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Synthesis of trifluoromethylthiolated alkenes and ketones via decarboxylative functionalization of cinnamic acids

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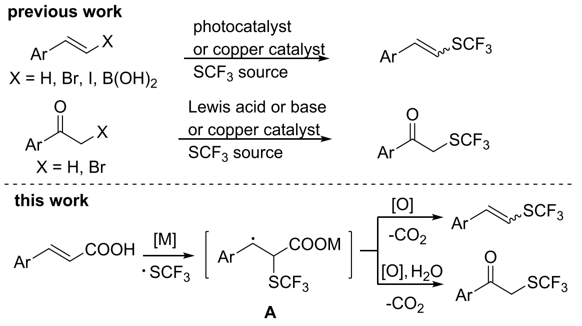
Abstract: A tunable decarboxylative trifluoromethylthiolation of cinnamic acids with $AgSCF_3$ was developed to afford trifluoromethylthiolated alkenes or ketones, respectively, via transition metal-mediated conditions.

The decarboxylative cross-coupling reaction of carboxylic acids is a fundamentally important transformation in organic chemistry, as carboxylic acids are abundant and inexpensive stock chemicals.[1] This reaction provides a powerful strategy for the formation of carbon–carbon[1c] and carbon–heteroatom bonds (e.g., C–F(Cl),[2] C–N,[3] C–P[4] and C–S[5]) through transition-metal catalysis and/or free radical mechanism.[6] More specifically, its application on the syntheses of fluorine-containing molecules have attracted much attentions during the past decades.[2c] For example, the decarboxylative trifluoromethylation has nicely achieved by Hu,[7] Liu,[8] Maiti,[9] Zhu,[10] Duan,[11] Cai[12] and Altman[13] using various trifluoromethylation reagents.[14] However, compared to large number reports on decarboxylative trifluoromethylation, the reports on decarboxylative trifluoromethylthiolation are very rare. Shen and co-workers reported a silver-catalyzed decarboxylative trifluoromethylthiolation of aliphatic carboxylic acids in aqueous emulsion to afford alkyl trifluoromethyl thioethers in high yields.[15] Glorius and co-workers achieved the same conversion by visible light promoted decarboxylation.[16] Among common fluorine-containing groups, SCF_3 has the highest lipophilicity value (π_x=1.44), which is much higher than those of SF_5 (π_x=1.23), OCF_3 (π_x =1.04), CF_3 (π_x =0.88), CH_3 (π_x =0.52).[17] So SCF_3-containing compounds are increasingly attractive for their potential applications in agrochemicals and pharmaceuticals as well as in materials science. Therefore, efficient methodologies for syntheses of SCF_3-containing molecules bearing C_{sp2}−SCF_3 and C_{sp3}−SCF_3 as well as C_{sp}−SCF_3 bonds have been developed.[18] However, facile construction of C_{vinyl}−SCF_3 bonds are limited, and prefunctionalized starting materials, such as enamines,[19] vinyl halides,[20] vinylboronic acids[21] or terminal alkynes[22] are usually used (Scheme 1).

Since 2012, we have been working on installations of SCF_3 group onto organic molecules.[23] We propose that decarboxylative trifluoromethylthiolation might be suitable strategy for the synthesis of vinyl trifluoromethylthioethers via a radical pathway (Scheme 1, bottom). First, SCF_3 radical can be generated at oxidative conditions. Then, the addition of SCF_3 radical to cinnamic acid will generate radical intermediate **A**, which further undergoes decarboxylation and oxidation may generate SCF_3-substituted alkenes or ketones depending on conditions such as oxidants and additional nucleophiles (e.g. water) (Scheme 1). Various efficient methods for synthesis of α-SCF_3-substituted ketones which act as important building blocks have been reported including the trifluoromethylthiolation of α-haloketones,[24] β-ketoesters,[25] silyl enol ethers[26] and simple ketones[27] with different SCF_3 sources. The decarboxylative trifluoromethylthiolation of α,β-unsaturated carboxylic acids would be another efficient method for synthesis of the α-SCF_3 substituted ketones. As part of our continuing studies on developing methodologies for introduction of SCF_3 into organic molecules, herein we present a tunable and efficient decarboxylative trifluoromethylthiolation of α,β-unsaturated carboxylic acids to afford vinyl trifluoromethyl thioethers and α-SCF_3 substituted ketones, respectively.



Scheme 1. Methods for the syntheses of SCF_3-substituted alkenes and α-SCF_3 substituted ketones.

We used trifluoromethylthiolation of cinnamic acid **1a** as the model system. The initiator, oxidant, and solvent critically affect the efficiency of this reaction (for the optimization of the reaction conditions, see ESI, Table S1). Initially, the reaction solvent was examined with CuI and Ag_2CO_3 as initiator and $K_2S_2O_8$ as oxidant at 50 °C. The results disclosed that no reaction occurred in neat solvent such as THF, DCE, CH_3CN, DMSO and DMF, however, the desired product **2a** was detected in 40 % yield when mixed solvents CH_3CN/HOAc (4:1) were used. Next, the copper salts including CuTC, CuOAc, CuCN, CuCl, CuBr, $(CH_3CN)_4CuPF_6$ $CuCl_2$, $CuSO_4$ and silver salts including Ag_2CO_3, $AgBF_4$, AgOAc, $AgNO_3$, AgOTf, Ag_2SO_4 as initiator was explored. The combination of CuI and Ag_2CO_3 was found to be the best initiator. The investigation of oxidants disclosed that peroxydisulfuric acid salts such as $K_2S_2O_8$, $Na_2S_2O_8$ and $(NH_4)_2S_2O_8$ were better than $PhI(OAc)_2$ and *tert*-butyl hydroperoxide (TBHP). The yield of the decarboxylative trifluoromethylthiolated alkene could be increased from 24% to 52% or 71% with the increase of reaction temperature from 50 °C to 70 °C or 90 °C, respectively. Further optimization of the

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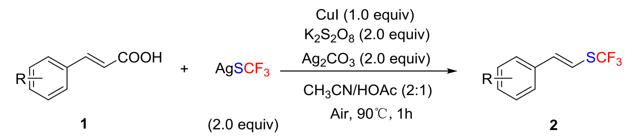
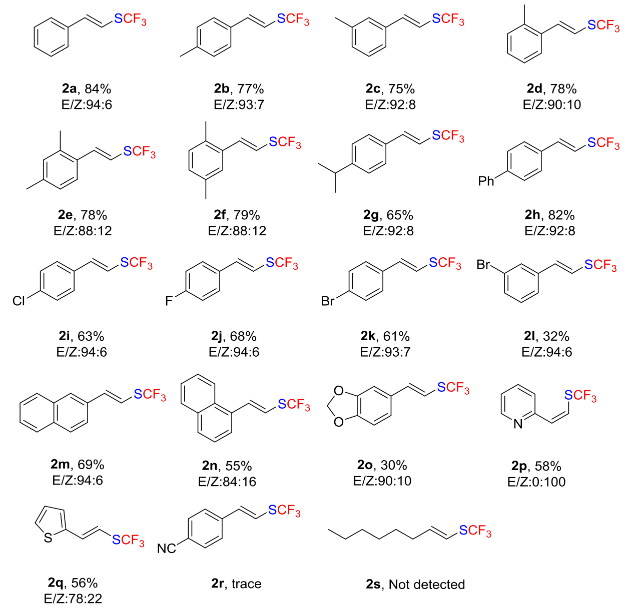
Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) reaction conditions revealed that using $AgSCF_3$ (2.0 equiv), CuI (1.0 equiv) and Ag_2CO_3 (2.0 equiv), $K_2S_2O_8$ (2.0 equiv) in $CH_3CN/HOAc$(2:1) at 90 °C for 1 h could give the desired vinyl trifluoromethyl thioether **2a** in 84% yield with excellent *E*/*Z* selectivity (94:6).

With the optimized conditions in hand, the scope of the Cu-mediated decarboxylative trifluoromethylthiolation for preparation of vinyl trifluoromethyl thioether was examined. A variety of aryl substituted α,β-unsaturated carboxylic acids can be transformed into the desired vinyl trifluoromethyl thioether in moderate to good yields (Table 1). Cinnamic acid with an alkyl substitution at *ortho*-, *meta*- or *para*-position gave comparative yield and *E*/*Z* selectivity (**2b**-**2d**, **2g** and **2h**). Halogen on the aromatic ring was well tolerated (**2i**-**2l**), providing a synthetic handle for further functionalization. Naphthyl and heteroaryl α,β-unsaturated carboxylic acids also gave corresponding vinyl trifluoromethyl thioether in moderate yields (**2m**-**2q**). In most cases, the *E*/*Z* selectivity was good with a ratio range of 78:22-94:6, however, the reversion of the *E*/*Z* selectivity was observed for pyridyl α,β-unsaturated carboxylic acid (**2p**, *E*/*Z* 0:100). Unfortunately, aliphatic substituted α,β-unsaturated carboxylic acids and cinnamic acids with a strong electron-withdrawing group such as nitro, cyano, formyl and trifluoromethyl groups were not suitable substrates.

Table 1. Copper-mediated decarboxylative trifluoromethylthiolation to form trifluoromethyl thioethers.[a,b]





2a, 84% E/Z:94:6
2b, 77% E/Z:93:7
2c, 75% E/Z:92:8
2d, 78% E/Z:90:10
2e, 78% E/Z:88:12
2f, 79% E/Z:88:12
2g, 65% E/Z:92:8
2h, 82% E/Z:92:8
2i, 63% E/Z:94:6
2j, 68% E/Z:94:6
2k, 61% E/Z:93:7
2l, 32% E/Z:94:6
2m, 69% E/Z:94:6
2n, 55% E/Z:84:16
2o, 30% E/Z:90:10
2p, 58% E/Z:0:100
2q, 56% E/Z:78:22
2r, trace
2s, Not detected

[a] Reaction conditions: **1** (1.0 equiv), $AgSCF_3$ (2.0 equiv), CuI (1.0 equiv) and Ag_2CO_3 (2.0 equiv), $K_2S_2O_8$ (2.0 equiv) in $CH_3CN/HOAc$ (2:1) at 90 °C for 1 h under atmosphere. [b] Isolated yields, the *E*/*Z* ratio were determined by ^{19}F NMR spectroscopy.

Based on the successful preparation of vinyl trifluoromethyl thioethers by decarboxylative trifluoromethylthiolation, we turned our interest to the synthesis of α-SCF_3 substituted ketones via the similar transformation. With cinnamic acid **1a** as the model substrate and $AgSCF_3$ as SCF_3 source, the reaction conditions for the synthesis of α-SCF_3 substituted ketone **3a** were optimized (for the optimization of the reaction conditions, see ESI, Table S2). First, the reaction was performed with CuI as a catalyst and $K_2S_2O_8$ as an oxidant in CH_3CN/H_2O (2:1) at 50°C for 12 h under O_2 atmosphere, however, no desired product was detected. Then, we investigated the effect of iron salts as catalyst instead of Cu salts. Among the tested iron salts, the best activity was observed with $Fe(OAc)_2$ affording **3a** in 13% yield. The presence of silver salt was crucial to the transformation, and Ag_2SO_4 was proved to be the most effective and led to an increase in the yield to 62%. Similar to the synthetic condition for vinyl trifluoromethyl thioether, peroxydisulfuric acid salts such as $K_2S_2O_8$, $Na_2S_2O_8$ and $(NH_4)_2S_2O_8$ were better than $PhI(OAc)_2$ and *tert*-butyl hydroperoxide (TBHP). Further screening of reaction conditions revealed that the solvent mixture of CH_3CN/H_2O (2:1) was superior to others, and prolonged reaction time from 12 h to 18 h resulted higher yield (62 % to 70 %). It is noteworthy that the transformation become sluggish under Argon atmosphere which indicated that oxygen as a second oxidant was essential.

The scope of substrates for the synthesis of α-SCF_3 substituted ketones under the optimized condition [$Fe(OAc)_2$ (1.0 equiv), $AgSCF_3$ (1.0 equiv), Ag_2SO_4 (2.0 equiv), $Na_2S_2O_8$ (2.0 equiv) in CH_3CN/H_2O (2:1) and O_2 at 50°C for 18 h] was then investigated. A variety of α,β-unsaturated carboxylic acids could be efficiently converted to the desired α-SCF_3 substituted ketones in moderate to good yields (Table 2). Electron-donating and electron-withdrawing substituents at the *ortho*-, *meta*- or *para* -positions on the aromatic ring of cinnamic acids have little influence on the reaction performance. The oxidative decarboxylative trifluoromethylthiolation of *para*- and *meta*-methoxyphenyl acrylic acid and *para*- and *meta*-tolyl acrylic acid proceeded smoothly to give **3b**-**3e** in good yields (45-63%).The α-SCF_3 substituted ketones with isopropyl (**3f**) and phenyl (**3g**) substituents were also obtained in yield of 55% and 65%, respectively. Halogen on the aromatic ring was well tolerated in the reaction. The yields of *para*-, *meta*- and *ortho*- chlorophenyl (**3h**-**3j**) and bromophenyl (**3k**-**3m**) α-SCF_3-substituted ketones were varied in the range of 35% to 75%. Unlike the synthesis of vinyl trifluoromethyl thioethers, cinnamic acids with strong electron-withdrawing substituents were also suitable substrates to afford the corresponding *para*-, *meta*-trifluoromethyl (**3n**-**3o**), *para*-, *meta*-cyanophenyl (**3q**-**3r**), *para*-fluorophenyl (**3p**), 3,4-dichlorophenyl (**3s**) and *para*-formyl (**3t**) α-SCF_3-substituted ketones in moderate to good yields (53-75%). The α,β-unsaturated carboxylic acid with an extra methyl group on the α position also gave 1-phenyl-2-((trifluoromethyl)thio)propan-1-one (**3x**) in 66% yield. However, the yields of acetamidophenyl (**3u**, 31%) and heterocycle aromatic (**3w**, 20%) substituted α-SCF_3 substituted ketones were poor. Surprisingly, when *p*-nitro-cinnamic acid was applied to the iron-mediated reaction system, the vinyl trifluoromethyl thioether (**2y**, 63%) was obtained as a major product along with α-SCF_3 substituted ketone (**3y**, 21%).

Table 2. Iron-mediated decarboxylative trifluoromethylthiolation to form α-SCF_3 substituted ketones.[a,b]

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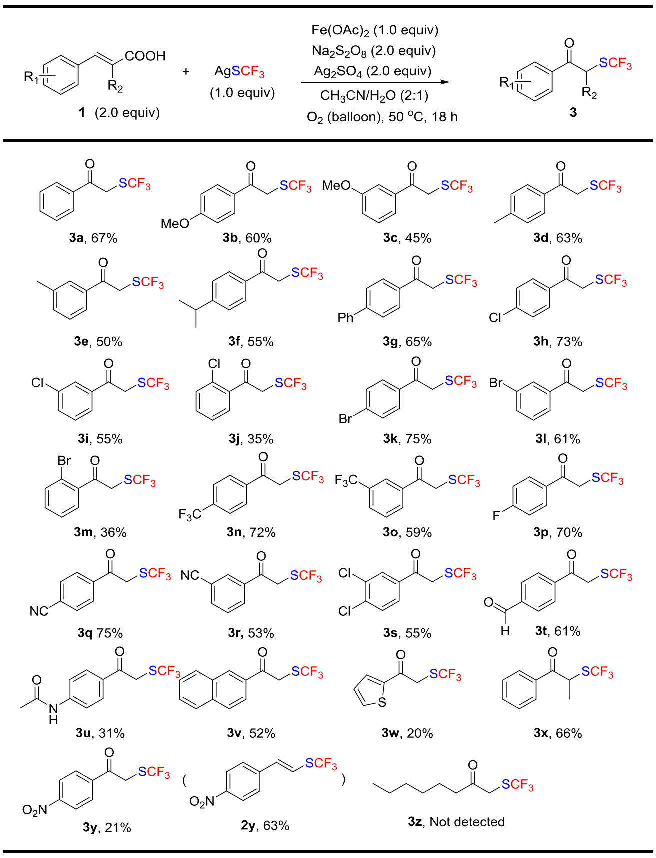
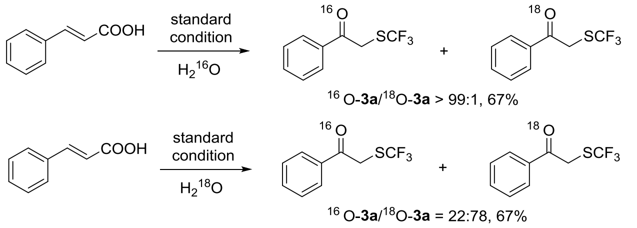


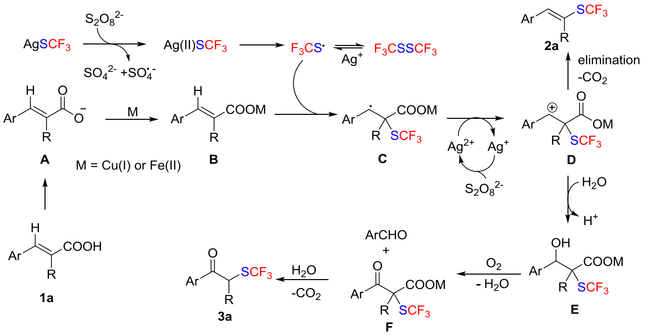
[a] Reaction conditions: **1** (2.0 equiv), $AgSCF_3$ (1.0 equiv), $Fe(OAc)_2$ (1.0 equiv), Ag_2SO_4 (2.0 equiv), $Na_2S_2O_8$ (2.0 equiv), O_2 (balloon) in CH_3CN/H_2O (2:1) at 50 °C for 18 h. [b] Isolated yields.

In order to understand the reaction mechanism, the radical trapping and isotope-labeling experiments were carried out. When 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) as radical scavenger was added to the reaction systems, the iron/copper mediated decarboxylative trifluoromethylthiolation between cinnamic acid and $AgSCF_3$ were both totally suppressed, suggesting that these transformation might proceed *via* a radical process (see ESI). Molecular oxygen is essential to the formation of α-SCF_3 substituted ketones. When the reaction was carried out under an argon atmosphere, the corresponding α-SCF_3 substituted ketone **3a** was not obtained, indicating that the formation of α-SCF_3 substituted ketones required the presence of oxygen. In an attempt to gain close insights into the origin of the oxygen in the newly formed carbonyl group of α-SCF_3-substituted ketones, isotope labeling experiments were performed by using ^{18}O-labeled water as a co-solvent instead of normal water. The content of ^{18}O-labeled product **3a** (^{18}O-**3a**) was increased to 78%, showing that the oxygen atom of carbonyl group in **3a** was from water instead of molecular oxygen (Scheme 2).



Scheme 2. Isotope-labeling experiments under the standard conditions.

On the basis of these observations and previous reports,[8,9,28] a plausible mechanism is proposed (Scheme 3). Initially, the oxidation of $AgSCF_3$ by peroxydisulfuric acid salt affords Ag(II)SCF_3 species, which triggers the F_3CS radical after the following single electron transfer course. Reaction of the cinnamic acid with Cu(I) or Fe(II) would produce a salt of **B**. The addition of F_3CS radical to **B** generates the corresponding alkyl radical intermediate **C**. Single electron transfer of **C** with Ag(II) to form the key intermediate **D**, which underwent elimination to afford vinyl trifluoromethyl thioethers **2**. The carbon cation intermediate **D** will quickly transformed into hydroxyl intermediate **E** in the presence of water. **E** was then oxidized by O_2 to produce **F** and byproduct aldehyde. Finally, decarboxylation of **F** leads to the desired α-SCF_3 ketones. $Fe(OAc)_2$ and CuI are likely to assist the elimination of CO_2.



Scheme 3. Proposed reaction mechanism.

In conclusion, the decarboxylative trifluoromethylthiolation of α,β-unsaturated carboxylic acids was achieved. Vinyl trifluoromethyl thioethers and α-SCF_3 substituted ketones can be selectively synthesized via adjusting the reaction systems with $AgSCF_3$ as SCF_3 source. These reactions have good functional group compatibilities, and provides novel pathway for the construction of C-SCF_3 bonds. Preliminary mechanism study revealed that these reactions proceeded *via* a radical mechanism, and oxygen atoms of carbonyl group of products **3** was found to be derived from water. Further investigation of these procedures focusing on using alkyl-substituted acrylic acids as substrates is currently underway in our laboratory.

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Keywords: Trifluormethylthiolation • decarboxylation • ketone • alkene • cinnamic acid

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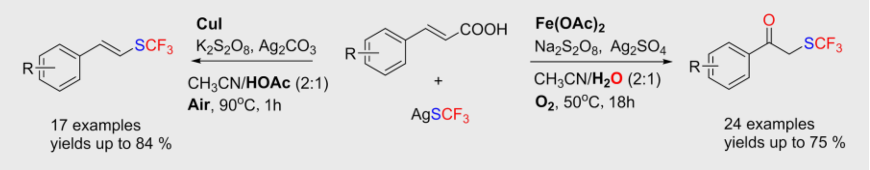

The decarboxylative trifluoromethylthiolation of cinnamic acids was achieved. Vinyl trifluoromethyl thioethers and α-SCF_3-substituted ketones can be selectively synthesized via adjusting the reaction systems with $AgSCF_3$ as SCF_3 source.

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Synthesis of trifluoromethylthiolated alkenes and ketones via decarboxylative functionalization of cinnamic acids