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ORIGINAL PAPER

Iodine-mediated acyloxyselenenylation of alkenes

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Abstract
In the presence of I_2, an acyloxyselenenylation of alkenes with diselenides and carboxylic acids is developed. This metal-free iodine-mediated acyloxyselenenylation proceeds efficiently under mild reaction conditions, affording a series of 2-acyloxy-1-selenides with high regioselectivity and in moderate to good yields.

Keywords Acyloxyselenenylation · Acetoxyselenenylation · Formyloxyselenylation · I_2

Introduction

2-Acetoxy-1-selenides are important organoselenium compounds; they can be prepared by acetoxyselenenylation of alkenes with selenenylating reagents in acetic acid, and after that an organylseleno group and an acetoxy are installed into the carbon–carbon double bond (Back 1987; Tiecco et al. 1990; Wirth 2000). In the electrophilic addition, the usually used selenenylating reagents PhSeX (X = Br, Cl) are commercially available (Paulmier 1986). 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 ions and the decrease in stereoselectivity. An alternative method for the formation of the electrophilic phenylselenium cation is the oxidation of cheaper and less toxic diphenyl diselenide with oxidants, such as ammonium peroxydisulfate (Tiecco et al. 1989, 1990), *m*-nitrobenzenesulfonyl peroxide (Masato et al. 1989, 1991), hypervalent iodine reagent $PhI(OAc)_2$ (Das et al. 2005; Mironov et al. 2004; Shi et al. 2005; Tiecco et al. 1998; Tingoli et al. 1991, 1993, 1994; Yu et al. 2007), and other oxidative systems (Bosman et al. 1994; Taniguchi 2006; Tiecco et al. 2001; Trost et al. 1978). Although there are a series of 2-acetoxy-1-selenides prepared by above methods, other 2-acyloxy-1-selenides, especially 2-formyloxy-1-selenides are less. Therefore, the development of simple and general methods for the preparation of 2-acyloxy-1-selenides and research on their unknown chemical and biological properties is highly desired.

Recently, we developed novel acetoxyselenenylation of alkenes using inorganic haloid salts as catalysts (Shi et al. 2015a, b). However, this procedure was not suitable for the preparation of 2-formyloxy-1-selenides when using formic acid to replace acetic acid. In our further research, we found that when a catalytic amount of PhI combined with an oxidant *m*CPBA was used, the acetoxyselenylation of alkenes proceeded efficiently. Furthermore, the formyloxyselenylation of alkenes was also occurred under the same reaction conditions, and some 2-formyloxy-1-selenides were synthesized successfully in moderate or poor yields (Zhang et al. 2017). More recently, we used molecular iodine to promote the cleavage of Se–Se bond in diselenides, which resulted in the active electrophilic selenium species, and a convenient procedure for the preparation of aminoselenides was developed (Wang et al. 2017). Based on this, we have investigated the acyloxyselenenylation of alkenes in the presence of I_2. To the best of our knowledge, this convenient iodine-mediated acyloxyselenenylation of alkenes has not been reported before.

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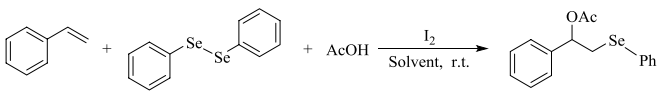
Results and discussion

Initially, we used AcOH as the representative of carboxylic acids to explore the reaction of styrene **1a**, diphenyl diselenide **2a**, and molecular I_2 with AcOH at room temperature. It was found that on simple stirring of the mixture of 1.2 equiv of 1**a**, 1.0 equiv of 2**a**, and I_2 in AcOH (3 mL) for 16 h, the expected addition product, 1-phenyl-2-(phenylselanyl) ethyl acetate 4**a** was obtained in 62% yield (Table 1, entry 1). Encouraged by the result, the acetoxyselenenylation of 1.2 equiv of **1a** and 1.0 equiv of **2a** with I_2 at room temperature was then optimized (Table 1). To improve the yield, solvents were first evaluated. As shown from Table 1, the yield increased when MeCN was used as solvent, and when the volume ratio of AcOH to MeCN was 2:1, the good yield of 84% was reached (entries 2–4). Other solvents such as CH_2Cl_2, CH_2ClCH_2Cl, THF, EtOAc, and water, when they were mixed with AcOH, the reaction resulted in **4a** in the yields ranging from 32 to 66% (entries 5–9). The amount of I_2 was also optimized, and 1.0 equiv proved to be the best choice (entries 3, 10, and 11). However, in the absence of I_2, 4**a** was not determined (entry 12). Finally, the suitable reaction time was determined: in 16 h the reaction was completed (entries 3, and 13–15).

With the optimal conditions in hand, the acyloxyselenenylation of 1.2 equiv of alkenes **1** with 1.0 equiv of diselenides **2**, I_2 and 2 mL of carboxylic acid **3** in MeCN (1 mL) proceeded efficiently, and after 16 h a series of corresponding 2-acyloxy-1-selenides **4** were obtained. The results are summarized in Table 2.

As depicted in Table 2, the acyloxyselenenylation was compatible with the studied alkenes when acetic acid was used, providing the corresponding 2-acetoxy-1-selenides with high regioselectivity and in moderate to good yields (Table 2, entries 1–6). It is obvious that when the substituents on the benzene ring were electron-withdrawing groups (bromo and chloro), the alkenes had higher yields than those bearing electron-donating groups (methyl and *t*-butyl) (entries 2–5). Cyclohexene **1f**, an aliphatic alkene, when it was treated under the same conditions, the addition proceeded in a *trans* fashion and the stereoisomer was obtained in 72% yield (entry 6). Dibenzyl diselenide **2b**, similar to **2a**, an aliphatic diselenide also reacted with alkenes easily, affording the similar results (entries 7–10). To explore the efficiency and generally of our methodology, formic acid was used to replace acetic acid, and consequently the formyloxyselenylation of alkenes proceeded smoothly, providing the corresponding 2-formyloxy-1-selenides in the yields ranging from 66 to 83% (entries 11–15). Compared with our reported method (Zhang et al. 2017), this protocol is more suitable for the formyloxyselenylation of alkenes. Finally, two alkenoic acids **1g** and **1h** were checked; the intramolecular reaction let to the corresponding products in good yields (entries 16, 17).

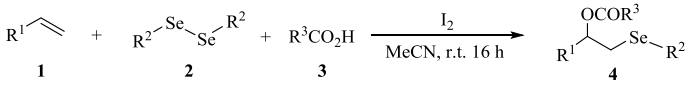
Table 1 Optimization of the acetoxyselenenylation of styrene mediated by I_2



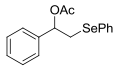
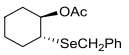
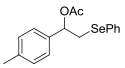
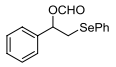
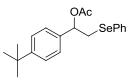
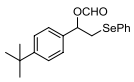
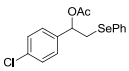
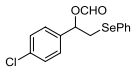
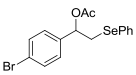
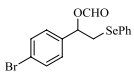
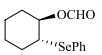
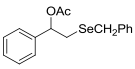
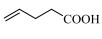
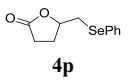
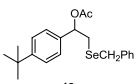
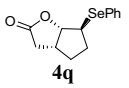
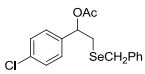
Entry	I_2 (equiv.)	AcOH (mL)	Solvent (mL)	Time (h)	Yield (%)[a]
1	1.0	3.0	-	16	62
2	1.0	1.5	MeCN (1.5)	16	74
3	1.0	2.0	MeCN (1.0)	16	84
4	1.0	2.0	MeCN (0.7)	16	78
5	1.0	2.0	CH_2Cl_2 (1.0)	16	42
6	1.0	2.0	CH_2ClCH_2Cl (1.0)	16	49
7	1.0	2.0	THF (1.0)	16	60
8	1.0	2.0	EtOAc (1.0)	16	66
9	1.0	2.0	H_2O (1.0)	16	32
10	1.4	2.0	MeCN (1.0)	16	86
11	0.6	2.0	MeCN (1.0)	16	64
12	-	2.0	MeCN (1.0)	16	0
13	1.0	2.0	MeCN (1.0)	12	70
14	1.0	2.0	MeCN (1.0)	6	55
15	1.0	2.0	MeCN (1.0)	24	85

[a] Isolated yields

Table 2 Preparation of 2-acyloxy-1-selenides 4



1 2 3 4

Entry	Alkene (1)	Diselenide (2)	Product (4)	Yield (%)[a]	Entry	Alkene (1)	Diselenide (2)	Product (4)	Yield (%)[a]
1	 **1a**	PhSeSePh **2a**	 **4a**	84	10	**1f**	**2b**	 **4j**	77
2	 **1b**	**2a**	 **4b**	58	11	**1a**	**2a**	 **4k**	81
3	 **1c**	**2a**	 **4c**	54	12	**1c**	**2a**	 **4l**	66
4	 **1d**	**2a**	 **4d**	77	13	**1d**	**2a**	 **4m**	77
5	 **1e**	**2a**	 **4e**	80	14	**1e**	**2a**	 **4n**	82
6	 **1f**	**2a**	 **4f**	72	15	**1f**	**2a**	 **4o**	83
7	**1a**	$(PhCH_2Se)_2$ **2b**	 **4g**	75	16	 **1g**	**2a**	 **4p**	80[b]
8	**1c**	**2b**	 **4h**	52	17	 **1h**	**2a**	 **4q**	81[b]
9	**1d**	**2b**	 **4i**	70					

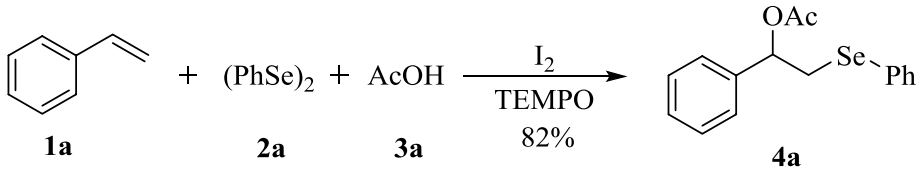
[a]Isolated yields

[b]Reaction conditions: **1** (1.2 equiv), **2a** (1.0 equiv), I_2 (1.0 equiv) in MeCN (2 mL), stirred at r.t. for 16 h

To demonstrate the practical utility of this method, a large-scale experiment was carried out. Thus, in MeCN (10 mL), **1a** (2.5 mmol), **2a** (1.04 mmol), I_2 (1.04 mmol), and AcOH (20 mL) were added successively. The mixture was vigorously stirred at r.t. for 16 h and worked up to provide product **4a** in 83% yield (552 mg, 1.73 mmol).

To explore the mechanism, a stoichiometric radical scavenger, 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), was added in the reaction of **1a** with **2a**, **3a**, and I_2 under the optimized conditions (Scheme 1). It was found that the acetoxyselenenylation was not affected by TEMPO, which meaning that the reaction may not undergo a radical pathway.

Scheme 1 A control experiment



1a **2a** **3a** **4a**

According to the above results and control experiments, a plausible electrophilic addition mechanism mediated by I_2 is shown in Scheme 2: I_2 first reacts with diselenide **2** smoothly to form the active intermediate **A**, followed by a rapid cleavage of Se–Se bond (Muangkaew et al. 2013; Shi et al. 2015a, b). The in situ generated active electrophilic selenium species then reacts with alkene **1** to produces the unstable cyclic seleniranium intermediate **B**. Finally, intermediate **B** is attacked by carboxylic acid **3** to provide the desired product **4** as a single isomer via an S_N1 mechanism. Accompanying the reaction, another active intermediate ArSeI (Huang et al. 1995) can further transfer a second equivalent of electrophilic selenium to alkene **1**. While aliphatic alkene **1f** is used as alkene substrate, the reaction provides the *trans* stereoisomers via an S_N2 mechanism.

Conclusions

We have developed an efficient iodine-mediated procedure for the synthesis of 2-acyloxy-1-selenides. This method has some advantages such as mild reaction conditions and simple procedure, which providing a series of corresponding compounds with high regioselectivity and in moderate to good yields. We have been interested in the acetoxyselenenylation of alkenes, and three methods have been developed by our group. The first one used KI as catalyst and *m*CPBA as the oxidant, which occurred smoothly and was completed in short time, affording the corresponding products in good to excellent yields (Shi et al. 2015a). However, this protocol was not suitable for the preparation of 2-formyloxy-1-selenides. With a catalytic amount of PhI combined and an oxidant *m*CPBA, the second method also proceeded efficiently and fast, resulting in 2-acetoxy-1-selenides in moderate to good yields, but 2-formyloxy-1-selenides were obtained in variable yields ranging from 37 to 69% (Zhang et al. 2017). Compared with our former studies, the present one using I_2 to mediate the acyloxyselenenylation of alkenes has milder reaction conditions. Although this method needs longer reaction time and gives products in moderate to good yields, it should be emphasized here that this methodology provides 2-formyloxy-1-selenides in good yields, which is more suitable to the synthesis of 2-acyloxy-1-selenides and extends the application scope of acyloxyselenenylation of alkenes.

Experimental section

General: 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, carboxylic acids, I_2, and solvents were commercially available.

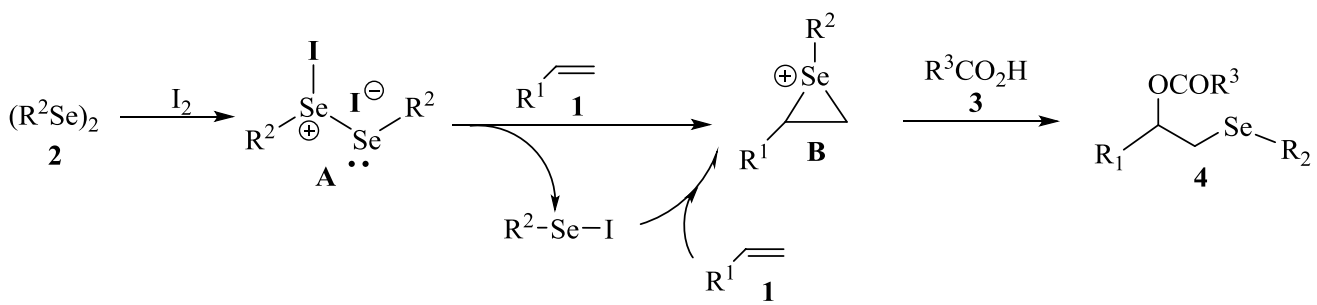
General procedure for the acyloxyselenenylation of alkenes mediated by I_2: in MeCN (1.0 mL), alkene **1** (0.24 mmol), diselenide **2** (0.1 mmol), carboxylic acid **3** (2.0 mL), and I_2 (0.1 mmol) were added successively. The mixture was vigorously stirred at r.t. for 16 h. Upon completion, the reaction 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-acyloxy-1-selenenylation compounds **4**.

1-Phenyl-2-(phenylselanyl)ethyl acetate (4a)

Colorless viscous oil (lit. of Tiecco et al. 1998).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.55–7.51 (m, 2H), 7.37–7.32 (m, 5H), 7.30–7.26 (m, 3H), 5.97 (dd, J = 8.0, 5.7 Hz, 1H), 3.41 (dd, J = 12.9, 8.0 Hz, 1H), 3.26 (dd, J = 12.9, 5.7 Hz, 1H), and 2.04 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 170.0, 139.4, 133.0, 129.8, 129.1, 128.5, 128.4, 127.2, 126.6, 75.2, 33.3, and 21.0.



Scheme 2 Proposed mechanism for the acyloxyselenenylation of alkene mediated by I_2

IR (KBr) ν: 3061, 3033, 1742, 1371, 1236, 1020, 738, and 698 cm^{-1}.

MS (ESI): *m/z* (%) 338 (M + 18, 4.8), 261 (100).

2-(Phenylselanyl)-1-(4-tolyl)ethyl acetate (4b)

Colorless viscous oil (lit. of Shi et al. 2015a, b).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.56–7.52 (m, 2H), 7.31–7.23 (m, 5H), 7.18 (d, J = 7.9 Hz, 2H), 5.94 (dd, J = 8.0, 5.9 Hz, 1H), 3.42 (dd, J = 12.8, 8.0 Hz, 1H), 3.25 (dd, J = 12.8, 5.9 Hz, 1H), 2.37 (s, 3H), and 2.04 (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, and 21.1.

IR (KBr) ν: 3055, 3027, 1742, 1370, 1236, 1020, 816, 738, and 692 cm^{-1}.

MS (EI): *m/z* (%) 334 (M^+, 6.5), 194 (100).

1-(4-*tert*-Butylphenyl)-2-(phenylselanyl)ethyl acetate (4c)

Colorless viscous oil (lit. of Shi et al. 2015a, b).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.55–7.49 (m, 2H), 7.40–7.36 (m, 2H), 7.31–7.25 (m, 5H), 5.98 (dd, J = 8.0, 5.7 Hz, 1H), 3.42 (dd, J = 12.8, 8.1 Hz, 1H), 3.27 (dd, J = 12.8, 5.6 Hz, 1H), 2.04 (s, 3H), and 1.35 (t, J = 2.9 Hz, 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, and 21.0.

IR (KBr) ν: 3057, 2963, 1745, 1370.0, 1235, 1021, 828, 737, and 691 cm^{-1}.

MS (EI): *m/z* (%) 376 (M^+, 14.1), 219 (100).

1-(4-Chlorophenyl)-2-(phenylselanyl)ethyl acetate (4d)

Pale yellow viscous oil (lit. of Shi et al. 2015a, b).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.52–7.46 (m, 2H), 7.33–7.28 (m, 2H), 7.29–7.24 (m, 5H), 5.89 (dd, J = 7.5, 6.2 Hz, 1H), 3.36 (dd, J = 12.9, 7.6 Hz, 1H), 3.20 (dd, J = 12.9, 6.1 Hz, 1H), and 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, and 21.0.

IR (KBr) ν: 3057, 1741, 1371, 1235, 1051, 1016, 824, 738, and 692 cm^{-1}.

MS (EI): *m/z* (%) 354 (M^+, 11.2), 214 (100).

1-(4-Bromophenyl)-2-(phenylselanyl)ethyl acetate (4e)

Pale yellow viscous oil (lit. of Shi et al. 2015a, b).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.54 (dd, J = 6.3, 3.2 Hz, 2H), 7.38–7.35 (m, 4H), 7.29 (dd, J = 4.9, 1.7 Hz, 3H), 5.97 (dd, J = 8.0, 5.7 Hz, 1H), 3.41 (dd, J = 12.9, 8.1 Hz, 1H), 3.26 (dd, J = 12.9, 5.7 Hz, 1H), and 2.04 (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, and 21.0.

IR (KBr) ν: 3056, 1741, 1481, 1072, 1007, 823, 736, and 690 cm^{-1}.

MS (EI): *m/z* (%) 398 (M^+, 58.5), 338 (100).

2-(Phenylselanyl)cyclohexyl acetate (4f)

Colorless viscous oil (lit. of Tiecco et al. 1998).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.61–7.56 (m, 2H), 7.30–7.25 (m, 3H), 4.89–4.80 (m, 1H), 3.26–3.17 (m, 1H), 2.20–2.13 (m, 1H), 2.11–2.05 (m, 1H), 1.96 (s, 3H), 1.75–1.61 (m, 2H), and 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, and 21.1.

IR (KBr) ν: 3056, 2936, 2858, 1738, 1373, 1238, 1036, 741, and 693 cm^{-1}.

MS (EI): *m/z* (%) 298 (M^+, 4.5), 81 (100).

2-(Benzylselanyl)-1-phenylethyl acetate (4g)

Pale yellow viscous oil (lit. of Shi et al. 2015a, b).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.40–7.20 (m, 10H), 5.86 (dd, J = 7.6, 6.3 Hz, 1H), 3.70 (d, J = 2.7 Hz, 2H), 2.96 (dd, J = 13.0, 7.8 Hz, 1H), 2.82 (dd, J = 13.0, 6.2 Hz, 1H), and 2.12 (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, and 21.1.

IR (KBr) ν: 3061, 3029, 1739, 1371, 1237, 1018, 758, and 698 cm^{-1}.

MS (ESI): *m/z* (%) 352 (M + 18, 11.0), 336 (100).

2-(Benzylselanyl)-1-(4-*tert*-butylphenyl)ethyl acetate (4h)

Pale yellow viscous oil (lit. of Zhang et al. 2017).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.39 (dd, J = 6.4, 2.0 Hz, 2H), 7.30 (d, J = 7.2 Hz, 2H), 7.28–7.21 (m, 5H), 5.85 (dd, J = 7.9, 6.2 Hz, 1H), 3.70 (s, 2H), 2.95 (dd, J = 13.0, 8.0 Hz, 1H), 2.80 (dd, J = 13.0, 6.1 Hz, 1H), 2.11 (s, 3H), and 1.33 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 169.9, 151.2, 138.8, 136.5, 128.9, 128.4, 126.7, 126.3, 125.3, 75.1, 34.5, 31.3, 28.8, 27.6, and 21.1.

IR (KBr) ν: 3028, 2962, 1744, 1370, 1237, 1017, 829, 758, and 698 cm^{-1}.

MS (ESI): *m/z* (%) 413 (M + 23, 3.5), 369 (100).

2-(Benzylselanyl)-1-(4-chlorophenyl)ethyl acetate (4i)

Colorless viscous oil (lit. of Shi et al. 2015a, b).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.37–7.20 (m, 9H), 5.77 (t, J = 7.0 Hz, 1H), 3.72 (d, J = 4.4 Hz, 2H), 2.91 (dd, J = 13.0, 7.6 Hz, 1H), 2.75 (dd, J = 13.0, 6.3 Hz, 1H), and 2.10 (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, and 21.1.

IR (KBr) ν: 3061, 3028, 1739, 1371, 1236, 1015, 825, 759, and 698 cm^{-1}.

MS (ESI): *m/z* (%) 369 (M + 1, 13.0), 289 (100).

2-(Benzylselanyl)cyclohexyl acetate (4j)

Colorless viscous oil (lit. of Zhang et al. 2017).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.36–7.17 (m, 5H), 4.88 (dd, J = 8.8, 4.8 Hz, 1H), 3.89 (dd, J = 19.5, 11.5 Hz, 2H), 2.90–2.84 (m, 1H), 2.17–2.10 (m, 2H), 2.09 (s, 3H), 1.75–1.54 (m, 3H), and 1.40–1.25 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 170.2, 139.2, 128.9, 128.4, 126.6, 75.7, 42.3, 32.0, 31.2, 27.1, 25.5, 23.3, and 21.3.

IR (KBr) ν: 3061, 3027, 2935, 1736, 1601, 1494, 1451, 1373, 1238, 1035, 759, and 697 cm^{-1}.

MS (ESI): *m/z* (%) 330 (M + 18, 17.0), 229 (100).

1-Phenyl-2-(phenylselanyl)ethyl formate (4k)

Colorless viscous oil (lit. of Zhang et al. 2017).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.09 (s, 1H), 7.53–7.49 (m, 2H), 7.38–7.25 (m, 8H), 6.03 (ddd, J = 8.0, 5.9, 0.8 Hz, 1H), 3.41 (dd, J = 12.9, 8.0 Hz, 1H), and 3.27 (ddd, J = 13.0, 5.9, 0.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 159.9, 138.7, 133.3, 129.4, 129.2, 128.7, 128.6, 127.4, 126.7, 75.0, and 33.1.

IR (KBr) ν: 3060, 2928, 1723, 1579, 1478, 1438, 1154, 737, and 698 cm^{-1}.

MS (ESI): *m/z* (%) 329 (M + 23, 16.8), 274 (100).

1-(4-*tert*-Butylphenyl)-2-(phenylselanyl)ethyl formate (4l)

Colorless viscous oil (lit. of Zhang et al. 2017).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.09 (s, 1H), 7.52–7.48 (m, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.31–7.23 (m, 5H), 6.03 (dd, J = 7.6, 6.2 Hz, 1H), 3.42 (dd, J = 12.9, 8.0 Hz, 1H), 3.28 (dd, J = 12.9, 5.8 Hz, 1H), and 1.33 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 160.0, 151.7, 135.6, 133.2, 129.5, 129.1, 127.4, 126.4, 125.5, 74.9, 34.6, 33.1, and 31.3.

IR (KBr) ν: 3057, 2962, 2868, 1726, 1478, 1163, 830, 737, and 691 cm^{-1}.

MS (ESI): *m/z* (%) 362 (M^+, 4.2), 478 (100).

1-(4-Chlorophenyl)-2-(phenylselanyl)ethyl formate (4m)

Colorless viscous oil (lit. of Zhang et al. 2017).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.07 (s, 1H), 7.51–7.45 (m, 2H), 7.35–7.23 (m, 7H), 5.98 (t, J = 6.9 Hz, 1H), 3.38 (dd, J = 12.9, 7.6 Hz, 1H), and 3.23 (dd, J = 12.9, 6.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 159.8, 137.1, 134.5, 133.3, 129.2, 129.1, 128.8, 128.1, 127.54, 74.3, and 32.9.

IR (KBr) ν: 3057, 2930, 1724, 1493, 1154, 1092, 1015, 825, 737, and 691 cm^{-1}.

MS (ESI): *m/z* (%) 358 (M + 18, 8.0), 301 (100).

1-(4-Bromophenyl)-2-(phenylselanyl)ethyl formate (4n)

Colorless viscous oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.06 (s, 1H), 7.50–7.44 (m, 4H), 7.29–7.24 (m, 3H), 7.21 (d, J = 7.5 Hz, 2H), 5.96 (t, J = 6.9 Hz, 1H), 3.37 (dd, J = 12.9, 7.6 Hz, 1H), and 3.22 (dd, J = 12.9, 6.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 159.7, 137.6, 133.4, 131.7, 129.2, 129.1, 128.5, 127.6, 122.7, 74.4, and 32.8.

IR (KBr) ν: 3057, 2926, 1726, 1478, 1163, 1072, 1011, 822, 738, and 691 cm^{-1}.

MS (ESI): *m/z* (%) 384 (M^+, 41.0), 338 (100).

HRMS (ESI): *m/z* [M^+] calcd for $C_{15}H_{13}BrO_2Se$: 383.9264; found: 383.9255.

2-(Phenylselanyl)cyclohexyl formate (4o)

Colorless viscous oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.05 (d, J = 0.6 Hz, 1H), 7.62–7.56 (m, 2H), 7.32–7.25 (m, 3H), 4.95 (td, J = 9.3, 4.1 Hz, 1H), 3.25–3.16 (m, 1H), 2.20–2.07 (m, 2H), 1.75–1.64 (m, 2H), 1.56–1.44 (m, 2H), and 1.40–1.31 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 160.3, 135.4, 128.9, 127.8, 74.9, 45.64, 32.2, 31.5, 30.6, 25.5, and 23.4.

IR (KBr) ν: 3056, 2936, 1725, 1176, 741, and 693 cm^{-1}.

MS (ESI): *m*/*z* (%) 307 (M + 23, 8.9), 81 (100).

HRMS (ESI): *m*/*z* [M^+] calcd for $C_{13}H_{16}NaO_2Se$: 307.0213; found: 307.0201.

5-Phenylselenomethyl-2-tetrahydrofuranone (4p)

Pale yellow oil (lit. of Tingoli et al. 2006).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.56–7.54 (m, 2H), 7.30–7.28 (m, 3H), 4.66 (dd, J = 7.2, 4.9 Hz, 1H), 3.29 (dd, J = 12.9, 4.9 Hz, 1H), 3.02 (dd, J = 12.9, 7.9 Hz, 1H), 2.63–2.47 (m, 2H), 2.46–2.33 (m, 1H), and 1.99–1.93 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 176.3, 133.2, 129.3, 128.9, 127.6, 79.3, 31.9, 28.7, and 27.6.

IR (KBr) ν: 3055.3, 1772.7, 1169.7, 739.6, and 692.0 cm^{-1}.

MS (ESI): *m*/*z* (%) 256 (M^+, 7.5).

2.2.17 6-(Phenylseleno)hexahydro-2H-cyclopenta[b]furan-2-one (4q)

Pale yellow oil (lit. of Nicolaou et al. 1979).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.56–7.53 (m, 2H), 7.31–7.29 (m, 3H), 4.90 (d, J = 6.4 Hz, 1H), 3.89 (d, J = 5.9 Hz, 1H), 3.12–3.09 (m, 1H), 2.82 (dd, J = 18.5, 10.0 Hz, 1H), 2.34 (dd, J = 18.4, 2.4 Hz, 1H), 2.28–2.15 (m, 2H), 1.87–1.82 (m, 1H), and 1.61–1.56 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 176.7, 133.6, 129.3, 128.7, 127.8, 90.5, 46.2, 37.1, 35.9, 32.4, and 30.1.

IR (KBr) ν: 3055.3, 2958.3, 1774.2, 1175.8, 1006.4, 740.6, and 692.0 cm^{-1}.

MS (ESI): *m*/*z* (%) 282 (M^+, 13.1).

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