Novel and convenient acetoxyselenenylation of alkenes catalyzed by potassium iodide

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A B S T R A C T

With KI as catalyst and *m*-chloroperbenzoic acid as the oxidant in acetic acid, a novel and efficient catalytic procedure has been developed for acetoxyselenenylation of alkenes, which providing a series of 2-acetoxy-1-selenenylation compounds with high regioselectivity and good yields in mild conditions. In this protocol, KI is first oxidized by *m*-chloroperbenzoic acid into acetylhypoiodite, which rapidly reacts with diselenide to form the active electrophilic selenenylating reagent, following an electrophilic addition of alkenes and 2-acetoxy-1-selenenylation compounds are obtained. The suitable equivalent ratio of alkene to diselenide is 1.2.

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Introduction

The oxyselenenylation reaction is a very useful procedure for the anti-l, 2-addition of an organylseleno group and an oxygen substituent (HO, RO, RCO$_2$) to an olefin [1]. The prepared products can also be transformed to the double-bond transpositioned allylic alcohols and ethers by oxidative deselenenylation sequence [2]. In the electrophilic addition, the most common selenenylating reagents PhSeX (X = Cl, Br) are usually commercially available, they are also prepared from oxidative cleavage of diphenyl diselenide by halogens [3]. However, the presence of toxic and moisture-sensitive nature of PhSeX, and the nucleophilic halide anions are sometimes responsible for some undesirable processes such as addition of the halide ion and the decrease in stereoselectivity, some new alternative methods have been developed such as cupric catalytic oxidation [4], electrolytic oxidation [2c,5] and photoelectron transfer [6]. Other production of the electrophilic phenylselenium cation can be effected by the reaction of diphenyl diselenide with ammonium peroxydisulfate [7] and *m*-nitrobenzenesulfonyl peroxide [8]. Using hypervalent iodine reagent PhI(OAc)$_2$, Tingoli and co-workers reported the successful oxidative cleave the Se—Se bond, and the electrophilic addition of the *in situ* generated reactive

electrophilic selenium species to alkenes proceeded smoothly [9]. Several further modifications of this reaction have recently been reported [10]. However, the catalytic oxyselenenylation using hypervalent iodine reagents as catalysts is developed rarely.

We have been interesting in oxidation and functionalization of organic compounds using hypervalent iodine reagents, especially the catalytic utilization of hypervalent iodine reagents in organic synthesis. In our new research, we have found that some inorganic iodides or molecular iodine can be used to replace hypervalent iodine reagents and the similar results have been obtained [11]. Recently, we have investigated the acetoxyselenenylation of alkenes with a catalytic amount hypervalent iodine reagent. In a parallel study, we found that when the hypervalent iodine reagent was replaced by KI, the acetoxyselenenylation of alkenes was carried out fluently with high regioselectivity and yields in mild conditions. Herein, we wish to report the novel and convenient acetoxyselenenylation of alkenes using KI as catalyst and *m*-chloroperbenzoic acid as the terminal oxidant, and to our knowledge this method has not been reported before.

Discussion and results

Initially, NH$_4$I was used as representative of inorganic iodides to attempt the novel catalytic acetoxyselenenylation of alkenes. When

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0.2 equiv. of NH_4I was added to the mixture of 1.0 equiv. of diphenyl diselenide (**2a**), 1.2 equiv. of *m*-chloroperbenzoic acid (*m*CPBA) and 1.5 equiv. of styrene (**1a**) in acetic acid (AcOH), it was found that the novel acetoxyselenenylation occurred smoothly at room temperature and after 6 h it afforded the predominated Markovnikov addition product, 1-phenyl-2-(phenylselanyl)ethyl acetate (**3a**) in 70% yield (Table 1, entry 1). If NH_4I was absent, a parallel experiment gave only 5% yield of **3a** (entry 2). Therefore, it was obvious that NH_4I played a key action in the reaction.

In light of the successful formation of **3a** in the presence of NH_4I, the reaction conditions were optimized and the results are summarized in Table 1. Firstly, several mixture solvents of acetic acid were used in the reaction, however, the yields were low (Table 1, entries 3–6). When CH_2Cl_2, CH_3CN and H_2O were used as sole solvent respectively, and 3.0 equiv. of AcOH was added in the reaction, the rather poor yields were determined (entries 7–9). When NaOAc took the place of AcOH as nucleophilic reagent in CH_3CN, no the desired product was observed (entry 10). With AcOH as the suitable solvent, two iodides NaI and KI were compared with NH_4I, and KI was the most effective one among them (entries 1, 11 and 12). Other oxidants, such as Oxone® and $NaBO_3 \cdot 4H_2O$ were active in the reaction, normally resulted in good yields (entries 13 and 14). The yields of **3a** dropped down when the amount of *m*CPBA was more or less then 1.0 equiv. due to the excess oxidant could lead to elimination reaction to produce the vinylic acetate α-acetoxystyrene (entries 12, 15–19) [2,12]. The amount of KI was investigated and 0.2 equiv. was the best choice (entries 17, 20 and 21). As the results showed that the reaction proceeded rapidly and it was completed in only 2 h (entries 17, 22–25). Finally, the amount of styrene was also checked, and 1.2 equiv. of it was optimal for the reaction (entries 26–28).

With the optimal conditions in hand, in order to assess the scope of this method, several alkenes **1** (1.2 equiv.) were treated with *m*CPBA (1.0 equiv.) and diselenide **2** (1.0 equiv.) in the presence of KI (0.2 equiv.) in AcOH for 2 h, a series of 2-acetoxy-1-selenenylation compounds, most new compounds were prepared (Table 2).

As shown in Table 2, the reaction was compatible with most of the studied alkenes except 2-methyl-3-buten-2-ol (**1k**), which provided the corresponding 2-acetoxy-1-selenenylation compounds in good to excellent yields (entries 1–11). It was also found that the groups on the benzene ring, no matter they were electron-donating or electron-withdrawing groups, did not influence on the yield (entries 2–7). Cyclohexene (**1i**) and bicyclo[2.2.1]hept-2-ene (**1j**), when they were treated under the same conditions, the addition proceeded in a *trans* fashion and single stereoisomers were isolated with excellent yields (entries 9 and 10). Compared with **2a**, dibenzyl diselenide (**2b**), an aliphatic diselenide also reacted easily with alkenes, but the yields slightly dropped down (entries 12–14).

Based on the remarkably catalytic effect of KI in the acetoxyselenenylation of alkenes, a plausible reaction pathway is suggested in Scheme 1 [2c,5]. Thus, KI is first oxidized by *m*CPBA to the corresponding acetylhypoiodite **A**, which reacts smoothly with diselenide **2** to form the active intermediate **B** [13], following a rapid cleavage of Se–Se bond, the electrophilic selenium species

Table 1
Optimization of the acetoxyselenenylation of alkenes using KI as catalyst.

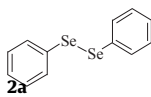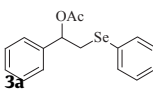| Entry	Styrene (equiv.)	Oxidant (equiv.)	I⁻ (equiv.)	Solvent	Time (h)	Yield (%)[a]
1	1.5	*m*CPBA (1.2)	NH_4I (0.2)	AcOH	6	70
2	1.5	*m*CPBA (1.2)	–	AcOH	6	5
3	1.5	*m*CPBA (1.2)	NH_4I (0.2)	AcOH-CH_2Cl_2 (1:1)	6	54
4	1.5	*m*CPBA (1.2)	NH_4I (0.2)	AcOH-CH_3CN (1:1)	6	47
5	1.5	*m*CPBA (1.2)	NH_4I (0.2)	AcOH-H_2O (1:1)	6	20
6	1.5	*m*CPBA (1.2)	NH_4I (0.2)	AcOH-EtOAc (1:1)	6	52
7	1.5	*m*CPBA (1.2)	NH_4I (0.2)	CH_2Cl_2	6	15[b]
8	1.5	*m*CPBA (1.2)	NH_4I (0.2)	CH_3CN	6	11[b]
9	1.5	*m*CPBA (1.2)	NH_4I (0.2)	H_2O	6	0[b]
10	1.5	*m*CPBA (1.2)	NH_4I (0.2)	CH_3CN	6	0[c]
11	1.5	*m*CPBA (1.2)	NaI (0.2)	AcOH	6	87
12	1.5	*m*CPBA (1.2)	KI (0.2)	AcOH	6	90
13	1.5	Oxone (1.2)	KI (0.2)	AcOH	6	89
14	1.5	$NaBO_3 \cdot 4H_2O$ (1.2)	KI (0.2)	AcOH	6	80
15	1.5	*m*CPBA (2.0)	KI (0.2)	AcOH	6	38
16	1.5	*m*CPBA (1.5)	KI (0.2)	AcOH	6	78
17	1.5	*m*CPBA (1.0)	KI (0.2)	AcOH	6	94
18	1.5	*m*CPBA (0.8)	KI (0.2)	AcOH	6	88
19	1.5	*m*CPBA (0.6)	KI (0.2)	AcOH	6	71
20	1.5	*m*CPBA (1.0)	KI (0.3)	AcOH	6	94
21	1.5	*m*CPBA (1.0)	KI (0.15)	AcOH	6	89
22	1.5	*m*CPBA (1.0)	KI (0.2)	AcOH	2	95
23	1.5	*m*CPBA (1.0)	KI (0.2)	AcOH	1.5	92
24	1.5	*m*CPBA (1.0)	KI (0.2)	AcOH	1	86
25	1.5	*m*CPBA (1.0)	KI (0.2)	AcOH	0.5	71
26	1.3	*m*CPBA (1.0)	KI (0.2)	AcOH	2	95
27	1.2	*m*CPBA (1.0)	KI (0.2)	AcOH	2	95
28	1.0	*m*CPBA (1.0)	KI (0.2)	AcOH	2	84
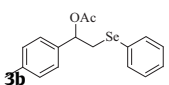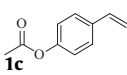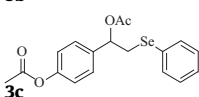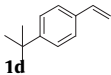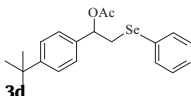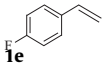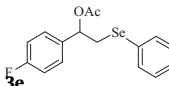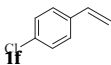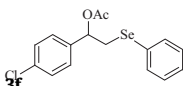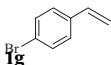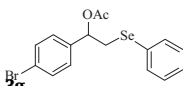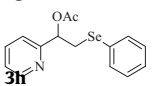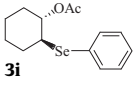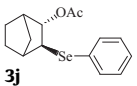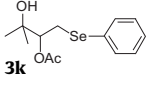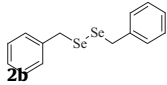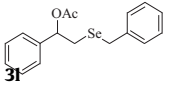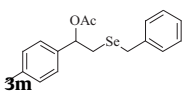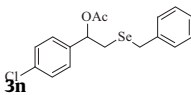
[a] Isolated yields.
[b] 3.0 equiv. HOAc was added.
[c] 3.0 equiv. NaOAc was added in CH_3CN.

reacts with alkene to produce the unstable cyclic intermediate **C**. The *in situ* generated active ArSeI [14] can further transfer a second equivalent of electrophilic selenium to alkenes to form the cyclic intermediate C. After a solvolysis of **C** in AcOH, the desired product 2-acetoxy-1-selenenylation compound **3** as a single isomer is obtained via an S_N1 mechanism for the aromatic alkenes.

When aliphatic alkenes such as **1i** and **1j** are used as alkene substrates, the reaction provides the *trans* single stereoisomers via an S_N2 mechanism, which supports the first formation of the cyclic selenium intermediate **C**, then acetate anion attacks the cyclic intermediate affording the corresponding anti-l, 2-addition products **3**.

Table 2
Preparation of 2-acetoxy-1-selenenylation compounds **3**.

Entry	Alkene 1	Diselenide 2	Product 3	Yield (%)[a]
1	1a	2a	3a	95
2	1b	2a	3b	93
3	1c	2a	3c	92
4	1d	2a	3d	88
5	1e	2a	3e	91
6	1f	2a	3f	84
7	1g	2a	3g	91
8	1h	2a	3h	67
9	1i	2a	3i	90
10	1j	2a	3j	86
11	1k	2a	3k	47
12	1a	2b	3l	72
13	1b	2b	3m	87
14	1f	2b	3n	70

 a Isolated yields.

Scheme 1. Proposed mechanism for the acetoxyselenenylation of alkenes using KI as catalyst.

Conclusions

We have developed a novel and efficient catalytic processor for synthesis of 2-acetoxy-1-selenenylation compounds by the electrophilic addition of alkenes with diselenides and mCPBA in the presence of catalytic amount of KI in AcOH at room temperature. This method has some advantages such as mild reaction conditions and simple procedure, which provided a series of 2-acetoxy-1-selenenylation compounds with high regioselectivity and good yields. Furthermore, the use of KI in the catalytic reaction will extend the application scope of inorganic iodides in organic synthesis. Other convenient anti-l, 2-addition of an organylseleno group and an oxygen substituent to unsaturated functions will be reported in due course.

Experimental

IR spectra were recorded on a Thermo-Nicolet 6700 instrument, ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker-AVANCE III (500 MHz) spectrometer, Mass spectra were determined on Waters-GCT Premier, Thermo-DECAX-60000 LCQ Deca XP and Thermo-ITQ 1100 mass spectrometers. Alkenes, diselenides, mCPBA, KI and AcOH (AR, 99.5%) were commercially available.

A typical procedure for acetoxyselenenylation of alkenes using KI as catalyst

In AcOH (1 mL), alkene **1** (0.24 mmol), diselenide **2** (0.1 mmol), KI (0.02 mmol) and m-CPBA (0.1 mmol) were added successively. The suspension mixture was vigorously stirred at r. t. for 2 h. Upon completion, the reaction was quenched by addition of sat. aq. $Na_2S_2O_3$ (2 mL), basified with sat. aq. Na_2CO_3 (8 mL) and H_2O (5 mL). The mixture was extracted with CH_2Cl_2 (3 × 5 mL) and the combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then purified on a silica gel plate (4:1 petroleum ether-ethyl acetate) to furnish 2-acetoxy-1-selenenylation compound **3**.

1-phenyl-2-(phenylselanyl)ethyl acetate (3a) [9d]
Yield: 95%; colorless viscous oil.
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.52 (dd, J = 6.5, 2.9 Hz, 2H), 7.39–7.30 (m, 5H), 7.30–7.24 (m, 3H), 5.96 (dd, J = 8.0, 5.7 Hz, 1H), 3.40 (dd, J = 12.9, 8.0 Hz, 1H), 3.25 (dd, J = 12.9, 5.7 Hz, 1H), 2.04 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm): 170.0, 139.4, 133.1, 129.8, 129.1, 128.5, 128.4, 127.2, 126.6, 75.2, 33.4, 21.0.

IR (KBr) ν: 3061, 3033, 1742, 1371, 1236, 1020, 738, 698 cm^{-1}.
MS (ESI): m/z (%) 320 (M$^+$, 1.8), 261 (100).

2-(phenylselanyl)-1-p-tolylethyl acetate (3b)
Yield: 93%; colorless viscous oil.
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.64–7.42 (m, 2H), 7.28 (dd, J = 4.9, 1.7 Hz, 3H), 7.24 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 5.93 (dd, J = 7.9, 5.9 Hz, 1H), 3.40 (dd, J = 12.8, 8.0 Hz, 1H), 3.24 (dd, J = 12.8, 5.9 Hz, 1H), 2.36 (s, 3H), 2.02 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm): 170.1, 138.3, 136.5, 133.1, 129.9, 129.3, 129.1, 127.2, 126.7, 75.2, 33.3, 21.2, 21.1.
IR (KBr) ν: 3055, 3027, 1742, 1370, 1236, 1020, 816, 738, 692 cm^{-1}.
MS (EI): m/z (%) 334 (M$^+$, 6.5), 194 (100).
HRMS: m/z [M]$^+$ calcd for $C_{17}H_{18}O_2Se$: 334.0472; found: 334.0451.

4-(1-acetoxy-2-(phenylselanyl)ethyl)phenyl acetate (3c)
Yield: 92%; pale yellow viscous oil.
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.54–7.48 (m, 2H), 7.37–7.33 (m, 2H), 7.27–7.23 (m, 3H), 7.09–7.04 (m, 2H), 5.96–5.92 (m, 1H), 3.41–3.34 (m, 1H), 3.21 (dd, J = 12.9, 5.7 Hz, 1H), 2.31 (s, 3H), 2.02 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm): 169.9, 169.3, 150.6, 137.0, 133.2, 129.7, 129.2, 127.9, 127.3, 121.7, 74.6, 33.3, 21.1, 21.0.
IR (KBr) ν: 3056, 1761, 1369, 1198, 1018, 840, 737, 691 cm^{-1}.
MS (EI): m/z (%) 378 (M$^+$, 2.8), 123 (100).
HRMS: m/z [M]$^+$ calcd for $C_{18}H_{18}O_4Se$: 378.0370; found: 378.0362.

1-(4-tert-butylphenyl)-2-(phenylselanyl)ethyl acetate (3d)
Yield: 88%; colorless viscous oil.
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.52–7.50 (m, 2H), 7.37–7.36 (m, 2H), 7.29–7.26 (m, 5H), 5.96 (dd, J = 8.0, 5.7 Hz, 1H), 3.40 (dd, J = 12.8, 8.1 Hz, 1H), 3.25 (dd, J = 12.8, 5.6 Hz, 1H), 2.03 (s, 3H), 1.33 (s, 9H).
^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm): 170.0, 151.4, 136.4, 133.1, 130.0, 129.1, 127.2, 126.4, 125.4, 75.1, 34.6, 33.4, 31.3, 21.0.
IR (KBr) ν: 3057, 2963, 1745, 1370.0, 1235, 1021, 828, 737, 691 cm^{-1}.
MS (EI): m/z (%) 376 (M$^+$, 14.1), 219 (100).
HRMS: m/z [M]$^+$ calcd for $C_{20}H_{24}O_2Se$: 376.0942; found: 376.0916.

1-(4-fluorophenyl)-2-(phenylselanyl)ethyl acetate (3e)
Yield: 91%; colorless viscous oil.
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.59–7.45 (m, 2H), 7.36–7.29 (m, 2H), 7.27–7.26 (m, 3H), 7.08–6.97 (m, 2H), 5.92 (dd, J = 7.5, 6.2 Hz, 1H), 3.38 (dd, J = 12.9, 7.7 Hz, 1H), 3.21 (dd, J = 12.8, 6.1 Hz, 1H), 2.02 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm): 170.0, 164.5, 162.1, 135.2 (d, J = 3.2 Hz), 133.2 (d, J = 5.3 Hz), 129.6, 129.2, 128.6 (d, J = 8.2 Hz), 127.4, 115.5 (d, J = 21.6 Hz), 74.7, 33.3, 21.0.
IR (KBr) ν: 3057, 1743, 1371, 1225, 1021, 836, 738, 691 cm^{-1}.
MS (EI): m/z (%) 338 (M$^+$, 19.7), 198 (100).
HRMS: m/z [M]$^+$ calcd for $C_{16}H_{15}FO_2Se$: 338.0221; found: 338.0219.

1-(4-chlorophenyl)-2-(phenylselanyl)ethyl acetate (3f)
Yield: 84%; pale yellow viscous oil.
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.54–7.44 (m, 2H), 7.33–7.29 (m, 2H), 7.29–7.20 (m, 5H), 5.93–5.85 (m, 1H), 3.42–3.30 (m, 1H), 3.26–3.14 (m, 1H), 2.02 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm): 169.9, 137.8, 134.2, 133.2, 129.5, 129.2, 128.7, 128.1, 127.4, 74.6, 33.1, 21.0.

IR (KBr) ν: 3057, 1741, 1371, 1235, 1051, 1016, 824, 738, 692 cm^{-1}.
MS (EI): m/z (%) 354 (M$^+$, 11.2), 214 (100).
HRMS: m/z [M]$^+$ calcd for C$_{16}$H$_{15}$ClO$_2$Se: 353.9926; found: 353.9902.

1-(4-bromophenyl)-2-(phenylselanyl)ethyl acetate (3g)

Yield: 91%; pale yellow viscous oil.
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.50–7.45 (m, 4H), 7.28–7.26 (m, 3H), 7.21–7.19 (m, 2H), 5.93–5.82 (m, 1H), 3.43–3.29 (m, 1H), 3.28–3.13 (m, 1H), 2.02 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm): 169.9, 138.3, 133.2, 131.6, 129.5, 129.2, 128.4, 127.4, 122.4, 74.7, 33.1, 21.0.
IR (KBr) ν: 3056, 1741, 1481, 1072, 1007, 823, 736, 690 cm^{-1}.
MS (EI): m/z (%) 398 (M$^+$, 58.5), 338 (100).
HRMS: m/z [M]$^+$ calcd for C$_{16}$H$_{15}$BrO$_2$Se: 397.9421; found: 397.9413.

2-(phenylselanyl)-1-(pyridin-2-yl)ethyl acetate (3h)

Yield: 67%; colorless viscous oil.
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 8.59–8.53 (m, 1H), 7.67 (td, J = 7.7, 1.8 Hz, 1H), 7.58–7.45 (m, 2H), 7.33 (d, J = 7.8 Hz, 1H), 7.29–7.21 (m, 4H), 6.14–5.96 (m, 1H), 3.52 (d, J = 6.0 Hz, 1H), 3.49 (d, J = 7.0 Hz, 1H), 2.05 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm): 170.2, 157.8, 149.5, 136.6, 133.0, 129.8, 129.1, 127.1, 123.2, 122.1, 75.7, 31.4, 21.0.
IR (KBr) ν: 3056, 1739, 1371, 1234, 1022, 739, 692 cm^{-1}.
MS (EI): m/z (%) 321 (M$^+$, 4.8), 183 (100).
HRMS: m/z [M]$^+$ calcd for C$_{15}$H$_{15}$NO$_2$Se: 321.0268; found: 321.0233.

2-(phenylselanyl)cyclohexyl acetate (3i) [9d]

Yield: 90%; colorless viscous oil.
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.68–7.49 (m, 2H), 7.28 (m, 3H), 4.95–4.78 (m, 1H), 3.33–3.10 (m, 1H), 2.22–2.05 (m, 2H), 1.96 (s, 3H), 1.79–1.61 (m, 2H), 1.54–1.29 (m, 4H).
^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm): 170.3, 135.0, 128.9, 128.7, 127.6, 75.4, 46.1, 32.3, 31.8, 25.8, 23.6, 21.1.
IR (KBr) ν: 3056, 2936, 2858, 1738, 1373, 1238, 1036, 741, 693 cm^{-1}.
MS (EI): m/z (%) 298 (M$^+$, 4.5), 81 (100).

3-(phenylselanyl)bicyclo[2.2.1]heptan-2-yl acetate (3j)

Yield: 86%; colorless viscous oil.
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.61–7.45 (m, 2H), 7.29–7.25 (m, 3H), 5.08–4.88 (m, 1H), 3.09 (t, J = 3.3 Hz, 1H), 2.62–2.60 (m, 1H), 2.30 (d, J = 3.9 Hz, 1H), 2.01 (s, 3H), 1.93–1.70 (m, 2H), 1.70–1.59 (m, 2H), 1.45–1.38 (m, 2H).
^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm): 170.4, 133.6, 130.1, 129.0, 127.2, 82.2, 49.5, 43.5, 41.3, 35.7, 29.9, 20.9, 20.2.
IR (KBr) ν: 3056, 2963, 1738, 1374, 1235, 1036, 738, 692 cm^{-1}.
MS (EI): m/z (%) 310 (M$^+$, 18.0), 91 (100).
HRMS: m/z [M]$^+$ calcd for C$_{15}$H$_{18}$O$_2$Se: 310.0472; found: 310.0466.

1-hydroxy-3-methyl-1-(phenylselanyl)butan-2-yl acetate (3k)

Yield: 47%; colorless viscous oil.
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.69–7.61 (m, 2H), 7.30–7.18 (m, 3H), 4.53 (dd, J = 11.9, 5.8 Hz, 1H), 4.41 (dd, J = 11.9, 6.8 Hz, 1H), 3.39 (dd, J = 6.7, 5.8 Hz, 1H), 2.65 (br, 1H), 2.01 (s, 3H), 1.42 (s, 3H), 1.36 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm): 170.6, 134.4, 129.7, 129.3, 127.9, 72.2, 65.5, 59.3, 28.1, 27.7, 20.9.
IR (KBr) ν: 3445, 3057, 2974, 1740, 1380, 1239, 1023, 740, 692 cm^{-1}.
MS (EI): m/z (%) 302 (M$^+$, 2.5), 184 (100).

HRMS: m/z [M]$^+$ calcd for C$_{13}$H$_{18}$O$_3$Se: 302.0421; found: 302.0399.

2-(benzylselanyl)-1-phenylethyl acetate (3l)

Yield: 72%; pale yellow viscous oil.
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.50–7.09 (m, 10H), 5.83 (dd, J = 7.6, 6.3 Hz, 1H), 3.67 (d, J = 2.4 Hz, 2H), 2.92 (dd, J = 13.0, 7.7 Hz, 1H), 2.78 (dd, J = 13.0, 6.2 Hz, 1H), 2.09 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm): 169.9, 139.7, 138.9, 129.0, 128.5, 128.3, 126.9, 126.7, 75.5, 29.0, 27.8, 21.1.
IR (KBr) ν: 3061, 3029, 1739, 1371, 1237, 1018, 758, 698 cm^{-1}.
MS (ESI): m/z (%) 334 (M$^+$, 3.1), 336 (100).
HRMS: m/z [M]$^+$ calcd for C$_{17}$H$_{18}$O$_2$Se: 334.0472; found: 334.0439.

2-(benzylselanyl)-1-p-tolylethyl acetate (3m)

Yield: 87%; pale yellow viscous oil.
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.33–7.17 (m, 9H), 5.83 (dd, J = 7.5, 6.5 Hz, 1H), 3.72 (d, J = 3.2 Hz, 2H), 2.95 (dd, J = 12.9, 7.7 Hz, 1H), 2.80 (dd, J = 12.9, 6.3 Hz, 1H), 2.36 (s, 3H), 2.10 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm): 169.9, 139.0, 138.1, 136.7, 129.2, 129.0, 128.5, 126.8 (d, J = 19.7 Hz), 75.4, 29.0, 27.8, 21.2.
IR (KBr) ν: 3059, 3027, 1741, 1370, 1237, 1018, 817, 759, 698 cm^{-1}.
MS (ESI): m/z (%) 348 (M$^+$, 3.5), 369 (100).
HRMS: m/z [M]$^+$ calcd for C$_{18}$H$_{20}$O$_2$Se: 348.0629; found: 348.0602.

2-(benzylselanyl)-1-(4-chlorophenyl)ethyl acetate (3n)

Yield: 70%; colorless viscous oil.
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.35–7.12 (m, 9H), 5.82–5.66 (m, 1H), 3.77–3.62 (m, 2H), 2.89 (dd, J = 13.0, 7.6 Hz, 1H), 2.74 (dd, J = 13.0, 6.4 Hz, 1H), 2.08 (s, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm): 169.8, 138.7, 138.2, 134.2, 129.0, 128.7, 128.6, 128.1, 126.9, 74.7, 28.7, 27.9, 21.1.
IR (KBr) ν: 3061, 3028, 1739, 1371, 1236, 1015, 825, 759, 698 cm^{-1}.
MS (ESI): m/z (%) 369 (M$^+$ + 1, 15.0), 289 (100).
HRMS: m/z [M]$^+$ calcd for C$_{17}$H$_{17}$ClO$_2$Se: 368.0082; found: 368.0058.

Acknowledgment

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