Organic LETTERS

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TfNHNHBoc as a Trifluoromethylating Agent for Vicinal Difunctionalization of Terminal Alkenes

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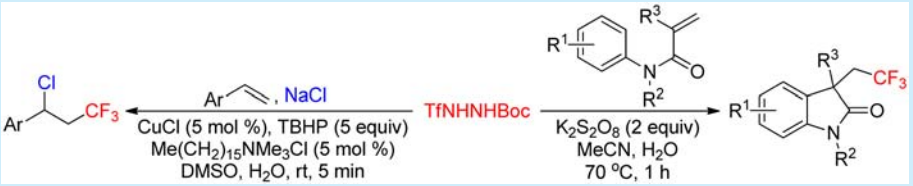
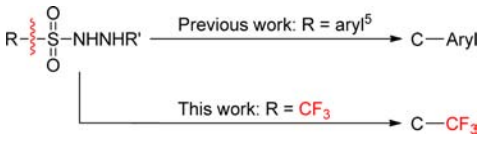
Supporting Information



ABSTRACT: An unprecedented application of trifluoromethanesulfonyl hydrazides as trifluoromethylating agents has been demonstrated in two vicinal difunctionalization reactions of terminal alkenes: the copper-catalyzed three-component vicinal chlorotrifluoromethylation of arylakenes with TfNHNHBoc and NaCl and the tandem trifluoromethylation/cyclization of *N*-arylacrylamides with TfNHNHBoc. The reactions proceeded in the presence of inexpensive oxidants under mild conditions and provided a range of structurally diverse trifluoromethyl-containing compounds with high regioselectivity.

Sulfonyl hydrazides are, in general, readily accessible solids, free of unpleasant odor, and compatible with air and water. For a long time, they have been widely employed to prepare hydrazones and nitrogen-containing heterocycles[1] and serve as reductants[2] and sulfonyl sources.[3] Recently, sulfonyl hydrazides have emerged as powerful sulfenylating agents for the synthesis of thioethers via S−N and S−O bond cleavage.[4] In contrast, much less progress has been disclosed on the synthetic applications of sulfonyl hydrazides via C−S bond cleavage. In this regard, we and others have recently explored arenesulfonyl hydrazides as alternative arylating agents for some oxidative cross-coupling reactions (Scheme 1).[5] Herein we report, for the first time, the application of sulfonyl hydrazides as trifluoromethylating agents (Scheme 1), which has been exemplified in the vicinal difunctionalization of terminal alkenes.

Scheme 1. Synthetic Applications of Sulfonyl Hydrazides via C−S Bond Cleavage



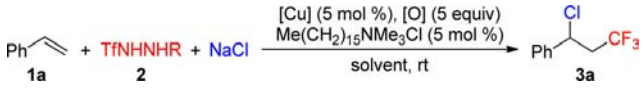
Much attention has been paid to the modification of pharmaceuticals, agrochemicals, and organic materials by introducing a trifluoromethyl group, which dramatically changes some of their properties such as lipophilicity, electronegativity, metabolic stability, and bioavailability.[6] Among the many trifluoromethylation reactions disclosed so far, particularly noteworthy is the vicinal difunctionalization of alkenes due to its high atom- and step-efficiency for the introduction of functional groups into target compounds.[7,8] One type of such reactions is the vicinal chlorotrifluoromethylation of alkenes, which has been realized by employing CF_3SO_2Cl,[9] Umemoto's reagent/TMSCl,[10] Togni's reagent/$SOCl_2$,[11] or Langlois' reagent/$FeCl_3$[12] as CF_3 and Cl sources.[13] These methods required highly corrosive liquids, an anhydrous atmosphere, an elevated temperature, and/or a long reaction time, and consequently, it is highly desirable to discover new CF_3 and Cl sources to facilitate the vicinal chlorotrifluoromethylation of alkenes. Inspired by the arylation reactions with arenesulfonyl hydrazides via C−S bond cleavage,[5] we investigated the possibility of using trifluoromethanesulfonyl hydrazides as CF_3 sources for the vicinal chlorotrifluoromethylation of alkenes.

While $TfNHNH_2$ is the simplest sulfonyl hydrazide having a CF_3 moiety,[14] the fact that it is very unstable persuaded us to turn to evaluate its derivatives **2**, which are stable solids prepared by treating triflic anhydride with monosubstituted hydrazines,[15] in the reaction with styrene (**1a**) and NaCl in dimethyl sulfoxide at room temperature using CuCl as a redox catalyst, $Me(CH_2)_{15}NMe_3Cl$ as a phase-transfer catalyst, and TBHP as an oxidant (Table 1, entries 1−5). The *N*′-substituent was found to significantly affect the ability of a trifluoromethanesulfonyl hydrazide to serve as a CF_3 source, and the best results were obtained with TfNHNHBoc (**2a**) (1.2 equiv), which furnished γ-chloro-α,α,α-trifluoroalkane **3a** in 53% yield with greater than 99% regioselectivity (entry 1). The yield decreased or even no desired product was obtained at all when replacing CuCl with another copper(I) salt or a copper(II) salt, TBHP with another oxidant, or dimethyl sulfoxide with another common solvent (entries 6−18). To our delight, addition of water to the reaction mixture enhanced the yield to 60% by

Received: June 27, 2016
Published: July 14, 2016

DOI: 10.1021/acs.orglett.6b01862
Org. Lett. 2016, 18, 3850−3853

Table 1. Optimization of the Reaction Conditions[a]



entry	2, R	[Cu]	[O]	solvent	yield (%)[b]
1	**2a**, Boc	CuCl	TBHP	DMSO	53
2	**2b**, Cbz	CuCl	TBHP	DMSO	40
3	**2c**, COPh	CuCl	TBHP	DMSO	46
4	**2d**, Ts	CuCl	TBHP	DMSO	36
5	**2e**, Ph	CuCl	TBHP	DMSO	0
6	**2a**	CuBr	TBHP	DMSO	50
7	**2a**	CuI	TBHP	DMSO	52
8	**2a**	CuCN	TBHP	DMSO	50
9	**2a**	$CuCl_2$	TBHP	DMSO	51
10	**2a**	$Cu(OAc)_2$	TBHP	DMSO	50
11	**2a**	CuCl	MCPBA	DMSO	0
12	**2a**	CuCl	DTBP	DMSO	0
13	**2a**	CuCl	H_2O_2	DMSO	0
14	**2a**	CuCl	O_2 (1 atm)	DMSO	0
15	**2a**	CuCl	TBHP	DMF	11
16	**2a**	CuCl	TBHP	dioxane	0
17	**2a**	CuCl	TBHP	MeCN	0
18	**2a**	CuCl	TBHP	EtOH	0
19	**2a**	CuCl	TBHP	DMSO/H_2O (4:1)	60
20[c]	**2a**	CuCl	TBHP	DMSO/H_2O (4:1)	80

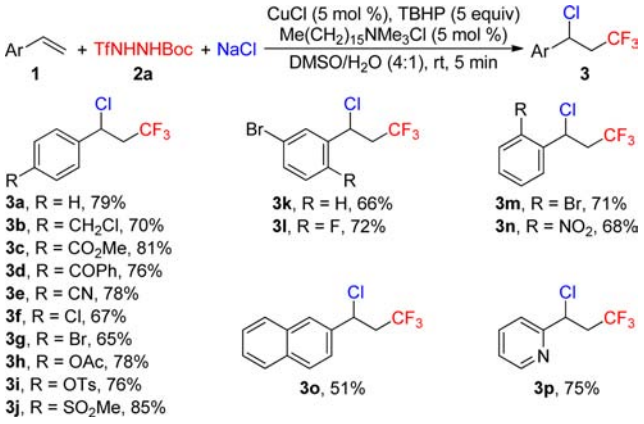
[a]Reaction conditions: **1a** (0.20 mmol), **2** (0.24 mmol), NaCl (1.0 mmol), [Cu] (5 mol %), [O] (1.0 mmol), $Me(CH_2)_{15}NMe_3Cl$ (5 mol %), solvent (0.5 mL), rt, 5 min. [b]Determined by ^{19}F NMR spectroscopic analysis using $PhCF_3$ as an internal standard. [c]**2a** (0.30 mmol) was used.

improving the solubility of NaCl (entry 19). Finally, increasing the amount of TfNHNHBoc (**2a**) to 1.5 equiv resulted in the formation of γ-chloro-α,α,α-trifluoroalkane **3a** in 80% yield (entry 20).

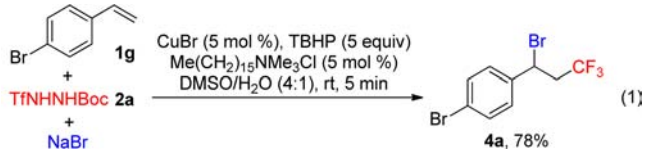
Under the optimized reaction conditions, a range of arylalkenes smoothly underwent copper-catalyzed three-component vicinal chlorotrifluoromethylation with TfNHNHBoc (**2a**) and NaCl, and in 5 min the reaction furnished structurally diverse γ-chloro-α,α,α-trifluoroalkanes in good yields with greater than 99% regioselectivity (Scheme 2). It is noteworthy that the reaction tolerated a variety of functional groups such as ester, ketone, nitrile, halo, sulfonate, sulfone, nitro, and pyridinyl. Compared to previous methods,[9−12] the substrate scope was extended to arylalkenes having ketone, sulfone, and pyridinyl groups. Nevertheless, the reaction of arylalkenes having strong electron-donating groups, such as methoxy and dimethylamino, gave complex mixtures. Moreover, the reaction was not applicable to alkylalkenes such as allylbenzene, electron-deficient terminal alkenes such as benzyl acrylate, and 1,2-disubstituted alkenes such as (*E*)-1,2-diphenylethylene due to lower reactivity.

By simply replacing NaCl and catalyst CuCl with NaBr and catalyst CuBr, respectively, the same reaction conditions were successfully applied to the vicinal bromotrifluoromethylation of arylalkene **1g**, which afforded γ-bromo-α,α,α-trifluoroalkane **4a** in 78% yield with greater than 99% regioselectivity (eq 1).[10,11,16] However, similar modification of the reaction conditions failed to execute the corresponding vicinal iodotrifluoromethylation of arylalkenes.[10,16b,17]

Scheme 2. Three-Component Vicinal Chlorotrifluoromethylation of Arylalkenes[a,b]



[a]Reaction conditions: **1** (0.20 mmol), **2a** (0.30 mmol), NaCl (1.0 mmol), CuCl (5 mol %), TBHP (1.0 mmol), $Me(CH_2)_{15}NMe_3Cl$ (5 mol %), DMSO/H_2O (4:1, 0.5 mL), rt, 5 min. [b]Isolated yields were given.



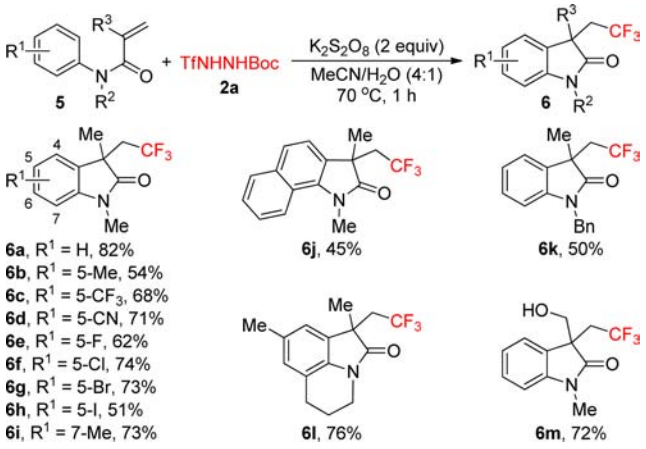
The synthetic application of TfNHNHBoc (**2a**) as a trifluoromethylating agent was further demonstrated in the tandem trifluoromethylation/cyclization of *N*-arylacrylamides for the construction of functionalized oxindoles, which has been found in many biologically relevant compounds.[18] The tandem trifluoromethylation/cyclization of *N*-arylacrylamides was initially reported to be catalyzed by transition metals,[19] and later several metal-free versions were disclosed using Togni's reagent, $TMSCF_3$, Langlois' reagent, and CF_3I as CF_3 sources.[20] While the metal-free versions are more environmentally benign, they required a large excess of CF_3 sources and a long reaction time. In this regard, we were happy to find that TfNHNHBoc (**2a**) (1.2 equiv) served as an effective CF_3 source for the tandem trifluoromethylation/cyclization of *N*-arylacrylamides (Scheme 3). This reaction required only 1 h in the presence of oxidant $K_2S_2O_8$ in a mixture of acetonitrile and water at 70 °C, and a range of structurally diverse 3-(β,β,β-trifluoroethyl)oxindoles were obtained in moderate to good yields with extremely high regioselectivity.

Addition of 2 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to the reaction mixture of alkene **1o** (Ar = 2-naphthyl), TfNHNHBoc (**2a**), and NaCl completely inhibited the formation of γ-chloro-α,α,α-trifluoroalkane **3o**. Similar inhibition was observed for the use of TEMPO in the reaction of *N*-arylacrylamide **5a** (R^1 = H, R^2 = R^3 = Me) with TfNHNHBoc (**2a**) under the standard conditions. These results suggest that the reaction may proceed via a radical pathway, which is substantially supported by the formation of compounds **7**[21] and **8**[22] as detected by ^{19}F NMR spectroscopic analysis and/or mass spectrometric analysis (eq 2). Clearly, both $CF_3^•$ and $CMe_3^•$ were generated by decomposition of TfNHNHBoc (**2a**) under the oxidative conditions.

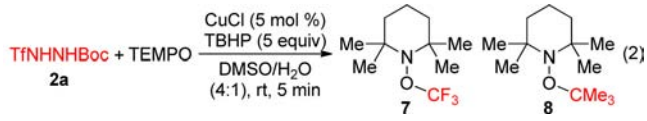
The above-mentioned experimental results and previous relevant studies permitted us to propose the following reaction

DOI: 10.1021/acs.orglett.6b01862
Org. Lett. 2016, 18, 3850−3853

Scheme 3. Tandem Trifluoromethylation/Cyclization of *N*-Arylacrylamides[a,b]

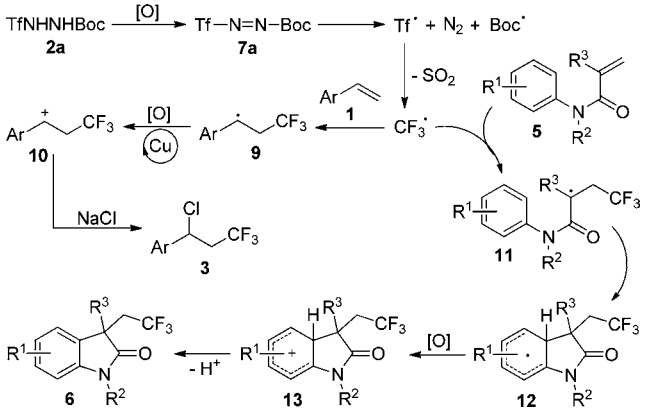


[a]Reaction conditions: **5** (0.20 mmol), **2a** (0.24 mmol), $K_2S_2O_8$ (0.40 mmol), MeCN/H_2O (4:1, 0.5 mL), 70 °C, 1 h. [b]Isolated yields were given.



pathways as depicted in Scheme 4. Oxidation of TfNHNHBoc (**2a**) either with or without a copper catalyst leads to the

Scheme 4. Proposed Reaction Pathways



formation of diazene **7a**,[3a−c] the decomposition of which followed by extrusion of SO_2 gives $CF_3^{\bullet}$.[19e] Regioselective addition of $CF_3^{\bullet}$ to arylalkene **1** followed by copper-catalyzed oxidation gives carbocation **10**, which reacts with Cl^- to give γ-chloro-α,α,α-trifluoroalkane **3**.[10] On the other hand, regioselective addition of $CF_3^{\bullet}$ to *N*-arylacrylamide **5** followed by cyclization gives radical **12**, which is subjected to sequential oxidation and deprotonation to give 3-(β,β,β-trifluoroethyl)-oxindole **6**.[20b,e]

In summary, we have demonstrated an unprecedented application of trifluoromethanesulfonyl hydrazides as trifluoromethylating agents in two vicinal difunctionalization reactions of terminal alkenes: the copper-catalyzed three-component vicinal chlorotrifluoromethylation of arylakenes with TfNHNHBoc and NaCl and the tandem trifluoromethylation/cyclization of *N*-arylacrylamides with TfNHNHBoc under oxidative conditions. All the starting materials and reagents are readily accessible and/or inexpensive, and the reactions proceeded under mild conditions to provide a range of structurally diverse CF_3-containing compounds with high regioselectivity. Preliminary mechanistic studies suggest that both reactions proceed via radical pathways involving oxidative decomposition of TfNHNHBoc to generate $CF_3^{\bullet}$. Further synthetic applications of TfNHNHBoc are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01862.

General information, experimental procedures, characterization data, and copies of ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra (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 (21472178 and 21232007) and the National Key Basic Research Program of China (2014CB931800).

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DOI: 10.1021/acs.orglett.6b01862
Org. Lett. 2016, 18, 3850−3853