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# A General and Efficient Method To Convert Selenides into Selenones by Using HOF·$CH_3CN$

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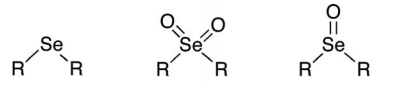
A general route for the preparation of selenones ($R_2SeO_2$) is presented. This task is achieved through the quick and high-yielding reaction of selenides ($R_2Se$) with HOF·$CH_3CN$. The reaction tolerates some elusive electron-deficient and sterically hindered selenides. Some mechanistic aspects are also investigated and discussed.

## Introduction

Over the past four decades, organoselenium chemistry has been proven highly valuable in the field of organic synthesis. The versatility of reactants and reagents based on this third chalcogen has led to a rapid development in this area, and organoselenium compounds have been broadly adopted in many useful reactions.[1,2] Today, many of these transformations revolve around the oxidation of selenides **1** (Scheme 1) to the corresponding monoxides, that is, selenoxides **3**, which can be used as intermediates in facile eliminations,[3] which were shown by Sharpless to proceed with *syn* stereospecificity.[4] Selenoxides have been also used in Pummerer-type[5] and [2,3] sigmatropic rearrangements[6] for the preparation of chiral alcohols,[7] in catalytic green chemistry,[8] and more.




**1** selenide **2** selenone **3** selenoxide

Scheme 1. Organoselenium derivatives.

Contrary to the developed selenoxide chemistry, hexavalent selenones **2** have received much less attention, as there is no general method for their preparation.[9] It has been established that only the most vigorous conditions and strong oxidizing agents can lead to selenones.[1b] It seems that the thermal instability of the fast-formed selenoxide intermediates and the sensitivity of many selenones to chromatographic procedures have impeded many selenone preparations. These works established the notion that the first oxidation of selenide to selenoxide is fast, opposed to the second sluggish oxidation step to selenone, probably because of the dominant preference of selenium for the $Se^{IV}$ oxidation state.[1b] Also, the decreased electron density on the selenium atom of selenoxides renders it less susceptible to further electrophilic oxygenation.[1b,10,11] This trend is quite different from homologous organosulfur chemistry.[3a] For rare cases in which selenones have been available, they were found to be useful intermediates in biologically important processes[12] and especially in some challenging substitution reactions, in which the selenones were usually not isolated.[13] This was attributed to the selenonyl anionic group ($RSeO_2^-$), which is an excellent leaving group in $S_N$-type displacements.[1b,1c,2c,14] It has been suggested that the selenonyl moiety can be replaced with almost any kind of nucleophile.[1c] The persisting problem, however, was the synthetic barrier that hampered their preparation, which thus prevented further development of their chemistry. We present in this work the first general method to form selenones that is very efficient and yet mild enough to keep this sensitive moiety intact. The method is based on the reaction of selenides with the acetonitrile complex of hypofluorous acid, HOF·$CH_3CN$.

HOF·$CH_3CN$ is easily prepared by passing dilute fluorine through aqueous acetonitrile.[15] Its forceful oxygen-transfer ability is derived from its highly electrophilic oxygen atom. Over the years, it has been successfully employed for the oxygenation of many sulfur-containing compounds, such as episulfides and very electron-deficient sulfides, thiophenes,[16] and oligothiophenes.[17] Oxygen-transfer reactions using the HOF·$CH_3CN$ complex are by no means limited to organosulfur derivatives, as other difficult oxygenations on a nitrogen atom of various families of compounds have also been performed.[18,19] In addition "impossible" epoxidations have been carried out,[20] tertiary hydroxylations have been achieved,[21] and many other diverse transformations that could not be otherwise completed were accomplished.[22] We found that this outstanding oxygen-transfer reagent can also play an important role in the syn-

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thesis of selenones. Notably, a theoretical study predicted that contrary to other reagents, which form considerable amounts of side reactions, HOF·$CH_3CN$ should smoothly convert selenides into selenones.[23]

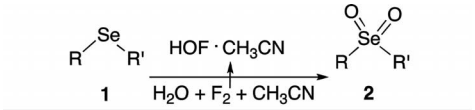
## Results and Discussion

It was reported that diphenyl selenide (**1a**) reacts with a 10-fold excess amount of hypochlorite to produce diphenyl selenone (**2a**) in 79% yield.[24] This result, however, could not be replicated by others.[25] We treated **1a** at 0 °C for 3 min with HOF·$CH_3CN$ (2.4 equiv., slight excess, as each equivalent is a source of one oxygen atom) to form $Ph_2SeO_2$ (**2a**) in quantitative yield. Dialkyl selenones are somewhat different, as the fully oxidized products, as well as the intermediate selenoxides, are sensitive to thermal eliminations and nucleophilic substitutions. The preparation of dibutyl selenone (**2b**), for example, has been previously achieved in two steps through the ozonolysis of dibutyl selenoxide (**3b**), which in its turn was prepared by separate oxidation of **1b**.[26] The mild conditions by which the HOF·$CH_3CN$ oxidation proceeds eliminates any side reaction, and when **1b** served as the reactant, **2b** was formed quantitatively after 5 min. Despite the fact that electron-rich aromatics are known to be oxidized by HOF·$CH_3CN$,[22b] the selenium atom reacts much faster and both mildly activated bis(4-methylphenyl) selenide (**1c**)[27] and electron-rich bis(4-methoxyphenyl) selenide (**1d**)[28] were treated with a slight excess amount of HOF·$CH_3CN$ to form the desired selenones without any ring over-oxidations (Table 1).

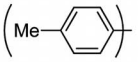
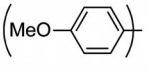
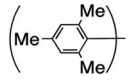
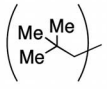
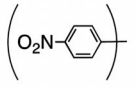
Alkyl aryl selenides were also treated with HOF·$CH_3CN$. These substrates appear to be a different case from the oxidation standpoint, as the intermediates – alkyl aryl selenoxides of type **3e**–**f** – are known to rapidly decompose through a *syn* elimination mechanism.[29] The reaction of butyl phenyl selenide (**1e**) with HOF·$CH_3CN$, however, resulted in clean oxidation to form selenone **2e** in almost quantitative yield after 3 min. The oxidation process of phenethyl phenyl selenide (**1f**) is even more sensitive to high temperatures and long reaction times, as intermediate selenoxide **3f** was found to be very unstable with a half-life of only 9 min at 38 °C.[29] This fact has prevented the prior preparation of **2f**, but under treatment of **1f** with a slight excess of HOF·$CH_3CN$, selenone **2f** was obtained in 90% yield after 3 min. This molecule seems to be more stable than the selenoxide, and no signs of any decomposition were observed after the reaction (Table 1).

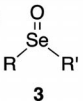
In the past, sterically hindered and electron-depleted selenides were too great of a challenge for contemporary oxidants, so they were never oxidized to the corresponding dioxides. This resulted from the fact that oxidation of selenoxides was known to be sensitive to steric hindrance[1b] and to electron-withdrawing substituents, which reduce the electron density around the selenium atom to the point at which it is no longer susceptible to orthodox electrophilic oxygenations. Thus, for example, when sterically congested dimesityl selenide (**1g**) was allowed to react with more than a 10-fold excess amount of $H_2O_2$ for 2 h, monoxide **3g** was formed exclusively.[30] Hypofluorous acid, which is a small molecule, has an advantage in the oxidation of such compounds, and its reaction with **1g** was complete within 10 min at 0 °C to afford selenone **2g** in 85% yield. Even when the HOF·$CH_3CN$ complex was added to dineopentyl selenide (**1h**), with its two bulky alkyl substituents, the result again was that selenone **2h** was formed in 91% yield (Table 1).

Table 1. Oxidation of selenides.




1 2

| Entry | 1 | R, R' | Yield [%] |
|---|---|---|---|
| 1 | **1a** | R = R' = Ph | >95 |
| 2 | **1b** | R = R' = Bu | >95 |
| 3 | **1c** | R = R' =  | >95 |
| 4 | **1d** | R = R' =  | >95 |
| 5 | **1e** | R = Ph, R' = Bu | >95 |
| 6 | **1f** | R = Ph, R' = $CH_2CH_2Ph$ | 90 |
| 7 | **1g** | R = R' =  | 85 |
| 8 | **1h** | R = R' =  | 91 |
| 9 | **1i** | R = R' =  | 87 |
| 10 | **1j** | R = $C_6F_5$, R' = Ph | >95 |
| 11 | **1k** | R = R' = $CH_2CF_3$ | >95 |
| 12 | **1l** | R = Ph, R' = $nC_8F_{17}$ | 91 |

The corresponding selenoxides: 

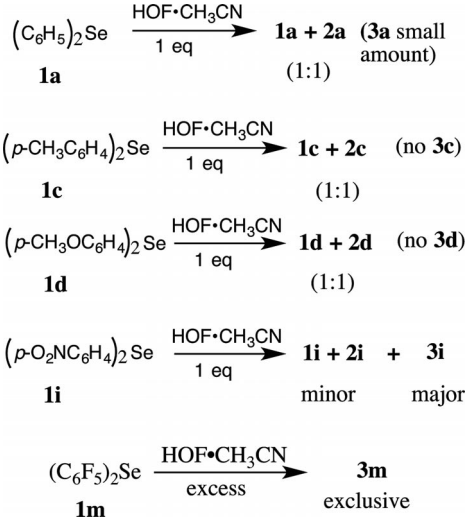
**3**

The oxygenation of **1i** bearing two electron-withdrawing nitrophenyl groups was previously attempted. In all cases, only the selenoxide **3i** was formed, with no evidence of the corresponding selenone.[31] Here, the strong electrophilic properties of hypofluorous acid were able to overcome the reduced susceptibility of the selenium atom in intermediate **3i** toward further electrophilic oxygenation, and so, selenone **2i** was obtained in 87% yield, although in this case, the reaction was somewhat slower and required 15 min to complete (Table 1).

Other electron-deficient selenides include polyfluorinated and perfluorinated selenides of type **1j**–**l**. The oxygenation of this class of materials has attracted some attention, and attempts to oxygenate them were undertaken by using various oxidizing agents, including neat and uncomplexed HOF. Most of these reactions failed, and the reactions with HOF ended in explosions, from which selenoxides could, in

some cases, be isolated.[32] Unlike the explosive nature of pure uncomplexed HOF and its troublesome preparation and handling, the acetonitrile complex of HOF is much easier to prepare, and it should not be isolated prior to its use, thus enabling mild and tunable reactions without the risk of explosions. The first attempt at the transformation of a perfluorinated selenide into a selenone was performed with pentafluorophenyl phenyl selenide (**1j**). First, an excess amount of *meta*-chloroperoxybenzoic acid (*m*CPBA) was used with a prolonged reaction time, but only the selenoxide **3j** was formed. A parallel reaction with dimethyldioxirane (DMDO) resulted in unidentified products. When, however, treated with HOF·$CH_3CN$, **1j** was transformed into the selenone **3j** in excellent yield. Much like the case of the oxygenation of **1i**, it took 15 min for the reaction to complete. We turned our attention also to electron-deficient **1k** and found that it could be transformed into selenone **2k** in very good yield. Lastly, **1l** with its strongly electron-withdrawing perfluoroalkyl chain directly bonded to the selenium atom was treated with HOF·$CH_3CN$ to afford **2l** in excellent yield as well (Table 1). All of the reported fluorine-containing selenones were previously unknown. However, when bis(perfluorophenyl) selenide (**1m**, Scheme 2) was treated with HOF·$CH_3CN$, the oxidation process stopped at the monoxide stage, as both the perfluoro substituents and the polarized Se–O bond reduced the electron density of the selenium atom to the point that it could no longer act as a nucleophile. Thus, in this extreme case selenoxide **3m** was exclusively obtained in quantitative yield (Scheme 2).




Scheme 2. Formation of selenones versus selenoxides by using an insufficient amount of HOF·$CH_3CN$.

It was of interest to examine some mechanistic aspects of the oxidation of selenides by using HOF·$CH_3CN$ and compare them with the parallel sulfide-to-sulfone oxidation. Reactions of sulfides with HOF·$CH_3CN$ were found to proceed generally directly to the sulfones, as clusters of HOF molecules were grouped around the sulfur atom through hydrogen bonding skipping the formation of the sulfoxide altogether. An insufficient amount of the reagent led to a mixture of the sulfone and the starting material.[16a]

On the basis of sulfur chemistry precedence, selenides should have been oxidized rapidly to selenones without forming considerable amounts of selenoxides. Selenium chemistry, however, is quite different, and the selenoxide-to-selenone oxidation proceeds with more difficulties than the parallel reactions leading to sulfones. Thus, when weakly nucleophilic bis(4-nitrophenyl) selenide (**1i**) was treated with approximately 1 equiv. of HOF·$CH_3CN$ (enough to transfer only one oxygen atom), selenoxide **3i** was formed almost exclusively, which points to a distinctive two-step reaction.

Aside from electronic factors, spatial factors may also be responsible for the deceleration of the second oxidation step, as the nonbonding electron pairs of the large selenium atom are fairly far from each other, and unlike the case of the sulfides, may allow the detachment of a second HOF molecule from the reagent's cluster near the reaction center resulting in partially oxidized selenoxide. However, when molecules possessing a selenium atom with stronger nucleophilic character, as in the case of electron-rich bis(4-tolyl) selenide (**1c**) and bis(4-methoxyphenyl) selenide (**1d**), were treated with approximately 1 equiv. of HOF·$CH_3CN$, mixtures of about 50% selenones **2c** and **2d** along with 50% of the starting materials were obtained. No signs of selenoxides **3c** and **3d** were observed, as indicated by analysis of the crude reaction mixtures by $^1H$ NMR spectroscopy, which points out that fast consecutive oxidation of the selenoxide to the selenone occurs, without the chance for the HOF cluster to detach from the reaction center, and this leaves only the doubly oxidized selenone along with unreacted selenide. When a less-reactive selenide, such as diphenyl selenide (**1a**), was treated with 1 equiv. of HOF·$CH_3CN$, selenone **2a** was the major product, accompanied by the starting selenide, although this time small amounts of selenoxide **3a** were also detected (Scheme 2).

## Conclusions

A very efficient and general method for the conversion of selenides into selenones by using HOF·$CH_3CN$ is described. For the first time, it is possible to prepare some sterically hindered and electron-deficient selenones, such as those possessing perfluorinated moieties. Mechanistic studies suggest some parallel behavior between the HOF·$CH_3CN$ oxidation of sulfides and electron-rich selenides, as in both cases the oxidation does not stop at the monoxide, but rather proceeds to form the corresponding dioxides. This feature is of synthetic value, as mixtures of selenoxides and selenones are in many cases difficult to separate, because they are prone to decomposition. In contrast, the HOF·$CH_3CN$ oxygenation of electron-deficient selenides displays a clear distinction between the two oxidative steps, and in one extreme case (**1m**), the reaction could not proceed to the selenone. These results also support the notion that electrophilic oxygenations with HOF·$CH_3CN$ are affected mainly by electronic factors

rather than steric ones, as the small size of the reagent has the ability to reach even sterically hindered spaces.

Regarding the use of $F_2$, which in the mind of many is somewhat problematic, it should be remembered that dilute fluorine (e.g., 10% $F_2$ in $N_2$) is less dangerous and easier to work with than chlorine (it is also less toxic than $Cl_2$[33]). Dilute fluorine is commercially available, and the reactions can be performed in standard glass vessels and only require a simple soda–lime trap at the reaction outlet. Technical-grade (>95%) $F_2$ can be diluted on the spot to the desired degree by using a simple vacuum line.[19a]

## Experimental Section

**General Experimental Procedures:** $^1$H, $^{19}$F, and $^{13}$C NMR spectra were obtained at 400, 376, and 100 MHz, respectively, with $Me_4Si$ as an internal standard for the $^1$H and $^{13}$C NMR spectra and with $CFCl_3$ as an internal standard for the $^9$F NMR spectra. MS data were measured under ASAP or APPI conditions.

**General Procedure for Working with Fluorine:** Fluorine is a strong oxidant and a corrosive material, so its reactions should be performed in a well-ventilated area. It should be used only with an appropriate vacuum line.[19a] For the occasional user, however, various premixed mixtures of $F_2$ in inert gases ($N_2$ or He) are commercially available, thereby simplifying the process. Unreacted fluorine should be captured by a simple trap containing a base such as soda–lime located at the outlet of the glass reactor. If elementary precautions are taken, the work with fluorine is simple, and we have never experienced any difficulties working with it.

**General Procedure for Producing HOF·$CH_3CN$:** Mixtures of 10–20% $F_2$ in nitrogen were used throughout this work. The gas mixture was prepared in a secondary container prior to the reaction and passed at a rate of about 400 mL min$^{-1}$ through a cold (–15 °C) mixture of $CH_3CN$ (10 mL) and $H_2O$ (1 mL) in a regular glass reactor. The development of the oxidizing power was monitored by treating aliquots with an acidic aqueous solution of KI. The liberated iodine was then titrated with thiosulfate. Typical concentrations of the oxidizing reagent were around 0.5–0.7 mol L$^{-1}$.

**General Procedure for Working with HOF·$CH_3CN$:** Selenide **1a**–**m** was dissolved in $CH_2Cl_2$, and the mixture was cooled to 0 °C. The oxidizing agent was then added in one portion to the reaction vessel. The reaction was monitored by GC or TLC and stopped after a few minutes. The mixture was then poured into water and extracted with ethyl acetate. The organic layer was washed with water until the aqueous phase was neutral and unreactive to KI. It was then dried with $MgSO_4$, and the solvent was evaporated. The crude selenone product was usually purified by recrystallization.

**Diphenyl Selenone (2a):** Prepared from commercial selenide **1a** (233 mg, 1.42 mmol) as described in the general oxygenation procedure by using 2.4 equiv. of the oxidizing agent for 3 min. The product was recrystallized from hexane/chloroform. A white solid (302 mg, 100%) was obtained. M.p. 132 °C (ref.[25] m.p. 131–132 °C). $^1$H NMR ($CDCl_3$): $\delta$ = 7.56–7.60 (m, 4 H), 7.62–7.66 (m, 2 H), 7.95–7.98 (m, 4 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 127.01, 130.34, 134.17, 142.64 ppm. HRMS (ASAP): calcd. for $C_{12}H_{11}O_2Se$ [M + H] 262.9951; found 262.9960.

**Dibutyl Selenone (2b):** Prepared from selenide **1b**[34] (260 mg, 1.00 mmol) as described in the general oxygenation procedure by using 2.4 equiv. of the oxidizing agent for 5 min. The product was recrystallized from hexane/chloroform. A white solid (265 mg, 100%) was obtained. M.p. 132 °C (ref.[26] m.p. 91 °C). $^1$H NMR ($CDCl_3$): $\delta$ = 0.982 (t, $J$ = 7.4 Hz, 6 H), 1.540 (sext, $J$ = 7.4 Hz, 4 H), 1.985 (quint, $J$ = 7.6 Hz, 4 H), 3.328 (t, $J$ = 8.0 Hz, 4 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 13.49, 22.16, 24.01, 57.13 ppm. HRMS (ASAP): calcd. for $C_8H_{19}O_2Se$ [M + H] 227.0556; found 227.0556.

**Bis(4-methylphenyl) Selenone (2c):** Prepared from selenide **1c**[27] (166 mg, 0.64 mmol) as described in the general oxygenation procedure by using 2.4 equiv. of the oxidizing agent for 3 min. The product was recrystallized from hexane/chloroform. A white solid (185 mg, 100%) was obtained. M.p. 183 °C (ref.[35] m.p. 183.5 °C). $^1$H NMR ($CDCl_3$): $\delta$ = 2.433 (s, 6 H), 7.386 (d, $J$ = 8.6 Hz, 4 H), 7.854 (d, $J$ = 8.4 Hz, 4 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 21.79, 126.99, 130.90, 139.89, 145.18 ppm. HRMS (ASAP): calcd. for $C_{14}H_{15}O_2Se$ [M + H] 291.0264; found 291.0269.

**Bis(4-methoxyphenyl) Selenone (2d):** Prepared from selenide **1d**[28] (199 mg, 0.68 mmol) as described in the general oxygenation procedure by using 2.4 equiv. of the oxidizing agent for 3 min. The product was recrystallized from hexane/chloroform. A white solid (218 mg, 99%) was obtained. M.p. 145–146 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 3.860 (s, 6 H), 7.045 (d, $J$ = 9.2 Hz, 4 H), 7.885 (d, $J$ = 8.8 Hz, 4 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 36.50, 116.11, 129.55, 134.69, 164.59 ppm. HRMS (ASAP): calcd. for $C_{14}H_{15}O_4Se$ [M + H] 323.0162; found 323.0172.

**Butyl Phenyl Selenone (2e):** Prepared from **1e**[36] (151 mg, 0.71 mmol) as described in the general oxygenation procedure by using 2.4 equiv. of the oxidizing agent for 3 min. The product was precipitated from hexane. A white solid (173 mg, 100%) was obtained. M.p. 56–60 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 0.822 (t, $J$ = 7.4 Hz, 3 H), 1.389 (sext, $J$ = 7.4 Hz, 2 H), 1.813 (quint, $J$ = 8.0 Hz, 2 H), 3.432 (t, $J$ = 8.0 Hz, 2 H), 7.54–7.58 (m, 2 H), 7.61–7.65 (m, 1 H), 7.87–7.89 (m, 2 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 14.07, 22.49, 25.01, 60.41, 127.72, 130.98, 135.02, 141.74 ppm. HRMS (APPI): calcd. for $C_{10}H_{15}O_2Se$ [M + H] 243.0264; found 243.0263.

**Phenethyl Phenyl Selenone (2f):** Prepared from **1f**[29] (140 mg, 0.54 mmol) as described in the general oxygenation procedure by using 2.4 equiv. of the oxidizing agent for 3 min. The product was precipitated from hexane. A white solid (142 mg, 90%) was obtained. M.p. 90 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 3.281 (t, $J$ = 8.6 Hz, 2 H), 3.718 (t, $J$ = 8.0 Hz, 2 H), 7.15–7.18 (m, 2 H), 7.20–7.29 (m, 3 H), 7.59–7.63 (m, 2 H), 7.68–7.72 (m, 1 H), 7.90–7.93 (m, 2 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 28.48, 60.53, 127.08, 127.51, 128.54, 129.09, 130.30, 134.31, 136.55, 141.57 ppm. HRMS (ASAP): calcd. for $C_{14}H_{15}O_2Se$ [M + H] 291.0264; found 291.0274. $C_{14}H_{14}O_2Se$ (293.22): calcd. C 57.35, H 4.81; found C 57.13, H 4.80.

**Dimesityl Selenone (2g):** Prepared from selenide **1g**[30] (210 mg, 0.66 mmol) as described in the general oxygenation procedure by using 2.4 equiv. of the oxidizing agent for 10 min. The product was recrystallized from hexane/chloroform. A white solid (196 mg, 85%) was obtained. M.p. 158 °C (blackens). $^1$H NMR ($CDCl_3$): $\delta$ = 2.278 (s, 6 H), 2.559 (s, 12 H), 6.902 (s, 4 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 21.24, 21.73, 132.93, 139.10, 142.19, 143.96 ppm. HRMS (APPI): calcd. for $C_{18}H_{22}O_2SeNa$ [M + Na] 369.0710; found 369.0707.

**Dineopentyl Selenone (2h):** Prepared from selenide **1h**[37] (201 mg, 0.91 mmol) as described in the general oxygenation procedure by using 2.4 equiv. of the oxidizing agent for 10 min. The product was recrystallized from hexane/chloroform. A white solid (210 mg, 91%) was obtained. M.p. 118 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 1.294 (s, 18 H), 3.280 (s, 4 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 30.41, 33.97, 73.79 ppm. HRMS (ASAP): calcd. for $C_{10}H_{23}O_2Se$ [M + H] 251.0890; found 251.0875. $C_{10}H_{22}O_2Se$ (253.24): calcd. C 47.43, H 8.76; found C 47.17, H 8.70.

**Bis(4-nitrophenyl) Selenone (2i):** Prepared from selenide **1i**[31b] (140 mg, 0.43 mmol) as described in the general oxygenation procedure by using 2.4 equiv. of the oxidizing agent for 15 min. The product was recrystallized from chloroform. An off-white solid (134 mg, 87%) was obtained. M.p. 277–278 °C. $^1$H NMR ([D$_6$]-DMSO): $\delta$ = 8.363 (d, $J$ = 9 Hz, 4 H), 8.510 (d, $J$ = 9 Hz, 4 H) ppm. $^{13}$C NMR ([D$_6$]DMSO): $\delta$ = 126.44, 129.40, 147.04, 151.77 ppm. HRMS (ASAP): calcd. for $C_{12}H_9N_2O_6Se$ [M + H] 352.9653; found 352.9655. $C_{12}H_8N_2O_6Se$ (355.17): calcd. C 40.58, H 2.27, N 7.89; found C 40.79, H 2.43, N 7.44.

**Pentafluorophenyl Phenyl Selenone (2j):** Prepared from selenide **1j**[38] (261 mg, 0.81 mmol) as described in the general oxygenation procedure by using 2.4 equiv. of the oxidizing agent for 15 min. The product was recrystallized from hexane/diethyl ether. A white solid (275 mg, 96%) was obtained. M.p. 104–105 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 7.68–7.72 (m, 2 H), 7.77–7.79 (m, 1 H), 8.12–8.14 (m, 2 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 126.95 (s), 130.80 (s), 135.50 (s), 136.7–137.0 (m), 139.3–139.6 (m), 143.9–144.1 (m), 144.46 (s), 146.5–146.7 (m) ppm. $^{19}$F NMR ($CDCl_3$): $\delta$ = –155.72 (t, $J$ = 18.8 Hz), –141.46 (t, $J$ = 19.9 Hz), –134.43 (d, $J$ = 19.9 Hz) ppm. HRMS (ASAP): calcd. for $C_{12}H_6F_5O_2Se$ [M + H] 352.9480; found 352.9472. $C_{12}H_5F_5O_2Se$ (355.12): calcd. C 40.59, H 1.42, F 26.75; found C 40.52, H 1.23, F 26.63.

**Bis(2,2,2-trifluoroethyl) Selenone (2k):** Prepared from selenide **1k**[39] (108 mg, 0.44 mmol) as described in the general oxygenation procedure by using 4 equiv. of the oxidizing agent for 10 min. The product was recrystallized from chloroform. An off-white solid (121 mg, 100%) was obtained. M.p. 239 °C (sublimes). $^1$H NMR ([D$_6$]acetone): $\delta$ = 4.99 (d, $J$ = 10 Hz, 4 H) ppm. $^{13}$C NMR ([D$_6$]-acetone): $\delta$ = 58.74 (q, $J$ = 127 Hz), 122.17 (q, $J$ = 1110 Hz) ppm. $^{19}$F NMR ($CDCl_3$): $\delta$ = 58.71 (s) ppm. HRMS (ASAP): calcd. for $C_4H_5F_6O_2Se$ [M + H] 274.9386; found 274.9389. $C_4H_4F_6O_2Se$ (277.02): calcd. C 17.34, H 1.46, F 41.15; found C 17.56, H 1.44, F 40.72.

**Perfluorooctyl Phenyl Selenone (2l):** Prepared from selenide **1l**[40] (210 mg, 0.36 mmol) as described in the general oxygenation procedure by using 4 equiv. of the oxidizing agent for 20 min. The product was recrystallized from hexane. A white solid (202 mg, 91%) was obtained. M.p. 70–71 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 7.77–7.81 (m, 2 H), 7.88–7.92 (m, 1 H), 8.09–8.12 (m, 2 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 128.54, 131.05, 136.33, 138.65 ppm. $^{19}$F NMR ($CDCl_3$): $\delta$ = –124.84 (s), –121.43 (s), –120.57 (s), –120.40 (s), –120.19 (s), –117.59 (s), –102.12 (s), –79.46 (s) ppm. HRMS (ASAP): calcd. for $C_{14}H_6F_{17}O_2Se$ [M + H] 604.9288; found 604.9276. $C_{14}H_5F_{17}O_2Se$ (607.12): calcd. C 27.70, H 0.83, F 53.20; found C 27.61, H 0.72, F 52.99.

**Bis(pentafluorophenyl) Selenoxide (3m):** Prepared from selenide **1m**[41] (214 mg, 0.52 mmol) as described in the general oxygenation procedure by using 2.2 equiv. of the oxidizing agent for 10 min. A white solid (220 mg, 100%) was obtained. M.p. 154 °C. $^{19}$F NMR ($CDCl_3$): $\delta$ = –156.7, –144.6, –136.5 ppm. HRMS (APPI): calcd. for $C_{10}HF_{10}OSe$ 430.9033 [M + H]; found 430.9029.

**Supporting Information** (see footnote on the first page of this article): Copies of the $^1$H, $^{13}$C, and $^{19}$F NMR spectra, HRMS data, and elemental analysis report.

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