Scheme 1. Reactivity of KSeCN (**1**)

These results suggest the possibility of generating the benzyl or alkylselenolate anion (RSe^-) from the corresponding organic selenocyanate in the presence of styryl bromide. Furthermore, these selenolate anions could react towards vinyl halides, such as alkane thiolate analogues,[15] giving the corresponding alkyl vinyl selenides in a one-pot procedure. We selected *n*-octyl bromide (**2**) as an alkylating reagent, (*E*)-β-bromostyrene (**3a**) as a model substrate, and the polar DMF as a solvent to start this study.

The organic selenocyanates (RSeCN) can be reduced to the corresponding RSe^- anions, $NaBH_4$ being one of the reagents more frequently used for this purpose.[17] With the aim of generating selenolate anions, we performed the reaction in the presence of this reduction reagent. Thus, a mixture of **1**, **2** and **3a** was allowed to react at 100 °C for 10 min in DMF as a solvent, in order to assure that the S_N2 reaction between **1** and **2** was completed. After that time, $NaBH_4$ was added and the reaction mixture was heated at 100 °C for one hour under nitrogen atmosphere. Fortunately, *n*-octyl styryl selenide (**4a**) was detected in 49% yield, together with the symmetric selenoether di-*n*-octyl selenide (**5**) (Scheme 2).This by-product probably comes from the nucleophilic attack of *n*-octyl selenolate anion at carbon 1 of *n*-octylselenocyanate.[18] To avoid this secondary reaction we increased the amount of **1**, **2** and $NaBH_4$ in relation to **3a**, and product **4** was obtained in 57% yield but with a lower amount of compound **5** and a new secondary product **6**, indentified as di-*n*-octyldiselenide (Scheme 2, Table 1, entry 1). Product **6** can proceed from a nucleophilic attack of the *in situ* generated *n*-octyl selenolate anion at the selenium electrophilic atom of *n*-octylselenocyanate.[17]

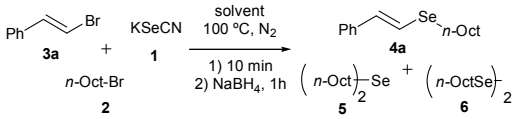


ratio **3a**: **1**: **2**: $NaBH_4$	% yield **4a**	ratio **5/6**
1: 1.2 : 1.1 : 2.4	49	99:1
1: 1.3 : 1.2 : 2.6	57	70:30

Scheme 2. One-pot synthesis of *n*-octyl styryl selenide (**4a**)

After these preliminary results, we performed a screening of solvents whose results are summarized in Table 1. Thus, the best results were obtained in the non protic solvent such as DMF, DMSO, MeCN and NMP, with 50-60% yields of **4a** (Table 1, entries 1-4). Conversely, the non polar toluene, dioxane and THF were not effective for this reaction (Table 1, entries 5-7).

Table 1. Solvent screening for the one-pot synthesis of selenide **4a**



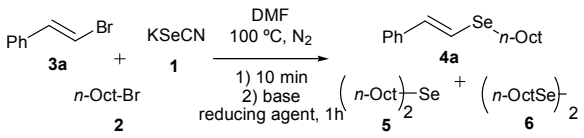
entry	solvent[a]	yield % **4a**[b]
1	**DMF**	**57**[c]
2	DMSO	56[c]
3	MeCN	48[c]
4	NMP	59[c]
5	Toluene	nd
6	Dioxane	nd
7	THF	nd
8	Ethanol	<5
9	PEG 300	53[c]

[a]The reaction was performed by using: 0.25 mmol of **3a** and a ratio of 1 : 1.3 : 1.2 : 2.6 for **3a**, **1**, **2** and $NaBH_4$, respectively. [b]Quantified by GC with internal standard. nd: no detected. [c]Together with ca. 20% of a mixture of **5** and **6** with a ratio **5/6** around 70/30-80/20.

Finally, only traces of **4a** were obtained when the reaction was performed in the polar protic ethanol and its yield increased to 53% in PEG 300 (Table 1, entries 8 and 9). The secondary products **5** and **6** were found in most of the solvents used, as minor by-products. Also, the amount of *n*-octylselenocyanate, formed in the first step, was detected in traces. It is important to mention that the reduction of one equivalent of **6** by two equivalents of $NaBH_4$ would generate two equivalents of *n*-octylselenolate anions. On the other hand, the presence of the secondary product **5** in moderate concentration is a disadvantage since its generation implies a minor availability of selenolate anions to react with styryl bromide **3a**.

Then, for a detailed study of the generation of *n*-octylselenolate anion from the corresponding alkylselenocyanate, diverse bases and reducing agents were screened (Table 2). Using NaH as a reducing species, the yield of **4a** dropped to 22% in comparison with that of the reaction performed employing $NaBH_4$ (Table 2, entries 1 and 2). When *t*-BuOK was used as a base instead of **4a,** a new product was obtained for the first time, indentified as *n*-octyl (2-phenylethynyl) selenide (Table 2, entry 3). This product was not detected in the previous reactions and its mechanistic study and synthetic scope are currently being developed. In the presence of other bases such as K_3PO_4, KOH, K_2CO_3 and DABCO, traces of **4a** were only detected in better conditions (Table 2, entries 4-7). Although these results did not seem to be encouraging, a detailed analysis of GC profiles showed that **6** was afforded as main product when the reaction was conducted in the presence of K_3PO_4 (Table 2, entry 4). In the presence of K_2CO_3, **6** was also obtained; yet, its yield was notably lower than with K_3PO_4 (Table 2, entry 6). The fact that neither **5** nor **6** were obtained in the presence of DABCO allows excluding the participation of DMF as reducing agent for the formation of selenolate anions from the alkyl selenocyanate. The generation of selenolate anions was ascribed to base-catalysed hydrolysis of *n*-octyl selenocyanate due to the presence of traces of water in DMF.[19,]

Table 2. Screening of reducing agents and bases



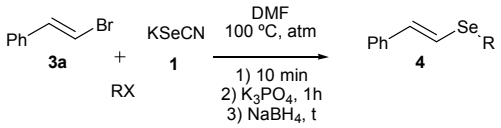
entry	red. /base[a]	**4a** %[b]	*n*-Oct-SeCN %[b]	(**5** + **6**)%, ratio **5/6**[b]
1	$NaBH_4$	57	6	17, 70/30
2	NaH	22	nd	52, 100/0
3[c]	*t*-BuOK	<5	<5	65, 32/68
4	**K_3PO_4**	**<5**	**<5**	**92, 0/100**
5	KOH	<5	nd	98, 10/90
6	K_2CO_3	nd	73	26, 0/100
7	DABCO	nd	98	nd

[a]The reaction was performed by using: 0.25 mmol of **3** and a ratio of 1 : 1.3 : 1.2 : 2.6 for **3a**, **1**, **2** and reducing agent or base, respectively. [b]Quantified by GC with internal standard; nd: not detected. [c]Phenylethynyl *n*-octyl selenide was also obtained in 33% yield.

In addition, the oxidation of selenolate anions to afford **6** can be excluded since these reactions were carried-out under an inert atmosphere and formation of **6** is only attributed to the presence of K_3PO_4 (Table 2, entry 4).

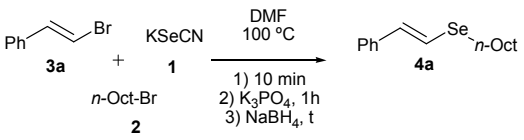
The results summarized in Table 2, evidence that under certain conditions it is possible to obtain only **6** without any trace of **5**. As mentioned above, alkyl selenolate anions can be generated by reduction of the corresponding dialkyldiselenide. In consequence, we planned to perform the same reaction in three steps: first, the S_N2 reaction between alkyl halide and KSeCN to afford alkylselenocyanate; then, the K_3PO_4-assisted generation of dialkyldiselenide from the previously obtained alkylselenocyanate; finally, the reduction of dialkyldiselenide to render alkylselenolate anion and the nucleophilic substitution of vinyl halides.

Scheme 3 shows the general strategy for the one-pot synthesis of alkyl vinyl selenide in three steps and Table 3 summarizes the results for the optimization conditions. First, we performed the reaction with a ratio of 1: 1.3 : 1.2 : 1.3 : 1.3 for **3a**, **1**, **2**, K_3PO_4 and $NaBH_4$ as a reducing agent, and the reaction time for the three previously mentioned steps was 10 min, 1 h and 1 h, respectively. Under these conditions compound **4a** was obtained in 66% yield (Table 3, entry 1). To improve the performance of the reaction, the equivalents of KSeCN and alkyl halide were increased to 1.5 and 1.35 relative to **3a**, affording an increase of vinyl selenide **4a** to 75% yield. Furthermore, when the reaction was conducted under air, the yield was not modified (76%) (Table 3, entries 2 and 3). The third step was performed for 2 h and the yield of **4a** increased to 80% quantified by GC and 71% isolated by column chromatography (Table 3, entry 4).



Scheme 3. One-pot three-step synthesis of alkyl vinyl selenides

Table 3. Optimization for the one-pot synthesis of **4a**[a]



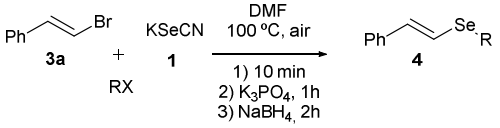
entry	Ratio[a] **3a**: **1**: **2:** K_3PO_4: $NaBH_4$	Cond.	% Yield[b] **4a**
1	1.0 : 1.3 : 1.2 : 1.3 : 1.3	1 h, N_2	66
2	1.0 : 1.5 : 1.35 : 1.5 : 1.5	1 h, N_2	75
3	1.0 : 1.5 : 1.35 : 1.5 : 1.5	1 h, Air	76
4	**1.0 : 1.5 : 1.35 : 1.5 : 1.5**	**2h, Air**	**80 (71)[c]**

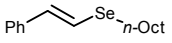
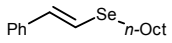
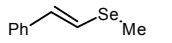
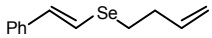
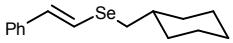
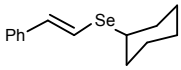
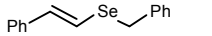
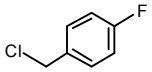
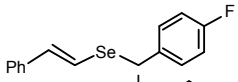
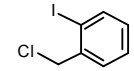
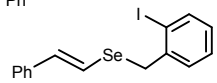
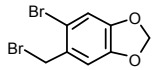
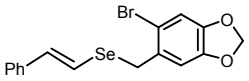
[a]The reaction was performed by using: 0.25 mmol of **3** and a ratio as indicated in the second column, in 2 mL of DMF. [b]Quantified by GC with the internal standard. [c]Isolated yield.

Next, we explored the scope and limitations of this methodology for the synthesis of alkyl styryl selenides with a variety of substituted styryl and alkyl halides (Table 4). In general, for different primary alkyl halides, including methyl iodide, 3-butenyl bromide, *n*-octyl bromide and cyclohexylmethyl bromide, the corresponding alkyl styryl selenides were obtained from moderate to excellent (71-95%) yields; *n*-octyltosylate afforded **4a** in good isolated yield (Table 4, entries 1-5). The secondary cyclohexyl bromide afforded only 21% yield of **4e** (Table 4, entry 6) while the tertiary *tert*-butyl chloride failed to render the alkane selenolate anion. Both results are clear evidences of a competitive E_2 reaction, and this is the main limitation of the present methodology. Benzyl bromide and *p*-fluorobenzyl chloride afforded the corresponding selenides **4f** and **4g** in 44% and 48% yield, respectively, while for *ortho*-substituted benzyl halides the yields of selenides **4h** and **4i** dropped to 25% and 21% respectively (Table 4, entries 7-10). These results can be ascribed to steric hindrance and secondary reactions involving the benzyl halide and benzyl selenocyanate under basic and reductive conditions (results not shown). Some examples were also performed in PEG 300 as solvent but the yields were not improved. (Table 4, entries 2 and 5).

Finally, the reactivity of a variety of substituted styryl halides with *n*-octyltosylate was also studied (Table 5). Both *E*-styryl bromide and chloride afforded **4a** in good isolated yields and *Z*-styryl bromide gave the corresponding *Z*-isomer ***Z*4a** in 84% yield (Table 5, entries 1-3). We also tested the effect of the substituents on the styryl moiety. The *p*-chloro derivative **3c** afforded the selenide **4j** in comparable yields with the unsubstituted styryl bromide (Table 5, entry 4); however, as the electron donor ability of the substituent increased (Me and MeO), the reactivity of the corresponding vinyl bromide decreased (Table 5, entries 5 and 6). Furthermore the presences of the MeO group at the *ortho* position decreased the yield to 52% due to steric hindrance, (Table 5, entry 7).

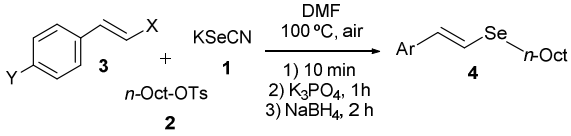
Table 4. One-Pot Synthesis of Alkyl (*E*) Styryl Selenides[a]

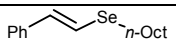
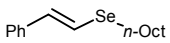
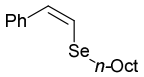
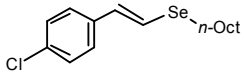
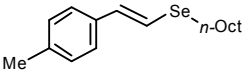
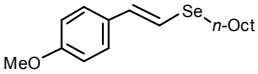
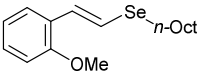


entry	R-X	product, yield(%)[b]		
1	*n*-OctylBr		**4a**	71
2	*n*-OctylOTs		**4a**	83[c]
3	MeI		**4b**	95
4	CH_2=$CHCH_2CH_2Br$		**4c**	71
5	Cy-CH_2Br		**4d**	85[d]
6	CyBr		**4e**	21
7	$PhCH_2Br$		**4f**	44
8			**4g**	48
9			**4h**	25
10			**4i**	21

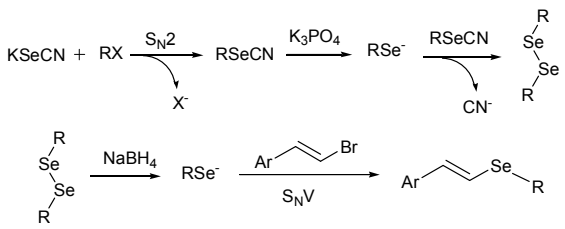
[a]Reaction conditions unless otherwise stated: (*E*)-β–bromostyrene (**3a**) (0. 25 mmol), KSeCN (**1**) (0.38 mmol), alkyl halide (0.34 mmol), K_3PO_4 (0.38mmol) and $NaBH_4$ (0.38 mmol) in 2 mL of DMF. [b]Isolated yields. [c]Performed in PEG 300, 51% isolated yield, with minor amount of **5** and **6**. [d]Performed in PEG 300, 70% isolated yield, with minor amount of **5** and **6**.

Table 5. One-Pot Synthesis of Arylvinyl *n*-Octyl Selenides[a]



entry	**3a-e** Y, X	product **4a, j-l**, yield(%)[b]		
1	H, Br **3a**		**4a**	83
2	H, Cl **3b**		**4a**	70
3	(*Z*)-H, Br[c]		(*Z*)**4a**	84[d]
4	Cl, Br **3c**		**4j**	83
5	Me, Br **3d**		**4k**	80
6	MeO, Br **3e**		**4l**	74
7	*o*-MeO, Br		**4m**	52

[a]Reaction conditions unless otherwise stated: aryl vinyl halide (**3a-e**) (0. 25 mmol), KSeCN (**1**) (0.38 mmol), *n*-octyl tosylate (0.34 mmol), K_3PO_4 (0.38mmol) and $NaBH_4$ (0.38 mmol) in 2 mL of DMF.[b]Isolated yields. [c]*Z*-Styryl bromide. [d]The starting *(Z)*-vinyl halide contained ca. 10% of (*E*)-isomer; this led to ca. 10% of the *trans*-isomer in the product.



Scheme 4. Proposed mechanism for one-pot formation of alkyl aryl vinyl selenide.

The effect of the substituents on the styryl halides, the stereochemical outcome of the reaction (configuration retention) and the occurrence of the reaction without catalysis suggest that the reaction of arylvinyl halides with alkyl selenolate anion follows a classical mechanism of concerted addition-elimination vinylic nucleophilic substitution similar to their analogue alkyl thiolate anion. Thus, the mechanism for the sequential one-pot synthesis of alkyl vinyl selenides follows (Scheme 4). First, alkyl halide reacts with KSeCN by a S_N2 mechanism to afford the corresponding alkyl selenocyanate. In the presence of K_3PO_4, this intermediate (RSeCN) is hydrolyzed by traces of water present in DMF[20] to produce alkyl selenolate anion which fast attacks the selenium atom of another molecule of RSeCN affording the corresponding dialkyl diselenide. The dialkyl diselenide was then reduced by $NaBH_4$ to yield alkane selenolate anion able to react with the vinyl halide by a vinylic nucleophilic substitution (S_NV).[21]

Experimental

Materials and methods: KSeCN, alkyl and benzyl halides were all high-purity commercial samples used without further purification. (*E*) and (Z)-β-bromostyrenes were prepared from cinnamic acids following literature procedures.[22] Di-Octyl selane (**5**)[23] and 1,2-dioctyl diselane (**6**)[24] were isolated from the reaction mixture by column chromatography and exhibited physical properties identical to those reported in the literature. DMF, acetonitrile and DMSO

absolute grade were used without further purification and stored over molecular sieves (4 Å). Toluene, dioxane, THF and pyridine were distilled by standard procedures and stored over molecular sieves (4 Å). PEG 300 and ethanol were used without further purification. All the reaction products were isolated by radial chromatography (silica gel, petroleum/diethyl ether) from the reaction mixture and characterized by ^{1}H, ^{13}C and ^{77}Se NMR and mass spectrometry. ^{1}H, ^{13}C and ^{77}Se NMR spectra were recorded at 400.16 and 100.62 MHz respectively on a Bruker 400 spectrometer, and all spectra were reported in δ (ppm) relative to Me_4Si, with $CDCl_3$ as a solvent. The chemical shifts in ^{77}Se specta were given in ppm using diphenyl diselenide (PhSeSePh) diluted in $CDCl_3$ as an external standard (δ 463 ppm at 25 ºC). Gas chromatographic analyses were performed on Agilent 5890 with a flame-ionization detector, on 30 m capillary column of a 0.32 mm x 0.25 μm film thickness, with a 5% phenylpolysiloxane phase. GS-MS analyses were conducted on Agilent 7890 employing a 30 m x 0.25 mm x 0.25 μm with a 5% phenylpolysiloxane phase column. HRMS spectra were recorded on a GCT Premie orthogonal acceleration time-of-flight (oa-TOF) GC mass spectrometer. Ionization was achieved by electronic impact (70eV) and detection setup positive mode.

Synthetic procedures

General experimental procedures for the reactions of 1 and benzyl, alkyl and vinyl bromides (Scheme 1). The reactions were carried out in a 10 mL three-necked Schlenk tube, equipped with a magnetic stirrer. The tube was charged with DMF (2.0 mL). Potassium selenocyanate (0.25 mmol) and benzyl, *n*-octyl or (*E*)-β-styryl bromides (0.25 mmol) were added and stirred at the corresponding temperature for 5 min (2 h for (*E*)-β-bromostyrene). The reaction mixture was cooled to room temperature. Diethyl ether (15 mL) and water (15 mL) were added and the mixture was stirred. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 15 mL). The combined organic extract was dried over anhydrous Na_2SO_4, and the product was isolated by column chromatography (silica gel, eluent: hexane). The identity of all the products was confirmed by ^{1}H, ^{13}C and ^{77}Se NMR and EI MS.

1-Selenocyanatooctane:[25] Following the general procedure, using potassium selenocyanate (36.0 mg, 0.25 mmol) and *n*-octyl bromide (48.3 mg, 0.25 mmol) for 5 min at 100 ºC. Purification was performed by column chromatography (pentane) providing the title compound as a pale yellow oil (53.5 mg, 95% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.06 (t, *J* = 7.4 Hz, 2H), 1.90 (quint, *J* = 7.3 Hz, 2H), 1.48 – 1.39 (m, 2H), 1.34 – 1.24 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 101.5, 31.7, 30.8, 29.7, 29.1, 29.0, 28.8, 22.6, 14.0. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 207.6. GC-MS (EI) *m/z* 219 (72) $[M]^+$, 137 (100), 101 (82), 75 (52), 50 (40).

(Selenocyanatomethyl)benzene:[26] Following the general procedure, using potassium selenocyanate (36.0 mg, 0.25 mmol) and benzyl bromide (42.7 mg, 0.25 mmol) for 5 min at room temperature. Purification was performed by column chromatography (pentane) providing the title compound as a white solid (53.5 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 – 7.32 (m, 5H), 4.31 (s, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.4, 129.2, 129.0, 128.7, 101.8, 32.8. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 281.9. GC-MS (EI) *m/z* 91 (100) $[M\text{-}SeCN]^+$, 65 (18).

General experimental procedures for one-pot synthesis of alkyl styryl selenides: The reactions were carried out in a 10 mL three-necked Schlenk tube, equipped with a magnetic stirrer. The tube was charged with DMF (2.0 mL). Potassium selenocyanate (0.375 mmol), alkyl halide (0.335 mmol), β-halostyrene (0.25 mmol) were added and stirred for 10 min at 100 ºC. K_3PO_4 (0.375 mmol) was then added and the mixture was stirred for 1 h. Finally, $NaBH_4$ (0.375 mmol) was also added and the mixture was stirred for 2 h. The reaction mixture was cooled to room temperature. Diethyl ether (15 mL) and water (15 mL) were added and the mixture was stirred. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 15 mL). The combined organic extract was dried over anhydrous Na_2SO_4 and the products were isolated by radial chromatography from the crude reaction mixture. The identity of all the products was confirmed by ^{1}H, ^{13}C, ^{77}Se NMR and EI MS.

(*E*)-Octyl(styryl)selane (4a): Following the general procedure, using potassium selenocyanate (54.0 mg, 0.375 mmol), *n*-octyl tosylate (95.7 mg, 0.337 mmol), (*E*)-β-bromostyrene (45.5 mg, 0.25 mmol) for 10 min at 100 ºC, potassium phosphate (79.9 mg, 0.375 mmol) for 1 h at 100 ºC and sodium borohydride (14.2 mg, 0.375 mmol) for 2 h at 100 ºC. Purification was performed by radial chromatography (pentane) providing **4a** as a pale yellow oil (61.4 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.24 (m, 4H), 7.24 – 7.15 (m, 1H), 7.04 (d, *J* = 15.9 Hz, 1H), 6.73 (d, *J* = 15.9 Hz, 1H), 2.81 (t, *J* = 7.3 Hz, 2H), 1.76 (q, *J* = 7.3 Hz, 2H), 1.46 – 1.37 (m, 2H), 1.34 – 1.23 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 132.1, 128.6, 127.1, 125.7, 119.5, 31.8, 30.4, 29.9, 29.2, 29.1, 26.3, 22.7, 14.1. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 267.6. GC-MS (EI) *m/z* 296 (69) $[M]^+$, 184 (100), 102 (39), 91 (39), 77 (21), 71 (39), 57 (75), 55 (33), 43 (82), 41 (70). HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{24}Se$ $[M]^+$ 296.1038, found 296.1040.

(*E*)-Methyl(styryl)selane (4b): Following the general procedure, using potassium selenocyanate (54.0 mg, 0.375 mmol), methyl iodide (21.0 μL, 0.337 mmol), (*E*)-β-bromostyrene (45.5 mg, 0.25 mmol) for 10 min at 100 ºC, potassium phosphate (79.9 mg, 0.375 mmol) for 1 h at 100 ºC and sodium borohydride (14.2 mg, 0.375 mmol) for 2 h at 100 ºC. Purification was performed by radial chromatography (pentane) providing **4b** as a pale yellow oil (47.0 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 – 7.31 (m, 4H), 7.18 – 7.23 (m, 1H), 7.07 (d, *J* = 15.8 Hz, 1H), 6.61 (d, *J* = 15.8 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.4, 130.4, 128.6, 127.0, 125.6, 120.0, 5.5. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 183.8. GC-MS (EI) *m/z* 198 (89) $[M]^+$, 183 (100), 102 (99), 77 (56), 63 (23), 51 (57). HRMS (ESI-TOF) *m/z* calcd for $C_9H_{10}Se$ $[M]^+$ 197.9942, found: 197.9943.

(*E*)-But-3-en-1-yl(styryl)selane (4c): Following the general procedure, using potassium selenocyanate (54.0 mg, 0.375 mmol), 4-bromobut-1-ene (34.2 μL, 0.337 mmol), (*E*)-β-bromostyrene (45.5 mg, 0.25 mmol) for 10 min at 100 ºC, potassium phosphate (79.9 mg, 0.375 mmol) for 1 h at 100 ºC and sodium borohydride (14.2 mg, 0.375 mmol) for 2 h at 100 ºC. Purification was performed by radial chromatography (pentane) providing **4c** as a pale yellow oil (72.2 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 – 7.28 (m, 4H), 7.24 – 7.18 (m, 1H), 7.04 (d, *J* = 15.9 Hz, 1H), 6.75 (d, *J* = 15.9

Hz, 1H), 5.86 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.11 (ddd, *J* = 16.9, 2.8, 1.9 Hz, 1H), 5.07 (ddd, *J* = 10.2, 2.8, 1.3 Hz, 1H), 2.87 (t, *J* = 7.5 Hz, 2H), 2.57 – 2.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.4, 137.0, 132.8, 128.6, 127.2, 125.7, 119.0, 116.1, 34.5, 25.0. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 270.2. GC-MS (EI) *m/z* 238 (45) $[M]^+$, 183 (54), 182 (40), 157 (19), 129 (58), 116 (87), 102 (77), 91 (65), 77 (53), 55 (100), 51 (37). HRMS (APCI) *m/z* calcd for $C_{12}H_{15}Se$ $[M+H]^+$ 239.03338, found:239.03357.

(*E*)-(Cyclohexylmethyl)(styryl)selane (4d): Following the general procedure, using potassium selenocyanate (54.0 mg, 0.375 mmol), bromomethyl cyclohexane (46.9 µL, 0.337 mmol), (*E*)-β-bromostyrene (45.5 mg, 0.25 mmol) for 10 min at 100 ºC, potassium phosphate (79.9 mg, 0.375 mmol) for 1 h at 100 ºC and sodium borohydride (14.2 mg, 0.375 mmol) for 2 h at 100 ºC. Purification was performed by radial chromatography (pentane) providing **4d** as a pale yellow oil (59.5 mg, 85% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.28 (m, 4H), 7.24 – 7.17 (m, 1H), 7.03 (d, *J* = 15.9 Hz, 1H), 6.72 (d, *J* = 15.9 Hz, 1H), 2.73 (d, *J* = 6.8 Hz, 2H), 1.93 – 1.85 (m, 2H), 1.79 – 1.69 (m, 2H), 1.69 – 1.63 (m, 1H), 1.63 – 1.55 (m, 1H), 1.32 – 1.20 (m, 2H), 1.19 – 1.09 (m, 1H), 1.06 – 0.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.6, 131.7, 128.6, 127.0, 125.6, 120.3, 38.6, 34.4, 33.5, 26.3, 26.1. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 239.4. GC-MS (EI) *m/z* 280 (12) $[M]^+$, 184 (32), 97 (28), 91 (12), 55 (100), 41 (22). HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{20}Se$ $[M]^+$ 280.0725, found: 280.0734.

(*E*)-Cyclohexyl(styryl)selane (4e): Following the general procedure, using potassium selenocyanate (54.0 mg, 0.375 mmol), bromocyclohexane (40.9 µL, 0.337 mmol), (*E*)-β-bromostyrene (45.5 mg, 0.25 mmol) for 10 min at 100 ºC, potassium phosphate (79.9 mg, 0.375 mmol) for 1 h at 100 ºC and sodium borohydride (14.2 mg, 0.375 mmol) for 2 h at 100 ºC. Purification was performed by radial chromatography (pentane) providing **4e** as a pale yellow oil (14.0 mg, 21% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.29 (m, 4H), 7.22 (td, *J* = 5.8, 2.6 Hz, 1H), 7.11 (d, *J* = 15.9 Hz, 1H), 6.83 (d, *J* = 15.9 Hz, 1H), 3.27 – 3.16 (m, 1H), 2.12 (d, *J* = 10.1 Hz, 2H), 1.78 (dd, *J* = 9.0, 4.3 Hz, 2H), 1.63 (dd, *J* = 10.3, 3.7 Hz, 2H), 1.43 – 1.26 (m, 4H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.6, 134.1, 128.6,0 127.2, 125.8, 118.3, 41.6, 34.4, 26.8, 25.7. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 338.4. GC-MS (EI) *m/z*266 (32) $[M]^+$, 184 (96), 102 (32), 91 (22), 77 (16), 55 (100), 51 (12), 41 (36). HRMS (APCI) *m/z* calcd for $C_{14}H_{19}Se$ $[M+H]^+$ 267.06469, found: 267.06476.

(*E*)-Benzyl(styryl)selane (4f): Following the general procedure, using potassium selenocyanate (54.0 mg, 0.375 mmol), benzyl bromide (64.1 mg, 0.337 mmol), (*E*)-β-bromostyrene (45.5 mg, 0.25 mmol) for 10 min at 100 ºC, potassium phosphate (79.9 mg, 0.375 mmol) for 1 h at 100 ºC and sodium borohydride (14.2 mg, 0.375 mmol) for 2 h at 100 ºC. Purification was performed by radial chromatography (pentane) providing **4f** as a light yellow solid (30.1 mg, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 – 7.26 (m, 8H), 7.25 – 7.19 (m, 2H), 7.03 (d, *J* = 15.9 Hz, 1H), 6.78 (d, *J* = 15.9 Hz, 1H), 4.04 (s, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3, 137.3, 133.6, 128.9, 128.6, 128.6, 127.3, 127.1, 125.8, 118.9, 29.9. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 340.9. GC-MS (EI) *m/z* 274 (10) $[M]^+$, 183 (5), 91 (100), 65 (13). HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{14}Se$ $[M]^+$ 274.0256, found 274.0260.

(*E*)-(4-Fluorobenzyl)(styryl)selane (4g): Following the general procedure, using potassium selenocyanate (54.0 mg, 0.375 mmol), 4-fluorobenzyl chloride (48.7 mg, 0.337 mmol), (*E*)-β-bromostyrene (45.5 mg, 0.25 mmol) for 10 min at 100 ºC, potassium phosphate (79.9 mg, 0.375 mmol) for 1 h at 100 ºC and sodium borohydride (14.2 mg, 0.375 mmol) for 2 h at 100 ºC. Purification was performed by radial chromatography (pentane) providing **4g** as a yellow solid (35.0 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.27 (m, 6H), 7.23 (dt, *J* = 9.2, 4.2 Hz, 1H), 7.02 – 6.97 (m, 3H), 6.77 (d, *J* = 15.8 Hz, 1H), 4.01 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8 (d, $^1J_{C\text{-}F}$ = 244.5 Hz), 137.2, 134.1, 134.1 (d, $^4J_{C\text{-}F}$ = 4.3 Hz), 130.4 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 128.7, 127.5, 125.8, 118.5, 115.5 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 29.1. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 343.1. GC-MS (EI) m/z 292 (6) $[M]^+$, 183 (7), 109 (100), 102 (8), 77 (3), 51 (4). HRMS (APCI) *m/z* calcd for $C_{15}H_{12}FSe$ $[M-H]^+$ 291.00832, found 291.00867.[27] HRMS (APPI) *m/z* calcd for $C_{15}H_{13}FSe$ $[M]^+$ 292.01669, found 292.01742.

(*E*)-(2-Iodobenzyl)(styryl)selane (4h): Following the general procedure, using potassium selenocyanate (54.0 mg, 0.375 mmol), 2-iodobenzyl chloride (84.6 mg, 0.337 mmol), (*E*)-β-bromostyrene (45.5 mg, 0.25 mmol) for 10 min at 100 ºC, potassium phosphate (79.9 mg, 0.375 mmol) for 1 h at 100 ºC and sodium borohydride (14.2 mg, 0.375 mmol) for 2 h at 100 ºC. Purification was performed by radial chromatography (pentane) providing **4h** as a yellow solid (25.0 mg, 25% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.3 Hz, 1H), 7.41 – 7.17 (m, 7H), 7.08 (d, *J* = 15.8 Hz, 1H), 6.91 (td, *J* = 7.7, 1.6 Hz, 1H), 6.79 (d, *J* = 15.8 Hz, 1H), 4.13 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.3, 139.9, 137.2, 134.8, 129.9, 128.7, 128.6, 128.5, 127.5, 125.9, 118.3, 100.6, 35.6. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 338.4. GC-MS (EI) *m/z* 400 (21) $[M]^+$, 217 (100), 183 (23), 102 (28), 91 (65), 90 (65), 89 (35), 77 (11), 63 (21), 51 (13). HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{13}INaSe$ $[M+Na]^+$ 422.9120, found: 422.9113.

(*E*)-5-Bromo-6-((styrylselanyl)methyl)benzo[d][1,3]dioxole (4i): Following the general procedure, using potassium selenocyanate (54.0 mg, 0.375 mmol), 5-bromo-6-(bromomethyl)benzo[d][1,3]dioxole (99.0 mg, 0.337 mmol), (*E*)-β-bromostyrene (45.5 mg, 0.25 mmol) for 10 min at 100 ºC, potassium phosphate (79.9 mg, 0.375 mmol) for 1 h at 100 ºC and sodium borohydride (14.2 mg, 0.375 mmol) for 2 h at 100 ºC. Purification was performed by radial chromatography (pentane) providing **4i** as a yellow solid (20.8 mg, 21% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.27 (m, 4H), 7.24 – 7.19 (m, 1H), 7.10 (d, *J* = 15.8 Hz, 1H), 7.00 (s, 1H), 6.85 (s, 1H), 6.79 (d, *J* = 15.8 Hz, 1H), 5.96 (s, 2H), 4.07 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.6, 147.5, 137.2, 134.4, 131.2, 128.6, 127.4, 125.9, 118.4, 114.8, 112.9, 110.2, 101.8, 30.4. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 342.3. GC-MS (EI) *m/z* 396 (2) $[M]^+$, 215 (100), 213 (93), 104 (17), 102 (22), 78 (37), 77 (25), 76 (32), 75 (29), 51 (24), 50 (22). HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{13}BrNaO_2Se$ $[M+Na]^+$ 418.9154, found 418.9145.

(*Z*)-Octyl(styryl)selane (*Z*4a): Following the general procedure, using potassium selenocyanate (54.0 mg, 0.375 mmol), *n*-octyl tosylate (95.7 mg, 0.337 mmol), (*Z*)-β-bromostyrene (45.5 mg, 0.25 mmol) for 10 min at 100 ºC, potassium phosphate (79.9 mg, 0.375 mmol) for 1 h at 100 ºC and sodium borohydride (14.2 mg, 0.375 mmol) for 2 h at 100 ºC. Purification was performed by radial chromatography (pentane) providing ***Z*4a** as a pale yellow oil (62.2 mg, 84% yield). The starting *(Z)*-vinyl halide contained ca. 10% of (*E*)-isomer; this led to ca. 10% of the *trans*-isomer in the product.^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 – 7.15 (m, 5H), 6.87 (d, *J* = 10.6 Hz, 1H), 6.60 (d, *J* = 10.6 Hz, 1H), 2.78 (t, *J* = 7.3 Hz, 2H), 1.75 (q, *J* = 7.3

Hz, 2H), 1.44 – 1.35 (m, 2H), 1.29 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.7, 129.3, 128.3, 126.8, 123.2, 31.8, 30.7, 29.7, 29.2, 29.1, 22.6, 14.1. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 263.1. GC-MS (EI) *m/z* 296 (58) $[M]^+$, 184 (97), 102 (59), 91 (30), 71 (36), 43 (100), 41 (55). HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{24}Se$ $[M]^+$ 296.1038, found 296.1041.

(*E*)-(4-Chlorostyryl)(octyl)selane (4j): Following the general procedure, using potassium selenocyanate (54.0 mg, 0.375 mmol), *n*-octyl tosylate (95.7 mg, 0.337 mmol), (*E*)-1-(2-bromovinyl)-4-chlorobenzene (54.4 mg, 0.25 mmol) for 10 min at 100 ºC, potassium phosphate (79.9 mg, 0.375 mmol) for 1 h at 100 ºC and sodium borohydride (14.2 mg, 0.375 mmol) for 2 h at 100 ºC. Purification was performed by radial chromatography (pentane) providing **4j** as a pale yellow oil (68.5 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.19 (m, 4H), 7.04 (d, *J* = 15.9 Hz, 1H), 6.66 (d, *J* = 15.9 Hz, 1H), 2.82 (t, *J* = 6.8 Hz, 2H), 1.76 (q, *J* = 6.8 Hz, 2H), 1.47 – 1.37 (m, 2H), 1.30 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.0, 132.6, 130.5, 128.8, 126.8, 120.6, 31.8, 30.3, 29.8, 29.2, 29.1, 26.3, 22.6, 14.1. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 271.6. GC-MS (EI) *m/z* 330 (40) $[M]^+$, 218 (28), 183 (40), 102 (20), 71 (51), 57 (78), 43 (100), 41 (71). HRMS (APCI) *m/z* calcd for $C_{16}H_{24}ClSe$ $[M+H]^+$ 331.07241, found: 331.07245.

(*E*)-(4-Methylstyryl)(octyl)selane (4k): Following the general procedure, using potassium selenocyanate (54.0 mg, 0.375 mmol), *n*-octyl tosylate (95.7 mg, 0.337 mmol), (*E*)-1-(2-bromovinyl)-4-methylbenzene (49.2 mg, 0.25 mmol) for 10 min at 100 ºC, potassium phosphate (79.9 mg, 0.375 mmol) for 1 h at 100 ºC and sodium borohydride (14.2 mg, 0.375 mmol) for 2 h at 100 ºC. Purification was performed by radial chromatography (pentane) providing **4k** as pale yellow oil (62.0 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 15.9 Hz, 1H), 6.71 (d, *J* = 15.9 Hz, 1H), 2.80 (t, *J* = 7.3 Hz, 2H), 2.31 (s, 3H), 1.75 (q, *J* = 7.3 Hz, 2H), 1.46 – 1.37 (m, 2H), 1.35 – 1.22 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.9, 134.8, 132.5, 129.3, 125.6, 118.0, 31.8, 30.4, 29.9, 29.9, 29.1, 26.3, 22.6, 21.2, 14.1. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 264.3. GC-MS (EI) *m/z* 310 (82) $[M]^+$, 198 (61), 197 (29), 183 (65), 115 (63), 105 (19), 91 (20), 71 (36), 57 (64), 43 (100), 41 (86).HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{26}Se$ $[M]^+$ 310.1195, found: 310.1169.

(*E*)-(4-Methoxystyryl)(octyl)selane (4l): Following the general procedure, using potassium selenocyanate (54.0 mg, 0.375 mmol), *n*-octyl tosylate (95.7 mg, 0.337 mmol), (*E*)-1-(2-bromovinyl)-4-methoxybenzene (53.2 mg, 0.25 mmol) for 10 min at 100 ºC, potassium phosphate (79.9 mg, 0.375 mmol) for 1 h at 100 ºC and sodium borohydride (14.2 mg, 0.375 mmol) for 2 h at 100 ºC. Purification was performed by radial chromatography (pentane) providing 4l as a white solid (60.3 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 – 7.21 (m, 2H), 6.87 (d, *J* = 15.8 Hz, 1H), 6.84 – 6.82 (m, 2H), 6.71 (d, *J* = 15.8 Hz, 1H), 3.80 (s, 3H), 2.79 (t, *J* = 6.8 Hz, 2H), 1.75 (q, *J* = 6.8 Hz, 2H), 1.46 – 1.37 (m, 2H), 1.34 – 1.22 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 132.5, 130.5, 126.9, 116.3, 114.1, 55.3, 31.8, 30.4, 29.8, 29.2, 29.1, 26.4, 22.6, 14.1. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 262.1. GC-MS (EI) *m/z* 326 (25) $[M]^+$, 214 (16), 198 (11), 134 (100), 57 (12), 43 (26), 41 (23).HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{26}OSe$ $[M+Na]^+$ 349.1042, found 349.1050.

(*E*)-(2-Methoxystyryl)(octyl)selane (4m): Following the general procedure, using potassium selenocyanate (54.0 mg, 0.375 mmol), *n*-octyl tosylate (95.7 mg, 0.337 mmol), (*E*)-1-(2-bromovinyl)-2-methoxybenzene (53.2 mg, 0.25 mmol) for 10 min at 100 ºC, potassium phosphate (79.9 mg, 0.375 mmol) for 1 h at 100 ºC and sodium borohydride (14.2 mg, 0.375 mmol) for 2 h at 100 ºC. Purification was performed by radial chromatography (pentane) providing **4m** as pale yellow oil (42.4 mg, 52% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.19 (ddd, *J* = 8.2, 7.5, 1.7 Hz, 1H), 7.09 (d, *J* = 16.0 Hz, 1H), 7.03 (d, *J* = 16.0 Hz, 1H), 6.91 (td, *J* = 7.5, 1.0 Hz, 1H), 6.85 (dd, *J* = 8.2, 0.8 Hz, 1H), 3.84 (s, 3H), 2.85 – 2.78 (m, 2H), 1.76 (q, *J* = 7.4 Hz, 2H), 1.47 – 1.38 (m, 2H), 1.35 – 1.23 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.0, 128.1, 127.2, 126.6, 126.5, 120.7, 120.1, 110.9, 55.4, 31.8, 30.4, 29.9, 29.2, 29.1, 26.2, 22.7, 14.1. ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 269.6. GC-MS (EI) *m/z* 326 (57) $[M]^+$, 214 (29), 198 (27), 183 (23), 134 (59), 119 (43), 105 (43), 91 (38), 77 (21), 57 (38), 41 (100). HRMS (APCI) *m/z* calcd for $C_{17}H_{27}OSe$ $[M+H]^+$ 327.12222, found 327.12075.

Conclusions

In summary, we have developed a new one-pot methodology for the stereoselective synthesis of alkyl arylvinyl selenides in moderate to excellent yields, free of any transition metal/ligand systems, from malodorous and air-sensitive selenolate anions and diselenide as starting reagents. This procedure employs the commercially available potassium selenocyanate, DMF as a solvent, short reaction time and air atmosphere

Acknowledgements

This work was supported partly by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and Fondo de Ciencia y Tecnología (FONCYT), Argentina. A. A. H. gratefully acknowledges the receipt of a fellowship from CONICET.

SUPPORTING INFORMATION: Spectra (^{1}H, ^{13}C and ^{77}Se NMR) for all the products (**4a-m** and **Z4a**).

Notes and references

1 a) Rappoport, Ed. *The Chemistry of Organic Selenium and Tellurium Compounds*; John Wiley & Sons: Chichester, 2014 (Vol. 4). b) Z. Rappoport, Ed. *The Chemistry of Organic Selenium and Tellurium Compounds*; John Wiley & Sons: Chichester, 2012 (Vol. 3). c) Wirth, T. Ed. *Organoselenium Chemistry. Modern Development in Organic Synthesis* in Topics in Current Chemistry 208, Springer-Verlag Berlin Heidelberg, 2000.

2 G. Perin, E. J. Lenardão, R. G. Jacob, and R. B. Panatieri, *Chem. Rev.* 2009, **109**, 1277.

3 a) F. Alonso, I. P. Beletskaya and M. Yus, *Chem. Rev.* 2004, **104**, 3079. b) I. P. Beletskaya and V. P. Ananikov, *Chem. Rev.* 2011, **111**, 1596.

4 O. Boutureira, M. I. Matheu, Y. Diaz and S. Castillon, *Carbohydr. Res.* 2007, **342**, 736.

5 a) E. J. Lenardao, M. S. Silva, M. Sachini, R. G. Lara, R. G. Jacob and G. Perin, *Arkivoc* **2009**, 221. b) N. Taniguchi, *Tetrahedron* 2009, **65**, 2782. c) G. Sartori, J. S. S. Neto, A. P. Pesarico, D. F. Back, C. W. Nogueira and G. Zeni, *Org. Biomol. Chem.* 2013, **11**, 1199. d) S. Braverman, M. Cherkinsky, Y. Kalendar, R. Jana, M. Sprecher and I. Goldberg, *Synthesis* 2014, **46**, 119. e) B. Battistelli, L. Testaferri, M. Tiecco and C. Santi, *Eur. J .Org. Chem.* 2011. 1848. f) C. Tidei, L. Sancineto, L. Bagnoli, B. Battistelli, F. Marini and C. Santi, *Eur. J. Org. Chem.* 2014, 5968.

6 a) S.-I. Fujiwara, M. Okuyama, S. Tsuda, T. Iwasaki, H. Kuniyasu and N. Kambe, *Tetrahedron* 2012, **68**, 10523. b) A. Ogawa, *Top. Organomet. Chem.*, 2013, **43**, 325.

7 a) T. Chatterjee and B. C. Ranu, *J. Org. Chem*. 2013, **70**, 7145. b) A. Saha, D. Saha and B. C. Ranu, *Org. Biomol. Chem.* 2009, **7**, 1652. c) L. C. Gonalves, G. F. Fiss, G. Perin, D. Alves, R. G. Jacob and E. J. Lenardao, *Tetrahedron Lett.* 2010, **51**, 6772.

8 T. Ozaki, M. Kotani, H. Kusano, A. Nomoto and A. Ogawa, *J. Organomet. Chem*. 2011**, 696***,* 450.

9 a) D. Kundu, N. Mukherjee and B. C. Ranu, *RSC Advances* 2013**, 3**, 117. b) A. L. Braga, T. Barcellos, M. W. Paixao, A. M. Deobald, M. Godoi, H. A. Stefani, R. Cella and A. Sharma, *Organometallics* 2008, **27**, 4009.

10 S. Kawaguchi, M. Kotani, S. Atobe, A. Nomoto, M. Sonoda and A. Ogawa, *Organometallics* 2011, **30**, 6766.

11 V. P. Reddy, K. Swapna, A. V. Kumar and K. R. Rao, *Tetrahedron Lett.* 2010, **51**, 293.

12 a) I. P. Beletskaya and V. P. Ananikov, *Eur. J. Org. Chem*. 2007, 3431. b) C. C. Silveira, P. C. S. Santo, S. R. Mendes and A. L. Braga, *J. Organomet. Chem.* 2008, **693**, 3787.

13 V. P. Ananikov, S. S. Zalesskiy and I. P. Beletskaya, *Curr. Org. Synth.*, 2011, **8**, 2.

14 a) B. Mohan, S. Hwang, H. Woo and K. H. Park, *Tetrahedron* 2014, **70**, 2699. b) G. W. Kabalka and B. Venkataiah, *Tetrahedron Lett.* 2002, **43**, 3703. c) R. G. Lara, P. C. Rosa, L. K. Soares, M. S. Silva, R. G. Jacob and G. Perin, *Tetrahedron* 2012**, 68**, 10414. d) G. Zeni, M. P. Stracke, C. W. Nogueira, A. L. Braga, P. H. Menezes and H. A. Stefani, *Org. Lett.* **2004***, 6,* 1135.

15 A. A. Heredia and A. B. Peñéñory, *Eur. J .Org. Chem*. 2013, 991.

16 A. A. Heredia, *Synlett* 2014, **25**, 748.

17 A. Krief, C. Delmotte and W. Dumont, *Tetrahedron* 1997, **53**, 12147.

18 M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli and M. Montanucci, *Tetrahedron Lett.* 1985, **26**, 2225.

19 The content of water present in DMF (3.1%) was determined by ^{1}H-NMR, and corresponds to 0.8 mmol of water in 2 ml of DMF used for each reaction.

20 a) S. Yavuz, A. Dioli, Y. Yildirir, L. Türker, *Molecules* 2005, **10**, 1000. b) Y. Tamura, M. Adachi, T. Kawasaki, Y. Kita, *Tetrahedron Lett.* 1979, **24**, 2251.

21 L. Testaferri, M. Tiecco, M. Tingoli and D. Chianelli, *Tetrahedron* 1986, **42**, 63.

22 a) S. Chowdhury and S. Roy, *J. Org. Chem.* 1997, **62**, 199. b) C. Kuang, H. Senboku and M. Tokuda, *Tetrahedron Lett*. 2001, **42**, 3893.

23 X.-B. Zhang, M.-B. Ruan and W.-Q. Fan, *Synth. Commun.* 1996, **26**, 4665.

24 T. Nakamura, S. Yasuda, T. Miyamae, H. Nozoye, N. Kobayashi, H. Kondoh, I. Nakai, T. Ohta, D. Yoshimura and M. Matsumoto,. *J. Am. Chem. Soc.* 2002, **124**, 12642.

25 S. Morimoto, *Nippon Kagaku Zasshi* 1954, **75**, 557; *Chem. Abstr*. 1957, 11234.

26 L. A. Jacob, B. Matos, C. Mostafa, J. Rodriguez and J. K. Tillotson, *Molecules* 2004, **9**, 622.

27 D. Q. Liu, M. Sun, *ISRN Spectroscopy*, 2012, **2012**, 1.

Graphical Abstract and Textual

One-pot synthesis of alkyl styryl selenides using KSeCN as selenium source