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Note

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Synthesis of Vinyl Trifluoromethyl Thioethers *via* Copper-Mediated Trifluoromethylthiolation of Vinyl Bromides

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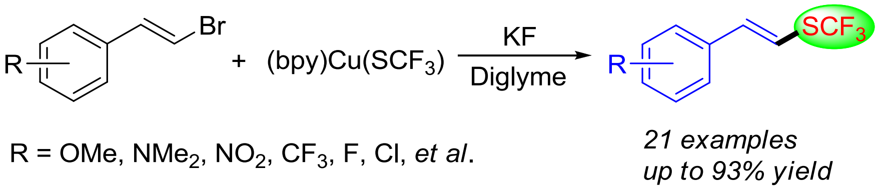
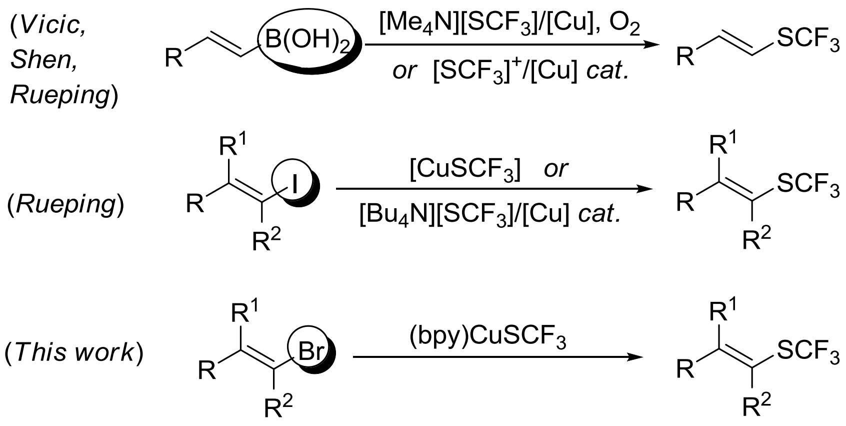
ABSTRACT:



A copper-mediated trifluoromethylthiolation of vinyl bromides has been developed. This method provides ready access to vinyl trifluoromethyl thioethers in good to high yields from simple, inexpensive starting materials. A broad substrate scope is achieved and the reaction is compatible with various functional groups, including cyano, nitro, trifluoromethyl, alkoxy, amino, halide, and heterocyclic groups.

Fluorine containing compounds are ubiquitous in pharmaceuticals, agrochemicals, and advanced materials.[1,2] Their fluorine moieties offer unusual chemical and physical properties, which can profoundly enhance the biological activity and metabolic stability.[3,4] The trifluoromethylthio group (CF_3S–) is of special interest, as it has one of the highest Hansch hydrophobicity parameter values ($\pi_R = 1.44$).[5] As a consequence, great synthetic efforts have been exerted to develop efficient methods for the incorporation of CF_3S– group into organic molecules.[6-11] In particular, transition-metal-catalyzed or -mediated trifluoromethylthiolation have experienced impressive progress and growth in recent years. For instance, Cu-catalyzed and -mediated trifluoromethylthiolation of aryl-,[12-14] and alkyl boronic acids,[15] aryl halides,[16] arenediazonium salts,[17] or related Cu-,[18,19,20] and Pd-promoted[21] trifluoromethylthiolation through the direct functionalization of C–H bonds, Ag-catalyzed decarboxylative trifluoromethylthiolation of aliphatic carboxylic acids,[22] Pd,[23] and Ni-catalyzed trifluoromethylthiolation of aryl halides,[24] have provided attractive access to compounds bearing C_{sp2}–SCF_3 and C_{sp3}–SCF_3, and C_{sp}–SCF_3 bonds.

However, synthetic processes for the direct construction of C_{vinyl}–SCF_3 bonds *via* transition-metal-catalyzed or -mediated trifluoromethylthiolation have not been well developed (Scheme 1). The Vicic,[13] Shen,[25] and Rueping[14] groups independently reported Cu-mediated and -catalyzed trifluoromethylthiolation of vinyl boronic acids to form vinyl trifluoromethyl thioethers. Most recently, Rueping and co-workers also developed a Cu-catalyzed trifluoromethylthiolation of vinyl iodides.[26] However, many of these procedures often require vinylboron compounds or vinyl iodides as substrates, and/or the use of electrophilic type trifluoromethylthiolation reagent.



Scheme 1. Methods for Preparation of Vinyl Trifluoromethyl Thioethers

We have therefore sought to develop a highly facile and cost-effective route to vinyl trifluoromethyl thioethers *via* copper-mediated trifluoromethylthiolation of vinyl bromides.

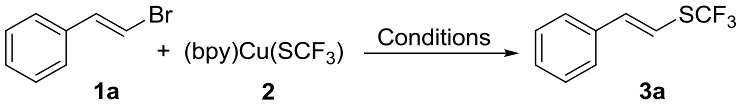
Copper-promoted coupling of vinyl bromides or iodides with *S*-nucleophiles has proven to be powerful method for synthesis of vinyl sulfides.[27-32] However, the coupling of vinyl bromides with SCF_3^- to give vinyl trifluoromethyl thioether products is a challenging task because of the reduced nucleophilicity of the SCF_3 anion.[26]

As part of our continuing studies on copper-mediated trifluoromethylthiolation,[33-38] we recently developed a novel C_{aryl}–SCF_3 bond formation mediated by a copper(I) trifluoromethylthiolate complex (bpy)Cu(SCF_3) (**2**;

bpy = 2,2'-bipyridine).[33] This complex reacted with various aryl iodides or activated aryl bromides to afford aryl trifluoromethyl thioethers in modest to excellent yields. These results encourage us to probe the feasibility of performing the trifluoromethylthiolation of more challenging substrates, such as vinyl bromides, using the copper reagent **2**.

Initially, trifluoromethylthiolation of phenylvinyl bromide (**1a**) with **2** to form styrenyl trifluoromethyl thioethers (**3a**) was investigated. The reaction first was conducted in CH_3CN at 100 °C for 16 h providing the desired product **3a** in 23% yield (Table 1, entry 1). Next, we examined the possible influence of some parameters like solvent and additive on the outcome of the reaction. Other solvents, such as DMF, DMSO and dioxane, were also ineffective (Table 1, entries 2, 3 and 6). When the solvent was changed to toluene and THF, the desired product **3a** was obtained in yields of 50% and 59%, respectively (Table 1, entries 4, and 5). It was found that diglyme was an optimal solvent, affording **3a** in 64% yield (Table 1, entry 7). Thus, diglyme was chosen as a solvent of choice for further studies. Since the addition of alkali metal fluorides could significantly enhance the reaction efficiency probably by facilitating the formation of active intermediate,[36,37] various these fluorides were screened in the reaction (Table 1, entries 8–13). It was found that KF was superior to all other screened additives for the reaction (Table 1, entry 10). Increasing the quantity of KF from 2 equiv to 4 equiv resulted in a higher yield of 80% (Table 1, entry 14). The reaction time was also examined. The results indicated that the yield of **3a** increased from 80% to 92% when the reaction time was prolonged from 16 to 24 h (Table 1, entry 15). Furthermore, lowering the reaction temperature to 80 °C resulted in a decreased yield of 71% (Table 1, entry 16).

Table 1. Optimization of the Trifluoromethylthiolation of Phenylvinyl Bromide [a]

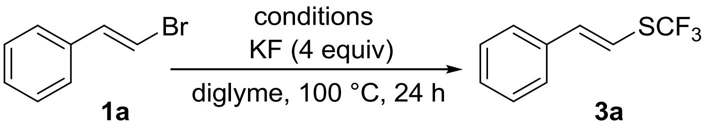


entry	additive (equiv)	solvent	temp (°C)	time (h)	yield (%)[b]
1		CH_3CN	100	16	23
2		DMF	100	16	28
3		DMSO	100	16	41
4		toluene	100	16	50
5		THF	100	16	59
6		dioxane	100	16	35
7		diglyme	100	16	64
8	LiF (2)	diglyme	100	16	63
9	NaF (2)	diglyme	100	16	57
10	KF (2)	diglyme	100	16	74
11	CsF (2)	diglyme	100	16	69
12	AgF (2)	diglyme	100	16	52
13	*n*-Bu_4NF (2)	diglyme	100	16	13
14	KF (4)	diglyme	100	16	80
15	KF (4)	diglyme	100	24	92
16	KF (4)	diglyme	80	24	71

[a] Reaction conditions: **1a** (0.050 mmol), **2** (0.060 mmol), solvent (1.0 mL), N_2. [b] The yield was determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as internal standard.

Subsequently, a comparison with other trifluoromethylthiolation reagents was performed (Table 2). Reaction with (phen)Cu(SCF$_3$) (phen = phenanthroline) generated product **3a** in moderate yield (55%; Table 2, entry 2). Similar behaviors were also observed in the previously reported for trifluoromethylthiolation of aryl iodides.[33] Moreover in the case of the Cu(I) catalyzed trifluoromethylthiolation using [Bu$_4$N][SCF$_3$] reagent, the reaction produced lower yield of **3a** (30%; Table 2, entry 3). This result shows a higher reactivity of (bpy)Cu(SCF$_3$) (**2**) compared to other reagents (Table 2, entry 1).

Table 2. Comparison of Copper-Mediated/-Catalyzed Trifluoromethylthiolation of Phenylvinyl Bromide.

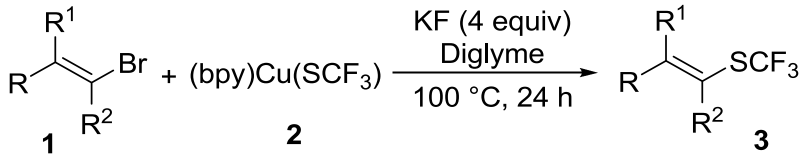


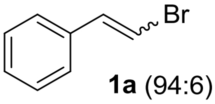
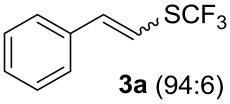
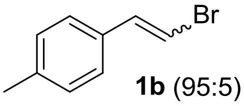
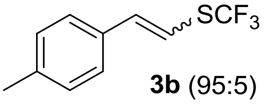
entry	conditions	yield (%)[a]
1	(bpy)Cu(SCF$_3$) (**2**) (1.2 equiv)	92
2	(phen)Cu(SCF$_3$) (1.2 equiv)	55
3	[Bu$_4$N][SCF$_3$] (2 equiv), CuI (20 mol-%), phen (20 mol-%)	30

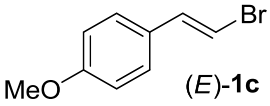
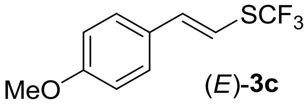
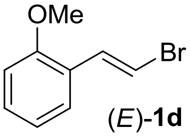
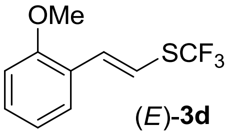
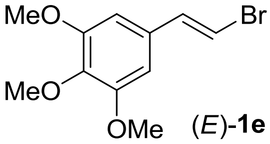
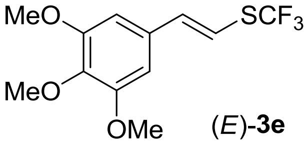
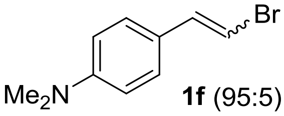
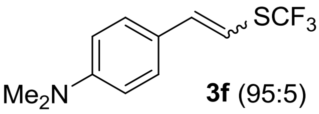
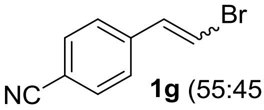
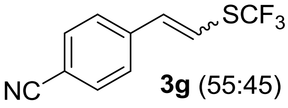
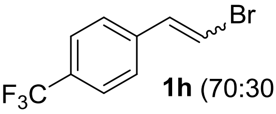
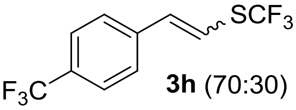
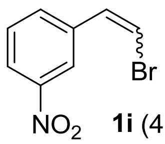
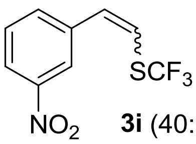
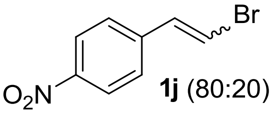
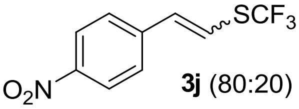
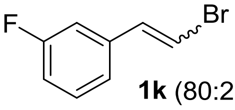
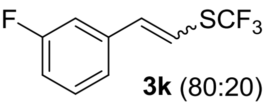
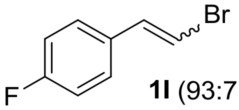
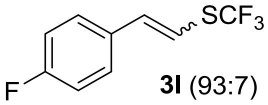
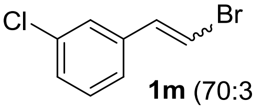
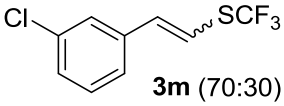
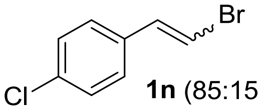
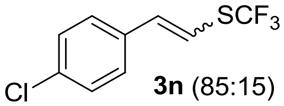
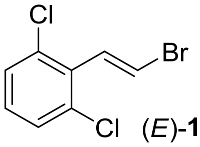
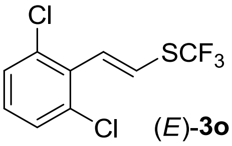
[a] The yield was determined by ^{19}F NMR spectroscopy with PhOCF$_3$ as internal standard.

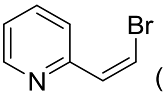
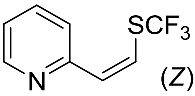
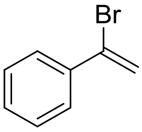
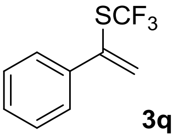
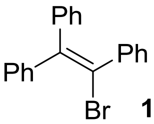
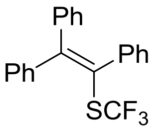
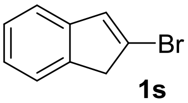
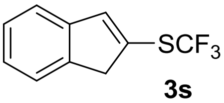
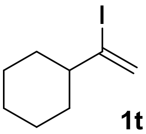
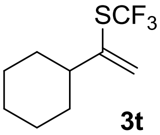
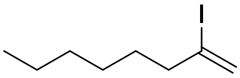
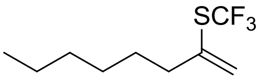
The generality of the reaction conditions was next tested on a variety of alkenyl bromides as illustrated in Table 3. A structurally diverse series of substituted β-bromostyrene underwent trifluoromethylthiolation with **2** by this procedure to produce the corresponding styrenyl trifluoromethyl thioethers in good to excellent yields. Moreover, no aryl acetylenes or homocoupled side products were observed. The products were characterized by IR, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, MS and HRMS spectra. The stereochemistry, easily assignable by the ^{1}H NMR coupling constant value of the olefinic protons (*trans* configuration: J = 15.0–15.4 Hz; *cis* configuration: J = 10.6–10.7 Hz), is in accordance with the results obtained in closely related molecules.[13,25,26] It also is worth noting that the *E*/*Z* stereochemistry of the styrenyl trifluoromethyl thioether bond corresponds to the starting vinyl bromide (Table 3, entries 1–16).

Table 3. Substrate Scope of Trifluoromethylthiolation of Vinyl Bromides [a]



entry	vinyl halides **1** (*E*/*Z*)	products **3** (*E*/*Z*)[b]	yield (%)
1	 **1a** (94:6)	 **3a** (94:6)	90
2	 **1b** (95:5)	 **3b** (95:5)	92

3	 (*E*)-**1c**	 (*E*)-**3c**	89
4	 (*E*)-**1d**	 (*E*)-**3d**	91
5	 (*E*)-**1e**	 (*E*)-**3e**	75
6	 **1f** (95:5)	 **3f** (95:5)	93
7	 **1g** (55:45)	 **3g** (55:45)	80
8	 **1h** (70:30)	 **3h** (70:30)	79
9	 **1i** (40:60)	 **3i** (40:60)	81
10	 **1j** (80:20)	 **3j** (80:20)	76
11	 **1k** (80:20)	 **3k** (80:20)	77
12	 **1l** (93:7)	 **3l** (93:7)	85
13	 **1m** (70:30)	 **3m** (70:30)	79
14	 **1n** (85:15)	 **3n** (85:15)	83
15	 (*E*)-**1o**	 (*E*)-**3o**	62

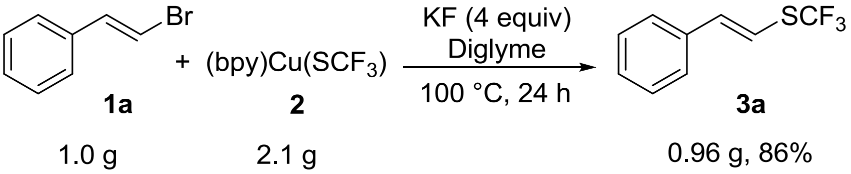
16	 (*Z*)-**1p**	 (*Z*)-**3p**	78
17	 **1q**	 **3q**	73
18	 **1r**	 **3r**	72
19	 **1s**	 **3s**	23[c]
20	 **1t**	 **3t**	70[c]
21	 **1u**	 **3u**	61[c]

[a] Reaction conditions: **1** (0.50 mmol), **2** (0.60 mmol), KF (2.0 mmol), diglyme (5.0 mL), N_2. [b] The E/Z isomer ratio was determined from the ^{19}F NMR analysis. [c] The yield was determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as internal standard.

For example, phenylvinyl bromides **1a** and **1b** afforded the corresponding products **3a** and **3b** in 90% and 92% yields, respectively (Table 3, entries 1 and 2). β-Bromostyrene having electron-donating groups on the phenyl ring were successfully converted to the desired products **3c**–**3f** in good to high yields (75%–93%; Table 3, entries 3–6). Furthermore, the introduction of electron-withdrawing substituents, including cyano, trifluoromethyl, and nitro groups, were well tolerated to give **3g–3j** in good yields (76–81%; Table 3, entries 7–10). This observation is consistent with our previous studies on trifluoromethylthiolation of α-halo-α,β-unsaturated carbonyl substrates.[36] Interestingly, the fluoro and chloro groups at the *ortho*-, *meta*-, or *para*-position of aromatic rings were also tolerated and the respective products **3k**–**3o** were afforded in 62–85 % yields (Table 3, entries 11–15). This method can be further extended to the heteroarylvinyl bromide systems. The reactions of (*Z*)-2-(2-bromovinyl)pyridine (**1p**) with **2** gave **3p** in 78% yield (Table 3, entry 16). Likewise, α-bromostyrene (**1q**) could also be reactive under the standard reaction conditions, leading to the desired product **3q** in 73% yield (Table 3, entry 17). Moreover, even 2-bromo-1,1,2-triphenylethylene (**1r**), a sterically highly demanding arylvinyl bromide, was a suitable substrate providing good yield of product **3r** (72%; Table 3, entry 18). Unfortunately, trifluoromethylthiolation of a cyclic vinyl bromide **1s** under the standard conditions, was less efficient, producting low yield of product **3s** (23% of ^{19}F NMR yield; Table 3, entry 19), along with dehalogenated and other unidentified side products. In addition to vinyl bromides, nonconjugated vinyl iodides are also suitable for the reaction. (1-Iodovinyl)cyclohexane (**1t**) and 2-iodooct-1-ene (**1u**) reacted with **2** to deliver good yields of the desired products **3t** and **3u** (70% and 61% of ^{19}F NMR yields, respectively; Table 3, entries 20 and 21).

To demonstrate the scalability and practicability of our synthesis, the trifluoromethylthiolation was conducted on a gram scale. Using 1.0 g of **1a** as the substrate, the trifluoromethylthiolated product **3a** was obtained in 86% yield (Scheme 2).

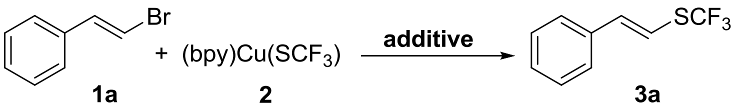
Scheme 2. Scalability of the Trifluoromethylthiolation of 1a



A series of experiments were conducted to probe whether any radical intermediates are involved in this transformation (Table 4). The reaction proceeds cleanly in the presence of the radical inhibitor 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT, 1.0 equiv) to afford the desired product **3a** in 93% yield. Similarly, carrying out the reaction in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), a radical scavenger, gave **3a** in 88% yield. Taken together, these two results and the complete retention of the double-bond stereochemistry after reaction appear inconsistent with a radical chain mechanism.[39]

Thus, it is likely that the reaction proceeds *via* an oxidative addition−reductive elimination pathway.[26,33]

Table 4. Inhibition Experiment on the Trifluoromethylthiolation of **1a** [a]



entry	additive (equiv)	yield (%)[b]
1	BHT (1.0)	93
2	TEMPO (1.0)	88

[a] Reaction conditions: **1a** (0.050 mmol), **2** (0.060 mmol), KF (0.20 mmol), diglyme (1.0 mL), N_2. [b] The yield was determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as internal standard.

In conclusion, we have demonstrated that a copper-mediated trifluoromethylthiolation of vinyl bromides to give vinyl trifluoromethyl thioethers in good to excellent yields. The reaction demonstrates a broad substrate scope and a variety of functional groups, including cyano, nitro, trifluoromethyl, alkoxy, amino, halide, and heterocyclic groups are tolerated. The complete retention of the olefin geometry, functional group tolerance, and scalability of this reaction make it an attractive protocol for the practical synthesis of these potentially important molecules.

EXPERIMENTAL SECTION

General Methods: All manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques. All glassware was oven or flame dried immediately prior to use. Solvents were freshly dried and degassed according to the procedures in Purification of Laboratory Chemicals prior to use. Deuterated solvents were purchased commercially, and were degassed and stored over activated 4 Å molecular sieves. β-Bromostyrene **1b−o**,[40,41] **1p**,[42] alkenyl iodides **1t−u**,[43] (bpy)Cu(SCF_3), (phen)Cu(SCF_3)[33] and [Bu_4N][SCF_3][44] were prepared according to the published procedures. All other reagents were obtained from commercial sources and used without further purification. The ^1H, ^{19}F and $^{13}C\{^1H\}$NMR spectra were recorded at 400, 376, and 101 MHz, respectively. ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as outside standard and low field is positive. Mass spectrometry was performed on GC/MS spectrometer under electron impact (EI) ionization technique. HRMS data were recorded on a GC-TOF instrument using EI technique.

General procedure for trifluoromethylthiolation of phenylvinyl bromide with (bpy)Cu(SCF_3). Phenylvinyl bromide **1** (0.50 mmol), [(bpy)Cu(SCF_3)] **2** (192 mg, 0.60 mmol, 1.2 equiv), KF (116 mg, 2.0 mmol), and diglyme (5.0 mL) were added to a reaction tube with Teflon screw cap equipped with a stir bar. The mixture was stirred at 100 °C for 24 hours. The reaction mixture was filtered through a pad of celite. The filtrate was added water (10 mL) at 0 °C. The resulting mixture was extracted with Et_2O (3×15 mL), and the combined organic layers was washed with water, and then dried over $MgSO_4$. The solvent was removed by rotary evaporation in an ice bath and the resulting product was purified by column chromatography on silica gel with pentane/Et_2O.

Styryl(trifluoromethyl)sulfane[14] (3a). Obtained as a yellow oil in 90% yield (91 mg) with *E*/*Z* ratio 94:6. R_f (*n*-pentane/diethyl ether 10:1) = 0.87. NMR of the major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.29 (m, 5H), 7.02 (d, *J* = 15.3 Hz, 1H), 6.75 (d, *J* = 15.3 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.7 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.2 (q, *J* = 1.2 Hz), 135.1 (s), 129.6 (q, *J* = 307.9 Hz), 129.2 (s), 128.9 (s), 126.8 (s), 111.7 (q, *J* = 3.3 Hz). IR(KBr): ν 1716, 1652, 1541, 1497, 1447, 1109, 953, 739, 757, 698, 590, 467 cm^{-1}. GC-MS m/z 204 (M^+), 135 (M^+-CF_3). HRMS (EI): calcd. for $C_9H_7F_3S$: 204.0221; found: 204.0217.

(4-Methylstyryl)(trifluoromethyl)sulfane[26] (3b). Obtained as a yellow oil in 92% yield (100 mg) with *E*/*Z* ratio 95:5. R_f (*n*-pentane/diethyl ether 10:1) = 0.87. NMR of the major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 15.3 Hz, 1H), 6.66 (d, *J* = 15.3 Hz, 1H), 2.35 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.9 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.8 (q, *J* = 1.3 Hz), 139.4 (s), 132.4 (s), 129.7 (q, *J* = 307.9 Hz), 129.6 (s), 126.8 (s), 110.3 (q, *J* = 3.2 Hz), 21.3 (s). IR(KBr): ν 2926, 2359, 1512, 1157, 1110, 958, 824, 787, 755, 505 cm^{-1}. GC-MS m/z 218 (M^+), 149 (M^+-CF_3). HRMS (EI): calcd. for $C_{10}H_9F_3S$: 218.0377; found: 218.0379.

(*E*)-(4-Methoxystyryl)(trifluoromethyl)sulfane[25] (3c). Obtained as a yellow oil in 89% yield (104 mg). R_f (*n*-pentane/diethyl ether 10:1) = 0.74. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 15.2 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 15.2 Hz, 1H), 3.83 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.1 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.5 (s), 142.2 (q, *J* = 1.1 Hz), 129.7 (q, *J* = 307.9 Hz), 128.4 (s), 127.9 (s), 114.3 (s), 108.4 (q, *J* = 3.0 Hz), 55.3 (s). IR(KBr): ν 2961, 2839, 2359, 1607, 1511, 1305, 1258, 1240, 1107, 1033, 959, 837, 796, 754 cm^{-1}. GC-MS m/z 234 (M^+), 165 (M^+-CF_3). HRMS (EI): calcd. for $C_{10}H_9F_3OS$: 234.0326; found: 234.0323.

(*E*)-(2-Methoxystyryl)(trifluoromethyl)sulfane (3d). Obtained as a yellow oil in 91% yield (106 mg). R_f (*n*-pentane/diethyl ether 10:1) = 0.65. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.37 – 7.26 (m, 2H), 7.01 – 6.92 (m, 2H), 6.87 (d, *J* = 15.4 Hz, 1H), 3.91 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.9 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.1 (s), 136.8 (q, *J* = 1.2 Hz), 130.3 (s), 129.8 (q, *J* = 307.7 Hz), 128.0 (s), 124.0 (s), 120.7 (s), 112.3 (q, *J* = 3.1 Hz), 111.0 (s), 55.5 (s). IR(KBr): ν 2965, 2840, 2360, 2341, 1487, 1250, 1106, 1027, 959, 749 cm^{-1}. GC-MS m/z 234 (M^+), 165 (M^+-CF_3). HRMS (EI): calcd. for $C_{10}H_9F_3OS$: 234.0326; found: 234.0327.

(*E*)-(Trifluoromethyl)(3,4,5-trimethoxystyryl)sulfane (3e). Obtained as a yellow oil in 75% yield (110 mg). R_f (*n*-pentane/diethyl ether 10:1) = 0.34. ^1H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, *J* = 15.3 Hz, 1H), 6.63 (d, *J* = 15.3 Hz, 1H), 6.61 (s, 2H), 3.88 (s, 6H), 3.86 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.8 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.5 (s), 141.7 (q, *J* = 1.1 Hz), 139.2 (s), 130.7 (s), 129.6 (q, *J* = 308.1 Hz), 110.7 (q, *J* = 3.2 Hz), 104.0 (s), 61.0 (s), 56.2 (s). IR(KBr): ν 2941, 1576, 1541, 1507, 1457, 1417, 1334, 1242, 1125, 1005, 953, 799, 755 cm^{-1}. GC-MS m/z 294 (M$^+$), 225 (M$^+$-CF$_3$). HRMS (EI): calcd. for $C_{12}H_{13}F_3O_3S$: 294.0537; found: 294.0532.

***N,N*-Dimethyl-4-(2-(trifluoromethylthio)vinyl)aniline (3f).** Obtained as a yellow oil in 93% yield (114 mg) with *E*/*Z* ratio 95:5. R_f (*n*-pentane/diethyl ether 10:1) = 0.69. NMR of the major isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 15.0 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.43 (d, *J* = 15.0 Hz, 1H), 2.99 (s, 6H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -43.6 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 151.1 (s), 144.3 (s), 129.8 (q, *J* = 308.0 Hz), 128.3 (s), 127.2 (s), 123.2 (d, *J* = 0.9 Hz), 112.0 (s), 40.3 (s). IR(KBr): ν 2925, 2854, 1608, 1522, 1446, 1362, 1185, 1153, 1110, 792 cm^{-1}. GC-MS m/z 247 (M$^+$), 178 (M$^+$-CF$_3$). HRMS (EI): calcd. for $C_{11}H_{12}F_3NS$: 247.0643; found: 247.0642.

4-(2-(Trifluoromethylthio)vinyl)benzonitrile (3g). Obtained as a yellow oil in 80% yield (91 mg) with *E*/*Z* ratio 55:45. R_f (*n*-pentane/diethyl ether 10:1) = 0.58. ^{1}H NMR (400 MHz, CDCl$_3$) *E* + *Z*: δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 2H), 6.92 (s, 2H), 6.83 (d, *J* = 10.7 Hz, 1H), 6.59 (d, *J* = 10.7 Hz, 1H). ^{19}F NMR (376 MHz, CDCl$_3$) *E* + *Z*: δ -42.2 (s, 3F) -42.9 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) *E* + *Z*: δ 139.3/139.2 (s), 136.4 (q, *J* = 1.2 Hz), 132.7 (s), 132.4 (s), 129.12/129.11 (q, *J* = 308.0 Hz), 129.12 (s), 127.1 (s), 117.9/117.0 (q, *J* = 3.8 Hz). IR(KBr): ν 2977, 2916, 2848, 2230, 1463, 1114, 734 cm^{-1}. GC-MS m/z 229 (M$^+$), 160 (M$^+$-CF$_3$). HRMS (EI): calcd. for $C_{10}H_6F_3NS$: 229.0173; found: 229.0169.

(Trifluoromethyl)(4-(trifluoromethyl)styryl)sulfane[26] (3h). Obtained as a yellow oil in 79% yield (107 mg) with *E*/*Z* ratio 70:30. R_f (*n*-pentane/diethyl ether 10:1) = 0.83. NMR of the major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 15.0 Hz, 1H), 6.86 (d, *J* = 15.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.4 (s, 3F), -62.8 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.3 (q, *J* = 1.3 Hz), 137.8 (s), 130.6 (s), 129.4 (q, *J* = 308.1 Hz), 128.8 (s), 126.9 (s), 125.9 (q, *J* = 3.8 Hz), 115.4 (q, *J* = 3.1 Hz). IR(KBr): ν 2955, 2924, 2854, 1457, 1326, 1168, 1135, 1110, 1068 cm^{-1}. GC-MS m/z 272 (M^+), 203 (M^+-CF_3). HRMS (EI): calcd. for $C_{10}H_6F_6S$: 272.0094; found: 272.0095.

(3-Nitrostyryl)(trifluoromethyl)sulfane (3i). Obtained as a yellow oil in 81% yield (100 mg) with *E*/*Z* ratio 40:60. R_f (*n*-pentane/diethyl ether 10:1) = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) *E* + *Z*: δ 8.26 – 8.14 (m, 4H), 7.73 – 7.64 (m, 2H), 7.63 – 7.53 (m, 2H), 7.04 – 6.87 (m, 2H), 6.61 (d, *J* = 10.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.2 (s) (E/Z), -42.8 (s) (E/Z). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *E* + *Z*: δ 134.2 (s), 132.4 (s), 129.9 (s), 129.6 (s), 129.3/129.1 (q, *J* = 308.2 Hz), 123.4/123.3 (s), 122.8 (s), 121.2 (s), 117.5/116.3 (q, *J* = 3.8 Hz). IR(KBr): ν 2926, 2855, 1609, 1532, 1458, 1351, 1111, 940, 806, 750, 737, 669 cm^{-1}. GC-MS m/z 249 (M^+), 180 (M^+-CF_3). HRMS (EI): calcd. for $C_9H_6F_3NO_2S$: 249.0071; found: 249.0066.

(4-Nitrostyryl)(trifluoromethyl)sulfane (3j). Obtained as a yellow solid in 76% yield (94 mg) with *E*/*Z* ratio 80:20. R_f (*n*-pentane/diethyl ether 10:1) = 0.67. NMR of the major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 6.97 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.0 (s, 3F). ^{13}C{^{1}H} NMR

(101 MHz, $CDCl_3$) δ 135.6 (q, *J* = 1.3 Hz), 129.3 (s), 129.2 (q, *J* = 308.2 Hz), 127.2 (s), 124.3 (s), 123.9 (s), 118.1 (q, *J* = 3.4 Hz). IR(KBr): ν 2955, 2924, 2854, 1457, 1326, 1168, 1135, 1110, 1068 cm^{-1}. GC-MS m/z 249 (M^+), 180 (M^+-CF_3). HRMS (EI): calcd. for $C_9H_6F_3NO_2S$: 249.0071; found: 249.0073.

(3-Fluorostyryl)(trifluoromethyl)sulfane (3k). Obtained as a yellow oil in 77% yield (85 mg) with *E*/*Z* ratio 80:20. R_f (*n*-pentane/diethyl ether 10:1) = 0.82. NMR of the major isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 1H), 7.20 – 6.99 (m, 3H), 6.94 (d, *J* = 15.4 Hz, 1H), 6.77 (d, *J* = 15.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.6 (s, 3F), -112.5 – -112.6 (m, 1F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.3 (s), 161.8 (s), 138.9 (q, *J* = 1.2 Hz), 130.5 (s), 130.4 (s), 129.5 (q, *J* = 308.0 Hz), 122.7 (s), 115.9 (s), 113.4 (s). IR(KBr): ν 1715, 1683, 1652, 1614, 1580, 1557, 1557, 1540, 1506, 1488, 1446, 1223, 1111, 949, 775, 757, 680 cm^{-1}. GC-MS m/z 222 (M^+), 153 (M^+-CF_3). HRMS (EI): calcd. for $C_9H_6F_4S$: 222.0126; found: 222.0123.

(4-Fluorostyryl)(trifluoromethyl)sulfane (3l). Obtained as a yellow oil in 85% yield (94 mg) with *E*/*Z* ratio 93:7. R_f (*n*-pentane/diethyl ether 10:1) = 0.85. NMR of the major isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.28 (m, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 15.3 Hz, 1H), 6.65 (d, *J* = 15.3 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.8 (s), -111.4 – -111.5 (m, 1F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.4 (s), 162.0 (s), 140.1-140.0 (m), 129.6 (q, *J* = 307.8 Hz), 128.6 (s), 116.1 (s), 111.6 – 111.2 (m). IR(KBr): ν 2926, 2856, 1602, 1508, 1457, 1234, 1159, 1111, 956, 933, 839, 798, 756, 527, 515 cm^{-1}. GC-MS m/z 222 (M^+), 153 (M^+-CF_3). HRMS (EI): calcd. for $C_9H_6F_4S$: 222.0126; found: 222.0128.

(3-Chlorostyryl)(trifluoromethyl)sulfane (3m). Obtained as a yellow oil in 79% yield (94 mg) with *E*/*Z* ratio 70:30. R_f (*n*-pentane/diethyl ether 10:1) = 0.83. NMR of the major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.37 – 7.21 (m, 3H), 6.93 (d, *J* = 15.2 Hz, 1H), 6.80 (d, *J* = 15.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.5 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 138.6 (q, *J* = 1.2 Hz), 136.8 (s), 134.9 (s), 130.1 (s), 129.4 (q, *J* = 307.9 Hz), 129.0 (s), 126.6 (s), 124.9 (d, *J* = 18.3 Hz), 113.8 (q, *J* = 3.2 Hz). IR(KBr): ν 1716, 1683, 1647, 1594, 1560, 1541, 1507, 1473, 1418, 1237, 1111, 950, 881, 792, 773, 756, 692, 679 cm^{-1}. GC-MS m/z 237 (M^+), 168 (M^+-CF_3). HRMS (EI): calcd. for $C_9H_6ClF_3S$: 237.9831; found: 237.9834.

(4-Chlorostyryl)(trifluoromethyl)sulfane[13] (3n). Obtained as a yellow oil in 83% yield (98 mg) with *E*/*Z* ratio 85:15. R_f (*n*-pentane/diethyl ether 10:1) = 0.82. NMR of the major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 4H), 6.89 (d, *J* = 15.4 Hz, 1H), 6.70 (d, *J* = 15.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.6 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.3 (s), 135.0 (s), 133.6 (s), 129.6 (q, *J* = 307.6 Hz), 129.1 (s), 128.0 (s), 112.6 (q, *J* = 3.2 Hz). IR(KBr): ν 2956, 2925, 2854, 1541, 1508, 1490, 1457, 1260, 1163, 1111, 1094, 1013, 792, 794 cm^{-1}. GC-MS m/z 237 (M^+), 168 (M^+-CF_3). HRMS (EI): calcd. for $C_9H_6ClF_3S$: 237.9831; found: 237.9829.

(*E*)-(2,6-Dichlorostyryl)(trifluoromethyl)sulfane (3o). Obtained as a yellow oil in 62% yield (84 mg). R_f (*n*-pentane/diethyl ether 10:1) = 0.83. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.09 (m, 1H), 7.05 – 6.88 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.1 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 134.4

(s), 132.3 (q, *J* = 1.6 Hz), 129.4 (d, *J* = 308.1 Hz), 129.3 (s), 128.7 (s), 121.8 (q, *J* = 3.4 Hz). IR(KBr): ν 1647, 1557, 1541, 1508, 1487, 1428, 1163, 1109, 946, 774, 757, 708 cm^{-1}. GC-MS m/z 271 (M$^+$), 202 (M$^+$-CF$_3$). HRMS (EI): calcd. for $C_9H_5Cl_2F_3S$: 271.9441; found: 271.9445.

(*Z*)-2-(2-(Trifluoromethylthio)vinyl)pyridine (3p). Obtained as a yellow solid in 78% yield (79 mg). R_f (*n*-pentane/diethyl ether 10:1) = 0.68. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.65 (d, *J* = 4.5 Hz, 1H), 7.67 (td, *J* = 7.7, 1.7 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.17 – 7.10 (m, 1H), 6.73 (s, 2H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -46.6 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 154.3 (s), 148.0 (s), 136.5 (s), 130.1 (q, *J* = 310.9 Hz), 124.6 (q, *J* = 1.2 Hz), 123.6 (s), 121.5 (s), 121.4 (s). IR(KBr): ν 1716, 1605, 1586, 1557, 1541, 1507, 1473, 1457, 1430, 1119, 997, 868, 795, 743, 688, 625, 541 cm^{-1}. GC-MS m/z 205 (M$^+$), 136 (M$^+$-CF$_3$). HRMS (EI): calcd. for $C_8H_6F_3NS$: 205.0173; found: 205.0175.

(1-Phenylvinyl)(trifluoromethyl)sulfane (3q). Obtained as a yellow oil in 73% yield (74 mg). R_f (*n*-pentane/diethyl ether 10:1) = 0.83. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65 – 7.61 (m, 2H), 7.41 – 7.36 (m, 3H), 6.08 (s, 1H), 5.99 (s, 1H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -41.2 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 135.5 (q, *J* = 1.9 Hz), 129.4 (q, *J* = 309.1 Hz), 129.1 (s), 128.5 (s), 127.4 (q, *J* = 1.8 Hz), 127.2 (s), 117.7 (s). IR(KBr): ν 1868, 1748, 1734, 1716, 1697, 1683, 1541, 1507, 1121, 771, 701 cm^{-1}. GC-MS m/z 204 (M$^+$), 135 (M$^+$-CF$_3$). HRMS (EI): calcd. for $C_9H_7F_3S$: 204.0221; found: 204.0222.

(Trifluoromethyl)(1,2,2-triphenylvinyl)sulfane (3r). Obtained as a white solid in 72% yield (128 mg). R_f (*n*-pentane/diethyl ether 10:1) = 0.79. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 7H), 7.22 – 7.15 (m, 3H), 7.11 – 7.01 (m, 3H), 6.98 – 6.88 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.5 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.4 (q, *J* = 1.5 Hz), 142.6 (s), 141.5 (s), 139.4 (s), 130.5 (s), 130.4 (s), 129.6 (s), 129.4 (q, *J* = 311.8 Hz), 128.3 (s), 128.0 (s), 127.9 (s), 127.8 (s), 127.7 (s), 127.4 (s), 126.1 (q, *J* = 1.5 Hz). IR(KBr): ν 1868, 1791, 1772, 1748, 1716, 1692, 1683, 1558, 1541, 1507, 1489, 1444, 1126, 1108, 1075, 755, 745, 696 cm^{-1}. GC-MS m/z 356 (M^+), 287 (M^+-CF_3). HRMS (EI): calcd. for $C_{21}H_{15}F_3S$: 356.0847; found: 356.0843.

(1*H*-Inden-2-yl)(trifluoromethyl)sulfane (3s). ^{19}F NMR analysis of the filtrate indicated that **3s** was produced in 23% yield. ^{1}H NMR (400 MHz, CD_3CN) δ 7.55 – 7.39 (m, 2H), 7.37 – 7.25 (m, 3H), 3.70 (s, 2H). ^{19}F NMR (376 MHz, CD_3CN) δ -42.6 (s). ^{13}C NMR (101 MHz, CD_3CN) δ 144.8 (s), 142.8 (s), 142.2 (q, *J* = 1.5 Hz), 129.6 (q, *J* = 307.9 Hz), 128.2 (q, *J* = 2.0 Hz), 126.9 (s), 123.8 (s), 121.8 (s), 117.3 (s), 43.8 (q, *J* = 1.0 Hz). HRMS (EI): calcd. for $C_{10}H_7F_3S$: 216.0221; found: 216.0225.

(1-Cyclohexylvinyl)(trifluoromethyl)sulfane (3t). Obtained as a yellow oil in 70% yield (73 mg). R_f (*n*-pentane) = 0.85. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (s, 1H), 5.64 (s, 1H), 2.18 (t, *J* = 11.4 Hz, 1H), 1.91 (dd, *J* = 58.1, 12.5 Hz, 4H), 1.43 – 1.09 (m, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.0 (s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.8 (q, *J* = 1.0 Hz), 129.9 (q, *J* = 307.7 Hz), 124.0 (q, *J* = 1.2 Hz), 46.2 (d, *J* = 0.9 Hz), 32.0 (s), 26.2 (s), 26.0 (s). IR(KBr): ν 2932, 2856, 2360, 1615, 1451, 1261, 1125, 1101, 929, 892, 806, 757, 606 cm^{-1}. GC-MS m/z 210 (M^+), 141 (M^+-CF_3). HRMS

(EI): calcd. for $C_9H_{13}F_3S$: 210.0690; found: 210.0692.

Oct-1-en-2-yl(trifluoromethyl)sulfane (3u). ^{19}F NMR analysis of the filtrate indicated that **3u** was produced in 61% yield. This volatile compound was inevitably contaminated with small amount of unidentified products. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.61 (s, 1H), 5.59 (s, 1H), 2.36 (t, *J* = 7.2 Hz, 2H), 1.37 – 1.22 (m, 8H), 0.89 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.4 (s). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 142.9 (q, *J* = 1.2 Hz), 129.8 (q, *J* = 308.1 Hz), 125.7 (q, *J* = 1.3 Hz), 38.4 (s), 31.5 (s), 28.4 (s), 27.6 (s), 22.6 (s), 14.0 (s). GC-MS m/z 212 (M^+), 143 (M^+-CF_3). HRMS (EI): calcd. for $C_9H_{15}F_3S$: 212.0847; found: 212.0852.

Gram scale reactions for synthesis of styrenyl trifluoromethyl thioethers (3a). Phenylvinyl bromide **1** (1.0 g, 5.5 mmol), [(bpy)Cu(SCF_3)] **2** (2.1 g, 6.6 mmol, 1.2 equiv), KF (1.28 g, 22.0 mmol), and diglyme (20.0 mL) were added to a reaction tube with Teflon screw cap equipped with a stir bar. The mixture was stirred at 100 °C for 24 hours. The reaction mixture was filtered through a pad of celite. The filtrate was added water (60 mL) at 0 °C. The resulting mixture was extracted with Et_2O (3×30 mL), and the combined organic layers was washed with water, and then dried over $MgSO_4$. The solvent was removed by rotary evaporation in an ice bath and the resulting product was purified by column chromatography on silica gel with pentane/Et_2O. **3a** was obtained as a yellow oil in 86% yield (0.96 g).

Procedure for the reaction of phenylvinyl bromide 1 with 2 in the presence of 1.0 equiv BHT. Phenylvinyl bromide **1** (0.050 mmol), [(bpy)Cu(SCF_3)] **2** (19.2 mg, 0.060 mmol, 1.2 equiv), KF (11.6 mg, 0.20 mmol), BHT (11.0 mg, 0.050 mmol, 1.0

equiv), and diglyme (1.0 mL) were added to a oven-dried 5 mL test tube with Teflon screw cap. The tube was sealed and the reaction solution was placed into a preheated 100°C oil bath for 24 h. The tube was removed from the oil bath and cooled to room temperature, and then 10 μL (trifluoromethoxy)benzene was added as an internal standard. The resulting mixture was filtered through a layer of Celite. The filtrate was analyzed by ^{19}F NMR and GC-MS. The yield of the styrenyl trifluoromethyl thioethers (**3a**) was calculated to be 93%.

Procedure for the reaction of phenylvinyl bromide 1 with 2 in the presence of 1.0 equiv TEMPO. Phenylvinyl bromide **1** (0.050 mmol), [(bpy)Cu(SCF$_3$)] **2** (19.2 mg, 0.060 mmol, 1.2 equiv), KF (11.6 mg, 0.20 mmol), TEMPO (7.80 mg, 0.050 mmol, 1.0 equiv), and diglyme (1.0 mL) were added to a oven-dried 5 mL test tube with Teflon screw cap. The tube was sealed and the reaction solution was placed into a preheated 100°C oil bath for 24 h. The tube was removed from the oil bath and cooled to room temperature, and then 10 μL (trifluoromethoxy)benzene was added as an internal standard. The resulting mixture was filtered through a layer of Celite. The filtrate was analyzed by ^{19}F NMR and GC-MS. The yield of the styrenyl trifluoromethyl thioethers (**3a**) was calculated to be 88%.

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Supporting Information

Full NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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