Organic LETTERS

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

Copper-Catalyzed Domino Cyclization/Trifluoromethylthiolation of Unactivated Alkenes: Access to SCF_3-Containing Pyrrolines

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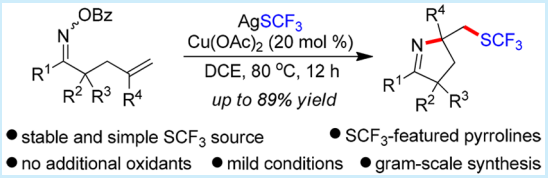
Supporting Information

ABSTRACT: A novel and efficient copper-catalyzed cascade cyclization/trifluoromethylthiolation of unactivated olefins has been achieved with the stable and readily available $AgSCF_3$ as the SCF_3 source. A range of SCF_3-substituted pyrrolines have been easily obtained under mild conditions in good yields via the present process. This method represents a facile and rapid access to valuable pyrrolines with fluorine-containing groups, and it is amenable to gram-scale synthesis.

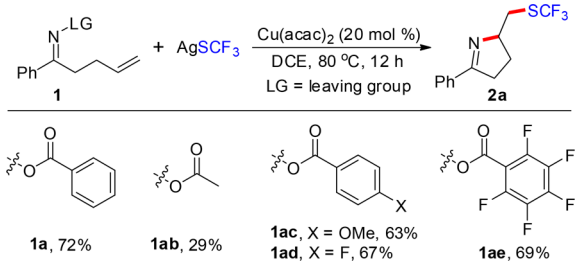


Compounds bearing fluorine-containing groups have been widely used as pharmaceuticals, agrochemicals, and materials, because of their unique physical, chemical, and biological properties.[1] Because of its strong electron-withdrawing capability and high lipophilicity, the incorporation of the trifluoromethylthio (SCF_3) group into an organic molecule often significantly improves the metabolic stability, bioavailability, and bioactivity.[2] Therefore, the development of effective strategies for the introduction of the SCF_3 group has attracted much attention from chemists.[3] Traditional indirect methods for the formation of the SCF_3 group include the trifluoromethylation of thiols and their derivatives[4] and the halogen-fluorine exchange reactions,[5] in which additional synthetic steps are needed. Recently, various direct strategies for the construction of C−SCF_3 bond, including nucleophilic,[6] electrophilic,[7] radical,[8] and oxidative[9] trifluoromethylthiolations have been developed. Because of its stability and ready availability, $AgSCF_3$ has recently been reported as an effective and straightforward trifluoromethylthiolating reagent in the C−SCF_3 bond-forming reactions.[6a,d−f,h−j,7f−h,8,9c,d] Despite significant progress, the difunctionalization-type trifluoromethylthiolation of alkenes with $AgSCF_3$ as the SCF_3 source has been less explored.[7h,8a,d,g] Thus, new and efficient C(sp^3)−SCF_3 bond-forming processes involving the difunctionalization of alkenes, especially unactivated alkenes, remain highly desirable.

O-Acyl oximes are exceptionally versatile building blocks for the construction of structurally diverse and valuable nitrogen-containing heterocycles via N−O bond cleavage.[10] To date, a variety of methods for the synthesis of *N*-heterocycles through the N−O bond cleavage of *O*-acyl oximes have been developed, mainly including transition-metal catalysis, such as Pd,[11] Rh,[12] Ru,[13] Fe,[14] Co,[15] Cu,[16] etc., microwave or UV irradiation,[17] and visible-light photoredox catalysis.[18] Difunctionalization of alkenes has become a powerful tool for the incorporation of two functional groups across a double bond in one step, and thus for a rapid increase of molecular complexity and diversity. Although much progress has been made in the construction of *N*-heterocycles with acyl oximes as the precursors, examples that involve the N−O bond cleavage of acyl oximes having an olefin moiety and the subsequent alkene difunctionalization process are rare.[11f,g,14b,16a,e,h,18b] Herein, we report a novel copper-catalyzed domino cyclization and trifluoromethylthiolation of acyl oxime-tethered unactivated olefins to deliver a range of SCF_3-featured pyrrolines in good yields, where the stable and easily available $AgSCF_3$ is employed as a SCF_3 source.

Our studies commenced with the examination of the effect of acyloxy leaving groups on the reactivity of olefinic *O*-acyl oximes and the product yield. As shown in Scheme 1, when *O*-benzoyl oxime **1a** was treated with $AgSCF_3$ in the presence of $Cu(acac)_2$ (20 mol %) in 1,2-dichloroethane (DCE) at 80 °C for 12 h, the desired SCF_3-containing pyrroline **2a** was obtained in 72% isolated yield. Other *O*-aroyl oximes with electron-donating or electron-withdrawing groups on the phenyl ring (**1ac**, **1ad**, and **1ae**) also gave product **2a**, albeit with slightly lower yields. However, less activated and more stable *O*-acetyl

Scheme 1. Screening of *O*-Acyl Oximes[a]



[a]All reactions were carried out with acyl oxime **1** (0.30 mmol), $AgSCF_3$ (0.45 mmol), and $Cu(acac)_2$ (0.060 mmol) in DCE (3.0 mL) at 80 °C under N_2 for 12 h. Isolated yield based on **1**.

Received: February 20, 2018

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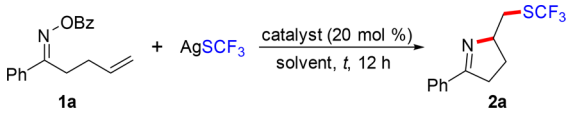
DOI: 10.1021/acs.orglett.8b00614
Org. Lett. XXXX, XXX, XXX−XXX

oxime **1ab** afforded a much lower yield of 29%. Thus, benzoyloxy group was chosen as a suitable leaving group of the acyl oxime substrates.

We next set out to optimize the reaction conditions with *O*-benzoyl oxime **1a** as a model substrate (Table 1). Various metal salt catalysts were first tested. No product was observed when $NiCl_2$(dme), $Fe(acac)_2$, or $Pd(OAc)_2$ was employed as the catalyst (Table 1, entries 2–4). Other Cu(II) and Cu(I) salts, including $Cu(OAc)_2$, $Cu(OTf)_2$, CuCl, CuBr, and $Cu(MeCN)_4PF_6$ were also found to be effective catalysts for this reaction (Table 1, entries 5–9). Among the copper salts surveyed, $Cu(OAc)_2$ proved to be the best catalyst, and gave product **2a** in 81% yield (Table 1, entry 5). Screening of solvents showed that DCE was superior to other solvents, such as CH_3CN, DMF, DMA, 1,4-dioxane, and toluene (Table 1, entries 5 and 10–14). The reaction temperature had a remarkable effect on this transformation, and a lower (50 °C) or a higher temperature (100 °C) resulted in inferior yields (Table 1, entries 15 and 16). The addition of ligands, such as PPh_3 and 2,2′-bipyridine, led to a lower yield and trace amounts of product, respectively (Table 1, entries 17 and 18).

Table 1. Optimization of the Reaction Conditions[a]



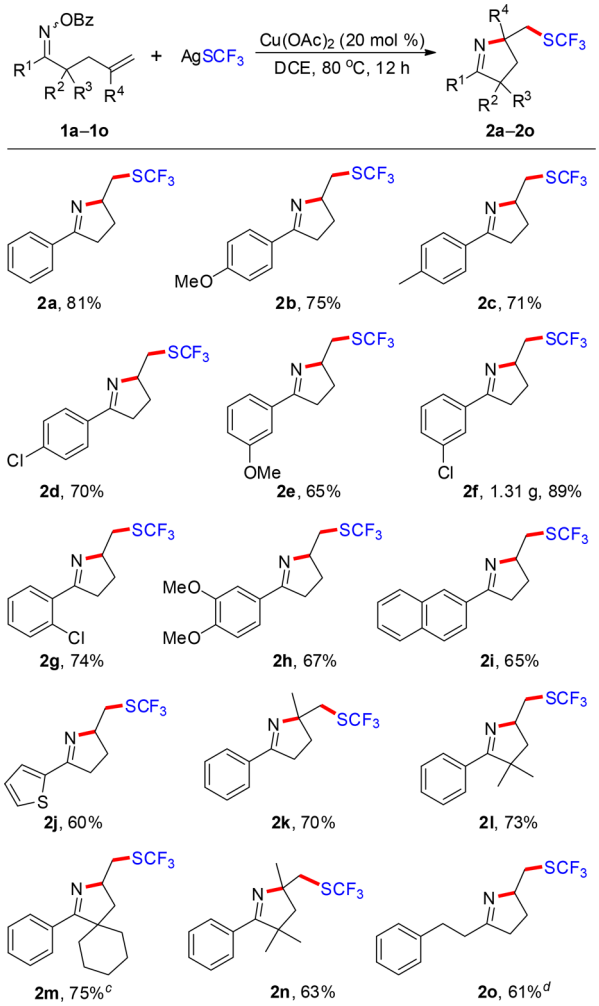
1a 2a

entry	catalyst	solvent	*t* (°C)	yield[b] (%)
1	$Cu(acac)_2$	DCE	80	72
2	$NiCl_2$(dme)	DCE	80	0
3	$Fe(acac)_2$	DCE	80	0
4	$Pd(OAc)_2$	DCE	80	0
5	**$Cu(OAc)_2$**	**DCE**	**80**	**81**
6	$Cu(OTf)_2$	DCE	80	67
7	CuCl	DCE	80	65
8	CuBr	DCE	80	60
9	$Cu(MeCN)_4PF_6$	DCE	80	68
10	$Cu(OAc)_2$	CH_3CN	80	61
11	$Cu(OAc)_2$	DMF	80	36
12	$Cu(OAc)_2$	DMA	80	46
13	$Cu(OAc)_2$	dioxane	80	26
14	$Cu(OAc)_2$	toluene	80	63
15	$Cu(OAc)_2$	DCE	50	trace
16	$Cu(OAc)_2$	DCE	100	51
17[c]	$Cu(OAc)_2$	DCE	80	67
18[d]	$Cu(OAc)_2$	DCE	80	trace

[a]All reactions were performed with **1a** (0.30 mmol), $AgSCF_3$ (0.45 mmol), and catalyst (0.060 mmol) in solvent (3.0 mL) at 80 °C for 12 h unless otherwise noted. [b]Isolated yields. [c]PPh_3 (0.060 mmol) was added. [d]2,2′-Bipyridine (0.060 mmol) was added.

Having established the optimized reaction conditions, we subsequently investigated the generality of this domino cyclization/trifluoromethylthiolation process. As exemplified in Scheme 2, the present reaction can be extended to a variety of olefinic *O*-acyl oximes to give the SCF_3-containing pyrroline products in 60%–89% yields. For the aryl-substituted *O*-acyl oximes with either electron-donating or electron-withdrawing groups at the *para*, *meta*, and *ortho* positions of the phenyl ring, the reaction proceeded smoothly and gave the desired products (**2a–2h**) in good yields. As illustrated in the case of acyl oxime **1f**, pyrroline **2f** can be obtained on gram scale in 89% yield. 2-

Scheme 2. Substrate Scope[a,b]



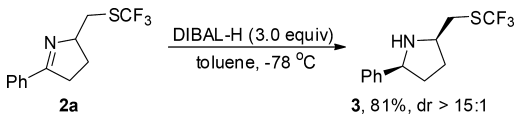
[a]All reactions were performed with acyl oxime **1** (0.30 mmol), $AgSCF_3$ (0.45 mmol), and $Cu(OAc)_2$ (0.060 mmol) in DCE (3.0 mL) at 80 °C under N_2 for 12 h unless otherwise noted. [b]Isolated yields. [c]Run for 24 h. [d]$Cu(CH_3CN)_4PF_6$ (20 mol %) was used.

Naphthyl- and 2-thienyl-substituted acyl oximes were also effective substrates, affording the corresponding products **2i** and **2j** in 65% and 60% yields, respectively. The aryl-substituted substrates bearing substitutions at the alkyl chain moieties were also compatible with the reaction, leading to the desired products (**2k–2n**) in satisfactory yields. The alkyl-substituted *O*-acyl oxime could also be transformed to the product (**2o**) in 61% yield.

To further demonstrate the synthetic utility of this method, reduction of the product **2a** was achieved by the use of diisobutylaluminum hydride (DIBAL-H), thus affording *cis*-pyrrolidine **3** in 81% yield and with good diastereoselectivity (dr >15:1) (see Scheme 3).

To understand the reaction mechanism, some control experiments were conducted using substrate **1a**. No reaction

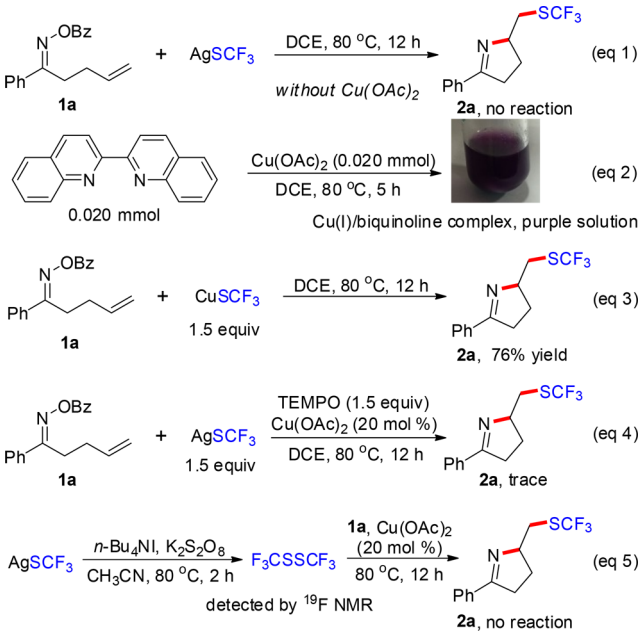
Scheme 3. Further Transformation of Product 2a



DOI: 10.1021/acs.orglett.8b00614
Org. Lett. XXXX, XXX, XXX–XXX

occurred in the absence of a copper catalyst, suggesting that the copper salt plays an important role in this transformation (Scheme 4, eq 1). When the mixture of 2,2′-biquinoline and

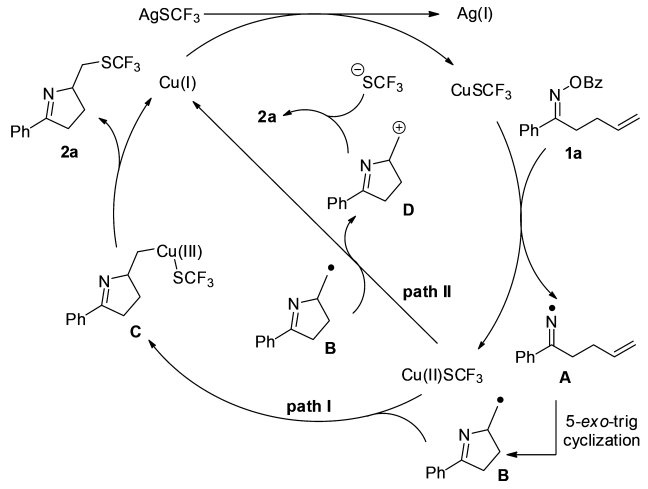
Scheme 4. Mechanistic Investigations



$Cu(OAc)_2$ in DCE was heated at 80 °C for 5 h, a purple solution was observed, indicating that a Cu(I)/biquinoline complex was formed in situ via reduction or disproportionation of $Cu(OAc)_2$ (Scheme 4, eq 2; see the Supporting Information (SI) for details).[16d] These results suggest that a Cu(I) species might be involved in the domino reaction. When isolated $CuSCF_3$ was used instead of $AgSCF_3$, product **2a** can be obtained in a good yield of 76% in the absence of a copper catalyst (Scheme 4, eq 3). The results indicate that $CuSCF_3$, which could be generated in situ from the copper salt and $AgSCF_3$,[6e,f] is likely to be an intermediate in the reaction. The reaction was almost completely suppressed upon the addition of the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) under standard conditions, and only trace amounts of **2a** were obtained, indicating that this reaction might proceed through a radical pathway (Scheme 4, eq 4). In order to investigate whether or not the SCF_3 radical is involved in this process, F_3CSSCF_3, which was reported to generate the SCF_3 radical in the presence of Ag(I),[8a] was prepared in situ and subjected to the reaction conditions (Scheme 4, eq 5). However, no reaction was observed, implying that the SCF_3 radical is not very likely to be involved in the domino cyclization and trifluoromethylthiolation process.

Based on the above results and the literature reports,[6e,f,16d,f,h,18b] a plausible catalytic pathway is proposed in Scheme 5. Initially, the metathesis between Cu(I) and $AgSCF_3$ generates $CuSCF_3$,[6e,f] which reductively cleaves the N−O bond of acyl oxime **1a** to form iminyl radical[16d,f,18b] **A** and Cu(II)SCF_3 species. Subsequently, an intramolecular 5-*exo*-trig cyclization of iminyl radical **A** gives C-centered radical **B**,[16d,h,18b] which is trapped by the Cu(II)SCF_3 species to produce Cu(III) intermediate **C**.[16d] Finally, reductive elimination of **C** leads to the desired product **2a** and regenerates the Cu(I) (path I). However, an alternative pathway cannot be ruled out. The C-centered radical **B** is oxidized by Cu(II)SCF_3

Scheme 5. Proposed Mechanism



to give the Cu(I) and carbocation **D**,[16g,h] which is then attacked by SCF_3 anion to produce the final product **2a** (path II).

In conclusion, we have developed a novel copper-catalyzed domino cyclization/trifluoromethylthiolation of unactivated alkenes bearing an *O*-acyl oxime moiety. A variety of SCF_3-containing pyrrolines can be effectively constructed in good yields from olefinic *O*-acyl oximes and the stable, easily handled, and readily available $AgSCF_3$. The reaction enables the simultaneous formation of a C−N bond and a C(sp^3)−SCF_3 bond, and is amenable to gram-scale synthesis. Preliminary mechanistic investigations indicated that the SCF_3 radical might not be involved in the process.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00614.

Experimental procedures and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for the financial support from the National Natural Science Foundation of China (No. 21502096), the Natural Science Foundation of Jiangsu Province (No. BK20150652), the Fundamental Research Funds for the Central Universities (No. KJQN201629), and "333 High Level Talent Project" of Jiangsu Province.

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DOI: 10.1021/acs.orglett.8b00614
Org. Lett. XXXX, XXX, XXX−XXX