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# New Catalytic Method for the Synthesis of β-Hydroxy Selenides

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In the presence of $NH_4I$ as catalyst and *m*-chloroperbenzoic acid as oxidant, the Se–Se bond cleavage of diselenides undergoes smoothly. The *in situ* generated reactive electrophilic Se species reacts with alkenes quickly, and a series of β-hydroxy selenides are prepared in good yields. This new catalytic method for synthesis of β-hydroxy selenides is a stereospecific *anti* addition, which occurs with a *Markovnikov* orientation.

**Keywords:** β-Hydroxy selenides, Hydroxyselenenylation, Diselenide, Alkenes, Catalysis.

## Introduction

In recent years, organoselenium compounds have been gaining importance due to their synthetic applications [1], biological activities, and other properties [2 – 9]. Among them, β-hydroxy selenides is a kind of valuable intermediates in the synthesis of allylic alcohols [10], olefins [11], bromohydrins [12], vinyl selenides [13][14], and some important natural compounds [15 – 17]. Several methods are available for the preparation of β-hydroxy selenides. The electrophilic addition of the commercially available selenenylating reagent PhSeCl to alkenes is a useful procedure [18][19]. However, the presence of toxic and moisture-sensitive nature of PhSeCl, and the nucleophilic $Cl^-$ anion is sometimes responsible for some undesirable processes, such as addition of the halide ion and the decrease in stereoselectivity. For this purpose, some novel alternative reagents, which do not contain nucleophilic counterions, such as $PhSeOSO_2Ar$, *N*-phenylselenophtalimide, and *N*-phenylselenosuccinimide, have been developed [20 – 22]. Since diphenyl diselenide is less expensive and less toxic, a simpler way for formation of the electrophilic phenylselenium cation is oxidation of diphenyl diselenide with oxidants, like DDQ, iodobenzene diacetate, or electrolytic system [23 – 25]. Using selenolate anions, the $S_N2$ ring opening of epoxides is another common method for access to β-hydroxy selenides. The selenolate anions can be generated by the treatment of diphenyl diselenide with Na, Zn, $NaBH_4$, zinc/aluminum (III) chloride, tributylphosphine in an alkaline medium and sodium hydroxymethanesulfinate [26 – 31]. They are also transformed from benzeneselenol under supramolecular catalysis in the presence of β-cyclodextrin [32] and promoted by $[Bmim]BF_4$ [33]. Treatment of commercially available PhSeX with Zn powder in refluxing THF can lead to the corresponding zinc selenolate [34]. However, these generated *in situ* selenolate anions are relatively unstable, they should be prepared under controlled anhydrous conditions, and above methods also have some disadvantages, such as long reaction times, the use of low temperatures, low to poor yields of products and multistep procedures, *etc*. Therefore, it is of significant interest to find mild and simple, especially catalytic methods for the synthesis of β-hydroxy selenides.

Recently, we have found that some inorganic haloid salts can catalyze the Se–Se bond cleavage of diselenides in the present of suitable oxidants. With the *in situ* generated electrophilic Se species, some new electrophilic reactions have been reported [35 – 37]. Based on the success, we have investigated the new synthetic method for preparation of β-hydroxy selenides. Herein, we wish to report a convenient hydroxyselenenylation of alkenes with diselenides, *m*-chloroperbenzoic acid (*m*CPBA), and $H_2O$ using $NH_4I$ as catalyst. To the best of our knowledge, this new catalytic method for synthesis of β-hydroxy selenides has not been previously reported.

## Results and Discussion

Initially, we investigated the hydroxyselenenylation of styrene **1a** with diphenyl diselenide **2a** and oxidant *m*CPBA in the presence of a catalytic amount of KI at room temperature. It was found that only stirring the mixture of 1.0 equiv. of **2a**, 1.2 equiv. of **1a**, and *m*CPBA with 0.1 equiv. of KI in a mixed solvent of $H_2O$ (1.5 ml) and MeCN (1.5 ml) for 3 h, the expected addition product 1-phenyl-2-(phenylselanyl) ethanol **3a** was obtained in 49% yield (*Table 1*, *Entry 1*). As a control experiment, **3a** was not observed in the absence of KI (*Entry 2*). Therefore, it was obvious that KI played a key role in the reaction. Then, the catalytic

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hydroxyselenenylation of **1a** with 1.0 equiv. of **2a** at room temperature for 3 h was optimized (*Table 1*).

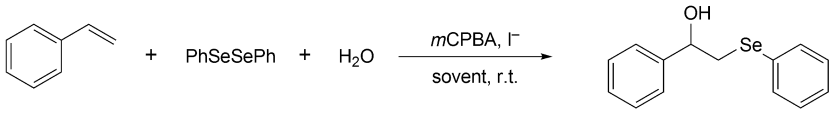
As shown in *Table 1*, several mixed solvents of $H_2O$ with $CH_2Cl_2$, DMF, THF, DMSO, and AcOEt (1:1 *v*/*v*) were first evaluated. As a result, in $H_2O$/AcOEt the reaction provided **3a** in moderate yield of 50%, while other mixed solvents or neat $H_2O$ usually resulted in poor or low yields (*Entries 3 – 8*). The reaction in $H_2O$/MeCN (1:1 *v*/*v*) or in $H_2O$/AcOEt (1:1 *v*/*v*) led closely to the same result. However, with $H_2O$/AcOEt (2:1 *v*/*v*), a better yield was observed (*Entries 9 – 14*). In the mixed solvent $H_2O$/AcOEt (2:1 *v*/*v*), the suitable amount of **1a** was determined: 1.2 equiv. of it was the best choice (*Entries 12, 15 – 16*). The appropriate amount of *m*CPBA was 1.0 equiv., and when it increased or decreased, the yields were not above 86% (*Entries 12, 17 – 21*). Compared with KI, $NH_4I$ had a better catalytic effect to the reaction; other iodine-containing catalysts, such as NaI and PhI, gave moderate to poor yields, and PrI had no catalytic effect at all (*Entries 22 – 25*). Finally, the optimum amount of $NH_4I$ was determined, 0.1 equiv. of it had the best effect to the reaction (*Entries 22, 26,* and *27*).

Having established the optimum conditions, the hydroxyselenenylation of 1.2 equiv. of alkenes **1** with 1.0 equiv. of diselenides **2**, 1.0 equiv. of *m*CPBA, and 0.1 equiv. of $NH_4I$ in $H_2O$/AcOEt (2:1 *v*/*v*) was carried out at room temperature for 3 h, and a series of corresponding *β*-hydroxy selenides **3** were obtained. The results are summarized in *Table 2*.

As shown in *Table 2*, the reaction was compatible with the studied alkenes, providing the corresponding *β*-hydroxy selenides **3** in moderate to good yields when **2a** was used (*Table 2*, *Entries 1 – 9*). Dibenzyl diselenide **2b**, an aliphatic diselenide similar to **2a**, also reacted with alkenes, resulting in the corresponding products **3j – 3n** in similar yields (*Entries 10 – 15*). This hydroxyselenenylation is a regiospecific reaction; all the obtained *β*-hydroxy selenides are *Markovnikov* orientation products. In order to investigate the stereospecificity of this reaction, cyclohexene **1h** was selected to react with **2a** and **2b**, and the obtained products **3h** and **3n** showed the *trans* stereoisomer mixtures (*Entries 8* and *15*).

According to the above results, a proposed catalytic cycle for the $NH_4I$-mediated hydroxyselenenylation of alkenes is shown in the *Scheme*. Thus, $NH_4I$ is first

Table 1. Optimization of the hydroxyselenenylation of styrene using $NH_4I$ as catalyst

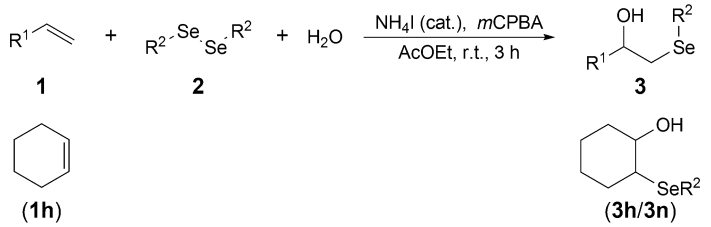



| *Entry* | Styrene (equiv.) | *m*CPBA (equiv.) | $I^-$ (equiv.) | $H_2O$ [ml] | Solvent [ml] | Yield [%][a]) |
|---|---|---|---|---|---|---|
| *1* | 1.2 | 1.2 | KI (0.1) | 1.5 | MeCN (1.5) | 49 |
| *2* | 1.2 | 1.2 | – | 1.5 | MeCN (1.5) | 0 |
| *3* | 1.2 | 1.2 | KI (0.1) | 1.5 | $CH_2Cl_2$ (1.5) | 12 |
| *4* | 1.2 | 1.2 | KI (0.1) | 1.5 | DMF (1.5) | 21 |
| *5* | 1.2 | 1.2 | KI (0.1) | 1.5 | THF (1.5) | 44 |
| *6* | 1.2 | 1.2 | KI (0.1) | 1.5 | DMSO (1.5) | 19 |
| *7* | 1.2 | 1.2 | KI (0.1) | 1.5 | AcOEt (1.5) | 50 |
| *8* | 1.2 | 1.2 | KI (0.1) | 3.0 | – | 38 |
| *9* | 1.2 | 1.2 | KI (0.1) | 1.0 | MeCN (2.0) | 58 |
| *10* | 1.2 | 1.2 | KI (0.1) | 2.0 | MeCN (1.0) | 42 |
| *11* | 1.2 | 1.2 | KI (0.1) | 1.0 | AcOEt (2.0) | 62 |
| *12* | 1.2 | 1.2 | KI (0.1) | 2.0 | AcOEt (1.0) | 73 |
| *13* | 1.2 | 1.2 | KI (0.1) | 1.8 | AcOEt (1.2) | 56 |
| *14* | 1.2 | 1.2 | KI (0.1) | 1.2 | AcOEt (1.8) | 68 |
| *15* | 2.0 | 1.2 | KI (0.1) | 2.0 | AcOEt (1.0) | 71 |
| *16* | 3.0 | 1.2 | KI (0.1) | 2.0 | AcOEt (1.0) | 73 |
| *17* | 1.2 | 1.5 | KI (0.1) | 2.0 | AcOEt (1.0) | 39 |
| *18* | 1.2 | 2.0 | KI (0.1) | 2.0 | AcOEt (1.0) | 10 |
| *19* | 1.2 | 1.0 | KI (0.1) | 2.0 | AcOEt (1.0) | 86 |
| *20* | 1.2 | 0.8 | KI (0.1) | 2.0 | AcOEt (1.0) | 81 |
| *21* | 1.2 | 0.6 | KI (0.1) | 2.0 | AcOEt (1.0) | 79 |
| *22* | 1.2 | 1.0 | $NH_4I$ (0.1) | 2.0 | AcOEt (1.0) | 92 |
| *23* | 1.2 | 1.0 | NaI (0.1) | 2.0 | AcOEt (1.0) | 65 |
| *24* | 1.2 | 1.0 | PhI (0.1) | 2.0 | AcOEt (1.0) | 12 |
| *25* | 1.2 | 1.0 | PrI (0.1) | 2.0 | AcOEt (1.0) | 0 |
| *26* | 1.2 | 1.0 | $NH_4I$ (0.2) | 2.0 | AcOEt (1.0) | 85 |
| *27* | 1.2 | 1.0 | $NH_4I$ (0.3) | 2.0 | AcOEt (1.0) | 83 |

[a]) Yield of isolated product.

Table 2. Preparation of β-hydroxy selenides **3**




| *Entry* | Alkene (**1**) | $R^1$ | Diselenide (**2**) | $R^2$ | Product (**3**) | Yield [%][a]) |
|---|---|---|---|---|---|---|
| *1* | **1a** | Ph | **2a** | Ph | **3a** | 92 |
| *2* | **1b** | 4-Me–$C_6H_4$ | **2a** | Ph | **3b** | 71 |
| *3* | **1c** | 4-AcO–$C_6H_4$ | **2a** | Ph | **3c** | 68 |
| *4* | **1d** | 4-$^t$Bu–$C_6H_4$ | **2a** | Ph | **3d** | 69 |
| *5* | **1e** | 4-F–$C_6H_4$ | **2a** | Ph | **3e** | 62 |
| *6* | **1f** | 4-Cl–$C_6H_4$ | **2a** | Ph | **3f** | 59 |
| *7* | **1g** | 4-Br–$C_6H_4$ | **2a** | Ph | **3g** | 61 |
| *8* | **1h** | | **2a** | Ph | **3h** | 58 |
| *9* | **1a** | Ph | **2b** | Bn | **3i** | 89 |
| *10* | **1b** | 4-Me–$C_6H_4$ | **2b** | Bn | **3j** | 71 |
| *11* | **1c** | 4-AcO–$C_6H_4$ | **2b** | Bn | **3k** | 72 |
| *12* | **1f** | 4-Cl–$C_6H_4$ | **2b** | Bn | **3l** | 55 |
| *13* | **1g** | 4-Br–$C_6H_4$ | **2b** | Bn | **3m** | 50 |
| *14* | **1h** | | **2b** | Bn | **3n** | 58 |

[a]) Yield of isolated products.

oxidized by *m*CPBA to the corresponding hypoiodous acid **A**, which reacts smoothly with diselenide **2** to form the active intermediate **B**, following a rapid cleavage of Se–Se bond [38]. The *in situ* generated active electrophilic selenium species then reacts with alkene to form the unstable cyclic intermediate **C**. Finally, intermediate **C** is attacked by $H_2O$ to provide the desired products, β-hydroxy selenides **3** as a single isomer *via* an $S_N1$ mechanism for the aromatic alkenes. When aliphatic alkene **1h** is treated in the reaction, the *trans* stereoisomer mixture *via* a $S_N2$ mechanism is obtained. In the cycle, another active intermediate ArSeI [39] can further transfer a second equivalent of electrophilic Se to alkene.

In summary, we have developed a novel and efficient catalytic procedure for the synthesis of β-hydroxy selenides. This method has some advantages, such as relatively short reaction times, mild reaction conditions, a simple workup, moderate to good yields of products, and remarkable regioselectivity. Furthermore, the scope of catalytic use of inorganic haloids in organic synthesis could be extended.

## Experimental Part

### *General*

Ammonium iodide, *m*CPBA, alkenes, and diselenides were commercially available. IR Spectra: *Thermo Nicolet 6700* instrument. $^1$H- and $^{13}$C-NMR spectra: in $CDCl_3$ on a *Bruker Avance III* (500 MHz) spectrometer. Mass spectra: *Thermo ITQ 1100* mass spectrometer.

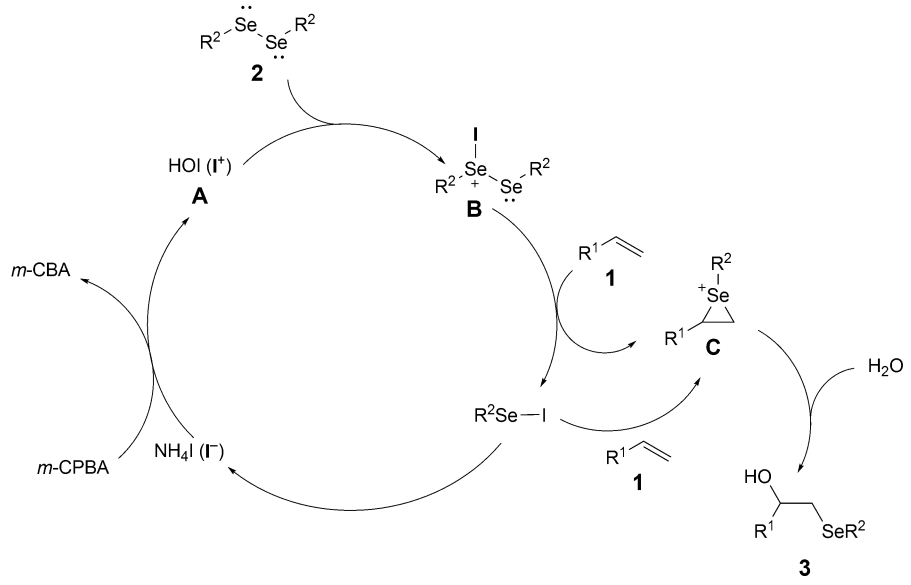
*Typical Procedure for the Catalytic Hydroxyselenenylation of Alkenes Using a Catalytic Amount of $NH_4I$.* To a mixed solvent of AcOEt (1.0 ml) and $H_2O$ (2.0 ml), alkene **1** (0.24 mmol), diselenide **2** (0.1 mmol), $NH_4I$ (0.02 mmol), and *m*CPBA (0.2 mmol) were added successively. The resulting suspension was vigorously stirred at r.t. for 3 h. Then, $H_2O$ (5 ml), sat. aq. $Na_2S_2O_3$ (2 ml), and sat. aq. $Na_2CO_3$ (2 ml) were poured into the mixture. The mixture was extracted with $CH_2Cl_2$ (3 × 5 ml) and the combined org. layer was washed with brine, dried over anh. $Na_2SO_4$, filtered, and concentrated under reduced pressure. The residue was purified by prep. TLC ($SiO_2$) with AcOEt/hexane (1:4) to give the pure product **3**.

**1-Phenyl-2-(phenylselanyl)ethanol** (**3a**) [18]. Pale yellow oil. Yield: 92%. IR (film): 3060 – 3010, 3059, 3030, 1578, 1477, 1437, 1054, 1023, 737, 700. $^1$H-NMR: 7.59 – 7.53 (*m*, 2 H); 7.40 – 7.25 (*m*, 8 H); 4.77 (*dd*, *J* = 9.4, 3.7, 1 H); 3.32 (*dd*, *J* = 12.8, 3.7, 1 H); 3.16 (*dd*, *J* = 12.8, 9.4, 1 H). $^{13}$C-NMR: 142.5; 133.1; 129.24; 129.20; 128.5; 127.9; 127.4; 125.8; 72.3; 38.4. ESI-MS: 295 (42, $[M + NH_4]^+$).

**1-(4-Methylphenyl)-2-(phenylselanyl)ethanol** (**3b**) [29]. Pale yellow oil. Yield: 71%. IR (film): 3600 – 3100, 3054, 3021, 1579, 1477, 1437, 1058, 1022, 818, 737, 691. $^1$H-NMR: 7.59 – 7.54 (*m*, 2 H); 7.32 – 7.23 (*m*, 5 H); 7.19 – 7.14 (*m*, 2 H); 4.75 (*dd*, *J* = 9.3, 3.8, 1 H); 3.30 (*dd*, *J* = 12.8, 3.8, 1 H); 3.17 (*dd*, *J* = 12.7, 9.3, 1 H); 2.36 (*s*, 3 H). $^{13}$C-NMR:

Scheme. Proposed mechanism for the catalyzed hydroxyselenenylation of alkenes.




139.6; 137.7; 133.0; 129.3; 129.23; 129.21; 127.3; 125.7; 72.1; 38.4; 21.1. ESI-MS: 309 (50, $[M + NH_4]^+$).

**4-[1-Hydroxy-2-(phenylselanyl)ethyl]phenyl Acetate** (**3c**). Pale yellow oil. Yield: 68%. IR (film): 3600 – 3100, 3056, 1757, 1579, 1506, 1370, 1198, 1165, 1018, 913, 847, 738, 692. $^1$H-NMR: 7.57 – 7.52 (*m*, 2 H); 7.37 – 7.33 (*m*, 2 H); 7.36 – 7.31 (*m*, 3 H); 7.12 – 7.01 (*m*, 2 H); 4.75 (*dd*, *J* = 9.4, 3.7, 1 H); 3.29 (*dd*, *J* = 12.8, 3.8, 1 H); 3.13 (*dd*, *J* = 12.8, 9.5, 1 H); 2.31 (*s*, 1 H). $^{13}$C-NMR: 169.5; 150.2; 139.9; 133.1; 129.3; 127.4; 126.9; 121.6; 71.7; 38.3; 21.1. ESI-MS: 353 (3.0, $[M + NH_4]^+$). HR-MS: 354.0601 ($C_{16}H_{20}NO_3Se^+$, $[M + NH_4]^+$; calc. 354.0608).

**1-(4-*tert*-Butylphenyl)-2-(phenylselanyl)ethanol** (**3d**). Pale yellow oil. Yield: 69%. IR (film): 3600 – 3100, 3056, 1579, 1477, 1438, 1057, 1022, 833, 736, 691. $^1$H-NMR: 7.58 – 7.52 (*m*, 2 H); 7.41 – 7.35 (*m*, 2 H); 7.32 – 7.25 (*m*, 5 H); 4.77 (*dd*, *J* = 9.3, 3.5, 1 H); 3.33 (*dd*, *J* = 12.8, 3.7, 1 H); 3.19 (*dd*, *J* = 12.8, 9.4, 1 H); 2.82 (*s*, 1 H); 1.33 (*s*, 9 H). $^{13}$C-NMR: 150.9; 139.5; 133.0; 129.4; 129.2; 127.3; 125.6; 125.4; 72.1; 38.2; 34.5; 31.32; 31.29. ESI-MS: 351 (46, $[M + NH_4]^+$). HR-MS: 352.1147 ($C_{18}H_{26}NOSe^+$, $[M + NH_4]^+$; calc. 352.1180).

**1-(4-Fluorophenyl)-2-(phenylselanyl)ethanol** (**3e**) [29]. Pale yellow oil. Yield: 62%. IR (film): 3600 – 3100, 3071, 1604, 1509, 1223, 1157, 1060, 836, 731, 691. $^1$H-NMR: 7.58 – 7.53 (*m*, 2 H); 7.34 – 7.27 (*m*, 5 H); 7.06 – 7.00 (*m*, 2 H); 4.74 (*dd*, *J* = 9.2, 3.8, 1 H); 3.28 (*dd*, *J* = 12.8, 3.9, 1 H); 3.12 (*dd*, *J* = 12.8, 9.3, 1 H). $^{13}$C-NMR: 163.3; 161.4; 138.25 (*d*, *J* = 2.6); 133.2; 129.3; 129.0; 127.5 (*d*, *J* = 8.1); 115.0; 71.6; 38.4. ESI-MS: 313 (23, $[M + NH_4]^+$).

**1-(4-Chlorophenyl)-2-(phenylselanyl)ethanol** (**3f**) [29]. Pale yellow oil. Yield: 59%. IR (film): 3600 – 3100, 3057, 1578, 1491, 1478, 1091, 1014, 828, 737, 691. $^1$H-NMR: 7.59 – 7.52 (*m*, 2 H); 7.33 – 7.25 (*m*, 7 H); 4.73 (*dd*, *J* = 9.2, 3.8, 1 H); 3.27 (*dd*, *J* = 12.8, 3.9, 1 H); 3.10 (*dd*, *J* = 12.9, 9.3, 1 H). $^{13}$C-NMR: 140.9; 133.5; 133.2; 129.3; 128.8; 128.6; 127.5; 127.2; 71.5; 38.4. ESI-MS: 330 (14, $[M + NH_4]^+$).

**1-(4-Bromophenyl)-2-(phenylselanyl)ethanol** (**3g**). Pale yellow oil. Yield: 61%. IR (film): 3600 – 3100, 3056, 1578, 1478, 1070, 1010, 823, 737, 690. $^1$H-NMR: 7.57 – 7.53 (*m*, 2 H); 7.49 – 7.43 (*m*, 2 H); 7.33 – 7.27 (*m*, 3 H); 7.24 – 7.20 (*m*, 2 H); 4.71 (*dd*, *J* = 9.2, 3.8, 1 H); 3.27 (*dd*, *J* = 12.8, 3.8, 1 H); 3.10 (*dd*, *J* = 12.8, 9.2, 1 H). $^{13}$C-NMR: 141.5; 133.2; 131.6; 129.3; 127.6; 121.7; 71.6; 38.3. ESI-MS: 374 (95, $[M + NH_4]^+$). HR-MS: 373.9645 ($C_{14}H_{17}BrNOSe^+$, $[M + NH_4]^+$; calc. 373.9659).

**2-(Phenylselanyl)cyclohexanol** (**3h**) [18]. Pale yellow oil. Yield: 61%. IR (film): 3600 – 3100, 3056, 1578, 1477, 1437, 1065, 740, 693. $^1$H-NMR: 7.63 – 7.58 (*m*, 2 H); 7.37 – 7.25 (*m*, 3 H); 3.34 (*td*, *J* = 10.2, 4.3, 1 H); 2.95 – 2.86 (*m*, 1 H); 2.24 – 2.11 (*m*, 2 H); 1.76 – 1.71 (*m*, 1 H); 1.67 – 1.60 (*m*, 1 H); 1.46 – 1.20 (*m*, 4 H). $^{13}$C-NMR: 136.1; 129.0; 128.1; 126.6; 72.3; 53.5; 33.9; 33.4; 26.8; 24.4. ESI-MS: 273 (100, $[M + NH_4]^+$).

**2-(Benzylselanyl)-1-phenylethanol** (**3i**). Pale yellow oil. Yield: 89%. IR (film): 3600 – 3100, 3060, 3027, 1601, 1493, 1453, 1054, 1029, 759, 698. $^1$H-NMR: 7.42 – 7.24 (*m*, 10 H); 4.69 (*dd*, *J* = 8.8, 4.1, 1 H); 3.78 (*s*, 2 H); 2.88 (*dd*, *J* = 13.0, 4.1, 1 H); 2.81 (*dd*, *J* = 13.0, 8.8, 1 H). $^{13}$C-NMR: 142.8; 138.9; 128.9; 128.6; 128.4; 127.8; 126.9; 125.7; 72.4; 34.1; 27.4. ESI-MS: 309 (11, $[M + NH_4]^+$). HR-MS: 310.0701 ($C_{15}H_{20}NOSe^+$, $[M + NH_4]^+$; calc. 310.0710).

**2-(Benzylselanyl)-1-(4-methylphenyl)ethanol** (**3j**). Pale yellow oil. Yield: 71%. IR (film): 3600 – 3100, 3059, 3026, 1600, 1514, 1494, 1453, 1179, 1066, 818, 758, 698. $^1$H-NMR: 7.40 – 7.18 (*m*, 9 H); 4.68 (*dd*, *J* = 8.7, 4.4, 1 H); 3.78 (*s*, 2 H); 2.87 (*dd*, *J* = 13.0, 4.4, 1 H); 2.82 (*dd*, *J* = 12.9, 8.7, 1 H); 2.39 (*s*, 1 H). $^{13}$C-NMR: 139.9; 138.9; 137.4; 129.1; 128.9; 128.5; 128.2; 127.8; 126.8; 125.6; 72.3;

34.0; 27.4; 21.1. ESI-MS: 323 (47, $[M + NH_4]^+$). HR-MS: 324.0861 ($C_{16}H_{22}NOSe^+$, $[M + NH_4]^+$; calc. 324.0867).

**4-[2-(Benzylselanyl)-1-hydroxyethyl]phenyl acetate** (**3k**). Pale yellow oil. Yield: 72%. IR (film): 3600 – 3100, 3061, 3027, 1756, 1602, 1506, 1369, 1198, 1016, 912, 848, 759, 698. $^1$H-NMR: 7.36 – 7.23 (*m*, 7 H); 7.07 (*dd*, *J* = 7.0, 1.6, 2 H); 4.64 (*dd*, *J* = 9.0, 4.0, 1 H); 3.79 (*s*, 2 H); 2.83 (*dd*, *J* = 13.1, 4.0, 1 H); 2.76 (*dd*, *J* = 13.1, 9.1, 1 H); 2.31 (*s*, 3 H). $^{13}$C-NMR: 169.5; 150.1; 140.4; 138.8; 128.9; 128.6; 126.9; 126.8; 121.5; 71.9; 34.0; 27.6; 21.1. ESI-MS: 367 (6.5, $[M + NH_4]^+$). HR-MS: 368.0743 ($C_{17}H_{22}NO_3Se^+$, $[M + NH_4]^+$; calc. 368.0765).

**2-(Benzylselanyl)-1-(4-chlorophenyl)ethanol** (**3l**). Pale yellow oil. Yield: 55%. IR (film): 3600 – 3100, 3061, 3027, 1598, 1492, 1453, 1091, 1014, 829, 758, 697. $^1$H-NMR: 7.36 – 7.20 (*m*, 9 H); 4.61 (*dd*, *J* = 9.0, 4.0, 1 H); 3.79 (*s*, 2 H); 2.82 (*dd*, *J* = 13.1, 4.0, 1 H); 2.73 (*dd*, *J* = 13.1, 9.0, 1 H). $^{13}$C-NMR: 141.3; 138.7; 133.4; 128.9; 128.62; 128.57; 127.1; 127.0; 71.7; 34.0; 27.5. ESI-MS: 343.5 (21, $[M + NH_4]^+$). HR-MS: 344.0319 ($C_{15}H_{19}ClNOSe^+$, $[M + NH_4]^+$; calc. 344.0320).

**2-(Benzylselanyl)-1-(4-bromophenyl)ethanol** (**3m**). Pale yellow oil. Yield: 50%. IR (film): 3600 – 3100, 3060, 3026, 1592, 1490, 1453, 1069, 1010, 823, 758, 697. $^1$H-NMR: 7.50 – 7.46 (*dd*, *J* = 6.8, 1.7, 2 H); 7.36 – 7.25 (*m*, 5 H); 7.18 (*d*, *J* = 8.4, 2 H); 4.59 (*dd*, *J* = 9.0, 3.9, 1 H); 3.80 (*s*, 2 H); 2.82 (*dd*, *J* = 13.1, 4.0, 1 H); 2.73 (*dd*, *J* = 13.1, 9.0, 1 H). $^{13}$C-NMR: 141.8; 138.7; 131.5; 128.9; 128.6; 127.4; 127.0; 121.5; 71.7; 33.9; 27.5. ESI-MS: 388 (6.5, $[M + NH_4]^+$). HR-MS: 387.9803 ($C_{15}H_{19}BrNOSe^+$, $[M + NH_4]^+$; calc. 387.9815).

**2-(Benzylselanyl)cyclohexanol** (**3n**) [27]. Pale yellow oil. Yield: 58%. IR (film): 3600 – 3100, 3060, 3027, 1600.4; 1494, 1449, 1067, 758, 697. $^1$H-NMR: 7.36 – 7.19 (*m*, 5 H); 3.87 (*dd*, *J* = 19.1, 11.7, 1 H); 3.39 (td, *J* = 10.1, 4.4, 1 H); 2.68 – 2.61 (*m*, 1 H); 2.15 – 2.12 (*m*, 2 H); 1.78 – 1.75 (*m*, 1 H); 1.67 – 1.51 (*m*, 2 H); 1.33 – 1.20 (*m*, 3 H). $^{13}$C-NMR: 139.2; 128.8; 128.6; 126.8; 72.8; 50.2; 34.0; 33.6; 26.9; 26.1; 24.5. ESI-MS: 287 (37, $[M + NH_4]^+$).

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