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Synthesis of α-phenylseleno-α,β-unsaturated esters by Wittig-type reactions. Studies on the Diels–Alder reaction

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Abstract

Ethyl α-phenylseleno-α,β-unsaturated esters were prepared by the reaction of tri-ethyl phosphonoacetate anion and ethoxycarbonyl(phenylselenenyl)methylidene(triphenyl)phosphorane with aliphatic and aromatic aldehydes. The α-phenylseleno unsaturated esters were obtained as mixtures of *E*/*Z*-isomers in medium to good yields and in moderate yields, respectively. α-Phenylselenenyl acrylate was used as dienophile in a Diels–Alder reaction. On reaction with isoprene only the *para* isomer was obtained while reaction with cyclopentadiene gave a 1:1 mixture of *exo*/*endo* isomers in good yield.

Keywords: Wittig reaction; Diels–Alder reactions; Selenium and compounds; Carboxylic esters; Microwave heating

1. Introduction

Organoselenium compounds play an important role in modern organic synthesis [1]. Of the different classes of organoselenium compounds, vinylic selenides constitute a very useful group. They have been reviewed recently [2].

Considerable efforts have been directed to extend the Wittig and Wittig–Horner reactions to the preparation of α-metal and non-metal substituted olefins [3], such as vinylic chalcogenides [2], in view of their applications in organic synthesis. The appropriate α-substituted phosphonium salt or phosphonate are the obvious starting materials for these reactions [2,4].

α-Phenylseleno-α,β-unsaturated esters, a potentially very useful class of vinylic selenides [5], are scarcely described in the literature, with few general methods reported for their preparation [5,6]. They have been prepared by a Wittig-type reaction of methoxycarbonyl(phenylselenenyl)methylidene(triphenyl)arsorane with aldehydes [7]. The reaction showed a medium to high *Z*-stereoselectivity. They have also been prepared from ethyl(phenylseleno)acetate and aromatic aldehydes, under acidic conditions [8]. These methods suffer from the high cost and the toxicity of arsenium compounds or from the low yields and selectivity of the second method. All other methods lack generality [6]. Recently we described the preparation of such compounds by the reaction of aldehydes with tellurium ylids of α-bromo-α-phenylseleno acetate [6].

In view of the fact that vinylic chalcogenides have great potential in organic synthesis [1,2] and in view of the advantages of the Wittig reaction, we developed methods for the synthesis of α-phenylseleno-α,β-unsaturated esters based on the reaction of sodium(phenylseleno)methanetriethylphosphono acetate and carboethoxy(phenylseleno)methylideno(triphenyl)phosphorane with aldehydes.

2. Results and discussion

2.1. Reaction of sodium(phenylseleno)methane triethylphosphonoacetate with aldehydes

In the first part of the present study, a new method for the synthesis of α-phenylseleno-α,β-unsaturated esters was developed, based on a Wittig–Horner-type reaction using as starting material triethylphosphonoac-

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etate (**1**). Thus, the treatment of a tetrahydrofuran solution of **1** at 0°C with a base, followed by phenylselenenyl bromide, generates the intermediate selenophosphonate **2**, which reacts in situ with another base equivalent, followed by an aldehyde, to give the desired olefinic product **3**, according to Scheme 1.

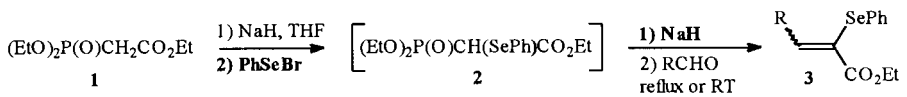
There have been reports in the literature [7,9] that the anion of **2** would be totally inert to the reaction with carbonyl compounds, in a Wittig–Horner-type reaction. This low reactivity of the anion of **2** would be anticipated as a result of three groups which stabilize a carbanion at the α-position. However, in order to achieve good yields in Wittig–Horner reactions, the presence of a further electron-withdrawing α-substituent on the phosphonate anions is required [10]. Thus, we decided to perform the reaction as shown in Scheme 1. Indeed desired products were obtained with both aromatic and aliphatic aldehydes, in yields ranging from 49 to 89% (Table 1).

In order to find the best experimental conditions, a detailed study was performed using benzaldehyde as the standard aldehyde. The selenophosphonate **2** was generated in situ for convenience in view of an observed low stability, although Paulmier described its preparation some years ago [11]. Initially, looking for the best base, lithium derived bases, like LDA, Li-hexamethyldisilylamide (Li-HMDS) and lithiumdicyclohexylamide were employed, but the yields were very low or the products were not formed. Better results were obtained by the use of sodium derivatives, like Na-HMDS and NaH. The best results were observed with NaH as base (73% yield) which was used for the present study with all other aldehydes. Among the solvents examined, THF turned out to be the best choice.

In all cases, for both aliphatic and aromatic aldehydes, the formation of a byproduct, identified as the α,β-unsaturated ester free of selenium, was isolated. The use of higher amounts of PhSeBr or the use of PhSeI (generated from PhSeSePh and I_2), did not reduce its formation. This byproduct could be easily removed by Kugelrohr distillation prior to the purification of the product by column chromatography. We observed that protection from light was useful, particularly when longer reaction times were necessary (benzaldehyde, *p*-chlorobenzaldehyde, furfural and tolualdehyde). It is noteworthy that the reaction worked well even for formaldehyde, to give acrylate **3f**, the simplest member of this class of compounds. It was used successfully as substrate for an investigation of the reactivity as a dienophile in a Diels–Alder reaction of such selenides (vide infra).

The reactions were also performed with several different ketones, but in all cases we were not able to detect the formation of the desired product, which it is not a surprising result in view of the expected low reactivity and the bulkiness of the tri-substituted carbanion **2a**-Na.

Concerning the stereochemistry of these olefinations, the formation of a mixture of *E* and *Z* isomers was observed, with a small preference for the *E* isomer. The ratios of the geometrical *E* and *Z* isomers and other experimental details are given in Table 1. The geometrical isomers were assigned by the chemical shifts of the vinylic hydrogens in the ^{1}H-NMR spectra. Thus, the signals of the vinylic hydrogen are shifted ca. 1 ppm downfield for the *Z*-isomers as compared to *E*-isomers. This absorption position has been well established in several previous studies [6]. For example, the *Z* isomer on the reaction with benzadehyde showed the vinylic hydrogen at $\delta = 8.15$ and the *E* isomer resonates at $\delta = 7.04$. The *Z*/*E* ratio was determined by GC analysis from both the crude reaction mixture and the purified compounds, and confirmed by comparing ^{1}H-NMR with some previously described compounds [6].

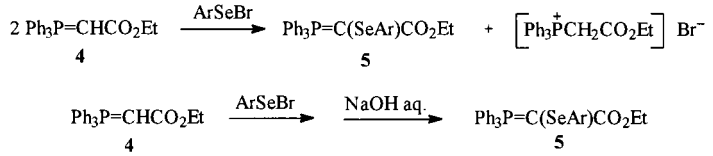


Scheme 1.

Table 1
Synthesis of α-phenylseleno-α,β-unsaturated esters according to Scheme 1

Entry	R in **3**	Conditions	Time (h)	Yield (%) [a]	*E*/*Z* [b]
3a	2-furyl	Reflux THF	6	87	65:35
3b	4-$NO_2C_6H_4$	Reflux THF	3	73	40:60
3c	4-ClC_6H_4	Reflux THF	12	65	60:40
3d	C_6H_5	Reflux THF	12	73	67:33
3e	4-$CH_3C_6H_4$	Reflux THF	6	49	60:40
3f	H	Reflux THF	0.45	76	
3g	*n*-$CH_3CH_2CH_2$	r.t.	1	89	65:35
3h	*n*-$CH_3(CH_2)_4$	Reflux THF	3	86	70:30

[a] Isolated yield after column chromatography.
[b] Determined by GC from the crude reaction mixture.



Scheme 2.

2.2. Reaction of ethoxycarbonyl(phenylseleno)-methylidene(triphenyl)phosphoranes with aldehydes under microwave irradiation

Some years ago, Petragnani and Moura Campos [12] described the preparation of the selenophosphorane **5**, a white crystalline solid, very stable to storage at room temperature, which was shown to be totally inert in Wittig-type reactions with carbonyl compounds [12]. The preparation of the phosphorane **5** has been formulated to proceed via a transylidation reaction between carbethoxymethylideno(triphenyl)phosphorane (**4**) and arylselenenyl bromide (Scheme 2) [12]. We found that the selenophosphorane **5** could also be prepared conveniently by the reaction of equimolar amounts of carbethoxymethylideno(triphenyl)phosphorane (**4**) and phenylselenenyl bromide, treating the resulting salt immediatly with aqueous sodium hydroxide solution, to give the desired phosphorane in 60% yield after recrystalization (Scheme 2).

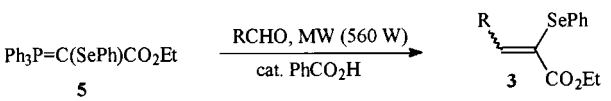
In recent years, microwave irradiation has been found to be a very useful tool for some transformations in organic synthesis [13]. Thus, we decided to study the Wittig-type reaction of phosphorane **5** with aldehydes under microwave irradiation. Several α-phenylseleno-α,β-unsaturated esters could be prepared successfully by this route (Scheme 3, Table 2).

Initially, with the standard conditions, with THF as solvent under reflux, products were not detected after 2 days, which is in accordance with previous observation [12]. For the microwave irradiation experiments, a domestic apparatus was used and the reactions were conducted in an open flask. The reaction was studied in detail having benzaldehyde as the standard aldehyde, following the reaction by TLC and GC. The first experiments were performed in the absence of catalyst and in toluene as the solvent, with very low yields of up to 15%. By removal of the solvent and the use of a catalytic amount of benzoic acid, better results were obtained. In the case of solid aldehydes, it was necessary to use a small amount of solvent (toluene), enough to give a homogeneous solution. The yields were also dependent on the power of the microwave apparatus used. The best results were obtained at 560 W of irradiation, with a reaction time ranging from 3 to 10 min.

The results, presented in Table 2, showed that moderate yields of the desired products could be obtained, which is quite acceptable, considering the very low reactivity of the starting phosphorane **5**. Noteworthy is the beneficial effect of microwave irradiation for the unreactive species, making possible reactions that by other methods might be very difficult. Unfortunately, the corresponding vinylic selenides were obtained as mixtures of isomers, but with reversed stereochemistry, compared to the products obtained by reactions via selenophosphonates (vide infra). In a similar way, in the present case the formation of the same byproducts was observed, the α,β-unsaturated ester, and variable amounts of diphenyl diselenide.

2.3. Study on the reactivity of *3f* in a Diels–Alder reaction

The Diels–Alder reaction is one of the most useful and powerful tools in preparative organic chemistry [14]. In this respect we decided to perform studies on the reaction of α-phenylseleno-α,β-unsaturated esters as dienophiles in Diels–Alder reactions with commercially available dienes. For our study, we decided to use the compound **3f**, the simplest reagent of this class of compounds. Although **3f** is expected to be a good

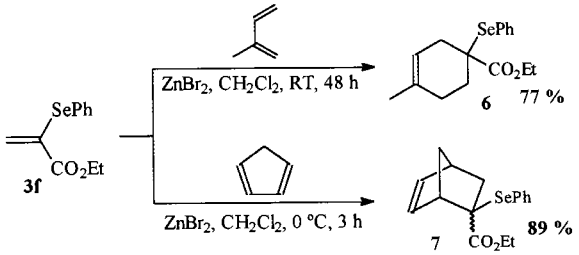


Scheme 3.

Table 2
α-Phenylseleno-α,β-unsaturated esters prepared by microwave (560 W) irradiation

Entry	R in **3**	Time (min)	Yield (%) [a]	*E*/*Z* [b] ratio
3a	2-furyl	9	41	22:78
3b	4-$NO_2C_6H_4$	10	41	30:70
3c	4-ClC_6H_4	6	25	23:77
3d	C_6H_5	6	40	25:75
3e	4-$CH_3C_6H_4$	3	10	43:57
3f	H	10	48	
3g	*n*-$CH_3CH_2CH_2$	6	44	12:88
3h	*n*-$CH_3(CH_2)_4$	6	50	17:83

[a] Isolated yield after column chromatography.
[b] Determined by GC from the crude reaction mixture.



Scheme 4.

dienophile, to the best of our knowledge, there are no reports on its Diels–Alder reactivity.

The first experiment with **3f** was performed with isoprene at high temperatures, which gave negative results. With cyclopentadiene it was possible to detect the formation of the desired product, albeit in low yield. The use of solvents like toluene and acetone does not improve the results. However, the use of $ZnBr_2$ as catalyst resulted in the formation of the desired adduct by reaction with cyclopentadiene in 89% isolated yield (Scheme 4). Under the same conditions, the reaction also gave a good result with isoprene as the diene.

The reactions were performed using an excess of the diene (up to 10 equivalents) and 1.2 equivalents of the Lewis acid in dichloromethane as the solvent. The Diels–Alder reaction of **3f** with isoprene proceeded regioselectively to give **6** in 77% isolated yield after 48 h at room temperature. The formation of the other regioisomer was not detected by NMR. The formation of the *para* isomer was also confirmed by a NOESY NMR study.

The reaction of **3f** with cyclopentadiene, under the conditions applied, showed no stereoselectivity, and the adduct **7** was obtained with an *endo*/*exo* ratio of 1:1.

The compounds **6** and **7** could serve as versatile synthetic intermediates for selenium-containing polycyclic systems. A significant feature of the reaction is that the dienophile can act as a propiolic ester synthon, through the removal of phenylseleninic acid from the corresponding selenoxide.

3. Experimental

3.1. General

^1H- and ^{13}C-NMR spectra of $CDCl_3$ solutions were recorded on a 200 MHz, or on a 400 MHz Bruker DPX-series NMR spectrometer. Chemical shifts are expressed as parts per million (ppm) downfield from tetramethylsilane as an internal standard. Mass spectra (EI) were obtained at 70 eV with a Hewlett Packard EM/CG HP-5988A spectrometer, infrared spectra were acquired on a Bruker IFS 28 spectrometer and elemental analyses were performed on a Vario EL elemental analysis system. The microwave reactions were performed on a domestic apparatus, Panasonic NN 6556. Merck silica gel 60 (230–400 mesh) was used for flash chromatography. THF was distilled over sodium–benzophenone immediately before use. Triethyl phosphonoacetate [15] and carbethoxymethylene(triphenyl)-phosphorane [16] were prepared by literature methods.

3.2. General procedure for the synthesis of α-phenylseleno-α,β-unsaturated esters (3a–3h) from the phosphonate 1

To a round bottom flask equipped with a reflux condenser containing a suspension of NaH (0.072 g, 3 mmol) in THF (10 ml), at 0°C under nitrogen, was added triethylphosphonoacetate (**1**) (0.231 g, 1 mmol), followed by a THF (5 ml) solution of phenylselenenyl bromide (0.35 g, 1.5 mmol). Immediate reaction was observed, with disappearance of the deeper color of PhSeBr, leaving the solution yellow. The aldehyde (1.5 mmol) was added after a few minutes, the ice-bath was removed and the reaction was heated under reflux for the time indicated in Table 1. The reaction mixture was cooled, treated with water (5 ml) and a saturated aqueous solution of NH_4Cl (50 ml) and extracted with ethyl acetate (2×25 ml). The organic phase was dried over $MgSO_4$ and the solvent removed in vacuo. The residue was purified by Kughelrohr distillation (to remove a byproduct, see text) followed by column chromatography in silica gel, eluting with hexane–ethyl acetate (99:1), to yield **3a**–**3h** [17].

3.3. Preparation of carbethoxymethylidene-(phenylseleno)triphenylphosphorane (5) [Ph_3P=C(SePh)CO_2Et]

In a 100 ml flask containing a solution of carbethoxymethylene (triphenyl)phosphorane [15] (3.48 g, 10 mmol) in dichloromethane (10 ml), was added, dropwise, a solution of phenylselenenyl bromide (2.3 g, 10 mmol) in dichloromethane (10 ml). The mixture was stirred at room temperature for 5 min and the solvent was removed under vacuum. The residue was dissolved in water (50 ml), a few drops of an aqueous solution of phenolphthaleine were added, followed by a 0.1 N aqueous solution of NaOH until a pink color remained. The aqueous solution was extracted with dichloromethane, dried over $MgSO_4$, the solvent removed in vacuo and the solid residue recrystallized from methanol to yield **5** (3.0 g, 60%); m.p. 178–180°C (literature value 182°C [12]).

3.4. General procedure for the synthesis of α-phenylseleno-α,β-unsaturated esters (3a–3h) from the phosphoranes 5

A 15 ml round bottom containing the selenophosphorane **5** (0.5 g, 1 mmol), benzoic acid ($\sim$10 mg) the aldehyde (5 mmol) and toluene (1 ml; for the solid aldehydes) was irradiated in a domestic microwave oven (560 W) for the time indicated in Table 2. The reaction mixture was cooled to room temperature, water was added and the reaction was extracted with ethyl acetate (2×25 ml). The combined organic phases were dried over $MgSO_4$ and the solvent was removed in vacuo. The product was purified as above.

Ethyl($E+Z$)-2-phenylseleno-3-(2-furyl)-2-propenoate (**3a**): oil. IR (film) 1716 cm^{-1} (C=O). δ_H (200 MHz, $CDCl_3$) 1.03 and 1.14 (2t, 3H, $J = 7.2$ Hz); 4.04 and 4.14 (2q, 2H, $J = 7.2$ Hz); 6.36 (dd, 1H, $J = 3.6$ and 2 Hz); 6.46 (dd, 1H, $J = 3.6$ and 2 Hz); 6.69 (dd, 1H, $J = 3.4$ and 0.4 Hz); 6.77 (s, E isomer); 8.03 (s, Z isomer) ($E+Z$; 1H); 7.14–7.6 (m, 6H).

Ethyl($E+Z$)-2-phenylseleno-3-(4-nitrophenyl)-2-propenoate (**3b**): yellow–orange oil. IR (film): 1699 cm^{-1} (C=O). δ_H (200 MHz, $CDCl_3$) 1.08 (t, 3H, $J = 7.2$ Hz); 4.05 (q, 2H, $J = 7.2$ Hz); 6.85 (s, E isomer); 8.05 (s, Z isomer) ($E+Z$; 1H); 7.19–7.73 (m, 7H); 8.11–8.20 (m, 2H).

Ethyl($E+Z$)-2-phenylseleno-3-(4-chlorophenyl)-2-propenoate (**3c**): oil. IR (film): 1715 cm^{-1} (C=O). δ_H (200 MHz, $CDCl_3$)1.04 and 1.05 (2t, 3H, $J = 7.0$ Hz); 4.02 and 4.06 (2q, 2H, $J = 7.0$ Hz); 6.94 (s, 1H, E vinylic H); 8.06 (s, 1H, Z vinylic H); 7.15–7.69 (m, 9H). Anal. Found: C, 55.8; H, 4.1. $C_{17}H_{15}ClO_2Se$ requires: C, 55.8; H, 4.0%.

Ethyl($E+Z$)-2-phenylseleno-3-phenyl-2-propenoate (**3d**): oil. IR (film): 1714 cm^{-1} (C=O). δ_H (200 MHz, $CDCl_3$) 1.00 and 1.03 (2t, 3H, $J = 7.0$ Hz); 4.02 and 4.05 (2q, 2H, $J = 7.0$ Hz); 7.16–7.62 (m, 10H); 7.04 (s, 1H, E vinylic H); 8.15 (s, 1H, Z vinylic H). Anal. Found: C, 61.8; H, 4.8. $C_{17}H_{16}O_2Se$ requires: C, 61.6; H, 4.8%.

Ethyl($E+Z$)-2-phenylseleno-3-(4-methylphenyl)-2-propenoate (**3e**): oil. IR (film): 1714 cm^{-1} (C=O). δ_H (200 MHz, $CDCl_3$) 1.03 (t, 3H, $J = 7.0$ Hz); 2.34 and 2.39 (2s, 3H); 4.05 (q, 2H, $J = 7.0$ Hz); 7.06–7.60 (m, 10H, includes E vinylic H); 8.15 (s, 1H, Z isomer; literature 8.19 [5]).

Ethyl-2-phenylseleno-acrylate (**3f**): oil. IR (film): 1725 cm^{-1} (C=O). δ_H (200 MHz, $CDCl_3$) 1.30 (t, 3H, $J = 7.0$ Hz); 4.26 (q, 2H, $J = 7.0$ Hz); 5.34 (s, 1H); 6.65 (s, 1H); 7.3–7.6 (m, 5H).

Ethyl($E+Z$)-2-phenylseleno-2-hexenoate (**3g**): oil. IR (film): 1710 cm^{-1} (C=O). δ_H (200 MHz, $CDCl_3$) 0.89 (t, 3H, $J = 7.0$ Hz); 0.98 (t, 3H, $J = 7.0$ Hz); 1.02–1.6 (m, 2H); 2.42 and 2.46 (2q, 2H, $J = 7.3$ Hz); 4.09 and 4.12 (q, 2H $J = 7.0$ Hz); 6.29 (t, $J = 7.7$, 1H, E isomer); 7.17–7.53 (m, 6H, includes Z isomer). m/z 298 (M, 97%), 252 (60), 172 (100).

Ethyl($E+Z$)-2-phenylseleno-2-nonenoate (**3h**): oil. IR (film): 1710 cm^{-1} (C=O). δ_H (200 MHz, $CDCl_3$) 0.87 (t, 3H, $J = 7.0$ Hz); 1.11 and 1.15 (2t, 3H, $J = 7.0$ Hz); 1.25–1.68 (m, 8H); 2.45 (q, 2H, $J = 7.0$ Hz); 4.06 and 4.10 (2q, 2H, $J = 7.0$); 6.28 (t, 1H, E isomer); 7.23–7.57 (m, 6H, includes Z isomer).

3.5. Typical procedure for the Diels–Alder reaction

To a suspension of dry $ZnBr_2$ (1.2 mmol, 0.27 g) in dichloromethane (2 ml) at 0°C was added a solution of **3f** (1 mmol, 0.25 g) in dichloromethane (2 ml). The mixture was stirred for 10 min and the diene (10 mmol) was added. The reaction was stirred for 48 h at room temperature (for isoprene) or for 3 h at 0°C (for cyclopentadiene). After completion, a saturated aqueous solution of $NaHCO_3$ (50 ml) was added, extracted with dichloromethane (2×25 ml); the organic phase was dried over $MgSO_4$ and the solvent removed in vacuo. The residue was purified by column chromatography on silica gel, eluting with hexane–ethyl acetate (99:1).

Ethyl-4-methyl-1-phenylselanyl-3-cyclohexene-1-carboxylate (**6**): oil. IR (film): 1720 cm^{-1} (C=O). δ_H (400 MHz, $CDCl_3$) 1.12 (t, 3H, $J = 7.0$ Hz); 1.62 (s, 3H); 1.97–2.18 (m, 4H); 2.43 (AB quart, 2d, $J = 18$ Hz); 4.02 (q, 2H, $J = 7.0$ Hz); 5.29 (s, 1H); 7.23–7.60 (m, 5H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C 13.74; 23.08; 28.37; 30.16; 33.45; 48.16; 60.49; 118.57; 125.64; 127.48; 128.41; 128.90; 131.28; 133.37; 137.14; 173.01. m/z 323 (M^+); 167 (40); 93 (100); 77 (40). Anal. Found: C, 59.55; H, 6.33. $C_{16}H_{20}O_2Se$ requires: C, 59.25; H, 6.22%.

Ethyl-2-phenylselanylbicyclo[2.2.1]hept-5-ene-2-carboxylate (**7**): oil. IR (film): 1727 cm^{-1} (C=O). ^{1}H-NMR δ_H (400 MHz, $CDCl_3$) *exo* + *endo*: 1.07 and 1.08 (2t, 3H, $J = 7.0$ Hz); 3.79–3.90 (m, 2H); 7.20–7.55 (m, 5H); *exo* isomer 1.22 (d, 1H, $J = 9.2$); 1.60–1.64 (m, 1H); 1.93 (dd, 1H, $J = 12.8$ and 3.6 Hz); 2.15 (dd, 1H, $J = 12.8$ and 2.4 Hz); 2.92 (br s, 1H); 3.44 (s, 1H); 6.15 (m, 1H); 6.22 (m, 1H); *endo* isomer 1.36 (dd, 1H, $J = 12.8$ and 2.8 Hz); 1.60–1.65 (m, 1H); 2.15 (d, 1H, $J = 8.4$ Hz); 2.61 (dd, 1H, $J = 12.8$ and 3.6 Hz); 2.92 (br s, 1H); 3.07 (s, 1H); 5.84 (m, 1H); 6.09 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C 13.75; 13.82; 37.80; 37.98; 41.93; 42.76; 47.50; 48.02; 49.38; 49.50; 55.17; 56.15; 60.40; 60.85; 128.26; 128.37; 128.60; 128.86; 133.82; 134.65 138.26; 138.88; 173.46; 174.03. Anal. Found: C, 60.2; H, 5.60. $C_{16}H_{18}O_2Se$ requires: C, 59.8; H, 5.60%.

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[17] All products were compared with authentic samples prepared and adequately characterized previously [6]. For compounds **3c** and **3d**, besides comparing with literature data, correct elemental analyses were also provided.