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Synthesis of Allylic and Propargylic Trifluoromethyl Thioethers by Copper(I)-Catalyzed Trifluoromethylthiolation of Allylic Bromides and Propargylic Chlorides

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An efficient method is reported for the copper(I)-catalyzed trifluoromethylthiolation of allylic bromides by using elemental sulfur and CF_3SiMe_3. This rate of this transformation was significantly accelerated in the presence of 18-crown-6, and the reaction afforded the desired products in moderate to excellent yields with high stereo- and regioselectivity. This method can tolerate a number of functional groups and provides facile access to a variety of allylic trifluoromethyl thioethers. The copper(I)-catalyzed trifluoromethylthiolation of propargylic chlorides was also investigated. A plausible mechanism that involves an allylcopper(III) intermediate is proposed.

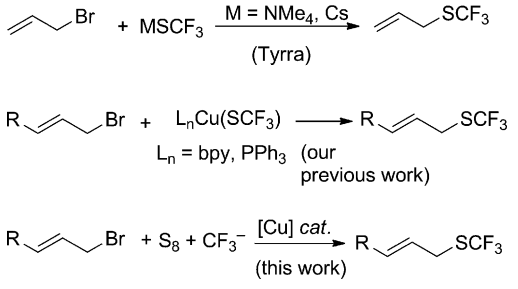
Introduction

Fluorinated allylic compounds have emerged as highly versatile synthons for the preparation of biologically active products such as drug molecules. These include herbicides, insecticides, and fungicides as well as fluorinated vitamin D and prostanoid analogues.[1,2] Additionally, these compounds can serve as an important skeletal motif that allows for further synthetic manipulations.[3] Accordingly, many effective methods for the synthesis of allylic fluorides have been developed such as nucleophilic[4,5] and electrophilic[6] fluorination reactions as well as the use of a fluorinated building block approach.[7] In addition, several methods to synthesize allylic trifluoromethylated compounds have emerged that rely on the copper-catalyzed electrophilic and oxidative allylic trifluoromethylation of terminal alkenes by using Togni's[8] and Umemoto's reagents[9] with CF_3SiMe_3 (Ruppert–Prakash reagent)[10] or the nucleophilic allylic trifluoromethylation of allylic halides.[11] The results of these investigations further demonstrate the value of these transformations in the synthesis of fluorine-containing allylic derivatives.

Allylic trifluoromethyl thioethers are of particular significance. These species that contain $–SCF_3$ groups have a high hydrophobicity parameter (π_R = 1.44),[12] and this property makes them increasingly attractive for their potential applications in agrochemicals and pharmaceuticals as well as in materials science. Therefore, an efficient synthetic approach to allylic trifluoromethyl thioethers is highly desirable.

In recent years, tremendous progress has been made in the direct introduction of the $–SCF_3$ group into organic molecules.[13] The development of Cu-catalyzed[14] and transition-metal-free oxidative trifluoromethylthiolation,[15] related Cu-promoted trifluoromethylthiolation through the direct functionalization of the C–H bonds of arenes,[16] and Pd-[17] and Ni-catalyzed processes[18] as well as the use new trifluoromethylthiolation reagents[19] has provided an attractive approach to the formation of $C_{sp^2}–SCF_3$, $C_{sp}–SCF_3$, and $C_{sp^3}–SCF_3$ bonds. Despite these advances, the development of new methods that catalytically generate allylic trifluoromethyl thioethers remains an important goal in synthetic organic chemistry.

Pioneering work by Tyrra and co-workers[20] demonstrated that allyl trifluoromethyl thioethers could be synthesized from the reaction between an allyl bromide and a sensitive, less-stable reagent such as $NMe_4(SCF_3)$ or $Cs(SCF_3)$ (see Scheme 1). Inspired by these results, we began to de-



Scheme 1. Methods for preparation of allylic trifluoromethyl thioethers.

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velop an expeditious synthetic process for the preparation of allylic trifluoromethyl thioethers with a broad substrate scope by using air- and moisture-stable copper reagents. The reactions of (bpy)Cu(SCF_3) (bpy = 2,2′-bipyridine) or (PPh_3)$_2$Cu(SCF_3) with a wide range of allylic bromides produced the desired allylic trifluoromethyl thioethers in good to excellent yields with high stereo- and regioselectivity.[21] In spite of the utility of these methods, stoichiometric amounts of copper reagents are required to achieve synthetically useful results.

To improve the potential of these reactions further, we set out to develop a metal-catalyzed process for trifluoromethylthiolation. We report herein our findings that a copper(I)/1,10-phenanthroline (phen) system[22] in the presence of 18-crown-6 efficiently catalyzes the trifluoromethylthiolation of allylic bromides with elemental sulfur and CF_3SiMe_3.

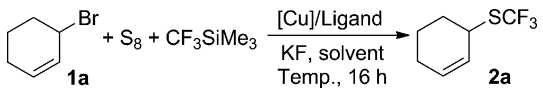
Results and Discussion

Initially, the reaction between 3-bromocyclohexene (**1a**), CF_3SiMe_3, and elemental sulfur in the presence of a copper catalyst was investigated. The trifluoromethylthiolation of **1a** in the presence of a catalytic amount of CuI (20 mol-%)/bpy (20 mol-%) in CH_3CN at 70 °C for 16 h afforded the desired cyclohexenyl(trifluoromethyl)sulfane **2a** in 47% yield (determined by ^{19}F NMR analysis; see Table 1, Entry 1). Encouraged by this initial result, we proceeded to optimize the reaction conditions. The use of phen as the ligand gave an improved yield for **2a** of 59%, whereas a 41% yield was achieved by using substrate **1a** with Me_2phen (2,9-dimethyl-1,10-phenanthroline) as the ligand (see Table 1, Entries 2 and 3). The investigation of various copper salts as the catalyst with phen as the ligand indicated that Cu(OTf)$_2$ (Tf = trifluoromethanesulfonyl) was almost as efficient a catalyst as CuI (see Table 1, Entry 7). Other copper salts such as CuCl, CuBr, and CuF_2 were less efficient (see Table 1, Entries 4–6). In addition, the yield of trifluoromethylthiolated product **2a** decreased in the absence of a copper source (13% yield; see Table 1, Entry 8), which indicates that copper may be involved in a catalytic cycle.

After screening various common organic solvents, we found that the trifluoromethylthiolation proceeded most efficiently in dioxane, which provided the product in 65% yield (see Table 1, Entry 16). The reactions that were performed in CH_3CN, THF, and toluene gave diminished product yields (see Table 1, Entries 2, 11 and 14), whereas other solvents such as DMF, CH_2Cl_2, diglyme, DMSO, and DME did not provide desirable results for this reaction (see Table 1, Entries 9, 10, 12, 13, and 15). Thus, dioxane was selected as the preferred solvent for the subsequent experiments because of its efficiency in the reaction and ease of handling during the workup procedure.

To accelerate the reaction, the copper(I)-catalyzed trifluoromethylthiolation was further examined in the presence of the additive 18-crown-6.[23] Interestingly, the yield of product **2a** significantly improved with the addition of this cation scavenger (78% yield; see Table 1, Entry 17). Furthermore, the reaction proceeded smoothly even at a lower temperature (50 °C) in the presence of 2 equiv. of 18-crown-6 to give **2a** at 76% yield (see Table 1, Entry 18).

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



Entry	[Cu]	Ligand	Additive	Solvent	T [°C]	Yield [%][b]
1	CuI	bpy	–	CH_3CN	70	47
2	CuI	phen	–	CH_3CN	70	59
3	CuI	Me_2phen	–	CH_3CN	70	41
4	CuCl	phen	–	CH_3CN	70	41
5	CuBr	phen	–	CH_3CN	70	36
6	CuF_2	phen	–	CH_3CN	70	30
7	Cu(OTf)$_2$	phen	–	CH_3CN	70	55
8	–	phen	–	CH_3CN	70	13
9	CuI	phen	–	DMF[c]	70	36
10	CuI	phen	–	CH_2Cl_2	40	31
11	CuI	phen	–	THF[c]	70	54
12	CuI	phen	–	diglyme	70	32
13	CuI	phen	–	DMSO[c]	70	21
14	CuI	phen	–	toluene	70	50
15	CuI	phen	–	DME[c]	70	21
16	CuI	phen	–	dioxane	70	65
17	CuI	phen	18-crown-6	dioxane	70	78
18	CuI	phen	18-crown-6	dioxane	50	76

[a] Reagents and conditions: **1a** (0.10 mmol), CF_3SiMe_3 (0.30 mmol, 3 equiv.), S_8 (0.30 mmol, 3 equiv.), KF (0.30 mmol, 3 equiv.), [Cu] (0.020 mmol), ligand (0.020 mmol), 18-crown-6 (0.20 mmol, 2 equiv.), solvent (2.0 mL), 16 h, under N_2 [b] Yields were determined by ^{19}F NMR spectroscopic analysis with $PhOCF_3$ as the internal standard. [c] DMF = *N*,*N*-dimethylformamide, THF = tetrahydrofuran, DMSO = dimethyl sulfoxide, DME = 1,2-dimethoxyethane.

Subsequently, the established optimal reaction conditions (see Table 1, Entry 18) were employed with other allylic bromides. Various types of substituted cinnamyl bromides were efficiently used in the present catalytic trifluoromethylthiolation to produce the linear allylic isomer regioselectively (see Table 2). The use of cyclic allylic bromide **1a** afforded the desired product **2a** in 67% yield. The reaction of cinnamyl bromide **1b** furnished the desired product **2b** in the high isolated yield of 94% (see Table 2, Entry 2). Furthermore, cinnamyl chloride **1b′** also underwent trifluoromethylthiolation, although it provided product **2b** in 58% yield (see Table 2, Entry 3). The reactions of cinnamyl bromides **1c**–**1e** with a methyl or isopropyl substituent at the *para* or *meta* position of the aromatic ring led to the isolation of products **2c**–**2e**, respectively, in 70–78% yield (see Table 2, Entries 4–6). On the other hand, when *p*-*tert*-butyl- and 2,4,6-trimethyl-substituted cinnamyl bromides **1f** and **1g** were employed in the reaction under the same conditions, relatively moderate yields were attained (58 and 40% yield, respectively; see Table 2, Entries 7 and 8). The electron-rich *o*-methoxy-substituted cinnamyl bromide **1h** worked well (82% yield; see Table 2, Entry 9), but the *m*-methoxy-substituted and the electron-poor *p*-trifluoro-

methyl-substituted substrates afforded a lower product yield (49 and 46% yield, respectively; see Table 2, Entries 10 and 11). Additionally, *p*-methylthio-substituted cinnamyl bromide **1k** enabled the efficient preparation of **2k** in excellent yield (90% yield, see Table 2, Entry 12). It is also worth noting that halogen functional groups were tolerated well in the reaction under the current conditions. The fluoro, chloro, and bromo substituents at the *para* position of cinnamyl bromides **1l**–**1n** underwent the reaction smoothly to give the corresponding products **2l**–**2n** in yields ranging from 53 to 71% (see Table 2, Entries 13–15). The ability to incorporate halogen substituents into the products provides opportunities for further functional manipulations through cross-coupling reactions. Furthermore, the trifluoromethylthiolation could also be performed with geranyl bromide (**1o**), which contained no conjugated aromatic ring, to give **2o** in good yield (78% yield, see Table 2, Entry 16) but with an *E*/*Z* ratio of 11:1. Ethyl 4-bromo-3-ethoxy-2-butenoate, led to the desired product **2p** in 60% yield (determined by ^{19}F NMR analysis; see Table 2, Entry 17).

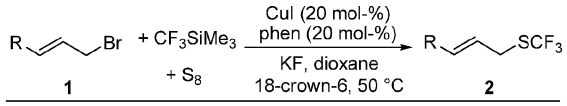
We subsequently proceeded to extend the scope of the reaction to include propargylic chlorides as electrophiles. As shown in Table 3, various propargylic chlorides **3** were examined to give the corresponding propargylic trifluoromethylthiolated products **4** in good yields. A larger amount of CuI (50 mol-%)/phen (50 mol-%) was, however, required. Interestingly, the process proceeded smoothly even in the absence of 18-crown-6. For example, the reaction of 3-phenylpropargyl chloride (**3a**) afforded the desired product **4a** in 81% yield (see Table 3, Entry 1). The reactions of 3-arylpropargyl chlorides **3b** and **3c**, which contained methyl- and *n*-amyl (*n*Am) substitutents at the *para* position of the benzene ring, took place to give the corresponding propargylic trifluoromethylthiolated products **4b** and **4c** in 77 and 85% yields, respectively (see Table 3, Entries 2 and 3). Notably, useful halogenated arenes were accommodated under the conditions. Thus, when *p*-fluoro- or *p*-chloro-substituted 3-arylpropargyl chlorides **3d** and **3e** were subjected to the reaction conditions, **4d** and **4e** were obtained in 77 and 75% yields, respectively (see Table 3, Entries 4 and 5).

To gain better insight into the mechanism of this copper(I)-catalyzed trifluoromethylthiolation of allylic halides, we performed several experiments as shown in Scheme 2.

To test whether any radical intermediates are involved in the reaction mechanism, the radical scavenger TEMPO (2 equiv.) was added to the reaction mixture. An excellent yield of **2b** was obtained (99% yield, determined by ^{19}F NMR analysis), which was similar to that of the reaction without TEMPO (94% yield; see Table 2, Entry 2). The trifluoromethylthiolation was unaffected by the addition of TEMPO, which suggests that no free radical intermediate was generated during the reaction.

On the basis of the above experimental results and our previous studies,[21a,24] a possible mechanism for the catalytic trifluoromethylthiolation of the allylic halides is shown in Scheme 3. The reaction of the copper source with CF_3SiMe_3, elemental sulfur, and KF in the presence of the ligand would easily give copper(I) trifluoromethylthiolate

Table 2. Copper(I)-catalyzed trifluoromethylthiolation of allylic halides.[a]



1 2

Entry	Allylic halides	Product	Yield [%][b]
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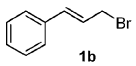
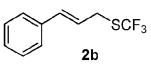
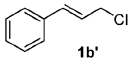
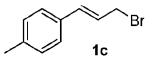
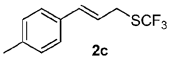
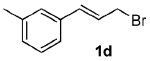
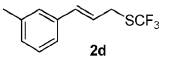
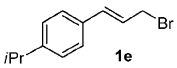
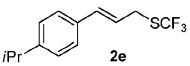
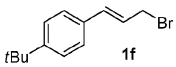
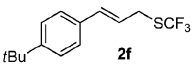
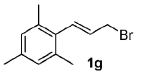
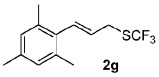
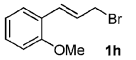
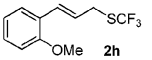
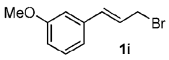
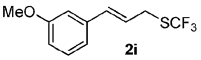
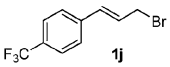
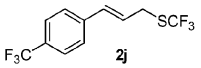
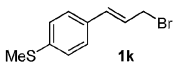
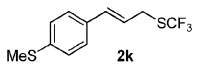
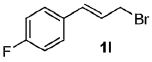
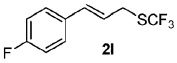
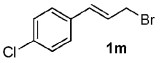
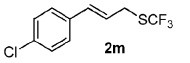
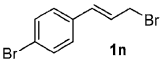
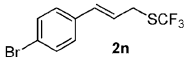
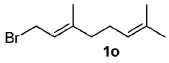
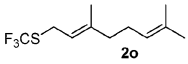
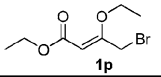
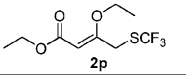
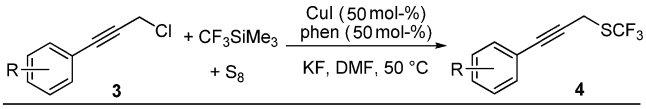
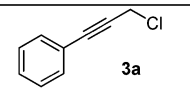
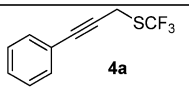
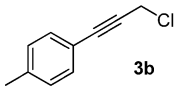
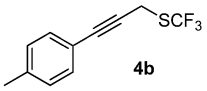
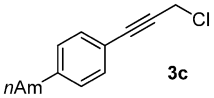
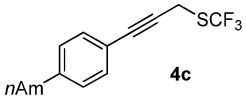
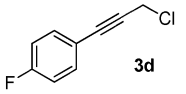
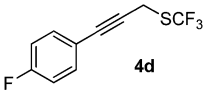
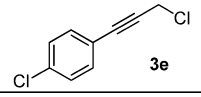
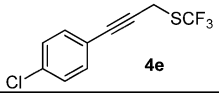
2	 1b	 2b	94
3	 1b'	2b	58[c]
4	 1c	 2c	73
5	 1d	 2d	78
6	 1e	 2e	70
7	 1f	 2f	58
8	 1g	 2g	40
9	 1h	 2h	82
10	 1i	 2i	49
11	 1j	 2j	46
12	 1k	 2k	90
13	 1l	 2l	71
14	 1m	 2m	55
15	 1n	 2n	53
16	 1o	 2o	78
17	 1p	 2p	60[c]

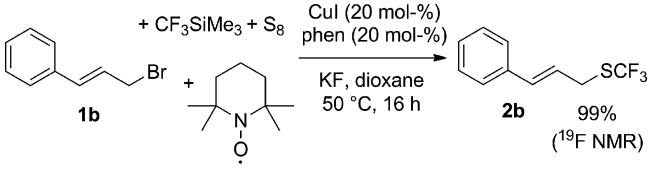
[a] Reagents and conditions: CuI (0.050 mmol), phen (0.050 mmol), allylic halides (0.25 mmol), CF_3SiMe_3 (0.75 mmol), S_8 (0.75 mmol), KF (0.75 mmol), 18-crown-6 (0.50 mmol), dioxane (2.0 mL), 50 °C, 16 h, under N_2. [b] Isolated yields. [c] Yield determined by ^{19}F NMR spectroscopic analysis.

Table 3. Copper(I)-catalyzed trifluoromethylthiolation of propargylic chlorides.[a]

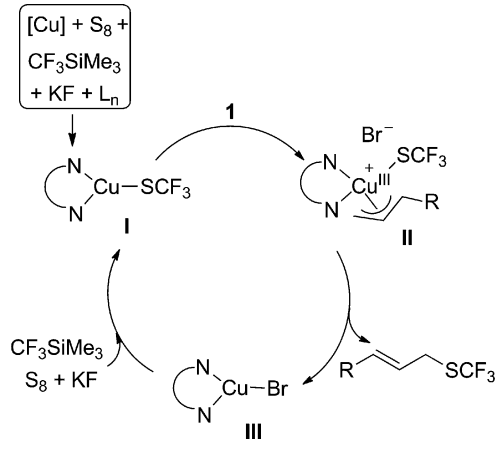


Entry	Propargylic bromide	Product	Yield [%][b]
1	 **3a**	 **4a**	81
2	 **3b**	 **4b**	77
3	 **3c**	 **4c**	85
4	 **3d**	 **4d**	77
5	 **3e**	 **4e**	75

[a] Reagents and conditions: CuI (0.25 mmol), phen (0.25 mmol), propargylic chloride (0.50 mmol), CF_3SiMe_3 (2.5 mmol), S_8 (2.5 mmol), KF (2.5 mmol), DMF (2.0 mL), 50 °C, 16 h, under N_2. [b] Isolated yields.



Scheme 2. Radical scavenger experiment with 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO).



Scheme 3. Proposed reaction mechanism.

complex **I**.[24] Then, the oxidative addition of allylic halide **1** to **I** would afford allylcopper(III) species **II**.[11a,25] The subsequent reductive elimination of **II** gives the desired trifluoromethylthiolated product and generates **III**. Intermediate **I** is then regenerated by the reaction of **III** with CF_3SiMe_3, S_8, and KF.

Conclusions

In summary, an efficient protocol has been developed for the synthesis of allylic and propargylic trifluoromethyl thioethers through the copper(I)-catalyzed trifluoromethylthiolation of allylic bromides and propargylic chlorides, respectively, with elemental sulfur and CF_3SiMe_3. This reaction is tolerant to a reasonable range of functional groups and provides facile access to a broad selection of trifluoromethylthiolated allylic and propargylic products in moderate to excellent yields with high stereo- and regioselectivity. The reaction mechanism that has been proposed involves an allylcopper(III) intermediate. The scope and synthetic applications of this transformation are under investigation.

Experimental Section

General Methods: The ^{1}H, ^{19}F, and ^{13}C NMR spectroscopic data were recorded with a Bruker AVIII 400 spectrometer. The ^{1}H and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane. The ^{19}F NMR chemical shifts were reported relative to $CFCl_3$ as the external standard, and low field is positive. Coupling constants (*J*) are reported in Hertz (Hz). The solvent peak was used as the internal reference for ^{1}H NMR (residual $CHCl_3$ at δ = 7.26 ppm) and ^{13}C NMR ($CDCl_3$ at δ = 77.0 ppm). The abbreviations that were used to describe the multiplicity of the signals are s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br. (broad). HRMS was performed with a Waters GCT-TOF at the Shanghai Institute of Organic Chemistry. Allylic bromides **1c**–**1n**[26] and propargylic chlorides **3a**–**3e**[27] were prepared according to published procedures. Other reagents were received from commercial sources. Solvents were freshly dried and degassed prior to use according to published procedures.[28] Purifications were performed by flash column chromatography using Merck silica gel 60.

General Procedure for Copper(I)-Catalyzed Trifluoromethylthiolation of Allylic Halides: In a dry glove box, CuI (19.0 mg, 0.10 mmol), phen (18.0 mg, 0.10 mmol), KF (87.2 mg, 1.5 mmol), S_8 (48.0 mg, 1.5 mmol), 18-crown-6 (264.3 mg, 1.0 mmol), CF_3SiMe_3 (222 μL, 1.5 mmol), and dioxane (2.5 mL) were added to an oven-dried 5 mL test tube that was equipped with a Teflon screw cap. The mixture was stirred at room temp. for 2 min, and then the allylic halide (0.50 mmol) was added. The tube was sealed, and the solution was placed into a preheated 50 °C oil bath for 16 h. The tube was removed from the oil bath and cooled to room temp. The reaction mixture was filtered through a layer of Celite, which was rinsed with diethyl ether. Water (5.0 mL) was added to the filtrate at 0 °C. The resulting mixture was extracted with ethyl ether (3 × 10 mL), and the combined organic layers were washed with water (3 × 10 mL) and then dried with magnesium sulfate. The solvent was removed by rotary evaporation using an ice bath, and the residue was purified by chromatography on a silica gel column (pentane) to give the product.

Cyclohex-2-enyl(trifluoromethyl)sulfane (2a): Colorless oil (61 mg, 67% yield); R_f = 0.83 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.96–5.91 (m, 1 H), 5.76–5.69 (m, 1 H), 4.01–3.95 (m, 1 H), 2.15–1.94 (m, 4 H), 1.88–1.77 (m, 1 H), 1.76–1.66 (m, 1 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –40.1 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 132.4 (s), 131.0 (q, J = 308.1 Hz), 125.0 (s), 41.2 (s), 29.8 (s), 24.6 (s), 18.8 (s) ppm. IR (KBr): $\tilde{\nu}$ = 2930, 2358, 2340, 1128, 1035, 748 cm^{-1}. GC–MS: m/z (%) = 182 $[M]^+$, 81 (100) $[M - SCF_3]^+$. HRMS (EI): calcd. for $C_7H_9F_3S$ 182.0379; found 182.0380.

(*E*)-Cinnamyl(trifluoromethyl)sulfane (2b):[21a] Colorless oil (102 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.29 (m, 5 H), 6.65 (d, J = 15.7 Hz, 1 H), 6.32–6.22 (m, 1 H), 3.76 (d, J = 7.4 Hz, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –40.8 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 136.1 (s), 134.4 (s), 130.8 (q, J = 306.9 Hz), 128.7 (s), 128.2 (s), 126.5 (s), 123.0 (s), 32.7 (q, J = 2.2 Hz) ppm.

(*E*)-[3-(*p*-Tolyl)allyl](trifluoromethyl)sulfane (2c):[21a] Colorless oil (85 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, J = 8.0 Hz, 2 H), 7.17 (d, J = 8.0 Hz, 2 H), 6.61 (d, J = 15.7 Hz, 1 H), 6.25–6.16 (m, 1 H), 3.75 (d, J = 7.4 Hz, 2 H), 2.38 (s, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –40.9 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.1 (s), 134.3 (s), 133.3 (s), 130.9 (q, J = 306.9 Hz), 129.4 (s), 126.4 (s), 121.9 (s), 32.8 (q, J = 2.4 Hz), 21.2 (s) ppm.

(*E*)-[3-(*m*-Tolyl)allyl](trifluoromethyl)sulfane (2d):[21a] Colorless oil (90 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.19 (m, 3 H), 7.13 (d, J = 7.2 Hz, 1 H), 6.61 (d, J = 15.7 Hz, 1 H), 6.30–6.20 (m, 1 H), 3.75 (d, J = 7.4 Hz, 2 H), 2.39 (s, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –40.9 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.3 (s), 136.1 (s), 134.5 (s), 130.9 (q, J = 306.9 Hz), 128.9 (s), 128.6 (s), 127.2 (s), 123.7 (s), 122.7 (s), 32.7 (q, J = 2.3 Hz), 21.3 (s) ppm.

(*E*)-[3-(4-Isopropylphenyl)allyl](trifluoromethyl)sulfane (2e):[21a] Colorless oil (91 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, J = 8.0 Hz, 2 H), 7.23 (d, J = 8.0 Hz, 2 H), 6.62 (d, J = 15.7 Hz, 1 H), 6.26–6.16 (m, 1 H), 3.75 (d, J = 7.4 Hz, 2 H), 2.94 (hept, J = 6.9 Hz, 1 H), 1.29 (d, J = 6.9 Hz, 6 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –40.8 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.1 (s), 134.3 (s), 133.7 (s), 130.8 (q, J = 306.9 Hz), 126.8 (s), 126.6 (s), 122.0 (s), 33.9 (s), 32.8 (q, J = 2.4 Hz), 23.9 (s) ppm.

(*E*)-{3-[4-(*tert*-Butyl)phenyl]allyl}(trifluoromethyl)sulfane (2f):[21a] Colorless oil (79 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, J = 8.3 Hz, 2 H), 7.35 (d, J = 8.3 Hz, 2 H), 6.62 (d, J = 15.6 Hz, 1 H), 6.27–6.17 (m, 1 H), 3.75 (d, J = 7.4 Hz, 2 H), 1.36 (s, 9 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –40.9 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.4 (s), 134.2 (s), 133.4 (s), 130.9 (q, J = 304.8 Hz), 126.3 (s), 125.6 (s), 122.1 (s), 34.6 (s), 32.8 (q, J = 2.4 Hz), 31.3 (s) ppm.

(*E*)-(3-Mesitylallyl)(trifluoromethyl)sulfane (2g): Brown oil (52 mg, 40% yield); R_f = 0.77 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (s, 2 H), 6.64 (d, J = 15.9 Hz, 1 H), 5.84–5.75 (m, 1 H), 3.79 (d, J = 7.2 Hz, 2 H), 2.32 (d, J = 5.6 Hz, 9 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –40.7 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 136.7 (s), 136.0 (s), 132.8 (s), 132.2 (s), 130.8 (q, J = 306.9 Hz), 128.7 (s), 128.1 (s), 33.0 (q, J = 2.3 Hz), 21.0 (s), 20.8 (s) ppm. IR (KBr): $\tilde{\nu}$ = 2922, 2861, 1612, 1481, 1446, 1241, 1114, 971, 854, 756 cm^{-1}. GC–MS: m/z (%) = 260 $[M]^+$, 159 (100) $[M - SCF_3]^+$. HRMS (EI): calcd. for $C_{13}H_{15}F_3S$ 260.0847; found 260.0848.

(*E*)-[3-(2-Methoxyphenyl)allyl](trifluoromethyl)sulfane (2h):[21a] Colorless oil (102 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, J = 7.6 Hz, 1 H), 7.28 (t, J = 7.8 Hz, 1 H), 7.00–6.93 (m, 2 H), 6.91 (d, J = 8.3 Hz, 1 H), 6.33–6.24 (m, 1 H), 3.89 (s, 3 H), 3.77 (d, J = 7.4 Hz, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –40.9 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.8 (s), 130.9 (q, J = 306.9 Hz), 129.5 (s), 129.2 (s), 127.2 (s), 125.2 (s), 123.5 (s), 120.7 (s), 111.0 (s), 55.5 (s), 33.2 (q, J = 2.3 Hz) ppm.

(*E*)-[3-(3-Methoxyphenyl)allyl](trifluoromethyl)sulfane (2i):[21a] Colorless oil (61 mg, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.27 (m, 1 H), 7.00 (d, J = 7.6 Hz, 1 H), 6.93 (s, 1 H), 6.85 (dd, J = 8.2, 2.3 Hz, 1 H), 6.60 (d, J = 15.7 Hz, 1 H), 6.30–6.19 (m, 1 H), 3.85 (s, 3 H), 3.74 (d, J = 7.4 Hz, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –40.9 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.8 (s), 137.5 (s), 134.2 (s), 130.8 (q, J = 306.9 Hz), 129.7 (s), 123.3 (s), 119.2 (s), 113.7 (s), 111.8 (s), 55.3 (s), 32.7 (q, J = 2.2 Hz) ppm.

(*E*)-(Trifluoromethyl){3-[4-(trifluoromethyl)phenyl]allyl}sulfane (2j):[21a] Colorless oil (66 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 8.2 Hz, 2 H), 7.49 (d, J = 8.1 Hz, 2 H), 6.66 (d, J = 15.7 Hz, 1 H), 6.41–6.31 (m, 1 H), 3.76 (d, J = 7.3 Hz, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –40.8 (s, 3 F), –62.6 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.5 (s), 132.8 (s), 130.7 (q, J = 307.0 Hz), 129.9 (q, J = 32.5 Hz), 126.7 (s), 126.0 (s), 125.6 (q, J = 3.9 Hz), 124.1 (q, J = 271.9 Hz), 32.4 (q, J = 2.4 Hz) ppm.

(*E*)-Methyl{4-[3-(trifluoromethylthio)prop-1-enyl]phenyl}sulfane (2k): White powder (119 mg, 90% yield); m.p. 39–41 °C. R_f = 0.65 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, J = 8.3 Hz, 2 H), 7.24 (d, J = 8.3 Hz, 2 H), 6.58 (d, J = 15.7 Hz, 1 H), 6.27–6.17 (m, 1 H), 3.74 (d, J = 7.4 Hz, 2 H), 2.52 (s, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –40.8 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.7 (s), 133.7 (s), 132.9 (s), 130.9 (q, J = 306.9 Hz), 126.9 (s), 126.5 (s), 122.3 (s), 32.8 (q, J = 2.2 Hz), 15.6 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3021, 2921, 1431, 1404, 1234, 1112, 967, 824, 801, 518 cm^{-1}. GC–MS: m/z (%) = 264 $[M]^+$, 163 (100) $[M - SCF_3]^+$. HRMS (EI): calcd. for $C_{11}H_{11}F_3S_2$ 264.0254; found 264.0253.

(*E*)-[3-(4-Fluorophenyl)allyl](trifluoromethyl)sulfane (2l): Colorless oil (84 mg, 71% yield); R_f = 0.65 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.34 (m, 2 H), 7.08–7.01 (m, 2 H), 6.59 (d, J = 15.7 Hz, 1 H), 6.22–6.10 (m, 1 H), 3.73 (d, J = 7.4 Hz, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –40.8 (s, 3 F), –113.5 (m, 1 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.6 (d, J = 247.6 Hz), 133.1 (s), 132.3 (d, J = 3.4 Hz), 130.8 (q, J = 306.9 Hz), 128.1 (d, J = 8.1 Hz), 122.8 (d, J = 2.3 Hz), 115.6 (d, J = 21.7 Hz), 32.6 (q, J = 2.4 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2360, 1603, 1509, 1233, 1112, 965, 841, 811, 755, 516 cm^{-1}. GC–MS: m/z (%) = 236 $[M]^+$, 135 (100) $[M - SCF_3]^+$. HRMS (EI): calcd. for $C_{10}H_8F_4S_1$ 236.0283; found 236.0281.

(*E*)-[3-(4-Chlorophenyl)allyl](trifluoromethyl)sulfane (2m):[21a] Colorless oil (69 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 4 H), 6.58 (d, J = 15.7 Hz, 1 H), 6.29–6.17 (m, 1 H), 3.73 (d, J = 7.3 Hz, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –40.8 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.6 (s), 133.8 (s), 133.1 (s), 130.7 (q, J = 307.0 Hz), 128.9 (s), 127.7 (s), 123.8 (s), 32.6 (q, J = 2.4 Hz) ppm.

(*E*)-[3-(4-Bromophenyl)allyl](trifluoromethyl)sulfane (2n):[21a] Colorless oil (78 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, J = 8.3 Hz, 2 H), 7.26 (d, J = 8.3 Hz, 2 H), 6.56 (d, J = 15.7 Hz, 1 H), 6.31–6.16 (m, 1 H), 3.73 (d, J = 7.4 Hz, 2 H) ppm. ^{19}F NMR

(376 MHz, $CDCl_3$): δ = –40.8 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 135.0 (s), 133.1 (s), 131.8 (s), 130.8 (q, J = 307.0 Hz), 128.0 (s), 123.9 (s), 122.0 (s), 32.6 (q, J = 2.4 Hz) ppm.

(*E*)-(3,7-Dimethylocta-2,6-dienyl)(trifluoromethyl)sulfane (2o):[21a] Colorless oil (93 mg, 78% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.30 (t, J = 7.8 Hz, 1 H), 5.09 (t, J = 6.7 Hz, 1 H), 3.59 (d, J = 7.9 Hz, 2 H), 2.09 (dt, J = 12.8, 5.9 Hz, 4 H), 1.72 (s, 6 H), 1.63 (s, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –41.4 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.1 (s), 132.0 (s), 131.0 (q, J = 306.7 Hz), 123.6 (s), 117.0 (s), 39.5 (s), 28.0 (q, J = 2.3 Hz), 26.2 (s), 25.7 (s), 17.7 (s), 16.0 (s) ppm.

(*Z*)-Ethyl 3-Ethoxy-4-(trifluoromethylthio)but-2-enoate (2p): Colorless oil (60% yield by ^{19}F NMR analysis; 18 mg, 14% yield); R_f = 0.45 (pentane). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.10 (s, 1 H), 4.17 (dd, J = 8.0, 6.2 Hz, 2 H), 4.15 (s, 2 H), 3.89 (q, J = 7.0 Hz, 2 H), 1.37 (t, J = 7.0 Hz, 3 H), 1.28 (t, J = 8.1, 6.3 Hz, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –41.6 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.1 (s), 167.0 (s), 130.8 (q, J = 306.7 Hz), 92.8 (s), 64.7 (s), 59.9 (s), 29.8 (q, J = 2.3 Hz), 14.2 (s), 13.8 (s) ppm. IR (KBr): $\tilde{\nu}$ = 2924, 1701, 1624, 1395, 1373, 1350, 1303, 1257, 1114, 1053, 816, 756 cm^{-1}. GC–MS: m/z (%) = 258 $[M]^+$, 157 (100) $[M – SCF_3]^+$. HRMS (EI): calcd. for $C_9H_{13}F_3O_3S$ 258.0538; found 258.0536.

Procedure for Copper(I)-Catalyzed Trifluoromethylthiolation of Cinnamyl Bromide (1b) in the Presence of TEMPO: In a dry glove box, CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), KF (17.4 mg, 0.30 mmol), S_8 (9.6 mg, 0.30 mmol), 18-crown-6 (52.9 mg, 0.20 mmol), TEMPO (31.3 mg, 0.20 mmol), and dioxane (1.0 mL) were added to a oven-dried 5 mL test tube that was equipped with a Teflon screw cap. CF_3SiMe_3 (45 μL, 0.30 mmol) was then added by syringe to the mixture. The reaction was stirred at room temp. for 2 min, and then cinnamyl bromide (**1b**, 19.7 mg, 0.10 mmol) was added. The tube was sealed, and the solution was placed into a preheated 50 °C oil bath for 16 h. The tube was removed from the oil bath and then cooled to room temp. (Trifluoromethoxy)benzene (10 μL) was then added as an internal standard. The reaction mixture was filtered through a layer of Celite, and the filtrate was analyzed by ^{19}F NMR spectoscopy. The yield of **2b** was calculated to be 99%.

General Procedure for Copper(I)-Catalyzed Trifluoromethylthiolation of Propargylic Chlorides: In a dry glove box, CuI (48.0 mg, 0.25 mmol), phen (45.0 mg, 0.25 mmol), KF (145.0 mg, 2.5 mmol), S_8 (80.0 mg, 2.5 mmol), CF_3SiMe_3 (370 μL, 2.5 mmol), and DMF (2.5 mL) were added to an oven-dried 5 mL test tube that was equipped with a Teflon screw cap. The mixture was stirred at room temp. for 2 min, and then the propargylic chloride (0.50 mmol) was added. The tube was sealed, and the solution was placed into a preheated 50 °C oil bath for 16 h. The tube was removed from the oil bath and cooled to room temp. The reaction mixture was filtered through a layer of Celite, which was rinsed with diethyl ether. Water (5.0 mL) was added to the filtrate at 0 °C. The resulting mixture was extracted with ethyl ether (3 × 10 mL), and the combined organic layers were washed with water (3 × 10 mL) and then dried with magnesium sulfate. The solvent was removed by rotary evaporation using an ice bath, and the residue was purified by chromatography on a silica gel column (pentane) to give the product.

(3-Phenylprop-2-ynyl)(trifluoromethyl)sulfane (4a): Brown oil (88 mg, 81% yield); R_f = 0.73 (pentane). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.41 (m, 2 H), 7.39–7.29 (m, 3 H), 3.92 (s, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –41.8 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 131.8 (s), 130.4 (q, J = 307.5 Hz), 128.7 (s), 128.4 (s), 122.2 (s), 84.6 (s), 82.2 (s), 19.5 (q, J = 3.4 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3059, 2927, 1491, 1443, 1271, 1243, 1113, 756, 690 cm^{-1}. GC–MS: m/z (%) = 216 $[M]^+$, 115 (100) $[M – SCF_3]^+$. HRMS (EI): calcd. for $C_{10}H_7F_3S$ 216.0221; found 216.0218.

(3-*p*-Tolylprop-2-ynyl)(trifluoromethyl)sulfane (4b): Brown oil (89 mg, 77% yield); R_f = 0.73 (pentane). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38 (m, 2 H), 7.17 (m, 2 H), 3.94 (s, 2 H), 2.40 (s, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –41.8 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.9 (s), 131.6 (s), 130.4 (q, J = 307.5 Hz), 129.1 (s), 119.2 (s), 84.8 (s), 81.4 (s), 21.4 (s), 19.5 (q, J = 3.3 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3031, 2924, 2360, 2342, 1510, 1457, 1409, 1275, 1245, 1114, 1021, 816, 756, 693 cm^{-1}. GC–MS: m/z (%) = 230 $[M]^+$, 129 (100) $[M – SCF_3]^+$. HRMS (EI): calcd. for $C_{11}H_9F_3S$ 230.0377; found 230.0373.

[3-(4-Pentylphenyl)prop-2-ynyl](trifluoromethyl)sulfane (4c): Brown oil (126 mg, 85% yield); R_f = 0.68 (pentane). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, J = 8.1 Hz, 2 H), 7.16 (d, J = 8.1 Hz, 2 H), 3.92 (s, 2 H), 2.71–2.46 (m, 2 H), 1.69–1.57 (m, 4 H), 1.39–1.28 (m, 3 H), 0.92 (t, J = 6.9 Hz, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –41.9 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.9 (s), 131.7 (s), 130.4 (q, J = 307.5 Hz), 128.5 (s), 119.4 (s), 84.8 (s), 81.4 (s), 35.9 (s), 31.4 (s), 30.9 (s), 22.5 (s), 19.6 (q, J = 3.4 Hz), 14.0 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3030, 2959, 2930, 2858, 2359, 2341, 2225, 1511, 1466, 1275, 1243, 1114, 837, 756 cm^{-1}. GC–MS: m/z (%) = 285 $[M – H]^+$, 185 (100) $[M – SCF_3]^+$. HRMS (EI): calcd. for $C_{15}H_{17}F_3S$ 286.1003; found 286.0999.

[3-(4-Fluorophenyl)prop-2-ynyl](trifluoromethyl)sulfane (4d): Yellow oil (90 mg, 77% yield); R_f = 0.68 (pentane). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.44 (dd, J = 8.7, 5.4 Hz, 2 H), 7.03 (t, J = 8.7 Hz, 2 H), 3.90 (s, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –41.9 (s, 3 F), –110.2 (m, 1 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.8 (d, J = 250.1 Hz), 133.7 (d, J = 8.4 Hz), 130.4 (q, J = 307.5 Hz), 118.4 (d, J = 3.5 Hz), 115.6 (d, J = 22.1 Hz), 83.5 (s), 82.0 (s), 19.3 (q, J = 3.4 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3059, 2927, 2225, 1491, 1443, 1271, 1243, 1113, 756, 690 cm^{-1}. GC–MS: m/z (%) = 233 $[M – H]^+$, 133 (100) $[M – SCF_3]^+$. HRMS (EI): calcd. for $C_{10}H_6F_4S$ 234.0126; found 234.0125.

[3-(4-Chlorophenyl)prop-2-ynyl](trifluoromethyl)sulfane (4e): Yellow oil (94 mg, 75% yield); R_f = 0.76 (pentane). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.0 Hz, 2 H), 7.32 (d, J = 8.0 Hz, 2 H), 3.90 (s, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –41.8 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.8 (s), 133.0 (s), 130.3 (q, J = 307.5 Hz), 128.7 (s), 120.7 (s), 83.4 (s), 83.3 (s), 19.4 (q, J = 3.4 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2962, 2360, 2341, 1490, 1275, 1243, 1112, 1015, 827, 757 cm^{-1}. GC–MS: m/z (%) = 249 $[M – H]^+$, 149 (100) $[M – SCF_3]^+$. HRMS (EI): calcd. for $C_{10}H_6ClF_3S$ 249.9831; found 249.9833.

Supporting Information (see footnote on the first page of this article): Copies of the ^1H, ^{19}F, and ^{13}C NMR spectra of all products.

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