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Geometrically Selective Denitrative Trifluoromethylthiolation of β-Nitrostyrenes with $AgSCF_3$ for (*E*)-Vinyl Trifluoromethyl Thioethers

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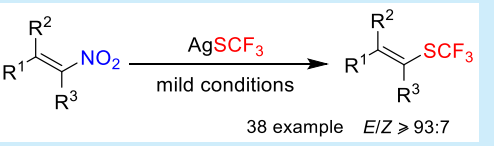
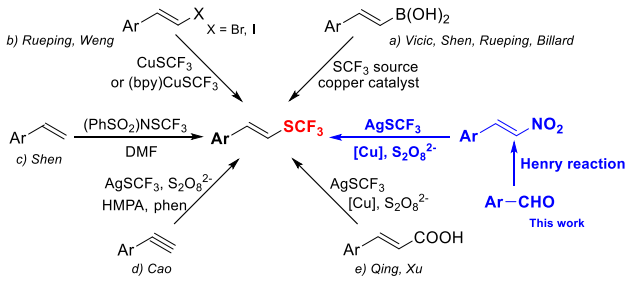
ABSTRACT: An efficient copper(II)-promoted denitrative trifluoromethylthiolation under mild reaction conditions has been developed for vinyl trifluoromethyl thioethers to construct C_{vinyl}–SCF_3 bonds with stable $AgSCF_3$ as a source of the trifluoromethylthio. This reaction system tolerates a broad range of functional groups to commendably achieve a high product yield and excellent stereoselectivity of *E*/*Z*.



The fluorinated organic compounds have always attracted significant interest with the continuous progress of synthetic methods, due to their unique properties in pharmaceuticals, agrochemicals, and advanced materials.[1] The incorporation of the trifluoromethylthio group (SCF_3) into parent organic molecules often dramatically improve the pharmacokinetic and physicochemical properties of the drug molecules, with its strong electron-withdrawing nature, higher Hansch's lipophilicity parameter, and better metabolic stability.[2] Many trifluoromethylthiolated organic compounds have been obtained through the construction of the aryl–SCF_3 bond, alkyl–SCF_3 bond, and alkynyl–SCF_3 bond.[3] The classical strategies for the synthesis of vinyl–SCF_3 compounds need excess amounts of toxic and corrosive gaseous trifluoromethylsulfenyl chloride (CF_3SCl).[4] Using electrophilic or nucleophilic trifluoromethylthiolating reagents, the vinyl–SCF_3 compounds have been synthesized straightforwardly through the transition-metal-mediated or catalyzed trifluoromethylthiolation of vinyl iodides,[5] vinyl bromides,[6] or vinylboron compounds by Zhang and Vicic,[7] Shen and co-workers,[8] Rueping and co-workers,[9] and Billard and co-workers[10] (Scheme 1). The amide-based electrophilic trifluoromethylthiolating reagent, $(PhSO_2)_2NSCF_3$, has been successfully prepared by Shen and co-workers and Shi and co-workers for direct trifluoromethylthiolation of styrene derivatives under a simple and mild condition.[11] The terminal alkyne substrates were also trifluoromethylthiolated by Cao and co-workers and Qing and co-workers to give two kinds of trifluoromethylthiolated vinyl–SCF_3 derivatives, Markovnikov and anti-Markovnikov products.[12] Although the above direct functionalization of C–H bonds has provided attractive access to compounds bearing C_{sp2}–SCF_3 and C_{sp3}–SCF_3 as well as C_{sp}–SCF_3 bonds for its atom and step economy, the facile synthetic processes for the direct construction of C_{vinyl}–SCF_3 bonds are still limited. Recently, the decarboxylative trifluoromethylthiolation of cinnamic acids was developed to afford trifluoromethylthiolated alkenes in moderate yield or *E*/*Z* selectivity by Qing and co-workers[13] and Xu and co-workers,[14] employing the facile trifluoromethylthiolating reagent $AgSCF_3$.

Scheme 1. Strategies for the Synthesis of Vinyl–SCF_3 Compounds



As significant and valuable substrates, nitro olefins can be easily available for the synthesis of complex target compounds, through the Henry reaction, nitration of alkenes, and decarboxylative nitration. The β-nitrostyrenes have been applied to the denitrative trifluoromethylation with CF_3SO_2Na[15] and Togni(II) reagent[16] as the trifluoromethylating reagent. However, there are very few examples for the transformation of β-nitrostyrenes into vinyl–SCF_3 compounds, especially for the vinyl trifluoromethyl thioethers with well-defined geometric configuration (*E* or *Z*). Inspired by the recent advance in trifluoromethylation of nitro olefins,[15−17] we have been trying to develop an efficient approach for the synthesis of vinyl–SCF_3 compounds, through the facile denitrative trifluoromethylthiolation of β-nitrostyrenes with

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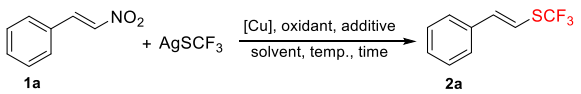
Table 1. Optimization of the Reaction Conditions[a]



entry	[Cu]	oxidant	additive	solvent	temp (°C)	time (h)	yield[b] (%)
1		$(NH_4)_2S_2O_8$		CH_3CN	25	24	0
2		$(NH_4)_2S_2O_8$	K_2HPO_4	CH_3CN	60	12	40
3	CuCl	$(NH_4)_2S_2O_8$	K_2HPO_4	CH_3CN	60	6	51
4	CuI	$(NH_4)_2S_2O_8$	K_2HPO_4	CH_3CN	60	6	26
5	$Cu(OAc)_2$	$(NH_4)_2S_2O_8$	K_2HPO_4	CH_3CN	60	6	38
6	$Cu(TFA)_2$	$(NH_4)_2S_2O_8$	K_2HPO_4	CH_3CN	60	6	65
7	$Cu(TFA)_2$	$(NH_4)_2S_2O_8$	K_2HPO_4	DMSO	60	6	95
8	$Cu(TFA)_2$	$(NH_4)_2S_2O_8$	K_2HPO_4	toluene	60	6	trace
9	$Cu(TFA)_2$	$(NH_4)_2S_2O_8$	K_2HPO_4	DCE	60	6	16
10	$Cu(TFA)_2$	$(NH_4)_2S_2O_8$	K_2HPO_4	THF	60	6	3
11	$Cu(TFA)_2$	$(NH_4)_2S_2O_8$	KH_2PO_4	DMSO	60	6	87
12	$Cu(TFA)_2$	$(NH_4)_2S_2O_8$	K_3PO_4	DMSO	60	6	68
13	$Cu(TFA)_2$	$(NH_4)_2S_2O_8$	Na_3PO_4	DMSO	60	6	83
14	$Cu(TFA)_2$	$(NH_4)_2S_2O_8$	K_2HPO_4	DMSO	40	6	64
15[c]	$Cu(TFA)_2$	$(NH_4)_2S_2O_8$	K_2HPO_4	DMSO	60	6	58

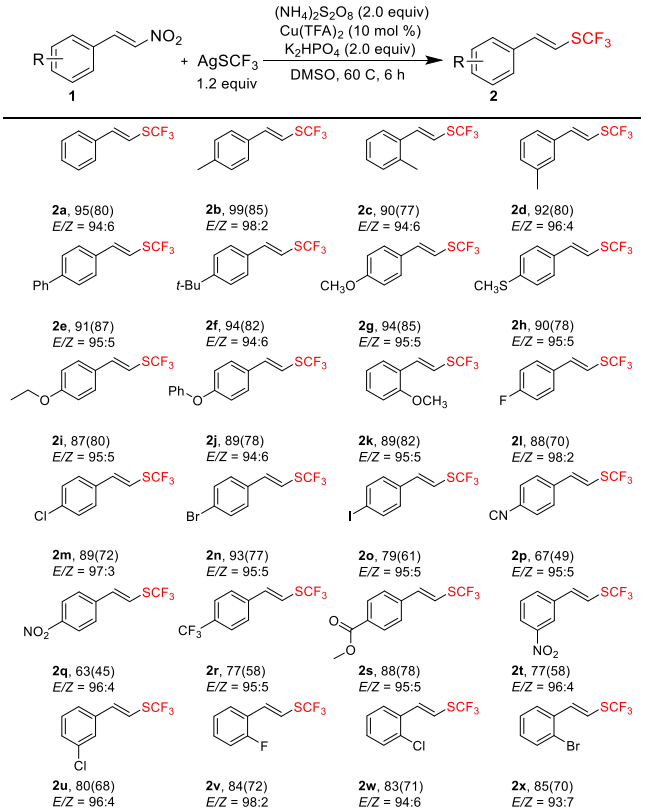
[a]Reaction conditions: **1** (0.1 mmol), $AgSCF_3$ (1.2 equiv), $Cu(TFA)_2$ (10% mol), $(NH_4)_2S_2O_8$ (2.0 equiv), K_2HPO_4 (2.0 equiv), 4,4-difluorobiphenyl (0.1 mmol, internal standard), solvent (1 mL). [b]Yields determined by ^{19}F NMR spectroscopy based on **1**. [c]Under air.

more stable $AgSCF_3$ as a source of the trifluoromethylthio (SCF_3).

The initial investigations were carried out using $AgSCF_3$ as a trifluoromethylthio source, **1a** as a model β-nitrostyrenes substrate, and $(NH_4)_2S_2O_8$ as the oxidant as shown in Table 1. No desired product was found in CH_3CN and at room temperature, in the absence of Cu salt and additive (Table 1, entry 1). Using K_2HPO_4 as an additive, β-trifluoromethylthiostyrene **2a** was obtained at 60 °C for 12 h, in 40% yield (entry 1) through computation by ^{19}F NMR spectroscopy with 4,4-difluorobiphenyl as the internal standard. Although the radicals SCF_3 and Ag^+ as reactive intermediates can be generated from $AgSCF_3$ in the presence of peroxide ($S_2O_8^{2-}$) as previously reported,[18] the additive K_2HPO_4 is obviously playing an important role in this reaction system (entry 2). We speculated that the formation and stability of the SCF_3 radical would benefit highly by the weakly basic condition resulting from K_2HPO_4.[17,18a,h−j] The addition of copper salts was still necessary to improve the weak reactivity of Ag^+ for the transformation. Using both K_2HPO_4 and $(NH_4)_2S_2O_8$ in CH_3CN at 60 °C, $Cu(TFA)_2$ was found to be an optimal catalyst among four examined copper salts, in the highest yield of 65% (Table 1, entries 3−6). In comparison with the nonpolar or less polar solvent (toluene, THF, and DCE), the higher yield in polar solvent (DMSO and CH_3CN) indicated that the strong polar aprotic solvents always do favor the transformation (entries 8−10). Generally, the stronger polar solvents can stabilize the polar intermediate of SCF_3 radicals with richer electron cloud density.[19] Compared with additives KH_2PO_4, K_3PO_4, and Na_3PO_4 (68−87%, entries 11−13), the K_2HPO_4 is still a favorable choice in higher yields of **2a** (95%, entries 7). At the lower temperature of 40 °C (entry 14) or in an air atmosphere (entry 15), the yield of the product decreases to 64% and 58%, respectively.

With the optimal reaction conditions established, the substrate scope of denitrative trifluoromethylthiolation to β-nitrostyrenes was explored. All monosubstituted substrates afforded the desired products in moderate to good yields and excellent selectivity of E/Z as summarized in Scheme 2. The

Scheme 2. Copper(II)-Promoted Denitrative Trifluoromethylthiolation of Monosubstituted β-Nitro-Styrenes with $AgSCF_3$[a,b]



[a]Reaction yields were determined by ^{19}F NMR spectroscopy using 4,4-difluorobiphenyl as internal standard. Values in parentheses are isolated yields using column chromatography. [b]The E/Z ratio was determined by ^{19}F NMR spectroscopy.

methyl substituted β-nitrostyrene can easily give the corresponding trifluoromethylthiolated products in good yields

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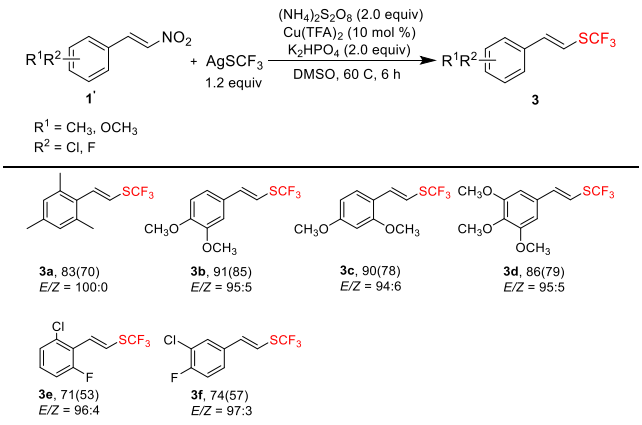
(Scheme 2, **2b**–**2d**). The pretty higher yield with the methyl substituent in the *ortho* position than *meta* and *para* positions (**2b**, 99%; **2c**, 90%; **2d**, 92%) can be ascribed to the steric hindrance effect of the substituent group, the same as methoxy substituted *β*-nitrostyrene (**2g**, 94%; **2k**, 89%). The *β*-nitrostyrenes with other electron-donating substituents, such as Ph, *t*-Bu, MeS, EtO, and PhO, were well tolerated under the reaction conditions, providing the corresponding target products (**2e**–**2j**) within the reasonable range of 78–87%. All halide substituted *β*-nitrostyrenes such as F, Cl, Br, and I can also tolerate the reaction system to give the corresponding products in moderate yields (**2l** and **2m** within the range of 79–93%). In particular, the iodo group in substrate **1o** can significantly survive the standard reaction conditions, affording the desired product **2o** in good yield. The *β*-nitrostyrene derivatives with electron-withdrawing groups, such as CN, NO_2, CF_3, and $COOCH_3$, afford the desired products under the standard conditions in pretty lower yield (**2p**–**2s**) than the electron-donating groups. Indeed, the electron-rich substrates always show relatively better reactivity than the electron-deficient substrates. Contrarily to the methyl substituted *β*-nitrostyrene, the higher yield of nitro substituted *β*-nitrostyrene was provided in the *meta* position of benzene ring rather than the *ortho* position (**2t**, 77%; **2q**, 63%).

Notably, the polysubstituted *β*-nitrostyrenes can also give the desired products through the reaction in slightly lower yields than the corresponding monosubstituted *β*-nitrostyrenes, as shown in Scheme 3, probably ascribed to the steric hindrance effect prior to the substituent electronic effect.

Scheme 3. Copper(II)-Promoted Denitrative Trifluoro-Methylthiolation of Di- or Trisubstituted *β*-Nitro-Styrenes with $AgSCF_3$[a,b]

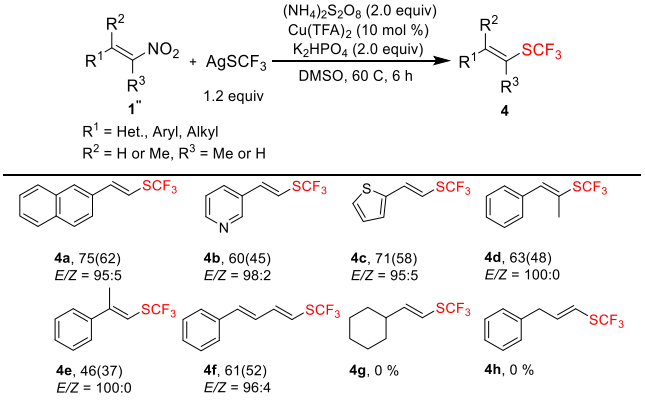


[a]Reaction yields were determined by ^{19}F NMR spectroscopy using 4,4-difluorobiphenyl as internal standard. Values in parentheses are isolated yields using column chromatography. [b]The *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy.

Impressively, the *E*/*Z* selectivity of the synthetic method was excellent in all cases with the high *E*/*Z* ratios of up to 92:8 determined by ^{19}F NMR spectroscopy. The highest *E*/*Z* ratios for 1,3,5-trimethyl-2-(2-nitrovinyl)benzene (**3a**, *E*/*Z* 100:0) suggest that the stereoselectivity can be improved perfectly by increasing the steric hindrance of the reactions (see the Supporting Information). Simultaneously, the higher the *E*/*Z* stereoselectivity, the better was the separation of the pure *E*-isomers. The highly geometrically selective trifluoromethylthiolated compound from *β*-nitrostyrenes was expected to possess fascinating properties for agricultural, pharmaceutical, and materials chemistry.[20]

Encouraged by the excellent suitability of the substrate for this reaction, we next drew our attention to the polycyclic and heterocyclic *β*-nitrostyrenes, such as naphthaline, pyridine, and thiophene. As shown in Scheme 4, the substrates underwent

Scheme 4. Scope of Other *β*-Nitrostyrenes for the Preparation of Vinyl Trifluoromethyl Thioesters[a,b]



[a]Yields were determined by ^{19}F NMR spectroscopy using 4,4-difluorobiphenyl as internal standard. Values in parentheses are isolated yields using column chromatography. [b]The *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy.

easy trifluoromethylthiolation under the optimal conditions to give the corresponding trifluoromethylthiolated compounds (**4a**, **4b**, and **4c**). With the methyl group in *α* or *β* position, the *β*-nitrostyrenes can still tolerate the reaction conditions to give products **4d** and **4e** in lower yields than the unsubstituted ones. Unfortunately, the aliphatic substrates, such as cyclic or aliphatic nitro-alkenes (**4g** and **4h**), were not suitable for this reaction condition. The substrate (1*E*,3*E*)-4-nitrobuta-1,3-dien-1-yl)benzene **4f** was afforded under the above optimized reaction conditions to give 52% yield of the corresponding product. Obviously, the conjugated structure of the substrates is the most important requirement for the reaction process.

Known as having unique pharmacological activity, the SCF_3 group often tended to generate some unexpected effects and unparalleled results. Exactly, a novel strategy of trifluoromethylthiolation always attracting attention is the focus for a medicinal chemist to use in the modification of known and common drugs. Similarly, this feasible method could be employed to introduce the SCF_3 group into complex molecules smoothly, such as coumarin and estrone (Scheme 5). The corresponding products, **5a** and **5b**, were obtained in 73% and 64% isolated yields, respectively. To illustrate the usefulness of this trifluoromethylthiolation procedure, the reaction of 2-nitrovinylbenzene **1a** with $AgSCF_3$ in a 1 mmol scale was carried out in the optimal conditions. The transformation proceeded successfully to give the corresponding product **2a** in 82% isolated yield (see the Supporting Information).

In order to provide a plausible mechanism for the reaction, the radical trapping experiment was carried out (Scheme 6). While 4.0 equiv of radical scavenger TEMPO (2,2,6,6-tetramethyl-1-oxylpiperidine) was added to the reaction systems under the optimal conditions (Scheme 6a), no desired product **2a** was detected by ^{19}F NMR spectroscopy, suggesting that the reaction was completely blocked by the radical

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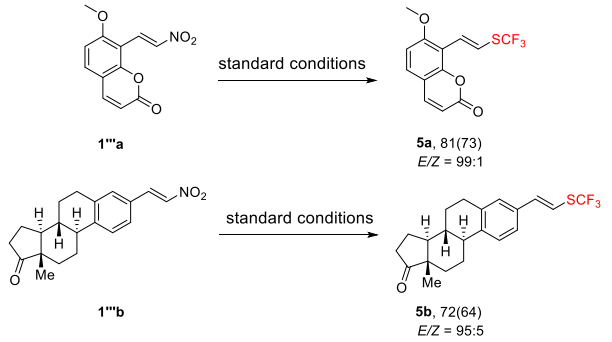
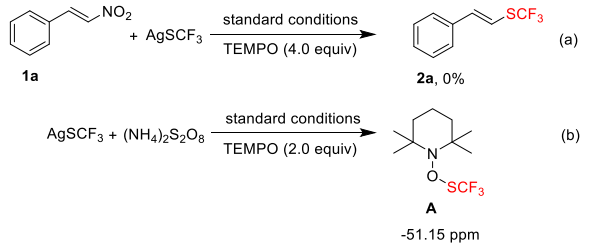
Scheme 5. Strategy to Introduce SCF_3 Groups to Complex Drug Molecules[a]



[a]All reactions were performed under standard conditions.

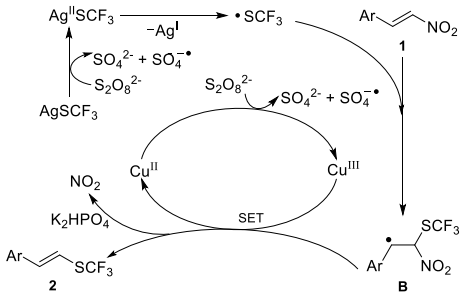
Scheme 6. Radical Trapping Experiment



scavenger. When TEMPO (2.0 equiv) was added into the reaction mixture of $AgSCF_3$ and $(NH_4)_2S_2O_8$ (Scheme 6b), a signal could be clearly observed at δ 51.15 ppm by ^{19}F NMR, ascribed to TEMPO−SCF_3 **A** (see the Supporting Information). These results suggest that the reaction may proceed via a radical pathway through the generation of a SCF_3 radical from $AgSCF_3$ treated with $(NH_4)_2S_2O_8$.

On the basis of the above results and previous studies,[12,13,18] a plausible mechanism is proposed as shown in Scheme 7.

Scheme 7. Plausible Mechanism for β-Nitrostyrenes Trifluoromethylthiolation



Initially, the oxidation of $AgSCF_3$ by $(NH_4)_2S_2O_8$ affords the Ag(II)SCF_3 species, which then triggers the SCF_3 radical and releases Ag(I) simultaneously.[13,14] The addition of the SCF_3 radical to β-nitrostyrene derivatives **1** generates a carbon-centered radical intermediate **B**. At the same time, the $(NH_4)_2S_2O_8$ reacts with Cu(II) to generate Cu(III). Subsequently, the intermediate **B** proceeds via a single-electron transfer (SET) by Cu(III) to give the expected products trifluoromethylthiolated alkenes **2**, along with the elimination of NO_2 and regeneration of Cu(II).

In summary, we have developed an efficient copper(II)-promoted denitrative trifluoromethylthiolation reaction to construct C_{vinyl}−SCF_3 bonds with $AgSCF_3$. This reaction system tolerates a broad range of functional groups to commendably achieve a high product yield and excellent stereoselectivity of *E*/*Z*. A preliminary mechanistic investigation suggests that this reaction proceeded via a radical pathway. This novel method provides an alternative strategy to construct C−SCF_3 bonds through the synthesis of trifluoromethylthiolated alkenes from β-nitrostyrene derivatives.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01714.

Experimental procedures and spectroscopic characterization data; ^1H and ^{13}C NMR spectra of the new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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