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Nickel-Catalyzed Trifluoromethylselenolation of Aryl Halides Using the Readily Available $[Me_4N][SeCF_3]$ Salt

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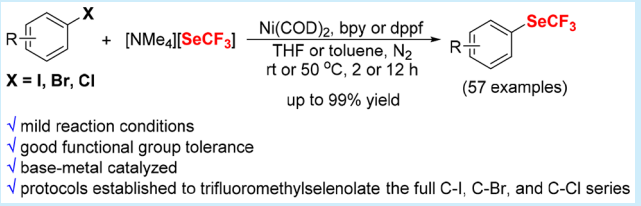
Supporting Information

ABSTRACT: A convenient and efficient method for the construction of aryl trifluoromethyl selenoethers from the corresponding aryl halides in the presence of $Ni(COD)_2$ and an appropriate ligand is reported. Various aryl iodides, bromides, and chlorides were smoothly converted in this reaction by simply varying the ligand, which afforded aryl and heteroaryl trifluoromethyl selenoethers in good to almost quantitative yields. The reaction was also applicable to the synthesis of druglike molecules. This work is the first report for trifluoromethylselenolation of aryl chlorides. Advantages of the present Ni-catalyzed approach include mild reaction conditions, good functional group tolerance, inexpensive reagents, easy operation, and no use of additional additives. This protocol allows for a straightforward and reliable access to trifluoromethyl selenides that are latent screening candidates for new pharmaceuticals and agrochemicals.



Fluorinated groups are important functionalities in bioactive molecules and advanced materials.[1] The systematic introduction of fluorine-containing moieties into a lead compound has become a commonly invoked procedure in modern day drug discovery units.[1] Among all fluorine-rich residues, the $SeCF_3$ functionality has attracted a growing interest in the past few years because of its unique electron-withdrawing ability and high lipophilicity that can significantly change the physicochemical and biological properties of a molecule.[2] Selenium is an essential element to humans and other living organisms. Basic and clinical studies have revealed that selenium supplements at an appropriate dosage have protective roles and therapeutic effects against various types of cancer[3a−d] and that inadequate levels of selenium increases the risk of cancer.[3] Since there has been no single $SeCF_3$-containing organic molecule found in nature, potential drugs or delivery agents bearing this functionality have to be synthesized.[1] Although the formation of C−SCF_3 bonds has been documented extensively, methods for direct trifluoromethylselenolation are much less developed owing to the limited types of $SeCF_3$ transfer reagents[4] and the relatively unexplored applications of selenium compounds compared to the sulfur derivatives.[5] In view of their potential applications in the pharmaceutical and agricultural industries, the development of a convenient method for the synthesis of $SeCF_3$-containing target molecules is a subject of great importance. In particular, late-stage trifluoromethylselenolation is highly sought-after to explore the pharmacological properties of the $SeCF_3$ group.

Traditionally, the incorporation of $SeCF_3$ moieties into organic scaffolds was mainly achieved by the nucleophilic trifluoromethylation of diselenides and selenocyanates by CF_3 anions, which were in situ generated from a mixture of $TMSCF_3$/fluoride,[6a−c] HCF_3/base,[6d,e] CF_3I/TDAE (tetrakis(dimethylamino)ethylene),[6f,g] and more.[6h,i] However, these trifluoromethylation reactions suffered from harsh conditions, low efficiencies, and/or a narrow range of substrates. To overcome these disadvantages, direct trifluoromethylselenolation was developed by using $SeCF_3$ reagents like $CuSeCF_3$,[7a] $Hg(SeCF_3)_2$,[7b] $[Me_4N][SeCF_3]$,[7c] $ClSeCF_3$,[7d,e] and $[(bpy)Cu(SeCF_3)]_2$.[8] Among these reagents, $[Me_4N][SeCF_3]$ is the most convenient and easily accessed $SeCF_3$ source.[9] Recently, the Cu-catalyzed/mediated reactions of $[Me_4N][SeCF_3]$ with aryl diazonium salts, α-diazo esters, boronic acids and their esters, and terminal alkynes allowed for several direct accesses to trifluoromethyl selenoethers (Scheme 1).[10] The Pd-catalyzed conversion of aryl iodides as well as a few bromides into the corresponding $ArSeCF_3$ was also harnessed, which represents the state-of-the-art method to incorporate the $SeCF_3$ group into aryl halides with $[Me_4N][SeCF_3]$.[11] Nevertheless, trifluoromethylselenolation of aryl chlorides with a practical $SeCF_3$ source still remains unknown. $[Me_4N][SeCF_3]$ is more thermally stable [decomposes at 207 °C (DTA/TG) or 215−217 °C (visible decomposition in sealed glass ampules)][9] than $[Me_4N][SCF_3]$ and, therefore, would survive better under sensitive reaction conditions. Despite the aforementioned studies, this reagent is poorly exploited in chemical synthesis relative to the $[Me_4N][SCF_3]$ analogue.[4]

Nickel has become an attractive alternative to palladium because of its higher abundance, low cost, and most

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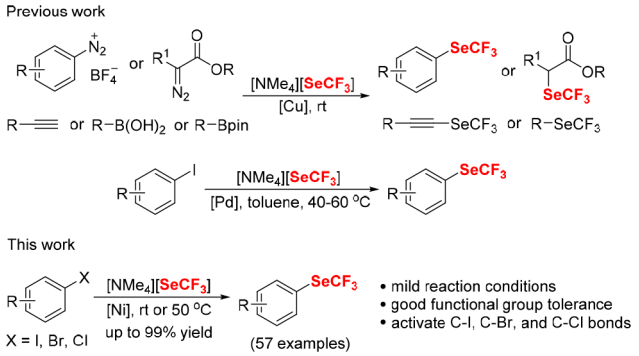
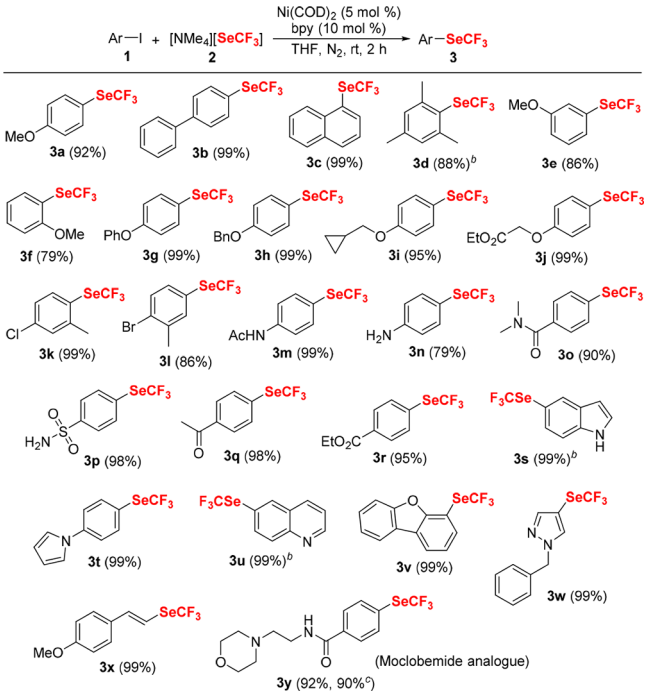
Scheme 1. Previously Described Trifluoromethylselenolations with $[NMe_4][SeCF_3]$



importantly, power to activate a larger array of C−X bonds (e.g., C−Cl) that are generally inert to palladium or copper.[12−15] In 2012, we reported the nickel-catalyzed trifluoromethylthiolation of aryl iodides and bromides with $[Me_4N][SCF_3]$ that proceeded at room temperature in the presence of bipyridine ligands.[12] Later, Schoenebeck and co-workers disclosed a nickel-catalyzed transformation of aryl chlorides to the corresponding trifluoromethyl sulfides with $[Me_4N][SCF_3]$ and a sterically hindered electron-rich phosphine ligand.[13] Inspired by these early works on nickel SCF_3 chemistry, we wondered whether a related nickel-catalyzed trifluoromethylselenolation of aryl halides (ArX, X = I, Br, Cl) with $[Me_4N][SeCF_3]$ would allow for a straightforward and efficient installation of the $SeCF_3$ group in aromatic and heteroaromatic systems under mild conditions.

To our delight, we found that reaction of 1-iodo-4-methoxybenzene (**1a**) with $[Me_4N][SeCF_3]$ (1.5 equiv) in the presence of 5 mol % of $Ni(COD)_2$ and 10 mol % of 2,2′-bipyridine (bpy) at room temperature for 6 h furnished (4-methoxyphenyl)(trifluoromethyl)selane (**3a**) in 96% yield (Table S1). Tables S1−S3 summarize important examples of our screenings and follow-up optimizations. The results of these screens indicated that diimine ligands outperformed diamine, phosphine, and diphosphine ligands and also indicated that THF, DME, and 1,4-dioxane were suitable solvents for the trifluoromethylselenolation of **1a**. Based on the exhaustive screening data, we chose a combination of **1**, $[Me_4N][SeCF_3]$ (1.2 equiv), $Ni(COD)_2$ (5 mol %), relatively cheap 2,2′-bipyridine (10 mol %), THF, room temperature, and 2 h as the standard reaction conditions for the trifluoromethylselenolation of aryl iodides (Scheme 2). Various aryl iodides bearing either electron-donating or -withdrawing groups on the phenyl rings under the standard reaction conditions were all smoothly converted to the corresponding trifluoromethyl selenoethers in good to quantitative yields (Scheme 2). The steric hindrance of the substrates had a considerable influence on the transformation. 1-Iodo-3-methoxybenzene (**1e**) and 1-iodo-2-methoxybenzene (**1f**) reacted with $[Me_4N][SeCF_3]$ yielded 86% of **3e** and 79% of **3f**, while the reaction of **1a** provided **3a** in 92% isolated yield. By increasing the amounts of $Ni(COD)_2$ and 2,2′-bipyridine to 10 and 12 mol %, respectively, the reaction of 2-iodo-1,3,5-trimethylbenzene (**1d**) with $[Me_4N][SeCF_3]$ supplied 88% of **3d**. The chloro, sterically hindered bromo, free amino, and keto groups, amides, and ester were all tolerated in the reaction (**3k−r**). Heteroaryl iodides such as 5-iodo-1*H*-indole (**1s**), 1-(4-iodophenyl)-1*H*-pyrrole (**1t**), 6-iodoquinoline (**1u**), 4-iododibenzo[*b*,*d*]furan (**1v**), and 1-

Scheme 2. Ni-Catalyzed Trifluoromethylselenolation of Aryl Iodides with $[Me_4N][SeCF_3]$ in the Presence of 2,2′-Bipyridine[a]



[a]Reaction conditions: **1** (0.2 mmol), $[NMe_4][SeCF_3]$ (0.24 mmol), $Ni(COD)_2$ (5 mol %), bpy (10 mol %), THF (2 mL), room temperature, 2 h. Isolated yields. [b]$Ni(COD)_2$ (10 mol %), bpy (12 mol %). [c]The reaction was run on a 1.0 mmol scale (see the SI).

benzyl-4-iodo-1*H*-pyrazole (**1w**) reacted with $[Me_4N][SeCF_3]$ in the presence of $Ni(COD)_2$ (5 or 10 mol %) and 2,2′-bipyridine (10 or 12 mol %) at room temperature for 2 h to form **3s−w** in almost quantitative yields. It is remarkable that treatment of (*E*)-1-(2-iodovinyl)-4-methoxybenzene (**1x**) with $[Me_4N][SeCF_3]$ under the standard reaction conditions gave **3x** in 99% yield (*E*-isomer only). Similarly, the reaction of 4-iodo-*N*-(2-morpholinoethyl)benzamide (**1y**, see the SI) with $[Me_4N][SeCF_3]$ afforded **3y**, a fluorinated analogue of the depression and anxiety drug moclobemide, in 92% yield.

Next, the nickel-catalyzed trifluoromethylselenolation of aryl bromides with $[Me_4N][SeCF_3]$ was studied. The reaction of 4-bromo-1,1′-biphenyl (**4a**) and $[Me_4N][SeCF_3]$ (1.2 equiv) in THF in the presence of 5 mol % of $Ni(COD)_2$ and 10 mol % of 2,2′-bipyridine at room temperature for 12 h produced **3b** only in 41% yield (Table S7). Increasing the catalyst loading of $Ni(COD)_2$ from 5 to 10 mol % could clearly promote the yield of **3b** (97%, Table S7). Diimine ligands such as 4,4′-di-Me-bpy, 4,4′-di-MeO-bpy, and 4,4′-di-*t*-Bu-bpy were also suitable ligands for the trifluoromethylselenolation of **4a**. It should be noted that the reaction of **4a** and $[Me_4N][SeCF_3]$ with 12, 15, or 20 mol % of diimine ligand and 10 mol % of $Ni(COD)_2$ gave lower yields of **3b** than that using 10 mol % of $Ni(COD)_2$ and 10 mol % of 2,2′-bipyridine (Tables S5 and S7). These results suggested that the excess bipyridine relative to $Ni(COD)_2$ inhibited the formation of **3b** (Tables S5 and S7). This consequence was different from the outcomes of **1a**, for which almost no obvious changes in the yields of the product were observed when amounts of bipyridine ligand equal or two times to Ni catalyst were used (Table S2).

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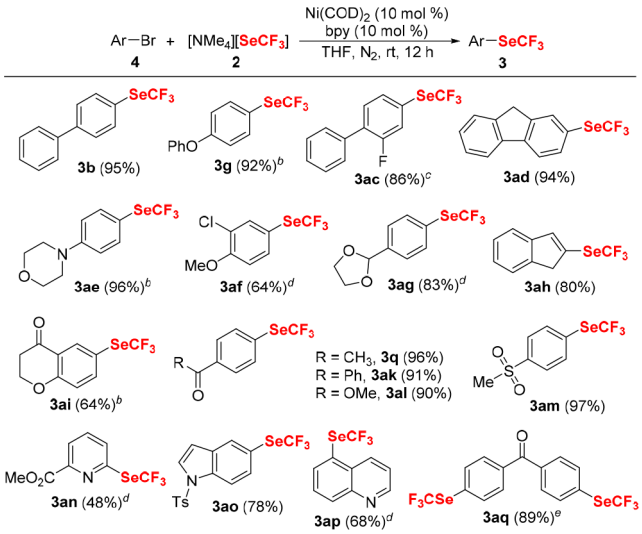
Scheme 3 summarizes the trifluoromethylselenolation of aryl bromides with $[Me_4N][SeCF_3]$ at room temperature in the presence of 10 mol % of $Ni(COD)_2$ and 10 mol % of 2,2′-bipyridine. For some elusive cases, satisfactory yields of the desired products were also obtained under the standard conditions, but increasing the catalyst loadings from 10 to 12, 15, or 20 mol % helped the complete conversion of the starting bromides, making the purification of the products easier (see the SI). Despite the catalyst loadings being relatively high at 15 or 20 mol %, these loadings are mitigated by the inexpensive combination of all the reagents employed in the reaction mixture. As a result, aryl bromides bearing either electron-donating or -withdrawing groups on the phenyl rings readily formed the corresponding trifluoromethyl selenoethers in good to high yields under the standard reaction conditions or modified ones (Scheme 3). This reaction was also applicable to heterocycles such as 4-(4-bromophenyl)morpholine (**4e**), 2-(4-bromophenyl)-1,3-dioxolane (**4g**), 6-bromochroman-4-one (**4i**), methyl 6-bromopicolinate (**4n**), 5-bromo-1-tosyl-1*H*-indole (**4o**), and 5-bromoquinoline (**4p**). In addition, bis(4-bromophenyl)methanone (**4q**) reacted with $[Me_4N][SeCF_3]$ (3 equiv) in the presence of 30 mol % of $Ni(COD)_2$ and 30 mol % of 2,2′-bipyridine at room temperature for 12 h to give **3aq** (89%) as a doubly trifluoromethylselenolated product.

When the $Ni(COD)_2$/bipyridine catalytic system was used for the transformation of aryl chloride at 40 °C, only a trace of the trifluoromethylselenolation product was formed (Table S9). It was known that modulation of the steric and electronic properties of the ligands can tremendously affect Ni-catalyzed reactions.[13−15] We envisioned that the bulky electron-rich phosphine ligands would have a good partnership with nickel for trifluoromethylselenolation of aryl chlorides,[13] even though such ligand gave poor catalytic efficiency in the nickel-catalyzed reactions of aryl iodides (Table S2). A variety of screens (Tables S9−S14) were carried out to determine the optimal conditions for the trifluoromethylselenolation of aryl chlorides with nickel. The combination of **5**, $[Me_4N][SeCF_3]$ (1.5 equiv), $Ni(COD)_2$ (10 mol %), dppf (20 mol %), 50 °C, and 12 h was ultimately used to probe the scope of the reaction (Scheme 4) with different aryl chlorides. For some challenging substrates, varying the catalyst/ligand loadings of $Ni(COD)_2$/dppf from 10 mol %/20 mol % to 15 mol %/30 mol % or 20 mol %/40 mol % could accelerate the conversion of the chlorides and consequently facilitate the formation of trifluoromethyl selenoethers (e.g., **3ba**, **3bb**, **3bg**, **3bk**, and **3bm**). Products with keto, formyl, or cyano substituent, ester, or sulfamine groups (**3ba−bd** and **3bf−bg**) were all successfully constructed. Heteroaryl chlorides like 6-chloroquinoline (**5h**), 8-chloroquinoline (**5i**), 7-chloro-2-methylquinoline (**5j**), 2-chloro-9*H*-thioxanthen-9-one (**5k**), 5-chlorobenzo[*b*]thiophene (**5l**), 5-chloro-2-methylbenzo[*d*]thiazole (**5m**), and 5-chloro-2-methylbenzo[*d*]oxazole (**5n**) reacted with $[Me_4N][SeCF_3]$ under the standard conditions or modified conditions to provide **3bh−bn** in 49−95% yields. Notably, the reaction of the cholesterol reducing drug Fenofibrate with $[NMe_4][SeCF_3]$ (1.5 equiv) in toluene in the presence of 20 mol % of $Ni(COD)_2$ and 40 mol % of dppf at 50 °C for 12 h gave the trifluoromethylselenolated analogue **3bo** in 78% isolated yields.

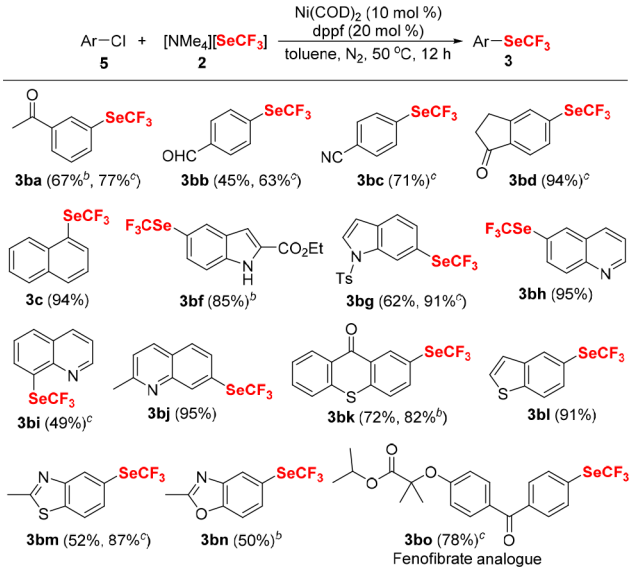
In conclusion, we have developed a comprehensive set of mild and efficient methods for the preparation of aryl trifluoromethyl selenoethers from the full aryl halide series (X = I, Br, Cl) in the presence of $Ni(COD)_2$ and ligand. In these strategies, various aryl and heteroaryl trifluoromethyl selenoethers were synthesized in good to almost quantitative yields with commonly used and relatively inexpensive reagents. The best conditions for a particular aryl halide were obtained simply by changing the ligand on nickel. Diimine ligands favored the

Scheme 3. Ni-Catalyzed Trifluoromethylselenolation of Aryl Bromides with $[Me_4N][SeCF_3]$ in the Presence of 2,2′-Bipyridine[a]



[a]Reaction conditions: **4** (0.2 mmol), $[NMe_4][SeCF_3]$ (0.24 mmol), $Ni(COD)_2$ (10 mol %), bpy (10 mol %), THF (2 mL), room temperature, 12 h. Isolated yields. [b]$Ni(COD)_2$ (12 mol %), bpy (12 mol %). [c]$Ni(COD)_2$ (15 mol %), bpy (15 mol %). [d]$Ni(COD)_2$ (20 mol %), bpy (20 mol %). [e]$[NMe_4][SeCF_3]$ (0.6 mmol), $Ni(COD)_2$ (30 mol %), bpy (30 mol %).

Scheme 4. Ni-Catalyzed Trifluoromethylselenolation of Aryl Chlorides with $[Me_4N][SeCF_3]$ in the Presence of dppf[a]



[a]Reaction conditions: **5** (0.2 mmol), $[NMe_4][SeCF_3]$ (0.3 mmol), $Ni(COD)_2$ (10 mol %), dppf (20 mol %), toluene (2 mL), 50 °C, 12 h. Isolated yields. [b]$Ni(COD)_2$ (15 mol %), dppf (30 mol %). [c]$Ni(COD)_2$ (20 mol %), dppf (40 mol %).

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trifluoromethylselenolation of aryl iodides and bromides. Aryl iodides appeared to require a low dosage of the catalyst, and excess bipyridine ligand relative to $Ni(COD)_2$ did not significantly affect the yields. Aryl bromides required a higher percentage of $Ni(COD)_2$ and bipyridine, and an excess of bipyridine relative to $Ni(COD)_2$ considerably inhibited the trifluoromethylselenolation reactions. These results suggest that the activation of aryl iodides occurs more readily than the bromides and that unproductive ligand coordination is competitive with the activation of the aryl bromide substrates. Importantly, the challenging aryl chloride substrates could be trifluoromethylselenolated by employing dppf as the optimal ligand on nickel. This work represents the first report for the direct trifluoromethylselenolation of aryl chlorides. Finally, the reactions developed herein are amenable to the synthesis of potentially bioactive molecules and drug analogues and could serve as a promising resource for the construction of trifluoromethyl selenides for life science applications. A more detailed investigation of the reaction mechanisms is currently underway in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01839.

Experimental information, reaction condition optimization, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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