

groups.

Letter

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

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lkenes are one of the most prevailing building blocks in A 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 CF₃Se group shows promising lipophilicity and electronic characteristics, which are beneficial to the development of bioactive compounds,³ the CF₃Se group might be promising in pharmaceutical research. In this aspect, the radical-initiated 1,2-carbotrifluoromethylselenolation of alkenes to introduce a trifluoromethylselenyl group⁴⁻⁶ 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 (TsSeCF₃) reagent which needs tedious synthesis^{7a,b} or a stoichiometric amount of bpyCuSeCF₃ 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 SeCF₃ compounds from readily available trifluoromethylselenolation reagents and diverse radical precursors under ambient conditions is highly desirable.

including various mono-, di-, and trisubstituted alkenes with many functional

Our group has focused on the copper-catalyzed radical 1,2difunctionalization 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 (Me₄N)SeCF₃ salt is a readily accessible and thermally stable trifluoromethyl-

Scheme 1. Radical 1,2-Trifluoromethylselenolation of Alkenes

(A) Previous Work on Radical 1,2-Carbotrifluoromethylselenolation of Alkenes



selenolation reagent,⁹ we wondered whether a coppercatalyzed radical 1,2-carbotrifluoromethylselenolation of alkenes could be achieved from (Me₄N)SeCF₃ 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).

Based on our assumption, we tried to initiate the alkene 1,2carbotrifluoromethylselenolation 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,





^{*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 ¹⁹F NMR spectroscopy using PhCF₃ as an internal standard. ^{*c*}Reaction was conducted at 60 °C (oil bath) for 4 h. ^{*d*}H₂O (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 % Cu₂O, 15 mol % L8, and 1.0 equiv of Cs₂CO₃ 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*}CCl₃CF₃ was used as the radical precursor.

25 77%

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

26, 61%^d

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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 arvlated 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-envne substrate to furnish the allene product 24. A preliminary trial with (Me₄N)SCF₃ 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 SCF₃containing 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



"Reaction conditions: 1 (0.20 mmol), 2a (0.30 mmol), 3 (0.60 mmol), Cu₂O (10 mol %), L8 (15 mol %), and Cs₂CO₃ (0.20 mmol) in 1,4-dioxane (3.0 mL) at room temperature for 48 h under argon.

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,Pligand 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.

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 TEMPOtrapping 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 (Me₄N)SeCF₃ 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 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 atomtransfer process followed by substitution by the SeCF₃ anion could not be excluded.¹⁵

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 SeCF₃-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 nildly oxidative radical **Notes**

The authors declare no competing financial interest.

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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

1 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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