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Letter

Copper-Catalyzed Radical 1,2-Carbotrifluoromethylselenolation of Alkenes under Ambient Conditions

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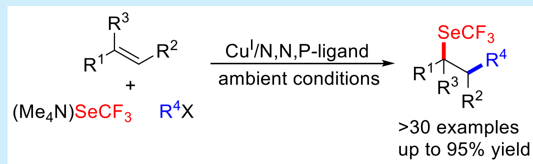
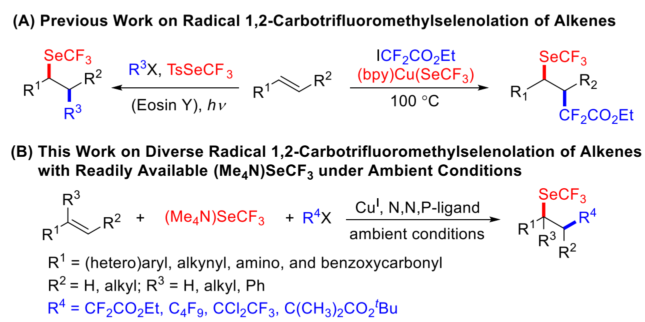
ABSTRACT: We have described a copper-catalyzed radical 1,2-carbotrifluoromethylselenolation of alkenes using the readily available alkyl halides and $(Me_4N)SeCF_3$ salt. Critical to the success is the use of a proline-based N,N,P-ligand to enhance the reducing capability of copper for easy conversion of diverse alkyl halides to the corresponding radicals via a single-electron transfer process. The reaction features a broad substrate scope, including various mono-, di-, and trisubstituted alkenes with many functional groups.



Alkenes are one of the most prevailing building blocks in organic synthesis, and straightforward transformation of alkenes is a powerful tool to allow for the expedient synthesis of complex molecules from simple feedstocks.[1] Among intensive research, the radical-initiated 1,2-difunctionalization of alkenes to install two new chemical bonds at the vicinal positions of alkenes has emerged as an appealing strategy due to its high reactivity and good functional group tolerance.[2] Since the CF_3Se group shows promising lipophilicity and electronic characteristics, which are beneficial to the development of bioactive compounds,[3] the CF_3Se group might be promising in pharmaceutical research. In this aspect, the radical-initiated 1,2-carbotrifluoromethylselenolation of alkenes to introduce a trifluoromethylselenyl group[4−6] as well as an additional functional group has gained increasing interest among chemists. Although this strategy has been realized in several reports,[7] they have to use either the trifluoromethyl tolueneselenosulfate ($TsSeCF_3$) reagent which needs tedious synthesis[7a,b] or a stoichiometric amount of $bpyCuSeCF_3$ complex (Scheme 1A).[7c] In addition, a high temperature or light irradiation strategy should be utilized in order to initiate the radical process (Scheme 1A).[7] Therefore, a catalytic radical 1,2-carbotrifluoromethylselenolation of alkenes to provide a number of β-functionalized $SeCF_3$ compounds from readily available trifluoromethylselenolation reagents and diverse radical precursors under ambient conditions is highly desirable.

Our group has focused on the copper-catalyzed radical 1,2-difunctionalization of alkenes to generate complex compounds from readily available starting materials.[8] During this course, we found that a multidentate N,N,P-ligand could significantly enhance the reducing capability of the copper catalyst, thus easily converting the mildly oxidative alkyl halides to alkyl radicals via a single-electron transfer (SET) process under ambient conditions.[8e] Given that the $(Me_4N)SeCF_3$ salt is a readily accessible and thermally stable trifluoromethylselenolation reagent,[9] we wondered whether a copper-catalyzed radical 1,2-carbotrifluoromethylselenolation of alkenes could be achieved from $(Me_4N)SeCF_3$ and diverse alkyl halides. However, the identification of a suitable ligand for radical generation from various mildly oxidative alkyl halides with copper catalyst is a challenging task.[10] Herein, we describe a copper/N,N,P-ligand catalysis for a radical 1,2-carbotrifluoromethylselenolation of alkenes from the readily available $(Me_4N)SeCF_3$ salt and diverse alkyl halides under ambient conditions (Scheme 1B).

Scheme 1. Radical 1,2-Trifluoromethylselenolation of Alkenes



Based on our assumption, we tried to initiate the alkene 1,2-carbotrifluoromethylselenolation of 4-phenyl-substituted styrene **1a**, with $(Me_4N)SeCF_3$ **2a** and ICF_2CO_2Et **3a** in the

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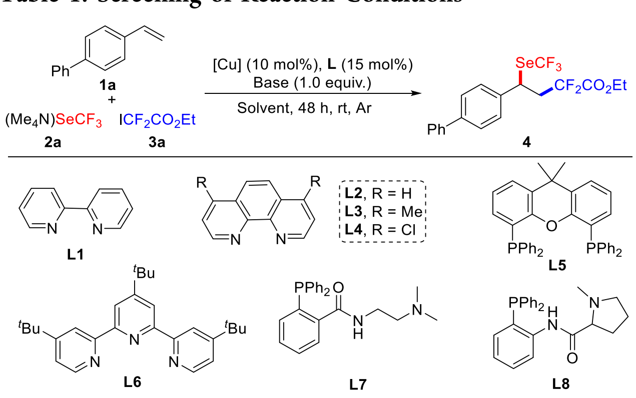
presence of 10 mol % Cu_2O and 1.0 equiv of Cs_2CO_3 by searching for a suitable ligand (Table 1). Bidentate ligands,

Table 1. Screening of Reaction Conditions[a]



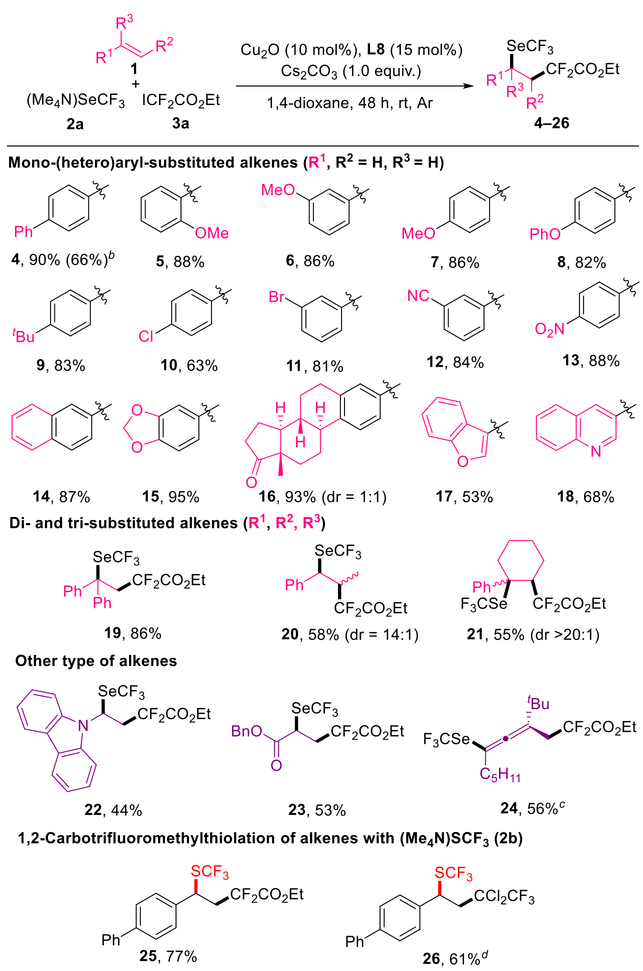
Entry	L	Base	[Cu]	Solvent	Yield (%)[b]
1	**L1**	Cs_2CO_3	Cu_2O	1,4-dioxane	0
2	**L2**	Cs_2CO_3	Cu_2O	1,4-dioxane	trace
3	**L3**	Cs_2CO_3	Cu_2O	1,4-dioxane	trace
4	**L4**	Cs_2CO_3	Cu_2O	1,4-dioxane	0
5	**L5**	Cs_2CO_3	Cu_2O	1,4-dioxane	0
6	**L6**	Cs_2CO_3	Cu_2O	1,4-dioxane	0
7	**L7**	Cs_2CO_3	Cu_2O	1,4-dioxane	0
8	**L8**	**Cs_2CO_3**	**Cu_2O**	**1,4-dioxane**	**87**
9	**L8**	Na_2CO_3	Cu_2O	1,4-dioxane	84
10	**L8**	K_3PO_4	Cu_2O	1,4-dioxane	5
11	**L8**	Cs_2CO_3	CuI	1,4-dioxane	7
12	**L8**	Cs_2CO_3	CuCN	1,4-dioxane	86
13	**L8**	Cs_2CO_3	Cu_2O	THF	11
14	**L8**	Cs_2CO_3	Cu_2O	DCM	78
15[c]	**L8**	Cs_2CO_3	Cu_2O	1,4-dioxane	92
16[d]	**L8**	Cs_2CO_3	Cu_2O	1,4-dioxane	15
17[e]	**L8**	Cs_2CO_3	Cu_2O	1,4-dioxane	0
18[f]	**L8**	Cs_2CO_3	Cu_2O	1,4-dioxane	43
19[g]	**L8**	Cs_2CO_3	Cu_2O	1,4-dioxane	0

[a]Reaction conditions: **1a** (0.10 mmol), **2a** (0.15 mmol), **3a** (0.30 mmol), [Cu] (10 mol %), **L** (15 mol %), and base (1.0 equiv) in solvent (1.5 mL) at room temperature for 48 h under argon. [b]Yields were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. [c]Reaction was conducted at 60 °C (oil bath) for 4 h. [d]H_2O (3.0 equiv) was added. [e]Reaction was performed under an air atmosphere. [f]Solvent (3.0 mL) was added. [g][Cu] (1 mol %) and **L8** (1.5 mol %) were used.

such as bipyridine **L1** and 1,10-phenanthroline ligands **L2**−**L4** with electron-donating or -withdrawing groups, could not afford the desired product **4** in a large amount (Table 1, entries 1−4). Further trials with the Xantphos ligand **L5** and tripyridine-tpye ligand **L6** revealed that they were not effective for the reaction (Table 1, entries 5 and 6). The N,N,P-ligand **L7**, which was utilized in our previous 1,2-carboalkynylation reaction,[8e] proved to be inapplicable in the 1,2-carbotrifluoromethylselenolation as well (Table 1, entry 7). We then tried the proline-based N,N,P-ligand **L8**,[11] and the reaction proceeded smoothly to deliver the desired product **4** in 87% yield (Table 1, entry 8). Further screening of different bases, copper salts, and solvents led to the optimal reaction conditions as follows: the reaction of **1a**, **2a**, and **3a** in the presence of 10 mol % Cu_2O, 15 mol % **L8**, and 1.0 equiv of Cs_2CO_3 in 1,4-dioxane gave rise to the carbotrifluoromethylselenolation product **4** in 87% NMR yield under ambient conditions (Table 1, entry 8). Control experiments were conducted to investigate the sensitivity of the reaction. Enhancing the reaction temperature to 60 °C dramatically increased the reaction rate, and a 92% yield of **4** can be obtained after 4 h (Table 1, entry 15). The exposure to moisture or air conditions greatly affected the reaction efficiency (Table 1, entries 16 and 17). The yield also decreased in a dilute condition (Table 1, entry 18). When Cu_2O was reduced to 1 mol %, the reaction afforded almost no product (Table 1, entry 19).

Having established the optimal reaction conditions, we next investigated the scope of alkenes (Table 2). The arylated

Table 2. Substrate Scope of Alkenes[a]

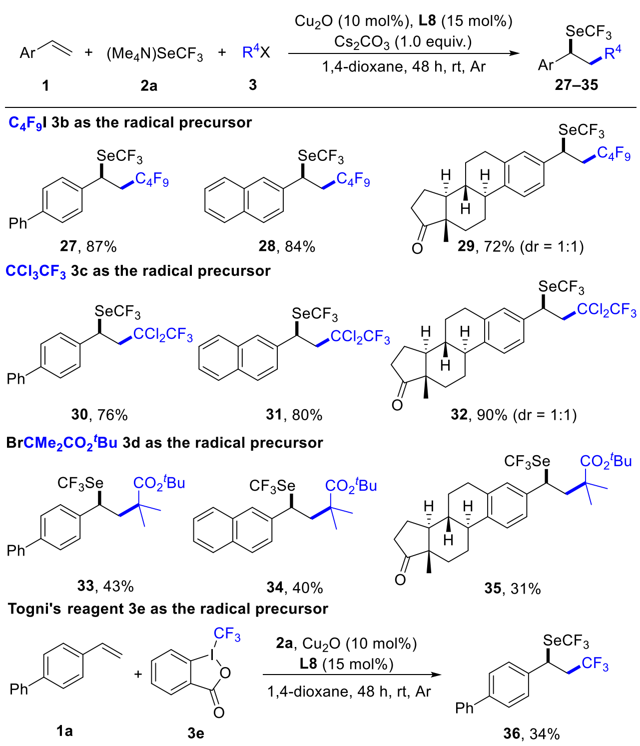


[a]Reaction conditions: **1** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.60 mmol), Cu_2O (10 mol %), **L8** (15 mol %), and Cs_2CO_3 (0.20 mmol) in 1,4-dioxane (3.0 mL) at room temperature for 48 h under argon. [b]Reaction was performed on a gram scale and **2a** (1 g) was used. [c]2,2-Dimethyl-3-methylenedec-4-yne was used as the starting alkene. [d]CCl_3CF_3 was used as the radical precursor.

alkenes with electron-rich or -deficient substituents at the *para*, *meta*, or *ortho* position of the aryl ring were applicable for the reaction to provide **4**−**15** in 63−95% yields. The reaction worked well on a gram scale, providing **4** with a slightly decreased yield (66%). A wide range of functional groups are well tolerated, such as the methoxyl (**5**−**7**), phenoxyl (**8**), halide (**10** and **11**), cyano (**12**), and nitro (**13**) group. Besides, the alkenes possessing a polycyclic aryl ring were also suitable for the reaction to generate **14** and **15** in excellent yields. For the estrone-derived alkene substrate, the reaction afforded **16** as a diastereomeric mixture (dr = 1:1). Furthermore, the alkenes containing heteroarenes, such as benzofuran and quinoline, are also amenable to the reaction to give **17** and **18** in good yields. In addition to the monosubstituted alkenes, the 1,1-disubstituted alkenes proceeded smoothly under the standard reaction conditions to furnish **19** in 86% yield. Moreover, the 1,2-disubstituted and trisubstituted alkenes also underwent the reaction to give rise to **20** and **21** with good diastereoselectivity, albeit in moderate yields. Notably, the reactions were not limited to arylated alkenes. For example, the electron-rich enamine was a viable substrate to deliver **22** in 44% yield. The electron-deficient alkene also worked well to provide the corresponding product **23** in 53% yield. Interestingly, the 1,4-carbotrifluoromethylselenolation was observed in the case of the 1,3-enyne substrate to furnish the allene product **24**. A preliminary trial with $(Me_4N)SCF_3$ **2b** as the nucleophile under the otherwise identical conditions demonstrated that the protocol was also applicable for the alkene 1,2-carbotrifluoromethylthiolation to provide the SCF_3-containing products **25** and **26** in good yields.

Encouraged by these results, we further focused on expanding the scope of radical precursors (Table 3). C_4F_9I is a cheap reagent which is used to introduce a C_4F_9 group into a molecule, but its reactivity is slightly low and a photoirradiation protocol is necessary to initiate the generation of the C_4F_9 radical species.[12] Having the idea that the N,N,P-ligand could enhance the reducing capability of copper catalyst, we targeted C_4F_9I as the radical source. To our delight, it could be successfully applied to the 1,2-carbotrifluoromethylselenolation process to afford **27−29** in good yields under the otherwise identical conditions. Further, CCl_3CF_3 was also a suitable radical precursor for the reaction to provide **30−32** in 76−90% yields. In addition, *tert*-butyl α-bromoisobutyrate was also a viable radical precursor, though the desired products **33−35** were formed in slightly lower yields. Notably, the radical precursors were not limited to alkyl halides and the Togni's reagent **3e** was also suitable for the reaction to deliver **36** in 34% yield.

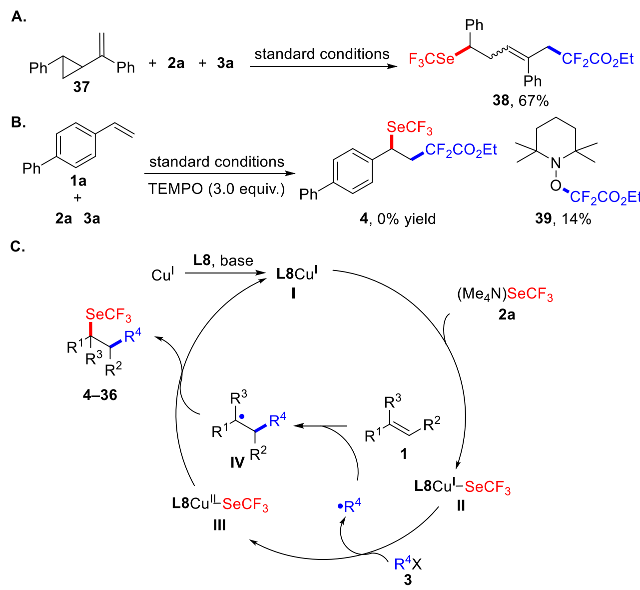
Table 3. Substrate Scope of Radical Precursors[a]



[a]Reaction conditions: **1** (0.20 mmol), **2a** (0.30 mmol), **3** (0.60 mmol), Cu_2O (10 mol %), **L8** (15 mol %), and Cs_2CO_3 (0.20 mmol) in 1,4-dioxane (3.0 mL) at room temperature for 48 h under argon.

In order to probe the possible mechanism, we performed the control experiments. The reaction of the radical clock substrate **37** with **2a** and **3a** led to the radical addition/ring-opening/nucleophile trapping product **38**, clearly illustrating a radical process (Scheme 2A). This is further demonstrated by the radical inhibition experiment with (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), which provided the TEMPO-trapping product **39**, and no desired product **4** was observed (Scheme 2B). Based on these results, we proposed a plausible reaction mechanism (Scheme 2C). Copper salt was first transformed into active catalytic species **I** in the presence of base and the ligand **L8**, which then reacted with $(Me_4N)SeCF_3$ to form the Cu^I Intermediate **II**.[13] A SET process occurred between the Cu^I complex **II** and alkyl halides to generate the Cu^{II} complex **III** and the corresponding alkyl radical $\cdot R^4$.[10] Afterward, the $\cdot R^4$ radical added to the alkenes **1** at the less sterically hindered positions to form the alkyl radical intermediate **IV**.[8] The resulting radical species further reacted with the Cu^{II} complex **III** to furnish the desired products and release the Cu^I complex for the next catalytic cycle.[14] With alkyl bromide or iodide as the radical precursors, although we cannot detect the bromide or iodide intermediate, the atom-transfer process followed by substitution by the $SeCF_3$ anion could not be excluded.[15]

Scheme 2. Mechanistic Study and Proposal



In summary, we have achieved a copper-catalyzed radical 1,2-carbotrifluoromethylselenolation of alkenes from the readily available alkyl halides and $(Me_4N)SeCF_3$ salt, providing expedient access to a range of $SeCF_3$-containing compounds. The utilization of a proline-based N,N,P-ligand is crucial to the success in that it can greatly enhance the reducing capability of

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the copper catalyst to convert the mildly oxidative radical precursors to the corresponding radicals via a SET process. A wide array of mono-, di-, and trisubstituted alkenes and alkyl halides are accommodated in the reaction.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00436.

Experimental procedures, characterization of compounds (PDF)

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Notes

The authors declare no competing financial interest.

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