Oxidation of Diphenyl Diselenide with 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ). A New Method for the Electrophilic Phenylselenenylation of Alkenes under Mild Conditions.

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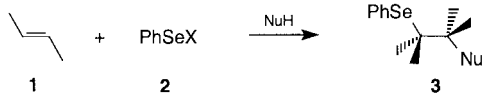
Abstract: The oxidation of diphenyl diselenide with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) represents a convenient mild method to produce a strongly electrophilic phenylselenium reagent. Clean phenylseleno methoxylations and hydroxylations of alkenes containing different types of functional groups can be effected by working in methanol or in acetonitrile and water, respectively. This new electrophilic reagent can also be employed to promote efficient cyclization reactions of alkenols to tetrahydrofurans or of alkenoic acids to lactones.

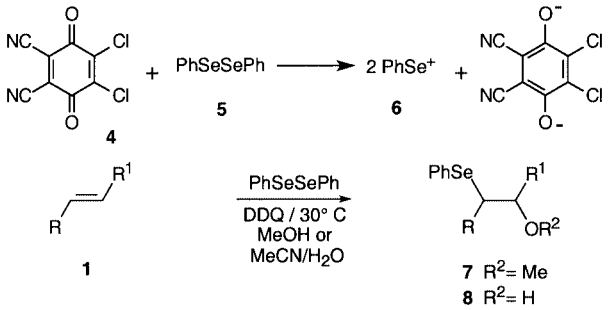
Key words: selenium, electrophilic additions, cyclization reactions

Organoselenium compounds are presently employed in organic synthesis as very useful and powerful reagents.[1–7] In most of the selenium promoted conversions the first step requires the introduction of a phenylseleno group into an organic molecule. Among the various methods available the most efficient and most largely used procedure consists in the reaction of an electrophilic phenylselenium reagent **2** with an alkene **1** in the presence of a nucleophile. In this way the alkyl phenyl selenides **3** are formed as the result of a stereospecific *anti*-addition reaction (Scheme 1).



Scheme 1

The use of the commercially available phenylselenenyl chloride and bromide often gives rise to undesirable processes such as incorporation of halide anions and decrease in regioselectivity. For this purpose new phenylselenenylating agents, which do not contain nucleophilic counterions have been introduced. Some of them were prepared from PhSeCl like the *N*-phenylselenophthalimide[8,9] or generated in situ with silver salts, like the hexafluorophosphate[10] or the triflate.[11,12] In other cases the electrophilic reagent was more conveniently produced in situ by the oxidation of the diphenyl diselenide with several reagents. Thus KNO_3,[13] $CuSO_4$,[13] $Ce(NH_4)_2(NO_2)_6$[13] were all successfully employed. Among these inorganic oxidizing agents the most efficient and versatile is the $(NH_4)_2S_2O_8$, which produces the strongly electrophilic phenylselenenyl sulfate.[13–16] Organic oxidizing agents, like *m*-nitrobenzenesulfonyl peroxide[17] or iodobenzene diacetate,[18] have also been used in some cases. The drawback of most of these methods is that the reaction conditions employed are often not compatible with sensitive functional groups, which may be present in the starting alkene. Thus, a method to effect the oxidation of diphenyl diselenide under mild experimental conditions is still desirable. On the basis of its known behavior,[19] we examined the possibility of using the 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) **4**. It was thus observed that an electron transfer reaction from the diphenyl diselenide **5** to the DDQ **4** occurred easily and afforded the strongly electrophilic phenylselenenylating agent **6** (Scheme 2). The reaction can be carried out in methanol, in acetonitrile or in a mixture of acetonitrile and water at 30 °C.



Scheme 2

Treatment of the diphenyl diselenide with DDQ represents therefore a new, very simple and convenient method to produce the electrophilic phenylselenium reagent under extremely mild experimental conditions. The efficiency of the method has been tested by studying the phenylseleno methoxylation and hydroxylation of different types of alkenes as well as the selenium promoted cyclization reactions of alkenols and alkenoic acids. As indicated in Scheme 2 the reactions of alkenes **1** in methanol or in acetonitrile and water afforded the β-methoxyselenide **7** or β-hydroxyselenide **8**, respectively.

The results obtained are summarized in Table 1. Reaction yields are good in almost every case. In the phenylseleno methoxylation reactions,[20] as already observed with other

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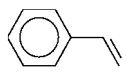
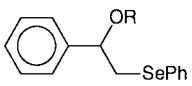
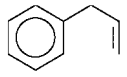
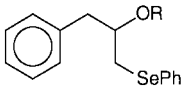
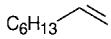
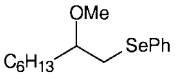
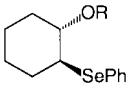
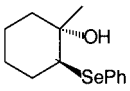
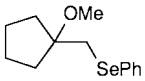
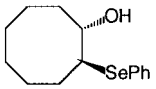
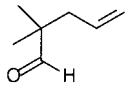
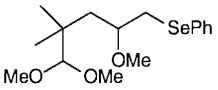
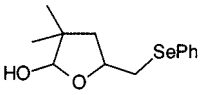
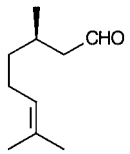
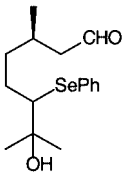
Table 1 Phenylseleno Methoxylation and Hydroxylation of Alkenes with PhSeSePh and DDQ in Methanol or in Acetonitrile and Water, respectively, at 30 °C.

Entry	Alkene **1**	β-Methoxyselenide **7** or β-Hydroxyselenide **8**	Yield (%)[a]
a			65 90
b			50[b] 45[c]
c			54[d]
d			98 78
e			78
f			93
g			64
h			49
			84[e]
i			50[f]

[a] The yields of the β-hydroxyselenides are reported in italic.
[b] A 32% of the other regioisomer was isolated.
[c] A 30% of the *anti*-Markovnikov product was isolated.
[d] A 8% of the other regioisomer was isolated.
[e] Isolated as a 2:1 mixture of diastereoisomers.
[f] Isolated as a 1:1 mixture of diastereoisomers.

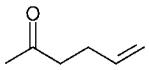
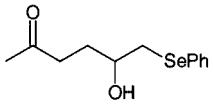
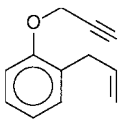
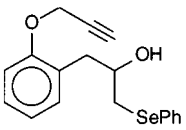
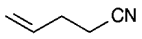
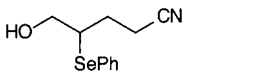
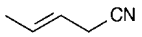
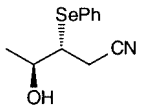
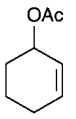
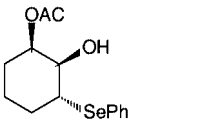
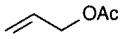
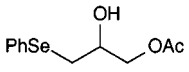
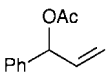
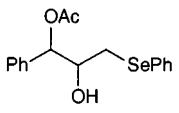
phenylselenenylating agents, the addition is not always regiospecific. Products deriving from a clean Markovnikov orientation were observed in the cases of **7a**, **7f** and **7h**, whereas a mixture of the two regioisomers was obtained in the cases of **7b** and **7c**. As expected, the reactions were completely stereospecific. Thus, the product of *anti*-addition **7d** was obtained as the sole reaction product. The formation of product **7h** is not unexpected since DDQ is known to behave as mild and efficient catalyst for the acetalization of carbonyl compounds.[21]

Similar results were obtained in the phenylseleno hydroxylation of alkenes.[20] β-Hydroxyselenides **8** were obtained in good yields. Compounds **8a**, **8h** and **8i** were obtained as single regioisomers. The reaction was not regiospecific in the case of **8b**. In this case also the reaction was a stereospecific *anti*-addition. In fact, the reactions of the alkenes **1d**, **1e** and **1g** afforded **8d**, **8e** and **8g**, respectively, as the sole reaction products. The cyclic hemiacetal **8h**, which is obtained in excellent yield as a 2:1 mixture of two diastereoisomers, is very likely produced from the initially formed γ-hydroxy aldehyde.

β-Hydroxyselenides can be transformed into several valuable derivatives and are therefore considered important intermediates in organic synthesis.[1–7,22] It seemed therefore interesting to investigate the scope of the present method and in particular its compatibility with other functional groups present in the starting alkenes.

Table 2 summarizes the results obtained from the phenylseleno hydroxylation of alkenes containing a carbonyl, a cyano, an acetylenic or an acetoxy as a second functional group. In every case the reaction occurs selectively at the C,C-double bonds and is not influenced by the presence of the other functional groups. Reaction yields are good in all cases. With the two terminal alkenes **1m** and **1n** the addition reaction is not regiospecific. In contrast, the β-hydroxyselenide **8l** was obtained as the sole reaction product.

Table 2 Conversion of functionalized Alkenes into β-Hydroxyselenides.

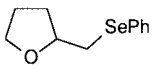
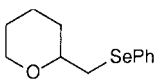
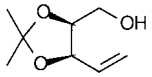
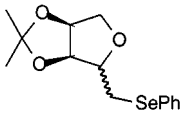
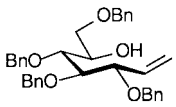
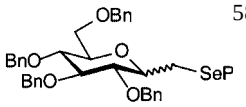
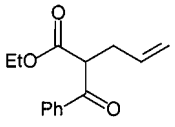
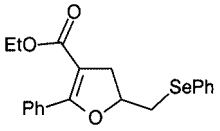
Entry	Alkene **1**	β-Hydroxyselenide **8**	Yield (%)
l			77
m			44[a]
n			66[a]
o			86
p			59
q			68[b]
r			80[c]

[a] A 17% of the other regioisomer was isolated.
[b] A 13% of 2-hydroxy-1-[(phenylseleno)methyl]ethyl acetate was obtained.
[c] Isolated as a 1:1 mixture of diastereoisomers.

The preference for Markovnikov addition observed in the reaction of the alkenes **1l**, **1q** and **1r** is not surprising since similar results were observed in the phenylseleno acetoxylation of terminal alkenes containing an acyloxy group in the allylic or homoallylic position.[23] The reactions of alkenes **1o** and **1p** proceed with high regio- and stereoselectivity. Remarkably, the reaction of **1p** with *N*-phenylselenophthalimide in the presence of water was not regiospecific.[24]

The new electrophilic phenylselenenylating agent produced from the oxidation of diphenyl diselenide with DDQ was then employed to promote ring-closure reactions of alkenes containing internal nucleophiles.[25] The reactions investigated were the cyclizations of alkenols **9** to the cyclic selenoethers **10**, and of alkenoic acids **11** to the lactones **12,** in acetonitrile at 30 °C. The results obtained are collected in Table 3 and in Table 4.

Table 3 Ring-closure Reactions of Alkenols promoted by PhSeSePh and DDQ in CH_3CN at 30 °C.

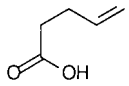
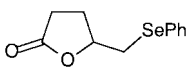
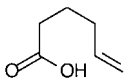
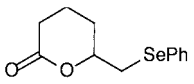
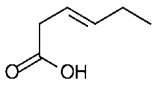
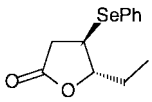
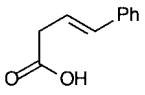
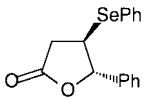
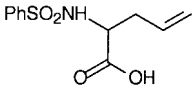
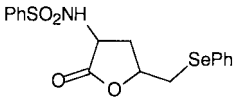
Entry	Alkenol **9**	Cyclic selenoether **10**	Yield (%)
a			86
b			70
c			57[a,c]
d			58[b,c]
e			70

[a] Isolated as a 1:1 mixture of diastereoisomers.
[b] Isolated as a 8:2 mixture of diastereoisomers.
[c] The ratios were determined by GC-MS.

The cyclizations of the alkenols **9** proceeded easily and afforded the expected five- or six-membered cyclic selenoethers **10** in good yields.[26] The formation of compounds **10c** and **10d** is interesting since these compounds[18] have been recently used for the synthesis of C-glycosides, potential inhibitors[27] of carbohydrate processing enzymes as well as for the synthesis of hydroxylated pyrrolizidines.[28]

The results collected in Table 4 show that the cyclizations of the alkenoic acids **11** in acetonitrile proceed smoothly in all the cases investigated and afforded the expected γ- or δ-lactones **12** in fairly good yields. The products **12c** and **12d** were obtained as single stereoisomers thus confirming that the ring-closure reaction is a stereospecific

Table 4 Ring-closure Reactions of unsaturated Acids promoted by PhSeSePh and DDQ in CH_3CN at 30 °C.

Entry	Alkenoic acid **11**	Lactone **12**	Yield (%)
a			95[a]
b			85
c			63
d			47
e			90[b]

[a] The reaction from the corresponding methyl ester furnished also the hydroxyphenylselenenylated product in appreciable yield.
[b] Isolated as a 1:1 mixture of diastereoisomers.

anti-addition as observed with other phenylselenenylating agents.[1–7]

In conclusion, the results described in the present paper indicate that the oxidation of diphenyl diselenide with DDQ represents a very simple method to produce the strongly electrophilic phenylselenenylating agent in the absence of nucleophilic counterions. Reaction conditions are very mild and allow alkenes containing other functional groups to be used as reagents. The examples described above demonstrate that this new procedure is general and that it favourably compares with the other methods described in the literature.[1–7,25]

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(20) All new compounds were fully characterized by MS, ^{1}H and ^{13}C NMR spectroscopy and by combustion analysis. Starting materials are commercially available or were prepared as described in the literature. **Phenylseleno methoxylation and hydroxylation of alkenes:** General Procedure. To the solution of the starting alkene (1 mmol), in anhyd MeOH (15 mL) or in CH_3CN and H_2O (98:2) (15 mL), diphenyl diselenide (0.6 mmol)and then DDQ (0.6 mmol) were added and the mixture was stirred at 30 °C. The initial deep red color of the solution gradually disappears. The progress of the reaction was monitored by TLC and GC-MS. Reaction times ranged from 8 h to 48 h. The reaction mixture was poured into 10% Na_2CO_3 solution to eliminate the formed hydroquinone and extracted with Et_2O. The organic layer was dried (Na_2SO_4) and evaporated. Chromatography of the residue through a silica gel column afforded the reaction products in pure form. Compounds **7a**,[17] **7c**,[17] **7d**,[14] **8a**,[8] **8b**, **8d**,[13] **8e**,[8] **8g**[8] and **8p**[17] have already been described. Physical, spectral and analytical data of some selected new compounds are reported below.
[(2,5,5-Trimethoxy-4,4-dimethylpentyl)seleno] Benzene (7h): Oil. ^{1}H NMR δ: 7.61–7.45 (m, 2 H), 7.31–7.16 (m, 3 H), 4.84 (s, 1 H), 3.58–3.4 (m, 1 H), 3.47 (s, 3 H), 3.25 (s, 3 H), 3.12 (dd, 1 H, *J* = 12.1 and 4.3 Hz), 2.93 (dd, 1 H, *J* = 12.1 and 7.1 Hz), 1.67–1.58 (m, 2 H), 0.93 (s, 3 H), 0.91 (s, 3 H). ^{13}C NMR δ: 132.7 (2 C), 128.8 (2 C), 128.7, 126.7, 113.6, 77.7, 58.2 (2 C), 55.6, 42.0, 38.9, 32.9, 22.9, 22.1. MS *m/z* (relative intensity): 346 (17), 175 (23), 143 (71), 111 (29), 75 (100), 47 (12). Anal. Calcd for $C_{16}H_{26}O_3Se$: C, 55.65; H, 7.59. Found: C, 55.77; H, 7.48.
3,3-Dimethyl-5-[(phenylseleno)methyl] tetrahydrofuran-2-ol (8h): Mixture of two diastereoisomers (2.6:1). Oil. Major diast. ^{1}H NMR δ: 7.60–7.45 (m, 2 H), 7.34–7.15 (m, 3 H), 4.9 (s, 1 H), 4.50–4.25 (m, 1 H), 3.82 (bs, 1 H), 3.24 (dd, 1 H, *J* = 12.2 and 5.7 Hz), 3.02 (dd, 1 H, *J* = 12.2 and 7.1 Hz), 1.84 (dd, 1 H, *J* = 12.2 and 6.5 Hz), 1.69 (dd, 1 H, *J* = 12.2 and 9.3 Hz), 1.08 (s, 3 H). ^{13}C NMR δ: 132.5 (2 C), 129.9, 128.9 (2 C), 126.8, 104.2, 78.2, 44.1, 43.1, 35.0, 25.2, 29.1. Minor diast. ^{1}H NMR δ: 7.60–7.45 (m, 2 H), 7.34–7.15 (m, 3 H), 5.04 (s, 1 H), 4.50–4.25 (m, 1 H), 3.92 (bs, 1 H), 3.12 (dd, 1 H, *J* = 12.1 and 6.0 Hz), 2.97 (dd, 1 H, *J* = 12.1 and 7.1 Hz), 2.04 (dd, 1 H, *J* = 12.6 and 7.7 Hz), 1.5 (dd, 1 H, *J* = 12.6 and 6.8 Hz), 1.08 (s, 3 H). ^{13}C NMR δ: 132.5 (2 C), 129.9, 128.9 (2 C), 126.8, 104.6, 76.3, 43.9, 43.1, 33.7, 27.1, 21.6; MS *m/z* (relative intensity): 286 (46), 172 (100), 157 (39), 97 (36), 83 (70), 55 (76), 41 (33). Anal. Calcd for $C_{13}H_{18}O_2Se$: C, 54.74; H, 6.36. Found: C, 54.88; H, 6.23.
(3*R*)-7-(*RS*)-Hydroxy-3,7-dimethyl-6-(phenylseleno) Octanal (8i): Mixture of two diastereoisomers (1:1). Oil. ^{1}H NMR δ: 9.74 (t, 1 H, *J* = 2.1 Hz), 9.63 (t, 1 H, *J* = 2.2 Hz), 7.66–7.52 (m, 4 H), 7.33–7.20 (m, 6 H), 3.08 (dd, 1 H, *J* = 5.8 and 2.4 Hz), 3.02 (dd, 1 H, *J* = 5.9 and 2.1 Hz), 2.9–2.55 (bs, 2 H), 2.5–2.1 (m, 4 H), 2.08–1.2 (m, 10 H), 1.36 (s, 6 H), 1.25 (s, 6 H), 0.95 (d, 6 H, *J* = 7.3 Hz). ^{13}C NMR δ: 202.5 (2 C), 133.6 (4 C), 129.3 (2 C), 129.1 (4 C), 127.2 (2 C), 72.8 (2 C), 64.9, 64.8, 51.1, 50.5, 36.2, 35.9, 30.2, 30.0, 28.0, 27.5, 26.9 (2 C), 26.8 (2 C), 20.2, 19.4; MS *m/z* (relative intensity): 328 (3), 270 (32), 158 (100), 113 (37), 95 (88), 69 (65), 43 (94). Anal. Calcd for $C_{16}H_{24}O_2Se$: C, 58.71; H, 7.39. Found: C, 58.84; H, 7.28.
5-Hydroxy-6-(phenylseleno)hexan-2-one (8l): Oil. ^{1}H NMR δ: 7.58–7.42 (m, 2 H), 7.34-7.12 (m, 3H), 3.74-3.6 (m, 1H), 3.07 (dd, 1H, *J* = 12.6 and 4.5 Hz), 2.90 (dd, 1 H, *J* = 12.6 and 7.8 Hz), 3.1–2.85 (bs, 1 H), 2.58 (dd, 1 H, *J* = 7.2 and 3.2 Hz), 2.55 (dd, 1 H, *J* = 7.2 and 3.0 Hz), 2.0–1.6 (m, 2 H), 2.13 (s, 3 H); ^{13}C NMR δ: 208.9, 132.6 (2 C), 129.0, 128.8 (2 C), 127.0, 69.3, 39.7, 36.4, 30.0. Anal. Calcd for $C_{12}H_{16}O_2Se$: C, 53.14; H, 5.95. Found: C, 53.27; H, 5.83.
2-Hydroxy-1-phenyl-3-(phenylseleno) Propyl Acetate (8r): Mixture of two diastereoisomers (1:1). Oil. ^{1}H NMR δ: 7.5–7.12 (m, 20 H), 5.78 (d, 1 H, *J* = 6.4 Hz), 5.3–5.1 (m, 2 H), 4.95 (d, 1 H, *J* = 4.8 Hz), 4.1–3.92 (m, 1 H), 3.15 (dd, 1 H, *J* = 13.0 and 5.5 Hz), 3.1–2.7 (m, 3 H), 2.8 (dd, 1 H, *J* = 13.0 and 8.0 Hz). ^{13}C NMR δ: 170.1 (2 C), 136.2 (2 C), 132.6 (2 C), 129.1 (2 C), 128.5 (4 C), 128.4 (4 C), 128.1 (4 C), 127.1 (2 C), 126.9 (2 C), 126.5 (2 C), 77.9, 76.5, 74.2, 72.6, 31.8, 27.6, 21.0, 20.6. MS *m/z* (relative intensity): 350 (14), 201 (29), 183 (37), 157 (30), 133 (41), 107 (100), 71 (28), 43 (64). Anal. Calcd for $C_{17}H_{18}O_3Se$: C, 58.46; H, 5.19. Found: C, 58.53; H, 5.28.
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(26) **Ring-Closure Reactions.** General Procedure. A solution of diphenyl diselenide (0.6 mmol), of DDQ (0.6 mmol) and of the alkenol or the alkenoic acid (1 mmol) in CH_3CN (15 mL) was stirred at 30 °C. The progress of the reaction was monitored by TLC and GC-MS, the reaction times ranged from 8 h to 30 h and during this time the color of the mixture gradually disappeared. The reaction mixture was poured into 10% Na_2CO_3 solution and extracted with diethyl ether. The organic layer was dried (Na_2SO_4) and evaporated. Chromatography of the residue through a silica gel column afforded the reaction products in pure form. Compounds **10a**,[15] **10b**,[15] **10c**,[18] **10d**,[18] **10e**,[15] **12a**–**c**[15] have already been described. Physical, spectral and analytical data of some selected compounds are reported below. **(4*RS*,5*SR*)-5-Phenyl-4-(phenylseleno)dihydrofuran-2(3*H*)-one(12d):**[29] Oil. ^{1}H NMR δ: 7.58–7.42 (m, 2 H), 7.4–7.28 (m, 8 H), 5.35 (d, 1 H, *J* = 7.3 Hz), 3.73 (dt, 1 H, *J* = 8.2 and 7.3 Hz), 3.02 (dd, 1 H, *J* = 17.6 and 8.2 Hz), 2.64 (dd, 1 H, *J* = 17.6 and 8.2 Hz). ^{13}C NMR δ: 173.3, 137.0, 135.9 (2 C), 129.4 (2 C), 128.8 (2 C), 128.6 (3 C), 125.7 (2 C), 86.0, 42.1, 35.9. MS *m/z* (relative intensity): 318 (20), 184 (100), 161 (21), 105

(48), 77 (38). Anal. Calcd for $C_{16}H_{14}O_2Se$: C, 60.58; H, 4.45. Found: C, 60.56; H, 4.46.

***N*-{2-Oxo-5-[(phenylseleno)methyl]tetrahydrofuran-3-yl}benzenesulfonamide (12e)**: Oil. First diastereoisomer. ^{1}H NMR δ: 7.92–7.8 (m, 2 H), 7.65–7.44 (m, 5 H), 7.35–7.24 (m, 3 H), 5.56 (d, 1 H, *J* = 4.5 Hz), 4.5 (ddt, 1 H, *J* = 10.1, 7.4 and 5.1 Hz), 4.03 (ddd, 1 H, *J* = 11.3, 8.3 and 4.5 Hz), 3.27 (dd, 1 H, *J* = 13.0 and 5.1 Hz), 3.0 (dd, 1 H, *J* = 13.0 and 7.4 Hz), 2.0–1.8 (m, 2 H). ^{13}C NMR δ: 173.5, 139.3, 132.7 (2 C), 129.5 (2 C), 129.3 (2 C), 128.3, 128.0, 127.2 (3 C), 76.8, 52.9, 36.4, 30.7. Second diastereoisomer. ^{1}H NMR δ: 7.92–7.80 (m, 2 H), 7.65–7.44 (m, 5 H), 7.35–7.24 (m, 3 H), 5.3 (d, 1 H, *J* = 4.3 Hz), 4.78 (dddd, 1 H, *J* = 7.5, 7.4, 4.8 and 1.7 Hz), 4.2 (ddd, 1 H, *J* = 9.5, 8.4 and 4.3 Hz), 3.15 (dd, 1 H, *J* = 13.3 and 4.8 Hz), 3 (dd, 1 H, *J* = 13.3 and 7.4 Hz), 2.5 (ddd, 1 H, *J* = 13.5, 8.4 and 1.7 Hz), 2.37 (ddd, 1 H, *J* = 13.5, 9.5 and 7.5 Hz). ^{13}C NMR δ: 173.0, 139.3, 133.3 (2 C), 129.5 (2 C), 129.3 (2 C), 128.3, 128.0, 127.2 (3 C), 77.6, 51.2, 34.3, 31.6. Anal. Calcd for $C_{17}H_{17}NO_4SSe$: C, 49.76; H, 4.18; N, 3.41. Found: C, 49.78; H, 4.21; N, 3.38.

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