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$CaCl_2$-Promoted Dehydroxytrifluoromethylselenolation of Alcohols with $[Me_4N][SeCF_3]$

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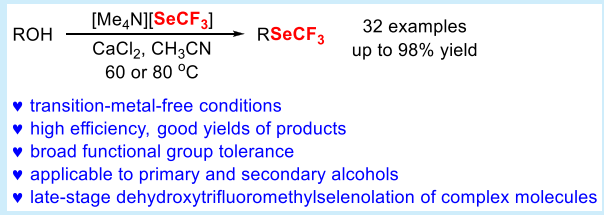
ABSTRACT: A direct trifluoromethylselenolation of alcohols with the readily accessible $[Me_4N][SeCF_3]$ salt has been reported. The reaction is significantly promoted by $CaCl_2$ and proceeds smoothly through unprecedented carbonoselenoate intermediates to form the corresponding alkyl trifluoromethyl selenoethers in good yields. This protocol is also applicable to the late-stage dehydroxytrifluoromethylselenolation of complex alcohols owing to its mildness, good compatibility, high efficiency, and broad functional group tolerance.



Fluorinated compounds have received broad interest in various research fields because of their unique physicochemical and biological properties.[1] Among all fluorine-containing functionalities, the XCF_3 (X = O, S) groups have found wide applications in the synthesis of agrochemicals, pharmaceuticals, and functional materials.[2] In recent years, the scientific attention has been shifted to the $SeCF_3$ moiety and the C−$SeCF_3$ bond formation.[3] Trifluoromethylselenolated compounds constitute a new class of valuable molecules with great potential for application in materials and life sciences.[3] Because the known CF_3Se-containing compounds are far more scarce, developing efficient methods to incorporate $SeCF_3$ groups into organic scaffolds is highly sought after.

The last several years have witnessed a flourish in the construction of C−$SeCF_3$ bonds along with advances in $SeCF_3$ reagents and catalytic systems.[3] Weng, Xiao, and Cook reported the Cu-mediated trifluoromethylselenolation of organic halides, terminal alkynes, α-diazo esters, and a series of Csp^3−H bonds with a copper(I) trifluoromethylselenolate complex ($[LCuSeCF_3]_2$), a $Ph_3P^+CF_2CO_2^-/Se_8/CsF$ mixture, and a $AgSeCF_3/CsBr$ system, respectively.[4−6] Billard, Tlili, and others disclosed the electrophilic or radical trifluoromethylselenolation of electron-rich arenes, Grignard reagents, carbonyl compounds, alkynes and their metal derivatives, alkenes, boronic acids, aryl diazonium salts, and alkyl halides with the powerful trifluoromethylselenenyl chloride (CF_3SeCl) and trifluoromethyl toueneselenosulfonate ($TsSeCF_3$).[7−9] However, these reagents suffered from high cost, low atomic economy, high volatility, toxicity, harsh reaction conditions, and tedious preparation procedures. Notably, tetramethylammonium trifluoromethylselenate ($[Me_4N][SeCF_3]$), synthesized from $TMSCF_3/Se_8/[Me_4N]F$, was investigated as a versatile nucleophilic trifluoromethylselenolation reagent under Cu, Pd, and Ni catalysis by the research groups of Rueping, Goossen, Schoenebeck, and Zhang.[10] Recently, the transition-metal-free trifluoromethylselenolation of alkynyl-(phenyliodonium) tosylates, organic halides, diaryliodonium triflates, aryl diazonium tetrafluoroborates, α-diazo carbonyls, electron-rich (hetero)arenes, alkyl carboxylic acids, and 1,3-dicarbonyls with $[Me_4N][SeCF_3]$ was also comprehensively harnessed, allowing the concise synthesis of various trifluoromethyl selenoethers.[11] These results proved that $[Me_4N][SeCF_3]$ is thermally stable, nonvolatile, readily accessible, and easy to handle, and it represents one of the most promising trifluoromethylselenolation reagents so far. Despite the aforementioned progress, trifluoromethylselenolation with $[Me_4N][SeCF_3]$ is still much less studied in comparison with the homologous trifluoromethylthiolation using $[Me_4N][SCF_3]$.[2,3] Thus the further search for new reactivities of $[Me_4N][SeCF_3]$ is very necessary for succeeding in more trifluoromethylselenolation approaches.

Alcohols are abundant, cheap, environmentally benign, easily accessible, and frequently used raw materials in organic synthesis.[12] The combination of alcohols with fluorination and fluoroalkylation reagents has constructed a large number of useful fluorine-containing molecules.[13] Qing et al. disclosed a direct trifluoromethylthiolation/fluorination of alkyl alcohols with $AgSCF_3/n\text{-}Bu_4NI$,[14] and Tang et al. uncovered a dehydroxytrifluoromethoxylation of alcohols using trifluoromethyl arylsulfonate as the OCF_3 reagent and $CsF/[Me_4N]Br$ as activators (Scheme 1).[15] These reactions took full advantage of the equilibria between $^-XCF_3$ (X = S, O) anions and X=CF_2 with fluoride ions to produce trifluoromethyl (thio)ethers. Nevertheless, as a comparison, the known $MSeCF_3$ complexes

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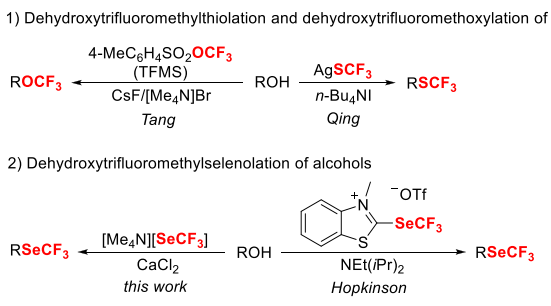
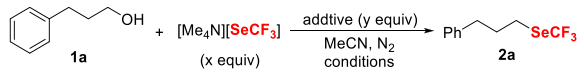
Scheme 1. Direct Trifluoromethylchalcogenation of Alcohols



(M = $SnMe_3$, 1/3B, 1/2Hg) decomposed to form carbonoselenoic difluoride ($Se{=}CF_2$) under very harsh conditions.[16] The decay of $MSeCF_3$ was slower and had a smaller tendency than that of the homologous $^-OCF_3$ and $^-SCF_3$ anions to $O{=}CF_2$ and $S{=}CF_2$, respectively,[16,17] according to the calculated free energies of the similar conversions.[17a] More seriously, the $Se{=}CF_2$ species was very easy to polymerize upon its formation under the reaction conditions.[16] These circumstances indicated that the synthesis and application of the $Se{=}CF_2$ intermediate is a challenging task. In this context, we envisioned that the removal of fluoride ions from the reversible decomposition of $^-SeCF_3$ anion would be conducive to the production of $Se{=}CF_2$ under mild conditions, which possibly slows down its polymerization. In other words, the use of a fluoride scavenger along with ionic $SeCF_3$ salt would accelerate the degradation of $^-SeCF_3$ to $Se{=}CF_2$ and benefit the targeted reactions. Very recently, Hopkinson et al. reported a deoxytrifluoromethylselenolation of alcohols with benzothiazolium salt ($BT{-}SeCF_3$) in the presence of $NEt(iPr)_2$,[18] which, however, suffered from the laborious synthesis of the $SeCF_3$ reagent from bis(2-benzothiazolyl)diselenide/CF_3I/MeOTf via stepwise procedures. As a part of our continuing interest in the development of facile trifluoromethylselenolation reactions, we examined in this Letter the dehydroxytrifluoromethylselenolation of alcohols with the readily accessible $[Me_4N][SeCF_3]$ reagent in the presence of a fluoride scavenger. This reaction is more convenient and efficient than Hopkinson's method and likely proceeds through a different mechanism from that of Qing and Tang's reactions.[14,15]

It is well known that calcium salt has been widely used as a cheap and strong scavenger for fluoride removal from water by chemists in both academic and industrial research fields,[19] which may be a good choice for our design to enhance the decomposition of the $^-SeCF_3$ anion to $Se{=}CF_2$ under mild conditions. The preliminary study showed that the treatment of 3-phenylpropan-1-ol (**1a**) with $[Me_4N][SeCF_3]$ (3 equiv) in CH_3CN at room temperature under a nitrogen atmosphere for 6 h gave no trifluoromethylselenolated product, and the starting materials could be recovered (entry 1, Table 1). Encouragingly, the use of $CaCl_2$ (1 equiv) in the same reaction led to (3-phenylpropyl)(trifluoromethyl)selane (**2a**) in 52% yield, suggesting that the trifluoromethylselenolation could be significantly promoted by $CaCl_2$ (entry 2, Table 1). Elevating the reaction temperature from room temperature to 40, 60, and 80 °C in the reactions of **1a**, $[Me_4N][SeCF_3]$ (3 equiv), and $CaCl_2$ (1 equiv) overnight provided **2a** in 63, 81, and 94% yield, respectively (entries 3−5, Table 1). The choice of calcium salts had an influence on the reaction. Taking

Table 1. Dehydroxytrifluoromethylselenolation of 1a by $[Me_4N][SeCF_3]$ under Different Reaction Conditions[a]



entry	**1a**/*x*/*y*	additive	conditions	yield (**2a**, %)[b]
1	1:3:0	none	r.t./6 h	0
2	1:3:1	$CaCl_2$	r.t./6 h	52[c]
3	1:3:1	$CaCl_2$	40 °C/overnight	63
4	1:3:1	$CaCl_2$	60 °C/overnight	81
5	1:3:1	$CaCl_2$	80 °C/overnight	94
6	1:3:1	$CaCl_2$	100 °C/ovenight	88
7	1:3:1	$Ca(COO)_2$	60 °C/overnight	30
8	1:3:1	$CaBr_2$	60 °C/overnight	76
9	1:3:1	$Ca(OTf)_2$	60 °C/overnight	63
10	1:3:1	CaF_2	60 °C/overnight	37
11	1:3:1	$CaSO_4$	60 °C/overnight	38
12[d]	1:3:1	HCl	80 °C/overnight	69[c]
13	1:3:1	LiI	80 °C/overnight	67[c]
14	1:3:2	$CaCl_2$	80 °C/overnight	57
15	1:2:1	$CaCl_2$	80 °C/overnight	54
16	1:2:0.5	$CaCl_2$	80 °C/overnight	(75)
17	1:3:1	$CaCl_2$	80 °C/2 h	92[c] (89)
18	1:3:1	$CaCl_2$	80 °C/1 h	81[c]

[a]Reaction conditions: **1a** (0.2 mmol), $[Me_4N][SeCF_3]$ (0.4 or 0.6 mmol), $CaCl_2$ (0, 0.1, 0.2, or 0.4 mmol), CH_3CN (2 mL), N_2, conditions. [b]Yields were determined by GC. [c]Yields were determined by ^{19}F NMR. Isolated yield is depicted in the parentheses. [d]Anhydrous HCl in 1,4-dioxane (4 mol/L) was used.

$Ca(COO)_2$ (calcium oxalate), $CaBr_2$, $Ca(OTf)_2$, CaF_2, and $CaSO_4$ instead of $CaCl_2$ in the reactions of **1a** and $[Me_4N][SeCF_3]$ (3 equiv) at 60 °C furnished **2a** in 30, 76, 63, 37, and 38% yield (entries 7−11, Table 1), which suggested that $CaCl_2$ and $CaBr_2$ are comparably effective promoters for the conversion. The frustrated results of $Ca(COO)_2$, CaF_2, and $CaSO_4$ might be attributed to their inertness and insolubility in CH_3CN. Other additives such as HCl and LiI under similar conditions supplied **2a** in 67−69% yield, implying that the Brønsted acid and lithium salt could moderately improve the reaction (entries 12 and 13, Table 1 and the SI). The equivalents of $CaCl_2$ and $[Me_4N][SeCF_3]$ also considerably affected the trifluoromethylselenolation. Varying the molar ratios of **1a**, $[Me_4N][SeCF_3]$, and $CaCl_2$ from 1:3:1 to 1:3:2, 1:2:1, and 1:2:0.5 at 80 °C resulted in 54, 57, and 75% of **2a**, indicating that superfluous $CaCl_2$ harmed the transformation, whereas excess $[Me_4N][SeCF_3]$ benefited the reaction (entries 14−16, Table 1). Furthermore, the reaction time could be reduced. A mixture of **1a**, $[Me_4N][SeCF_3]$ (3 equiv) and $CaCl_2$ (1 equiv) heated to 80 °C for 2 or 1 h furnished **2a** in 92 or 81% yield, implying a fast trifluoromethylselenolation (entries 17 and 18, Table 1).

Next, the substrate scope of this dehydroxytrifluoromethylselenolation was tested by using a combination of **1**, $[Me_4N][SeCF_3]$ (3 equiv), $CaCl_2$ (1 equiv), 80 °C, N_2, and 2 h or overnight as the optimal conditions (entry 17, Table 1, Scheme 2). To our delight, a series of benzyl alcohols bearing either electron-withdrawing (e.g., F, Cl, Br, I, CN, CHO, CO_2Me) or electron-donating groups (e.g., OMe, CH_3, $O(CH_2)O$) on the phenyl rings were smoothly converted to form the corresponding products (**2b−k**) in good yields (48−98%). Aliphatic alcohols such as 2-phenylethan-1-ol (**1l**),

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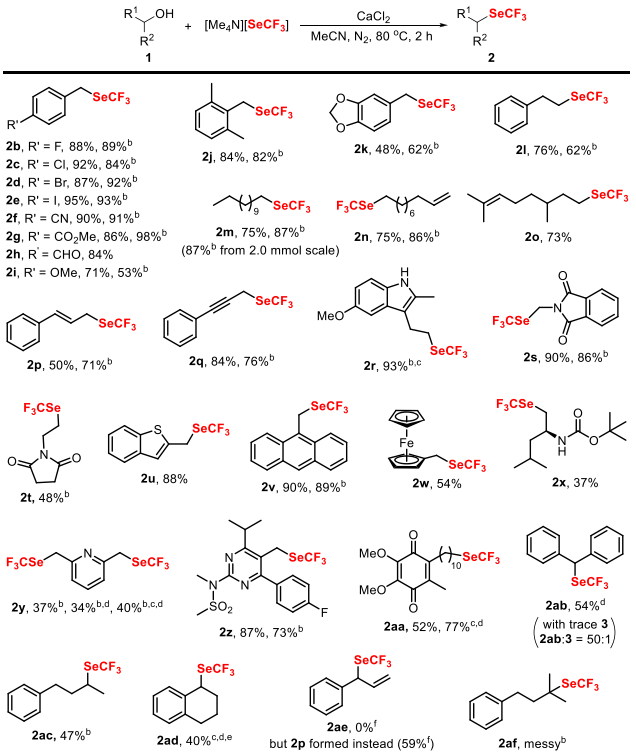
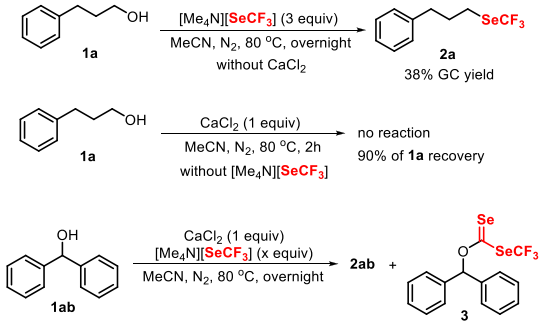
Scheme 2. $CaCl_2$-Promoted Dehydroxytrifluoromethylselenolation of Alcohols by $[Me_4N][SeCF_3]$[a]



[a]Reaction conditions: **1** (0.2 mmol), $[Me_4N][SeCF_3]$ (0.6 mmol), $CaCl_2$ (0.2 mmol), MeCN (2 mL), N_2, 80 °C (oil bath), 2 h, isolated yield. [b]Overnight. [c]60 °C. [d]$[Me_4N][SeCF_3]$ (1.0 mmol). [e]2 days. [f]$[Me_4N][SeCF_3]$ (0.8 mmol).

dodecan-1-ol (**1m**), dec-9-en-1-ol (**1n**), and 3,7-dimethyloct-6-en-1-ol (**1o**) reacted with $[Me_4N][SeCF_3]$ and $CaCl_2$ under the standard conditions to provide **2l**–**o** in 62–87% yields. (*E*)-3-Phenylprop-2-en-1-ol (**1p**) and 3-phenylprop-2-yn-1-ol (**1q**) were also successfully trifluoromethylselenolated in the reaction, giving products (**2p**–**q**) in 50–84% yields. Other complex alcohols like 2-(5-methoxy-2-methyl-1*H*-indol-3-yl)-ethan-1-ol (**1r**), 2-(hydroxymethyl)isoindoline-1,3-dione (**1s**), 1-(2-hydroxyethyl)pyrrolidine-2,5-dione (**1t**), benzo[b]-thiophen-2-ylmethanol (**1u**), anthracen-9-ylmethanol (**1v**), ferrocenemethanol (**1w**), and *tert*-butyl (*S*)-(1-hydroxy-4-methylpentan-2-yl)carbamate (**1x**) reacted similarly with $[Me_4N][SeCF_3]$ and $CaCl_2$ to furnish **2r**–**x** in 37–93% yields. These results demonstrated that the carbon–carbon double bonds and triple bond, heterocycles, imides, ferrocene, and carbamate groups in alcohols were well tolerated in the dehydroxytrifluoromethylselenolation. When pyridine-2,6-diyl-dimethanol (**1y**) was mixed with $[Me_4N][SeCF_3]$ and $CaCl_2$ under the same conditions, the doubly trifluoromethylselenolated product (**2y**) was obtained in 37% yield. Increasing the equivalents of $[Me_4N][SeCF_3]/CaCl_2$ or decreasing the reaction temperature did not obviously change the yield of **2y**. Moreover, the drug and drug-like molecule, for example, *N*-(4-(4-fluorophenyl)-5-(hydroxymethyl)-6-isopropyl-4,5-dihydropyrimidin-2-yl)-*N*-methylmethanesulfonamide (**1z**) and idebenone (**1aa**), reacted under the standard conditions to give **2z** in 87% (or 73%) yield and **2aa** in 52% yield. The reaction of **1aa** could be further improved by increasing the equivalent of $[Me_4N][SeCF_3]$ (5 equiv) and lowering the reaction temperature (60 °C), which afforded **2aa** in 77% yield. In addition, the dehydroxytrifluoromethylselenolation was applicable to secondary alcohols. The treatment of diphenylmethanol (**1ab**), 4-phenylbutan-2-ol (**1ac**), and 1,2,3,4-tetrahydronaphthalen-1-ol (**1ad**) with $[Me_4N][SeCF_3]/CaCl_2$ under the slightly modified conditions supplied **2ab**–**ad** in 40–54% yields. Interestingly, the reaction of 1-phenylprop-2-en-1-ol (**1ae**) with $[Me_4N][SeCF_3]$ and $CaCl_2$ in the same way formed cinnamyl(trifluoromethyl)-selane (**2p**) rather than **2ae** as the product, which might be attributed to the thermodynamically preferable rearrangement of the independent carbon–carbon double bond (**1ae**) to the conjugated one (**2p**). The use of excess $[Me_4N][SeCF_3]$ or the relatively low reaction temperature in some cases was beneficial to transforming the intermediates (e.g., **3**, see Scheme 3) or inhibiting the elimination byproducts. Nonetheless, tertiary alcohol (e.g., **1af**) reacted with $[Me_4N][SeCF_3]$ and $CaCl_2$ under either standard or modified conditions provided a complicated mixture.

Scheme 3. Studies for Mechanistic Insights



To probe the possible reaction mechanisms, several control experiments were carried out (Scheme 3 and the SI). It was found that a mixture of **1a** and $[Me_4N][SeCF_3]$ (3 equiv) at room temperature for 6 h gave no trifluoromethylselenolated product, whereas the treatment of **1a** with $[Me_4N][SeCF_3]$ (3 equiv)/$CaCl_2$ (1 equiv) under the same conditions provided **2a** in 52% yield (entries 1 and 2, Table 1). Further exploration showed that the reaction of **1a** with $[Me_4N][SeCF_3]$ (3 equiv) in the absence of $CaCl_2$ at 80 °C overnight formed **2a** in 38% yield (Scheme 3). It seemed that $[Me_4N][SeCF_3]$ itself could also initiate the dehydroxytrifluoromethylselenolation at an elevated temperature but with much poorer efficiency than that using $CaCl_2$. Additionally, when **1a** was mixed with $CaCl_2$ (1 equiv) without $[Me_4N][SeCF_3]$ at 80 °C for 2 h, no reaction occurred, and the starting alcohol was recovered (Scheme 3). In contrast, the treatment of $[Me_4N][SeCF_3]$ with $CaCl_2$ in the absence of **1a** at room temperature led to the rapid conversion of $[Me_4N][SeCF_3]$ as the signals of $[Me_4N][SeCF_3]$ disappeared within 1 h in the ^{19}F NMR spectra of the reaction mixtures. (See the SI.) The expected peaks of Se=CF_2 and its polymers were not observed; nonetheless, Se=$C(SeCF_3)_2$ was detected by ^{19}F NMR and GC–MS analyses of the mixtures, which might work as an intermediate for the reactions of $[Me_4N][SeCF_3]/CaCl_2$/**1a**.[16] Moreover, the standard reaction of **1ab** with $[Me_4N][SeCF_3]$ (3 equiv) and $CaCl_2$ (1 equiv) formed **2ab** in 39% total yield, accompanied

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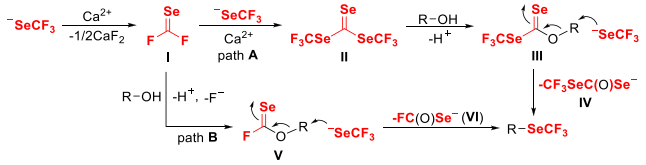
by a considerable amount of $Ph_2CHOC(Se)SeCF_3$ (**3**, Condition A, Scheme 3). This byproduct could not be separated from **2ab** by column chromatography but could almost completely be transformed in the reaction with 5 equiv of $[Me_4N][SeCF_3]$ under the same conditions (47%) or in the reaction with 3 equiv of $[Me_4N][SeCF_3]$ overnight followed by treatment with another 3 equiv of $[Me_4N][SeCF_3]$ for 8 h at 80 °C (39%) (Condition B or C, Scheme 3 and the SI), indicating that the dehydroxytrifluoromethylselenolation possibly involves a carbonoselenoate intermediate ($ROC(Se)SeCF_3$).

On the basis of these results and the knowledge that the calcium cation has a strong affinity for fluoride and that $^-SeCF_3$ has high nucleophilicity, a plausible reaction mechanism is suggested in Scheme 4. Carbonoselenoic

Scheme 4. Proposed Reaction Mechanism for $CaCl_2$-Promoted Dehydroxytrifluoromethylselenolation



difluoride (**I**) is first generated from the decomposition of $^-SeCF_3$ with $CaCl_2$ as a fluoride scavenger, which, upon generation, reacts with another two equivalents of $^-SeCF_3$ in the presence of Ca^{2+} cations to form bis(trifluoromethyl)carbonotriselenoate (**II**) as a key intermediate (path **A**). In the latter step, the Ca^{2+} species might behave as both a fluoride scavenger and a Lewis acid to promote the formation of **II** from **I**. Because there were no signals of selenocarbonyl fluorides detected by ^{19}F NMR during the reactions, this process may be rapid and complete. Subsequently, the nucleophilic substitution of **II** by ROH provides a carbonoselenoate (**III**), which is finally attacked by the $^-SeCF_3$ anion to provide the trifluoromethylselenolated product (path **A**). Furthermore, the production of $RSeCF_3$ via a straightforward reaction of **I** and ROH followed by the nucleophilic attack of $FC(Se)OR$ (**V**) with $^-SeCF_3$ cannot be excluded in this stage (path **B**). This pathway is not likely the major process in the Ca-mediated dehydroxytrifluoromethylselenolation, especially when using a large excess $[Me_4N][SeCF_3]$. Combining all of the observations might hint at a different reaction profile of $[Me_4N][SeCF_3]/CaCl_2$ for alcohols from those of $AgSCF_3/n$-Bu_4NI and $ArSO_2OCF_3/CsF/[Me_4N]Br$,[14,15] wherein alcohols probably reacted solely with $X{=}CF_2$ (X = S, O) to yield the corresponding trifluoromethylchalcogenated products. Nevertheless, the exact roles of $CaCl_2$ in these reactions remain unclear.

In conclusion, we have developed an efficient method for the $CaCl_2$-promoted dehydroxytrifluoromethylselenolation of alcohols with $[Me_4N][SeCF_3]$. A variety of primary and secondary alcohols, including complex bioactive molecules, were readily converted to form the respective alkyl trifluoromethyl selenoethers in good yields. A mechanistic study showed that this reaction might mainly proceed though a bis(trifluoromethyl)carbonotriselenoate (**II**) intermediate, which was *in situ* generated from $Se{=}CF_2$ and $^-SeCF_3$ anions. The advantages of the method include its simplicity, convenience, high efficiency, mild reaction conditions, good functional group tolerance, wide range of substrates, and easily accessible starting materials. The application of $[Me_4N][SeCF_3]$ as a useful $Se{=}CF_2$ source for other systems is currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02109.

Brief description of screening the optimal reaction conditions, general procedure for $CaCl_2$-promoted dehydroxytrifluoromethylselenolation, control experiments for mechanistic insights, characterization data, and NMR spectra of the products (PDF)

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Notes

The authors declare no competing financial interest.

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