Synthetic Methods

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Copper-Catalyzed Trifluoromethylazidation of Alkynes: Efficient Access to CF_3-Substituted Azirines and Aziridines**

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Dedicated to Professor Xuelong Hou on the occasion of his 60th birthday

Abstract: *A novel method for convenient access to CF_3-containing azirines has been developed, and involves a copper-catalyzed trifluoromethylazidation of alkynes and a photocatalyzed rearrangement. Both terminal and internal alkynes are compatible with the mild reaction conditions, thus delivering the CF_3-containing azirines in moderate to good yields. The azirines can be converted into various CF_3-substituted aziridines.*

Aziridines and azirines, the smallest nitrogen-containing heterocycles, have been recognized as important precursors of more complex molecules.[1] Meanwhile, these structures are also prevalent in medicines and pesticides. For instance, the molecules in Figure 1 are representative of biologically relevant compounds bearing the related skeletons.[2] Therefore, the development of synthetic methodologies toward aziridines and azirines have been of broad interest for at least half a century.[3] Owing to the unique characteristics of the trifluoromethyl group, CF_3-containing molecules were extensively studied and widely applied as pharmaceutical and agricultural chemicals.[4] We surmized that the introduction of a CF_3 group into aziridines and azirines would further enrich the related compound library, which is beneficial for new drug discovery. Because of the easy access to aziridines from azirines, exploration of new methods for the efficient synthesis of CF_3-containing azirines is much more attractive. Unfortunately, the related transformations are quite rare.[5] Herein, we exploited an efficient approach to the selective synthesis of valuable CF_3-containing azirines from simple alkynes, an approach enabled by a sequential process including copper-catalyzed trifluoromethylazidation of alkynes and photocatalyzed rearrangement of CF_3 vinyl azides (Scheme 1).

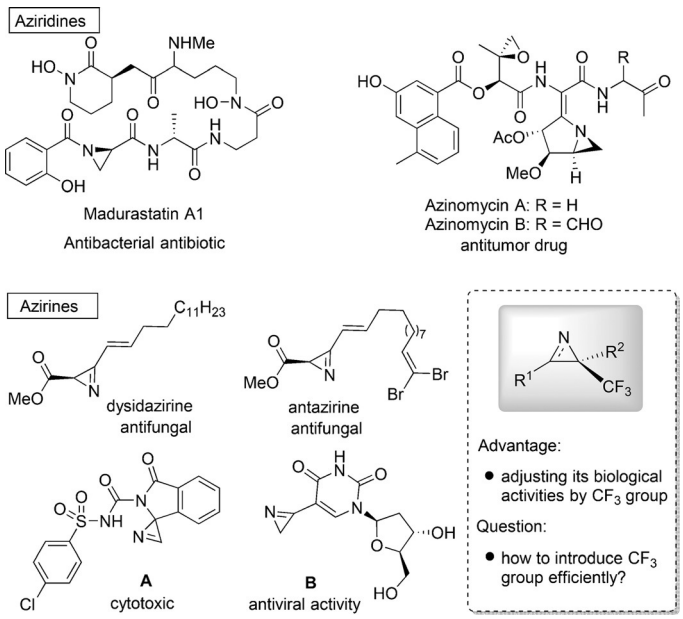
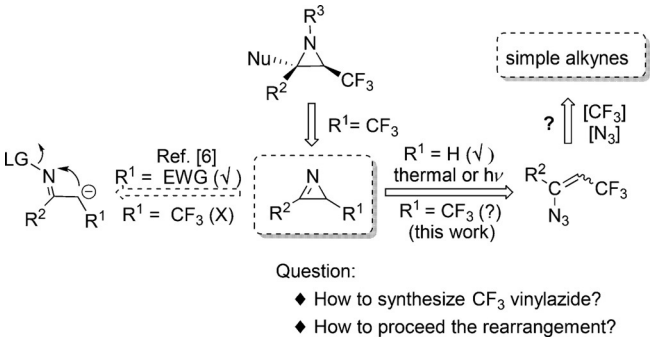


Figure 1. Representative biologically active compounds containing aziridine and azirine moieties.



Scheme 1. Synthetic strategies for CF_3-containing azirines. EWG = electron-withdrawing group.

So far, the Neber reaction[6] (Scheme 1; left) and the rearrangement of vinyl azides[7] (Scheme 1; right) have been the major methods used for the synthesis of azirines. However, reaction conditions of the former are not suitable for CF_3-containing substrates because the key intermediate, an α-trifluoromethylated carbanion, is prone to β-fluoride

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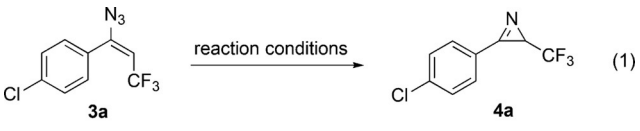
elimination.[8] In contrast, the latter method provides a promising approach, but the rearrangement of bulky and electron-deficient CF_3 vinyl azides is a formidable challenge. From this aspect, exploration of an efficient method for access to CF_3-substituted vinyl azides is an essential requirement.

Recently, tremendous progress on trifluoromethylation reactions has been achieved.[9] Among them, trifluoromethylation of alkenes presents a useful method for the synthesis of CF_3-containing aliphatic compounds or heterocycles.[10] In contrast, the catalytic trifluoromethylation of alkynes are still underdeveloped. Recently, the groups of Chen,[11a] Hu,[11b] and Cho[11c] reported the halotrifluoromethylation of alkynes. The groups of Szabó[10e] and Maiti[11d] reported the intermolecular oxytrifluoromethylation of alkynes, and in these reactions, addition of CF_3 radical to alkynes was proposed to provide a key CF_3 vinyl radical intermediate. We speculated that, if this vinyl radical could be trapped by an azide, the desired trifluoromethylazidation of alkynes might be expected to deliver the CF_3 vinyl azides efficiently, thus providing an opportunity for the synthesis of CF_3 azirines.

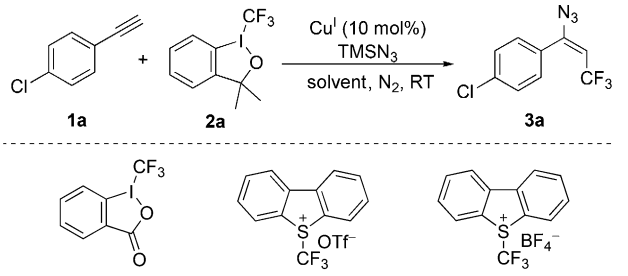
Our group recently developed a mutual activation mode between Togni's reagent **2a** (for structure see Table 1) and either TMSNu or $ArB(OH)_2$, and it facilitates the copper-catalyzed trifluoromethylation of alkenes.[12] Inspired by these studies, a copper(I) catalyst combined with **2a** and $TMSN_3$ was initially applied to test the above hypothesis.[12a] To our delight, the reaction of **1a** and $[Cu(CH_3CN)_4]PF_6$ indeed occurred to give the desired trifluoromethylazidation product **3a** in 42% yield at room temperature (Table 1, entry 1). After screening various solvents, MeOH turned out to be the best (entries 1–5). Furthermore, catalyst screening demonstrated that both copper(I) and copper(II) catalysts could deliver **3a**, but CuBr gave the best yield (entries 6–10). Either lowering or increasing the temperature deteriorated the reaction yields (entries 8, 11, and 12). Meanwhile, other CF_3^+ reagents, **2b–d**, were either less effective or inactive for affording **3a** (entries 13–15). Further optimization of the reaction conditions revealed that the best yield was obtained with a slightly lower catalyst loading (5 mol%) as well as a smaller amount of **2a** (entry 16). Finally, no reaction occurred in the absence of a copper catalyst. And some other metal catalysts, such as $CoCl_2$, $CrCl_2$, and $[Mn(acac)_3]$, were proven to be inert for this reaction (see the Supporting Information). It is worthy to note that a single isomer, (*E*)-**3a**, was observed in all of the reactions.

With the above results in hand, the rearrangement of **3a** was surveyed [Eq. (1)]. The thermolysis pathway was



explored by using different solvents, but the reaction of **3a** only afforded trace amounts of the desired CF_3-substituted azirine product **4a**. We discovered that after removal of the copper catalyst, the unpurified **3a**, which was kept in a flask?

Table 1: Optimization of the reaction conditions.[a]



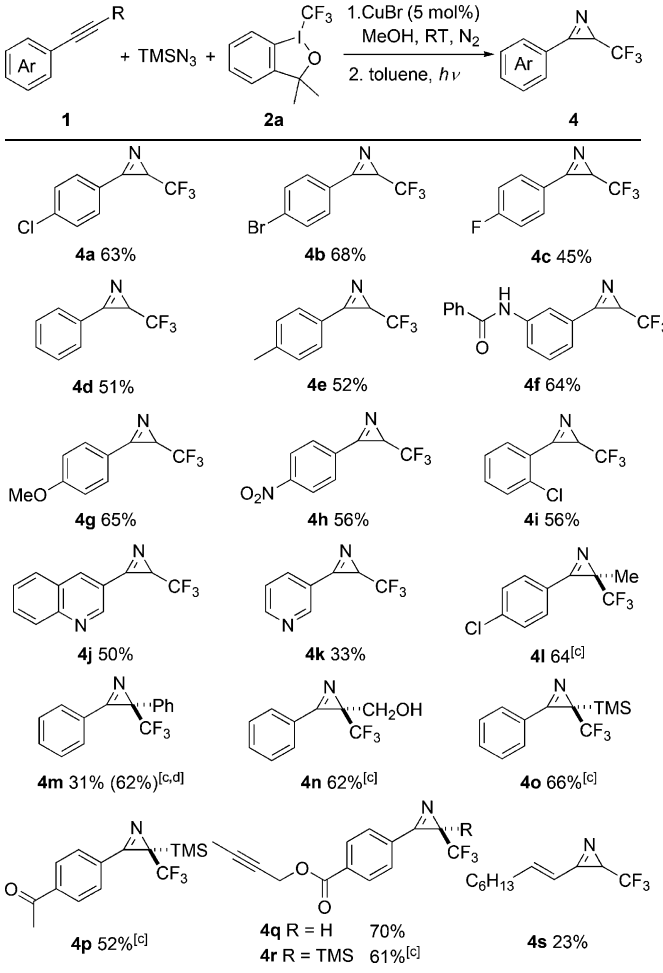
Entry	Solvent	Catalyst	$[CF_3^+]$	Yield [%][b]
1	DMAc	$[Cu(CH_3CN)_4]PF_6$	**2a**	42
2	DMSO	$[Cu(CH_3CN)_4]PF_6$	**2a**	34
3	$CHCl_3$	$[Cu(CH_3CN)_4]PF_6$	**2a**	24
4	MeOH	$[Cu(CH_3CN)_4]PF_6$	**2a**	57
5	Et_2O	$[Cu(CH_3CN)_4]PF_6$	**2a**	20
6	MeOH	$[Cu(CH_3CN)_4]OTf$	**2a**	57
7	MeOH	CuI	**2a**	59
8	MeOH	CuBr	**2a**	64
9	MeOH	$Cu(OAc)_2$	**2a**	60
10	MeOH	$CuBr_2$	**2a**	50
11[c]	MeOH	CuBr	**2a**	48
12[d]	MeOH	CuBr	**2a**	35
13	MeOH	CuBr	**2b**	20
14	MeOH	CuBr	**2c**	0
15	MeOH	CuBr	**2d**	0
16[e]	*MeOH*	*CuBr*	***2a***	*75*
17	MeOH	–	**2a**	0

[a] Reaction conditions: **1a** (0.1 mmol), Cu catalyst (10 mol%), $[TMSN_3]$ (0.2 mmol), and $[CF_3^+]$ reagent (0.15 mmol) in solvent (0.6 mL) at room temperature. [b] Yield determined by ^{19}F NMR spectroscopy. [c] At 0°C. [d] At 40°C. [e] Cu^I catalyst (5 mol%), $[CF_3^+]$ reagent (0.13 mmol). DMAc = *N*,*N*-dimethylacetamide, DMSO = dimethylsulfoxide, Tf = trifluoromethanesulfonyl, TMS = trimethylsilyl.

on the bench, gradually generated **4a** but at a very slow rate. Given this observation, further optimization of the reaction conditions with respect to the irradiation source was pursued, and an excellent yield of **4a** was obtained when using a high-pressure mercury lamp (100 W) and toluene. Thus, this process combines trifluoromethylazidation of alkynes with the rearrangement of CF_3 vinyl azides and presents an efficient synthetic approach to **4a**.

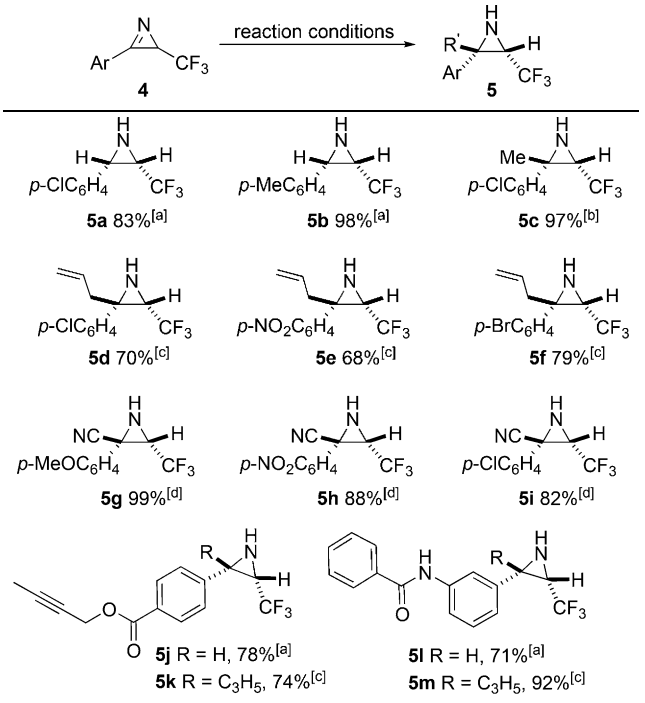
With the established sequential process, the substrate scope of the terminal alkynes was investigated and the results are summarized in Table 2. Arylacetyenes having a series of substituents on the aromatic ring, including electron-donating and electron-withdrawing groups, were compatible with the current transformation (**1a–i**). And various functional groups, such as halogen, ester, nitro, and amide groups, were tolerated in these two steps to give the desired products **4a–i** in good yields. Interestingly, substrates with heteroaryl groups, such as quinolinyl (**1j**) and pyridyl (**1k**), also proceeded smoothyl to give **4j** and **4k**, respectively, in satisfactory yields. Inspired by the above results, we turned our attention to internal alkynes. Gratifyingly, when the substrate **1l** was subjected to the standard reaction conditions, the trisubstituted CF_3-containing azirine **4l** was obtained in 51% yield along with 28% recovery of **1l**. With slightly modified reaction conditions

Table 2: Substrate scope of alkynes.[a,b]



[a] Reaction conditions: Alkyne **1** (0.4 mmol), $TMSN_3$ (0.8 mmol), **2a** (0.52 mmol), and CuBr (0.02 mmol) in MeOH (1.5 mL) at room temperature for 8 h. After removal of the Cu catalyst, the residue in toluene (2 mL) was irradiated for 3 h. [b] Yield of isolated product. [c] After the standard reaction for 2 h, extra $TMSN_3$ (0.8 mmol) and **2a** (0.2 mmol) were added and stirred for another 6 h; then followed with the same process. [d] Yield was based on recovery of the starting material.

Table 3: Further transformation of azirines into aziridines.

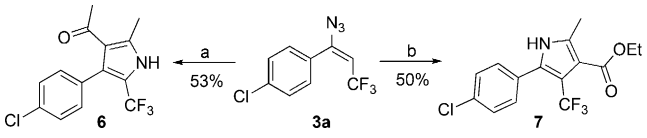


Reaction conditions: [a] $NaBH_4$ (2.0 equiv), MeOH, 0 °C–RT. [b] MeMgBr (2.0 equiv), Et_2O, −20 °C. [c] 3-Bromoprop-1-ene (3.0 equiv), In (2.0 equiv), THF, RT. [d] CuCl (0.1 equiv), TMSCN (2.0 equiv), $nBu_4NF{\cdot}3H_2O$ (2.0 equiv), DCE, 50 °C. DCE = 1,2-dichloroethane, THF = tetrahydrofuran.

(addition of extra amount of $TMSN_3$ and **2a**), the yield of **4l** could be increased to 64%. Furthermore, a range of internal alkynes (**1m–p**) bearing hydroxy, silyl, and ketone groups, were also compatible to the reaction conditions and provided the desired azirine products **4m–p** in moderate to good yields. Interestingly, when substrates have two carbon–carbon triple bonds, such as **1q** and **1r**, the reactions only occurred at the aryl-conjugated triple bond to deliver the related products **4q** (70%) and **4r** (61%), respectively, with the alkyl-substituted alkynyl group intact, a group which is useful for further transformations. Finally, it is notable that the conjugated alkenyl acetylene **1s** could also furnish the desired product **4s**, albeit in low yield (23%). Unfortunately, the alkyl-substituted alkynes showed poor reactivity and only provided trace amounts of desired products.

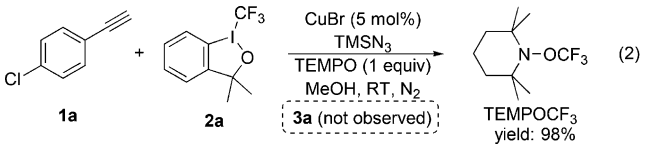
Because of the utility of aziridines,[1,3] further conversion of the CF_3-containing azirines **4** into the related aziridines were investigated.[13a–b] As shown in Table 3, the CF_3-containing azirines **4** were coupled with different nucleophiles to deliver the corresponding multisubstituted aziridines **5** in good to excellent yields with excellent diastereoselectivities. For example, the reduction products **5a** and **5b** were obtained with excellent yields and diaselectivities under when treated with $NaBH_4$, and the methylated product **5c** with MeMgBr. When treated with an allylindium reagent generated in situ, the related products **5d–f** were successfully provided in good yields as a single isomer. Excitingly, the cyanation of azirines also proceeded smoothly to yield the corresponding aziridines **5g–i** when using a copper(I) catalyst. Furthermore, the complex azirines **4f** and **4q** were also compatible with these reaction conditions to give **5j–m** in good to excellent yields. Gratifyingly, the CF_3 moiety survived under these reaction conditions, and all these reactions presented excellent diastereoselecitvity because of the steric bulky of the CF_3 group. Finally, further transformation of **3a** was also conducted.[13c–d] Besides triazole from the click reaction (see the Supporting Information), the pyrazoles **6** and **7** were efficiently obtained, each having a CF_3 group in a different position (Scheme 2).

To gain more insight into the mechanism of the trifluoromethylazidation of alkynes, some control experiments were examined: 1) when the radical scavenger 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) was added, the trifluoromethyl-

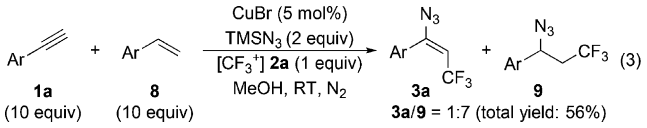


Scheme 2. Further transformation of **3a**. Reaction conditions: a) Pentane-2,4-dione (5.0 equiv), toluene, 150 °C; b) Ethyl 3-oxobutanoate (1.5 equiv), $Mn(OAc)_3{\cdot}H_2O$ (0.1 equiv), AcOH (2.0 equiv), MeOH, 40 °C.

azidation reaction was completely inhibited, and only the TEMPO-CF_3 product was obtained [Eq. (2)]; 2) a competi-

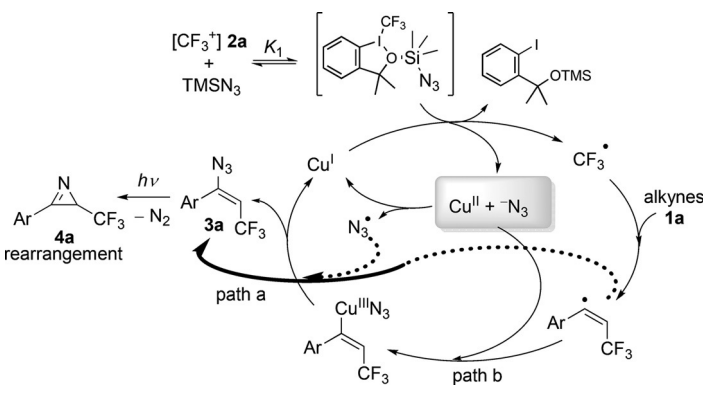


tion reaction with the same number of equivalents of **1a** and styrene (**8**) proceeded through the predominant trifluoromethylation of alkenes to give **9** as a major product [Eq. (3);



Ar = *p*-C_6H_4Cl]. These results revealed that a CF_3 radical is involved in the reaction,[14] and its addition into alkynes might occur to give a CF_3 vinyl radical species. However, this process is much slower than that with an alkene. Furthermore, the electronic effects on the aryl groups were evaluated, and alkynes with electron-rich aryl groups reacted faster than those with electron-poor aryl groups. A significant Hammett ρ-value of -0.29 was observed (see the Supporting Information), and is in agreement with a mechanism involving radical addition to the triple bond.[15]

For the final C–N bond formation, there are two scenarios to address (Scheme 3): Path a: the released azide ion from $TMSN_3$ is oxidized by copper(II) to give the azide radical,



Scheme 3. Proposed mechanism for the trifluoromethylazidation of alkynes.

which is then trapped by a CF_3 vinyl radical to give the final product **3a**. Path b: the azide anion may act as an X-type ligand to coordinate with copper(II), and then the CF_3 vinyl radical is trapped by this $[Cu^{II}(X)N_3]$ species to form a copper(III) intermediate, which undergoes reductive elimination to yield **3a**. With the current experimental data, neither pathway could be excluded at this stage.

In summary, we have developed a novel method for convenient access to CF_3-containing azirines, which can be easily converted into the related CF_3-substituted aziridines. This process includes a sequential copper-catalyzed trifluoromethyl/azidation of alkynes and photoirradiated rearrangement of CF_3 vinyl azides. Both terminal and internal alkynes are compatible with the mild reaction conditions and the reaction demonstrates good functional-group tolerance. Further investigation on the mechanism and synthetic applications of the reaction are underway in our laboratory.

Keywords: alkynes · copper · heterocycles · rearrangements · synthetic methods

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