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Article

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Structure-Reactivity Relationship (SAR) of Trifluoromethanesulfenates: Discovery of An Electrophilic Trifluoromethylthiolating Reagent

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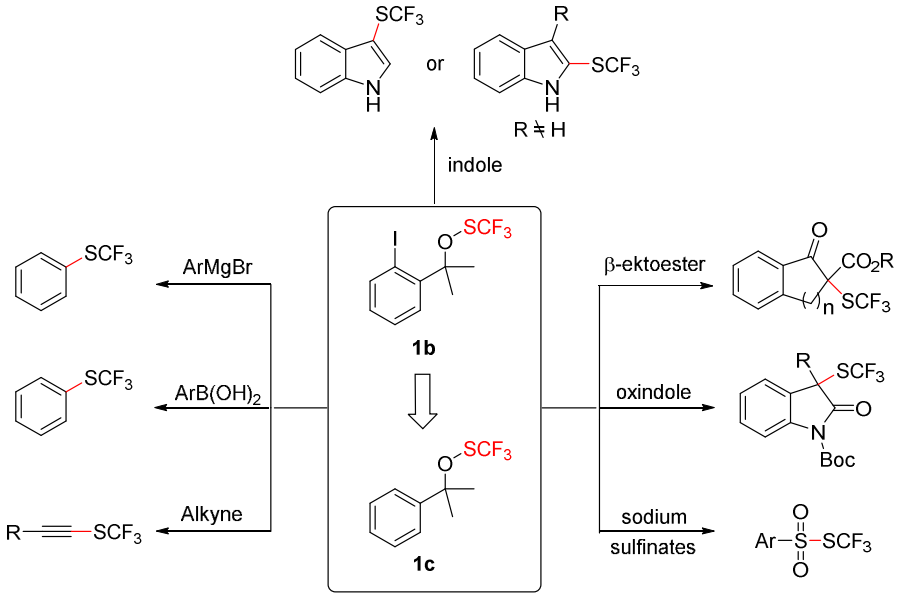
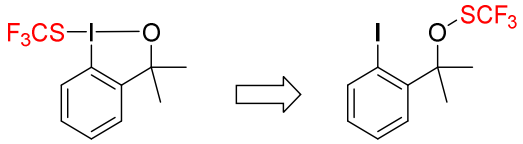


Abstract

A family of electrophilic trifluoromethanesulfenates was prepared. Structure-reactivity relationship studies showed that the substituted groups on the aryl ring of the trifluoromethylthiolating reagent didn't have obvious influence on their reactivities. A simplified electrophilic trifluoromethylthiolating reagent **1c** was then identified that can react with a wide range of nucleophiles such as Grignard reagents, arylboronic acids, alkynes, indoles, β-ketoesters, oxindoles and sodium sulfinates under mild reaction conditions. A variety of functional groups were tolerated under these conditions.

Introduction

In 2013, we reported the preparation of an air and moisture stable trifluoromethylthiolating reagent **1a,** which was isolated as a colorless liquid with a boiling point 151-153 ^{o}C. Reagent **1a** was characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, as well as elemental analysis. Reagent **1a** is a powerful trifluoromethylthiolating reagent that allows the trifluoromethylthiolation of a variety of nucleophiles such as aryl, vinyl, alkyl boronic acids, alkynes, indoles, carbonyl derivatives such as β-ketoesters, aldehydes, or amides.[1] In addition, a quinine-catalyzed highly enantioselective trifluoromethylthiolation of β-ketoesters and oxindoles with reagent **1a** was achieved under mild conditions.[2] Furthermore, using reagent **1a** as the radical trap, a silver-catalyzed decarboxylative trifluoromethylthiolation of secondary and tertiary aliphatic carboxylic acids in aqueous emulsion was also described.[3] The structure of reagent **1a** was initially proposed to be a trifluoromethylthio-substituted hypervalent iodine reagent. Very recently, Buchwald and co-workers[4] revised the structure of the reagent as a trifluoromethanesulfenate **1b**, based on a combination of spectroscopic techniques, derivatization experiments and the crystal sponge method (Figure 1).



1a initially proposed structure **1b** revised structure

Figure 1. Electrophilic trifluoromethylating reagent: its initial proposed structure **1a** and revised structure **1b**.

One question that arose from the structure revision is the role of the iodide atom

for the reactivity of the reagent **1**. One possible scenario is that structure **1a** and **1b** may exist as a tautomeric equilibria where structure **1b** is the major form. If **1a** is much more reactive than **1b** when a nucleophile reacts with the electrophilic trifluoromethylthiolating reagent, the reaction might proceed via nucleophilic substitution with structure **1a** and the equilibrium might then shift toward right (Figure 2).

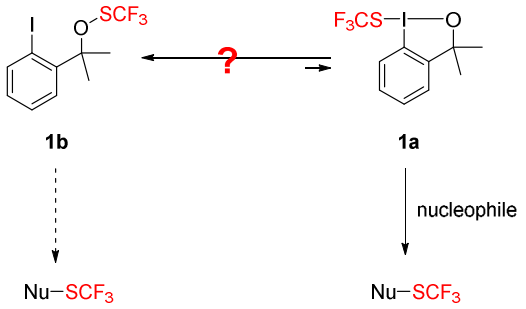


Figure 2. Tautomeric equilibrium between **1a** and **1b** and one possible reaction pathway when reagent **1** reacts with nucleophiles.

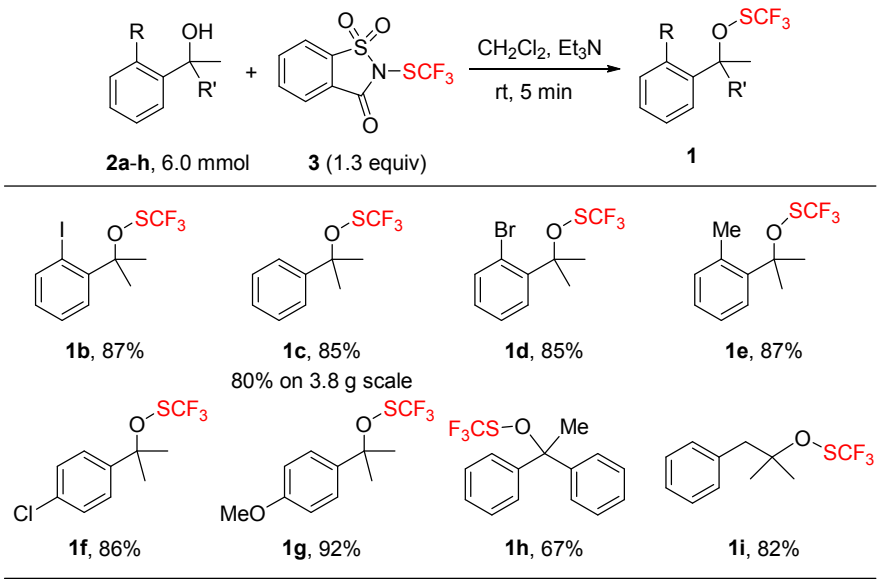
To probe if this is the case and the role of the iodide for the reactivity of the trifluoromethylthiolating reagent, we synthesized a family of substituted trifluoromethanesulfenates and studied their structure-reactivity relationship (SAR). We found that substituted trifluoromethanesulfenates with or without iodide atom showed similar reactivities toward a variety of nucleophiles. Subsequent studies showed that a simplified trifluoromethanesulfenate **1c**, which is shelf stable and easily handled, can be used as an equally effective electrophilic trifluoromethylthiolating reagent as **1b**. Herein, we disclose these findings and report the scope of the trifluoromethylthiolating reagent **1c** with a variety of different nucleophiles.

Results and Discussion

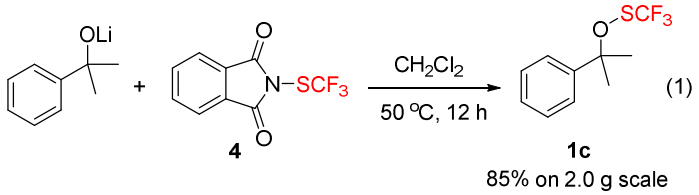
1. Preparation of substituted electrophilic trifluoromethanesulfenates.

The substituted trifluoromethanesulfenates were readily synthesized from corresponding tertiary alcohols **2a**-**h** with trifluoromethylthiolated saccharin, an electrophilic trifluoromethylthiolating reagent **3** developed in our own group.[5] Typically, the tertiary alcohols were converted to the trifluoromethanesulfenates in good to excellent yields within 5 min at room temperature using Et_3N as the base (Table 1). Notably, these reactions can be easily scaled up without loss of the yields. For example, reaction of 2-phenylpropan-2-ol (20 mmol) with reagent **3** generated the trifluoromethanesulfenate **1c** in 80% yield on 3.8 g scale. Alternatively, trifluoromethanesulfenate **1c** could be synthesized by reaction of lithium 2-phenylpropan-2-olate and trifluoromethylthiolated phthalimide **4** in 85% yield on 2.0 g scale under mild conditions (Eq 1).[6] These substituted trifluoromethanesulfenates are bench stable compounds except for compound **1g**. They are usually stored at 0-4 ^oC and no obvious decomposition was observed for at least 5 months as determined by ^{19}F NMR spectroscopy. Compound **1g** is much less stable since it was found that compound **1g** was completely decomposed when we tried to purify it by flash chromatography.

Table 1. Preparation of Substituted Trifluoromethanesulfenates.[a]



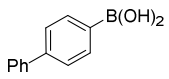
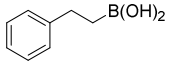
[a]Reaction conditions: alcohol (6.0 mmol), reagent **3** (7.8 mmol), Et_3N (2.0 mL) in CH_2Cl_2 (40 mL) at room temperature for 5 min. Isolated yield.

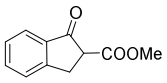
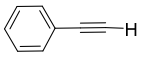
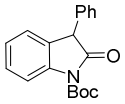
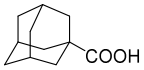


2. Structure-reactivity Relationship (SAR) studies of the trifluoromethanesulfenates. With reagents **1b-i** in hand, we began to study their structure-reactivity relationship (SAR) with a variety of different nucleophiles such as aryl and alkyl boronic acids,[7] *β*-ketoester,[1] indole,[8] alkyne, 2-phenyl-oxindole[9] and 1-adamamtame carboxylic acid[3] under the previously optimized conditions, and the results were summarized in Table 2. Interestingly, the SAR studies showed that in most cases, trifluoromethanesulfenates with or without iodide displayed similar reactivities when reacted with the same nucleophile under the same reaction conditions. These results clearly indicated that the iodide in reagent **1b** does not play an important role for the high reactivity of the reagent and the scenario described in Figure 2 is likely not going to take place. Interestingly, these studies also showed

reagents **1b**, **1c**, **1d** and **1f** showed different reactivities from reagents **1g**, **1h** and **1i** when reacted with some nucleophiles. For example, in the presence of the copper catalyst, reactions of 2-phenylethyl boronic acid with trifluoromethanesulfenates **1b**, **1c**, **1d** or **1f** generated the corresponding trifluoromethylthiolated products in 80%, 74%, 70% and 70%, respectively, while the same reaction with reagent **1g**, **1h** and **1i** gave the products in trace, 37% and 52% yields respectively (Table 2, entry 2). Similar trends were also observed when these reagents were subjected to the conditions of the silver-catalyzed decarboxylative trifluoromethylthiolation with 1-adamantane carboxylic acid (Table 2, entry 7). Notably, it was discovered that reagent **1g** is less thermally stable than other reagents. Heating of reagent **1g** in 1,2-dichloroethane at 120 ^{o}C for 12 h led to complete decomposition as determined by ^{19}F NMR spectroscopy. The low yield for the reaction of reagent **1g** with indole in the presence of 10 mol% of camphorsulfonic acid may also due to the low stability of the reagent in the presence of the Brønsted acid. Considering the easy availability of the starting materials, the cost and the atom economy of the reagent, we chose reagent **1c,** which is shelf stable and easily handled, as an equally effective electrophilic trifluoromethylthiolating reagent as **1b**.

Table 2. Structure-reactivity Relationship (SAR) studies of the trifluoromethanesulfenates with Different Nucleophiles.[a]

		Trifluoromethanesulfenates							
		1b	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**
1[b]		99%	57%	57%	54%	81%	70%	81%	52%
2[c]		80%	74%	70%	21%	70%	trace	37%	52%

3[d]		98%	95%	92%	99%	91%	99%	94%	95%
4[e]		99%	92%	94%	59%	57%	23%	57%	70%
5[f]		99%	98%	73%	90%	92%	86%	80%	36%
6[g]		85%	85%	85%	99%	77%	88%	79%	91%
7[h]		98%	95%	94%	68%	96%	trace	50%	75%

[a]Yields were determined by ^{19}F NMR spectroscopy with benzotrifluoride as an internal standard; Reaction conditions: [b]4-Biphenyl boronic acid (0.1 mmol), electrophilic trifluoromethylthiolating reagent (0.1 mmol), $Cu(MeCN)_4PF_6$ (10 mol %), 2,2'-bipyridine (20 mol %) and K_2CO_3 (2.0 equiv) in diglyme (0.5 mL) at 35 °C for 15 h; [c]Alkylboronic acid (0.15 mmol), electrophilic trifluoromethylthiolating reagent (0.1 mmol), $CuCl_2 \bullet 2H_2O$ (20 mol %), 2,2'-bipyridine (40 mol %) and K_2CO_3 (2.0 equiv) in 1,2-dichloroethane (0.5 mL) at 120 °C for 12 h; [d]β-Ketoester (0.1 mmol), electrophilic trifluoromethylthiolating reagent (0.2 mmol), DMAP (0.11 mmol) in CH_2Cl_2 (0.5 mL) room temperature for 12 h; [e]Indole (0.1 mmol), electrophilic trifluoromethylthiolating reagent (0.11 mmol), camphorsulfonic acid (10 mol %) in 0.5 mL of 1,2-dichloroethane 40 °C for 20 h; [f]Alkynes (0.20 mmol, 2.0 equiv), $CuBr(SMe_2)$ (20 mol %), 2,2'-biyridine (40 mol %), K_2CO_3 (2.0 equiv) and electrophilic trifluoromethylthiolating reagent (0.1 mmol) in 1,2-dichloroethane (0.5 mL) at 80 °C for 14 h; [g]Reaction conditions for oxindole (0.1 mmol), electrophilic trifluoromethylthiolating reagent (0.15 mmol), DMAP (0.11 mmol) in CH_2Cl_2 (0.5 mL), room temperature for 12 h; [h]1-Adamantane carboxylic acid (0.1 mmol), electrophilic trifluoromethylthiolating reagent (0.2 mmol), sodium 1-dodecanesulfate (0.02 mmol), $AgNO_3$(0.03 mmol), $K_2S_2O_8$ (0.1 mmol) in H_2O (0.5 mL), 50 °C for 12 h.

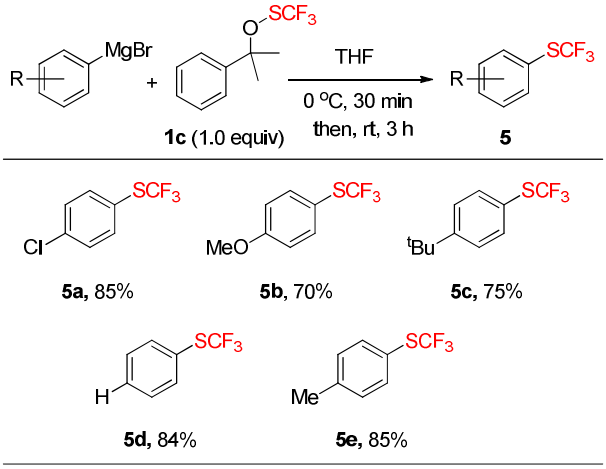
3 Scope of reagent 1c with different nucleophiles.

3.1 Reactions of reagent 1c with Grignard reagents.

Trifluoromethylthiolated arenes are important structural motif found in many drug molecules and agrochemicals.[10] As a result, development of efficient methods for the preparation of trifluoromethylthiolated arenes is of great interest in the field of medicinal chemistry and argochemistry.[11-12] One straightforward way for the synthesis of the trilfluoromethylthiolated arenes is direct trifluoromethylthiolation of Grignard reagents with electrophilic trifluoromethylthiolating reagent, which has been

previously reported by Billard and coworkers.[13] It was found that reactions of a variety of Grignard reagents with electrophilic trifluoromethylthiolating reagent **1c** occurred smoothly in THF to give the corresponding trifluoromethylthiolated arenes in good to excellent yields. The reactions are facile and full conversions were observed after 3 h at room temperature (Table 3). Grignard reagents with functional groups such as chloride or methoxy group also gave the corresponding products in good yields.

Table 3. Substrate Scope for Reaction of Reagent 1c with Grignard Reagents.[a]



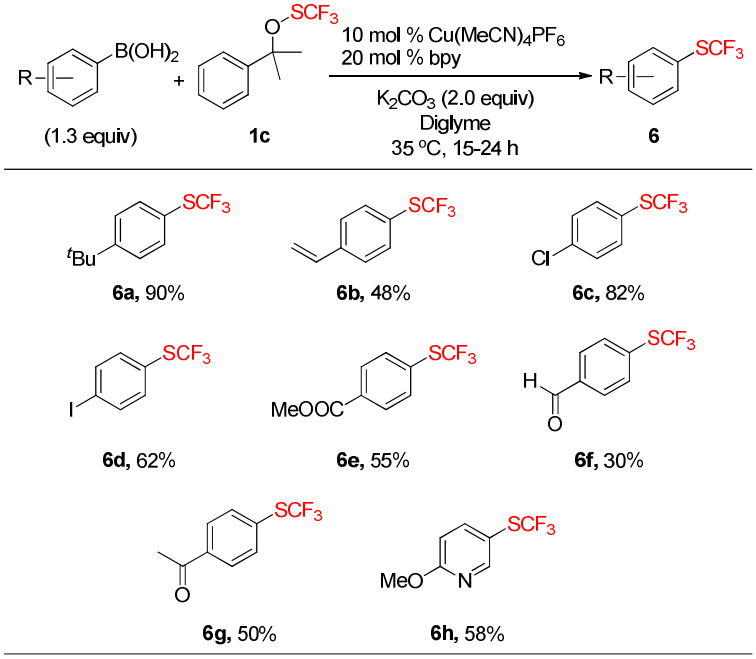
[a]Reaction conditions: RMgBr (0.5 mmol), reagent **1c** (0.5 mmol), in THF (2.5 mL), 0 °C for 30 min, then room temperature for 3 h. Isolated yield.

3.2 Reactions of Reagent 1c with Arylboronic Acids.

Even though Grignard reagents react with reagent **1c** under mild conditions, there is one drawback of using Grignard reagents for the preparation of trifluoromethylthiolated arenes. In general, Grignard reagents are incompatible with various functional groups. To address this disadvantage of using Grignard reagents, we previously have developed a copper-catalyzed trifluoromethylthiolation of aryl boronic acids with reagent **1b** under mild conditions.[1] Likewise, reactions of a variety of electron-rich and electron-deficient arylboronic acids with reagent **1c** gave the

corresponding products in good to excellent yields, although the yields for reactions of some aryl boronic acids with reagent **1c** were less than those with reagent **1b**. Various functional groups, including ethers, alkenes, ketones, esters, chloride and iodine were tolerated under the standard reaction conditions. In addition, reaction of 2-methoxy-3-pyridylboronic acid with reagent **1c** gave the trifluoromethylthiolated pyridine derivative in 58% yield (Table 4, **6h**).

Table 4. Substrate Scope for Reaction of Reagent 1c with Arylboronic Acids.[a]



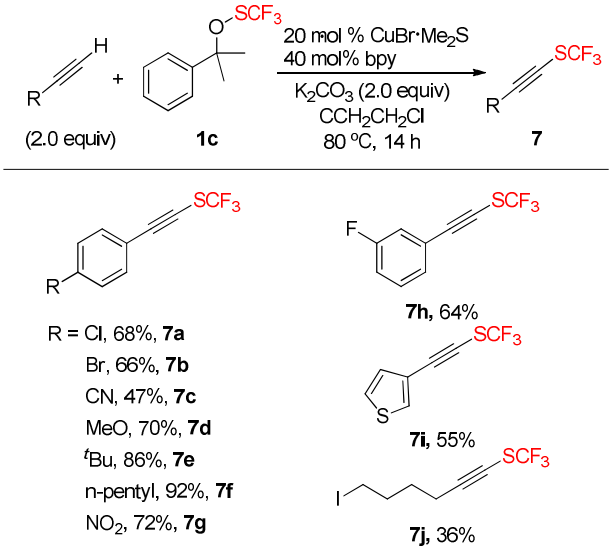
[a]Reaction conditions: arylboronic acid (0.65 mmol), reagent **1c** (0.5 mmol), $Cu(MeCN)_4PF_6$ (10 mmol %), bpy (20 mmol %), K_2CO_3 (1.0 mmol) in diglyme (2.5 mL) at 35 °C for 15–24 h. Isolated yields.

3.3 Reactions of Reagent 1c with Alkynes.

Trifluoromethylthiolated alkynes, which could be converted to other functionalized trifluoromethylthioethers, are also important structural motif found in many drug molecules and agrochemicals. In 2012, Qing reported a transition-metal free oxidative trifluoromethylthiolation of alkynes with moderate yields at room temperature.[14] Billard reported that trifluoromethylthiolated alkynes could be easily accessed from

reaction of alkynyl lithium with trifluoromethanesulfanamide, an electrophilic trifluoromethylthiolating reagent developed in Billard's laboratory.[15] We have previously reported that in the presence of a copper catalyst, reactions of a variety of alkynes with reagent **1b** occurred in good to excellent yields.[1] Under the same conditions, reaction of various alkynes with reagent **1c** at 80 °C after 14 h generated the corresponding trifluoromethylthiolated alkynes in good to excellent yields. A wide range of functional groups, including nitro, chloride, ester, fluoride and bromide were compatible with the reaction conditions (Table 5, **7a-7h**). Aliphatic and hetero alkynes also reacted under these conditions to give the corresponding alkynyl-trifluoromethylthioethers in satisfactory yields (Table 5, **7i-j**).

Table 5. Substrate Scope for Reaction of of Reagent 1c with Terminal Alkynes.[a]



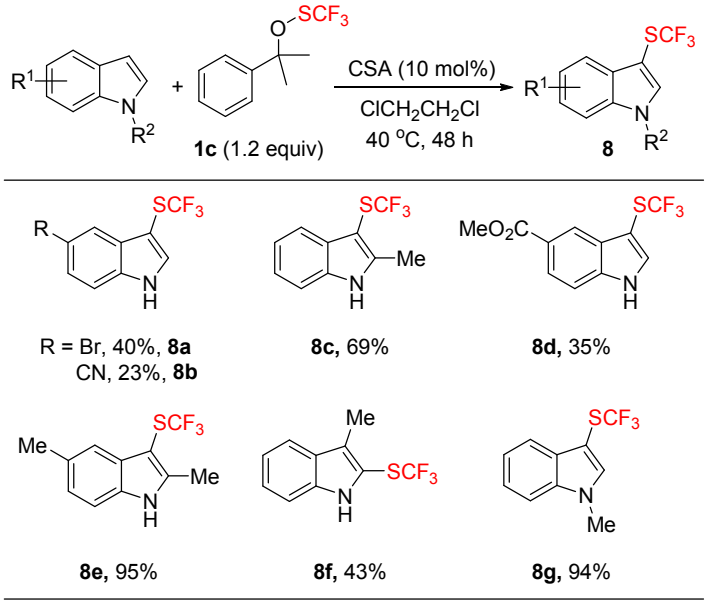
[a]Reaction conditions: alkyne (0.60 mmol), reagent **1c** (0.3 mmol), $CuBr{\cdot}SMe_2$ (20 mol %), bpy (40 mol %), K_2CO_3 (0.60 mmol) in 1,2-dichloroethane (1.5 mL) at 80 °C for 14 h. Isolated yields.

3.4 Reaction of Reagent 1c with Indoles.

Indole is among one of the privileged structural motif in biologically active natural products such as amino acids and alkaloids.[16] Development of efficient methods for

functionalization including trifluoromethylthiolation of indole is, therefore, of great current interests. Notably, Billard and Langlois reported the first BrØsted acid-mediated electrophilic trifluoromethylthiolation of indoles under mild conditions.[13b] In 2013, Shibata described a copper-catalyzed trifluoromethylthiolation of indoles with an electrophilic trifluoromethanesulfonyl hypervalent iodonium ylide via an *in situ* reduction of the CF_3SO_2 group to form a trifluoromethylthiolated ammonia salt that was responsible for the trifluoromethylthiolation.[17] It was found that in the presence of 10 mol% of camphorsulfonic acid, reactions of indoles with electron-donating or withdrawing groups with the electrophilic trifluoromethylthiolating reagent **1c** gave the corresponding trifluoromethylthiolated indoles in moderate to good yields (Table 6). Reaction of 3-methyl-indole formed the corresponding 2-trifluoromethylthiolated indole in 43% yield (Table 6, **8f**). *N*-Methyl indole also reacted under standard conditions to give the corresponding product in 94% yield (Table 6, **8g**).

Table 6. Substrate Scope for Reaction of Reagent 1c with Indoles.[a]

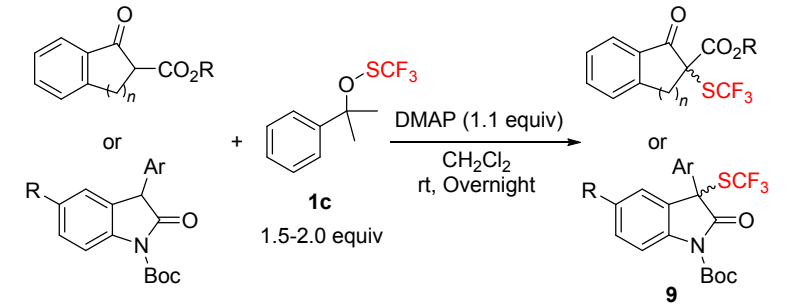


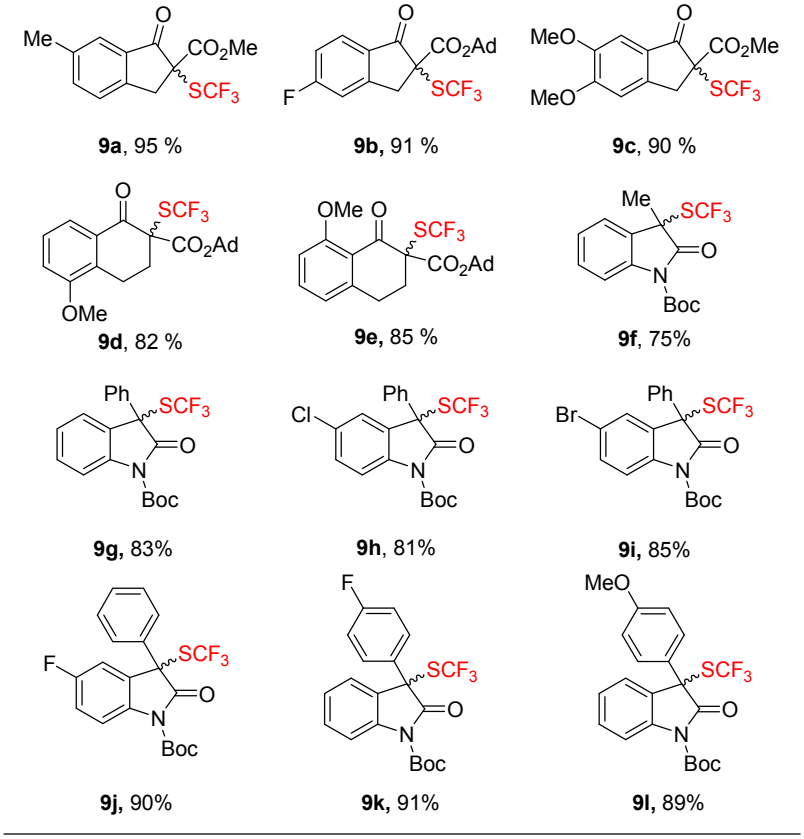
[a]Reaction conditions: indole (0.3 mmol), reagent **1c** (0.33 mmol), catalyst(10 mol %) in 1.5 mL of 1,2-dichloroethane for 20-48 h. Isolated yields.

3.5 Reaction of Reagent 1c with β-ketoesters and Oxindoles

We have previously showed that reactions of β-ketoesters and oxindoles with the electrophilic trifluoromethylthiolating reagent **1b** occurred in good to excellent yields in presence of 4-dimethylaminopyridine (DMAP) as the base.[1,9] The same reaction conditions were applied for the reactions of β-ketoesters and oxindoles with reagent **1c**. It was found that reactions of various β-ketoesters derived from indanone, tetralone, or 1-benzosuberone gave the corresponding products in good to excellent yields (Table 7, **9a-e**). Likewise, reactions of oxindoles generated the corresponding trifluoromethylthiolated products also in good to excellent yields (Table 7, **9f-l**).

Table 7. Substrate Scope for Reaction of of Reagent 1c with β-ketoesters and Oxindoles.[a]





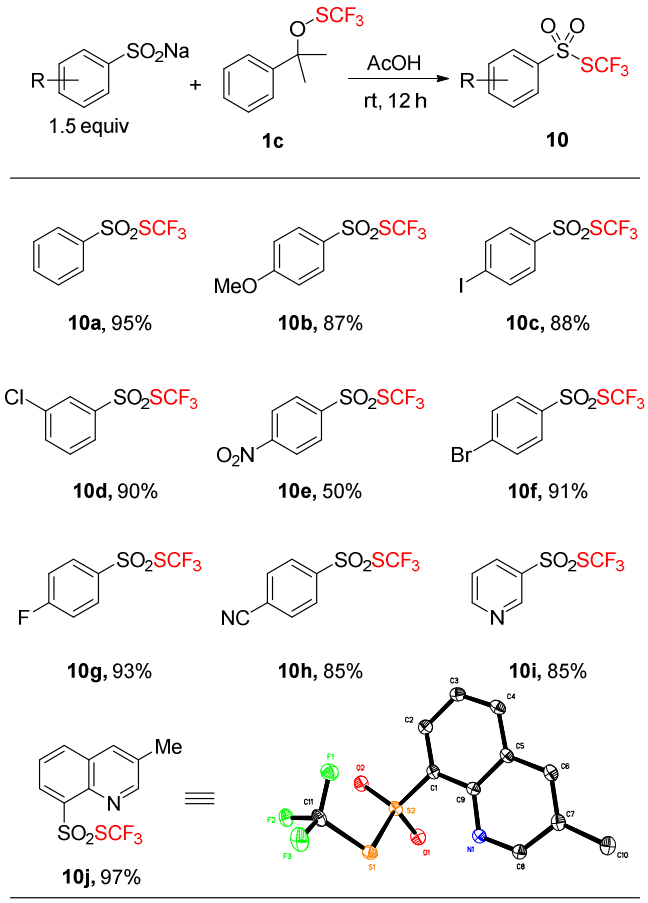
[a]Reaction conditions for β-ketoester (0.3 mmol), reagent **1c** (0.6 mmol), DMAP (0.33 mmol) in CH_2Cl_2 (1.5 mL), room temperature for 12 h; Reaction conditions for oxindole (0.3 mmol), reagent **1c** (0.45 mmol), DMAP (0.33 mmol) in CH_2Cl_2 (1.5 mL), room temperature for 12 h. Isolated yields.

3.6 Reaction of Reagent 1c with Sodium Sulfinates.

Thiosulfonates are a family of valuable compounds that have shown insecticidal activity in azuki bean weevils and rice stem borer larvae.[18] In addition, thiosulfonates can act as a thio-transfer reagent for the preparation of a variety of thiolated compounds.[19] Interestingly, no methods for the preparation of trifluoromethylthiolated sulfonates have been reported previously. It was found that treatment of sodium

sulfinates with reagent **1c** in acetic acid after 12 h at room temperature generated the corresponding trifluoromethylthiolated sulfonates in good to excellent yields. The reaction was compatible with a variety of functional groups such as chloride, bromide, fluoride, nitrile, nitro and ester group (Table 8, **10a-h**). Sodium heteroarylsulfinates also reacted with reagent **1c** under the standard conditions to give the corresponding products in excellent yields (Table 8, **10i-j**). The structure of compound **10j** was further confirmed by x-ray diffraction of its single crystals.

Table 8. Substrate Scope for Reactions of Reagent 1c with Sodium Sulfinates.[a]

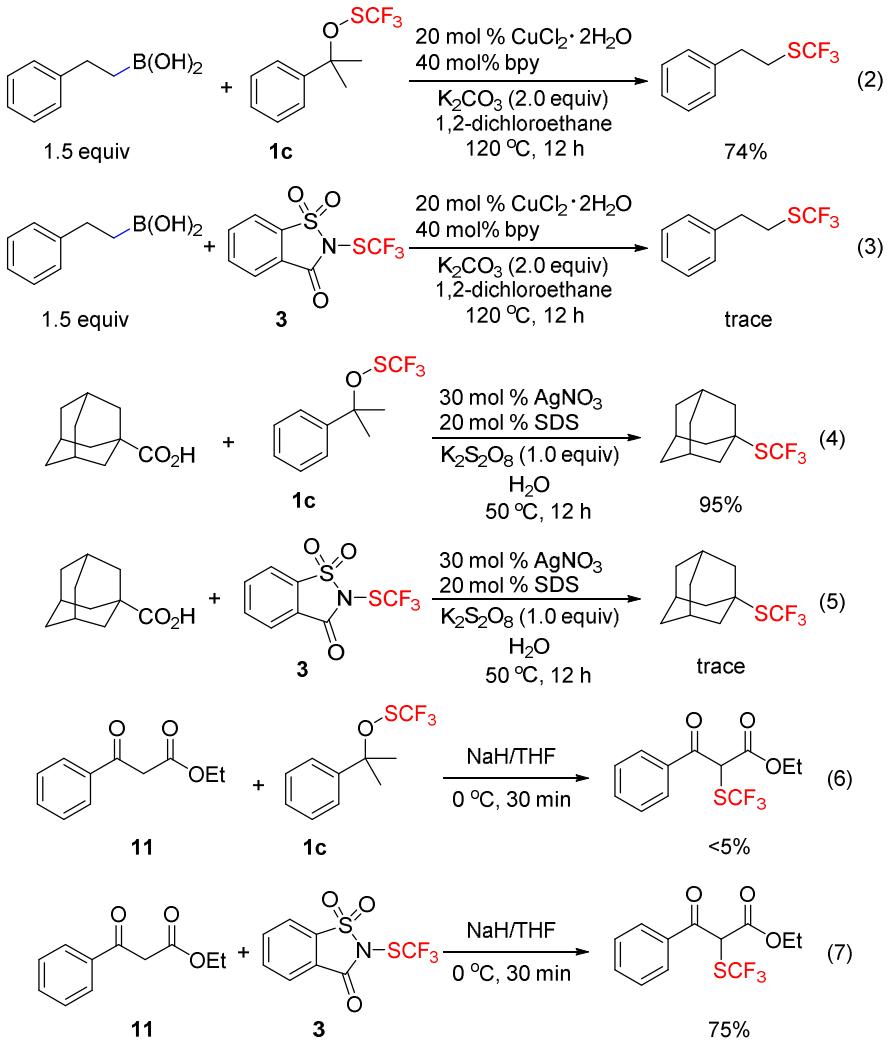


[a]Reaction conditions: sodium sulfinates (0.75 mmol), reagent **1c** (0.5 mmol), in AcOH (2.5 mL), room temperature for 12 h. Isolated yields.

4. Comparasion of the Reactivity of Reagent 1c and 3.

Both reagents **1c** and **3** can act as highly reactive electrophilic trifluoromethylthiolating reagent for a wide range of the substrates. Nevertheless, the substrate scope of two reagents is complementary. Reagent **1c** shows better reactivity than reagent **3** in copper-catalyzed trifluoromethylthiolation of aryl/alkyl boronic acids and silver-catalyzed decarboxylative trifluoromethylthiolation of aliphatic carboxylic acids. For example, reaction of 2-phenylethylboronic acid with reagent **1c** in the presence of 20 mol% of $CuCl_2 \bullet 2H_2O$ and 40 mol% 2,2'-bipyridine as the catalyst occurred to 74% yield after 12 h at 120 ^oC, while the same reaction using reagent **3** as the electrophilic trifluoromethylthiolating reagent gave trace amount of the coupled product (Eqs. 2-3). Likewise, silver-catalyzed Hunsdiecker-type decarboxylative trifluoromethylthiolating reaction of adamantine carboxylic acid using reagent **1c** afford the corresponding trifluoromethylthiolated product in 95% yield, while the same reaction using reagent **3** did not generate the trifluoromethylthiolated product (Eqs. 4-5). On the other hand, reagent **3** displays much higher reactivity than reagent **1c** in direct nucleophilic trifluoromethylthiolating reactions such as reactions with alcohols, amines, thiols and β-ketoesters.[5] For these nucleophiles, no products were observed when reagent **1c** was used as the electrophilic trifluoromethylthiolating reagents. One obvious example of the higher reactivity of reagent **3** in direct nucleophilic substitution reaction is that reagent **1c** itself was prepared from reagent **3**. Similarly, reaction of β-ketoester **11** with reagent **3** formed the mono-trifluoromethylthiolated product in 75% yield, while the same reaction with reagent **1** was messy and the monotrifluoromethylthiolated product was

observed in less than 5% yield as determined by ^{19}F NMR spectroscopy (Eqs. 6-7).



Summary

In this work, we described the preparation of a family of substituted trifluoromethanesulfenates. Structure-reactivity relationship (SAR) studies showed that substituted trifluoromethanesulfenates with or without iodide atom display similar reactivities toward a variety of nucleophiles. As a result, a simplified trifluoromethanesulfenate **1c**, which is shelf stable and easily handled, was identified as an equally effective electrophilic trifluoromethylthiolating reagent as **1b.** Reaction of reagent **1c** with various nucleophiles such as aryl Grignard reagents, aryl boronic

acids, alkynes, indoles, β-ketoesters, 2-substituted oxindoles and sodium sulfinates under mild conditions have thus been developed. The ease in preparation, thermal and moisture stability and broad range of reactivity toward different nucleophiles under mild reaction conditions make reagent **1c** attractive as a general electrophilic trifluoromethylthiolating reagent for the incorporation of the trifluoromethylthio group into small molecules. The investigation of reactions of reagent **1c** with other nucleophiles are undergoing currently in our laboratory.

Experimental Section

General information. All solvents were purified by standard method. ^{1}H, ^{19}F NMR and ^{13}C NMR spectra were recorded on 300 MHz, 282 MHz and 100 MHz spectrometer, respectively. ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm and ^{19}F NMR chemical shifts were determined relatived to $CFCl_3$ as inter standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All reactions were monitored by TLC or ^{19}F NMR. Flash column chromatograph was carried out using 300-400 mesh silica gel at medium pressure.

Materials. All reagents were received from commercial sources. Pure CuI was freshly prepared under the condition of the reference (Dieter, R. K. *J. Am. Chem. Soc.* **1985**, *107*, 4679). Solvents were freshly dried and degassed according to the purification handbook *Purification of Laboratory Chemicals* before using.

Synthesis of tertiary alcohols

A dry and nitrogen-flushed 25 mL flask equipped with a magnetic stirrer and a septum was charged with 56.25 mL of 2.0 M MeMgBr in Et_2O. 40 mL of methyl benzoates (50 mmol) in Et_2O was added dropwise in 30 min and the reaction was allowed to warm slowly to room temperature. The reaction was stirred for overnight and was quenched with an NH_4Cl solution (70 mL contain 10 mL ice water). 80 mL of Et_2O was added and the organic phase was separated. The aqueous phase was extracted with Et_2O (3 × 40 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated in vacuo. The product was purified by flash chromatography on silica gel to give the tertiary alcohol as a colorless liquid.

2-(2-Bromophenyl)propan-2-ol.[20] Colorless liquid (6.74 g, 63%). Eluent: ethyl acetate/petroleum ether = 1 /10, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.59 (d, *J* = 8.0 Hz, 1 H), 7.49 (d, *J* = 8.0 Hz, 1 H), 7.21 (t, *J* = 8.0 Hz, 1 H), 7.01 (t, *J* = 8.0 Hz, 1 H), 2.77 (s, 1 H), 1.69 (s, 6 H) ppm

2-(*O*-tolyl)propan-2-ol.[21] White solid (4.58 g, 61%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.48-7.45 (m, 1 H), 7.18-7.16 (m, 3 H), 2.62 (s, 3 H), 1.85 (s, 1 H), 1.67 (s, 6 H) ppm

2-(4-Chlorophenyl)propan-2-ol.[22] Colorless liquid (6.55 g, 77%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.42 (d, *J* = 8.8 Hz, 2 H), 7.29 (d, *J* = 8.8 Hz, 2 H), 1.82 (s, 1 H), 1.57 (s, 6 H) ppm

2-(4-Methoxyphenyl)propan-2-ol.[22] Colorless liquid (5.90 g, 71%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ

7.41 (d, J = 8.8 Hz, 2 H), 6.87 (d, J = 8.8 Hz, 2 H), 3.81(s, 3 H), 1.87 (s, 1 H), 1.57 (s, 6 H) ppm.

General procedure for the preparation of trifluoromethanesulfenates.

General method 1. A 50 mL round-bottomed flask with a magnetic stirrer was charged with alcohols (6.0 mmol), *N*-trifluoromethylthiosaccharin (2.2 g, 7.8 mmol) , Et_3N (2.0 mL, 14.4 mmol) and CH_2Cl_2 (40 mL). The mixture was stirred at room temperature for 5 min. The resulting mixture was purified by flash column chromatography (Eluent: petroleum ether) to give trifluoromethanesulfenate as a light yellow liquid. The light yellow liquid was further purified by flash column chromatography (Eluent: petroleum ether) to give a colorless liquid.

General method 2. A 50 mL round-bottomed flask with a magnetic stirrer was charged with lithium 2-phenylpropan-2-olate (10 mmol), trifluoromethylthiolated phthalimide (10 mmol) in 40 mL of CH_2Cl_2. The reaction was stirred at 50 ^oC and monitored by ^{19}F NMR spectroscopy until the disappearance of the trifluoromethylthiolating reagent. The mixture was filtered through a pad of Celite and the solvent was removed in vacuo. The product was purified by flash chromatography on silica gel to give reagent **1c** as a colorless liquid (2.0 g, 85% yield).

((2-Phenylpropan-2-yl)oxy)(trifluoromethyl)sulfane 1c.[5] Colorless liquid (3.8 g, 80%). Eluent: petroleum ether, R_f = 0.8. ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.42-7.32 (m, 5 H), 1.70 (s, 6 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.1 (s, 3 F) ppm.

((2-(2-Bromophenyl)propan-2-yl)oxy)(trifluoromethyl)sulfane 1d. Colorless liquid

(1.6 g, 85%). Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.66 (d, *J* = 8.0 Hz, 1 H), 7.47 (d, *J* = 8.0 Hz, 1 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.17 (t, *J* = 7.9 Hz, 1 H), 1.86 (s, 6 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -51.5 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 141.8, 136.2, 130.7 (q, *J* = 312.9 Hz), 129.8, 128.6, 126.0, 121.4, 87.6, 26.6 ppm. IR (KBr): ν = 2990, 2935, 1590, 1566, 1470, 1386, 1368, 1278, 1251, 1124, 1048, 1023, 933, 585, 756, 724 cm^{-1}. Elemental Analysis for $C_{10}H_{10}F_3OBrS$: Calculated: C, 38.11; H, 3.20, Found: C, 37.72; H, 3.12.

((2-(O-tolyl)propan-2-yl)oxy)(trifluoromethyl)sulfane 1e. Colorless liquid (1.3 g, 87%). Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.34-7.32 (m, 1 H), 7.25-7.18 (m, 3 H), 2.58 (s, 3 H), 1.79 (s, 6 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -51.6 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 141.1, 136.9, 133.3, 130.8 (q, *J* = 312.1 Hz), 128.5, 127.0, 125.9, 87.9, 27.4 (q, *J* = 1.4 Hz), 21.7 ppm. IR (KBr): ν = 2990, 1490, 1458, 1383, 1367, 1293, 1259, 1128, 1108, 1057, 849, 805, 761, 726, 582 cm^{-1}. Elemental Analysis for $C_{11}H_{13}F_3OS$: Calculated: C, 52.79; H, 5.24, Found: C, 52.69; H, 5.21.

((2-(4-Chlorophenyl)propan-2-yl)oxy)(trifluoromethyl)sulfane 1f. Colorless liquid (1.4 g, 86%). Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.37 (s, 4 H), 1.71 (s, 6 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -51.6 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 142.9, 135.3, 130.6 (q, *J* = 312.9 Hz), 128.9, 128.7, 87.2, 27.6 ppm. IR (KBr): ν = 2990, 2935, 1590, 1566, 1470, 1386, 1368, 1278, 1251, 1124, 1048, 1023, 933, 585, 756, 724 cm^{-1}. Elemental Analysis for $C_{10}H_{10}F_3OClS$: Calculated: C, 44.37; H, 3.72, Found: C, 44.19; H, 3.68.

((2-(4-Methoxyphenyl)propan-2-yl)oxy)(trifluoromethyl)sulfane 1g. Colorless liquid (1.5 g, 92%). Eluent: petroleum ether, R_f = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K, TMS) δ 7.36 (d, *J* = 8.0 Hz, 2 H), 6.91 (d, *J* = 8.0 Hz, 2 H), 3.84 (s, 3 H), 1.71 (s, 6 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.1 (s, 3 F); ^{13}C NMR (125.0 MHz, $CDCl_3$, 293 K, TMS) δ 136.3, 130.8 (q, *J* = 313.0 Hz), 127.2, 126.8, 113.9, 86.4, 55.4, 27.6 ppm. IR (KBr): ν = 2692, 2837, 1608, 1582, 1513, 1465, 1442, 1413, 1366, 1291, 1252, 1155, 1113, 1038, 829 cm^{-1}. Elemental Analysis for $C_{11}H_{13}F_3O_2S$: Calculated: C, 49.62; H, 4.92, Found: C, 49.75; H, 5.19.

(1,1-Diphenylethoxy)(trifluoromethyl)sulfane 1h. Colorless liquid (1.2 g, 67%). Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.36-7.33 (m, 10 H), 2.07 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -51.7 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 144.6, 130.8 (q, *J* = 312.7 Hz), 128.5, 128.2, 127.1, 89.8, 25.9 (q, *J* = 1.5 Hz) ppm. IR (KBr): ν = 3062, 3030, 2992, 1599, 14894, 1447, 1316, 1252, 1221, 1124, 1069, 1043, 1029, 589, 792, 698, 627, 582 cm^{-1}. Elemental Analysis for $C_{15}H_{13}F_3OS$: Calculated: C, 60.39; H, 4.39, Found: C, 59.94; H, 4.30.

((2-Methyl-1-phenylpropan-2-yl)oxy)(trifluoromethyl)sulfane 1i.[5] Colorless liquid (1.2 g, 80%). Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.36-7.29 (m, 3 H), 7.23-7.21 (m, 2 H), 2.91 (s, 2 H), 1.32 (s, 6 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.9 (s, 3 F) ppm.

General Procedure for electrophilic trifluoromethylthiolation of Grignard reagents with reagent 1c.

A dry and nitrogen-flushed 25 mL flask equipped with a magnetic stirrer and a septum was charged with RMgBr (0.5 mL, 2.0 M in THF, 1.0 mmol). The reaction mixture was cooled to 0 °C, and reagent **1c** (118.2 mg, 0.5 mmol) in 1.0 mL was added dropwise. After 30 min of stirring, the reaction temperature was increased to room temperature. The reaction was stirred for further 3 h and monitored by ^{19}F NMR spectroscopy until the disappearance of the electrophilic trifluoromethylthiolating reagent **1c** (typically 24 h). 15 mL of brine and 10 mL of CH_2Cl_2 was added and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated in vacuo. The product was purified by flash chromatography on silica gel.

(4-Chlorophenyl)(trifluoromethyl)sulfane 5a.[23] Colorless liquid (90.1 mg, 85%). Eluent: petroleum ether, R_f = 0.9. ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.60 (d, *J* = 8.4 Hz, 2 H), 7.41 (d, *J* = 8.4 Hz, 2 H) ppm; ^{19}F NMR (375 MHz, $CDCl_3$) δ -42.9 (s, 3 F) ppm.

1-(Methoxy)-4-[(trifluoromethyl)thio]benzene 5b.[12f] Colorless liquid (72.8 mg, 70%). Eluent: petroleum ether, R_f = 0.6. ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.58 (d, *J* = 8.8 Hz , 2 H), 6.93 (d, *J* = 8.8 Hz , 2 H), 3.84 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -44.0 (s, 3 F) ppm.

(4-(*tert*-Butyl)phenyl)(trifluoromethyl)sulfane 5c.[12e] Colorless liquid (87.8 mg, 75%). Eluent: petroleum ether, R_f = 0.9. ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.59 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 1.35 (s, 9 H); ^{19}F NMR (375 MHz,

$CDCl_3$) δ -43.0 (s, 3 F) ppm.

Phenyl(trifluoromethyl)sulfane 5d.[13c] Colorless liquid (74.8 mg, 84%). Eluent: petroleum ether, R_f = 0.9. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.66 (d, *J* = 7.2 Hz , 2 H), 7.50-7.41 (m, 3 H) ppm; ^{19}F NMR (375 MHz, $CDCl_3$) δ -42.8 (s, 3 F) ppm.

P-tolyl(trifluoromethyl)sulfane 5e.[12h] Colorless liquid (81.6 mg, 85%). Eluent: petroleum ether, R_f = 0.9. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.53 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 2.37 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -42.3 (s, 3 F) ppm.

General Procedure for copper-catalyzed trifluoromeththiolation of aryl boronic acids with 1c.

$Cu(MeCN)_4PF_6$ (18.6 mg, 0.05 mmol, 10 mol%), 2,2'-biyridine (16.0 mg, 0.20 mmol, 20 mol%), aryl boronic acid (0.65 mmol, 1.3 equiv), K_2CO_3 (138.2 mg, 1.0 mmol, 2.0 equiv), and reagent **1c** (118.1 mg, 0.50 mmol, 1.0 equiv) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. The tube was quickly sealed with a rubber stopper and 2.5 mL of freshly distilled diglyme was added. The reaction was stirred at 35 ^{o}C and monitored by ^{19}F NMR spectroscopy until the disappearance of reagent **1c** (typically 15 h). 25 mL of distilled water and 10 mL of Et_2O was added and the organic phase was separated. The aqueous phase was extracted with Et_2O (5 x 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The product was purified by flash chromatography on silica gel, and further purified by Kugelrohr distillation.

(4-(tert-Butyl)phenyl)(trifluoromethyl)sulfane 6a.[12e] Colorless liquid (105.3 mg,

90%). Eluent: petroleum ether (R_f = 0.9). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.59 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 1.35 (s, 9 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -43.0 (s, 3 F) ppm.

1-Ethenyl -4-[(trifluoromethyl)thio]benzene 6b.[12e] Colorless liquid (48.9 mg, 48%). Eluent: petroleum ether, R_f = 0.9. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.61 (d, *J* = 8.0 Hz, 2 H), 7.50 (d, *J* = 8.0 Hz , 2 H), 6.73 (dd, *J* = 17.6 Hz, *J* = 11.2 Hz, 1 H), 5.84 (d, *J* = 17.6 Hz, 1 H), 5.39 (d, *J* = 10.8 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -42.9 (s, 3 F) ppm.

(4-Chlorophenyl)(trifluoromethyl)sulfane 6c.[23] Colorless liquid (86.9 mg, 82%). Eluent: petroleum ether, R_f = 0.9. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.60 (d, *J* = 8.4 Hz, 2 H), 7.41 (d, *J* = 8.4 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -42.9 (s, 3 F) ppm.

(4-Iodophenyl)(trifluoromethyl)sulfane 6d.[24] Light brown liquid (94.2 mg, 62%). Eluent: petroleum ether, R_f = 0.9. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.74 (d, *J* = 8.0 Hz, 2 H), 7.37 (d, *J* = 8.0 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -42.7 (s, 3 F) ppm.

Methyl 4-[(trifluoromethyl)thio]benzoate 6e.[12e] Colorless liquid (59.5 mg, 55%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.8). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.07 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 7.8 Hz, 2 H), 3.94 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -41.8 (s, 3 F) ppm.

4-((Trifluoromethyl)thio)benzaldehyde 6f.[25] Colorless liquid (30.9 mg, 30%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$,

293 K, TMS) δ 10.07 (s, 1 H), 7.93 (d, *J* = 8.0 Hz, 2 H), 7.82 (d, *J* = 8.0 Hz , 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -41.6 (s, 3 F) ppm;

1-(4-Trifluoromethylsulfanyl-phenyl)-ethanone 6g.[1] Colorless liquid (55.0 mg, 55%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.98 (d, *J* = 8.0 Hz, 2 H), 7.73 (d, *J* = 8.0 Hz, 2 H), 2.62 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -41.8 (s, 3 F) ppm;

2-Methoxy-3-[(trifluoromethyl)thio]pyridine 6h.[1] Colorless liquid (60.6 mg, 58%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.4. (d, *J* = 2.4 Hz, 1 H), 7.80 (dd, *J* = 7.6, 2.0 Hz, 1 H), 7.79 (d, *J* = 8.8 Hz, 1 H), 3.97 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -43.9 (s, 3 F) ppm.

General procedure for copper-catalyzed trifluoromethylthiolation of terminal alkynes with 1c.

$CuBr(SMe_2)$ (12.0 mg, 0.06 mmol, 20 mol%), 2,2'-biyridine (19.2 mg, 0.12 mmol, 40 mol%), alkynes (0.60 mmol, 2.0 equiv), K_2CO_3 (82.9 mg, 0.60 mmol, 2.0 equiv), and reagent **1c** (70.9 mg, 0.30 mmol, 1.0 equiv) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. The tube was quickly sealed with a rubber stopper and 1.5 mL of freshly distilled solvent was added. The reaction was stirred at 80 ^{o}C and monitored by ^{19}F NMR spectroscopy until the disappearance of **3** (typically 14 h). 25 mL of distilled water and 10 mL of CH_2Cl_2 was added and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (5 x 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The product was purified by flash chromatography on silica

gel.

((4-Chlorophenyl)ethynyl)(trifluoromethyl)sulfane 7a.[26] Light yellow liquid (48.1 mg, 68%). Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.43 (d, *J* = 8.4 Hz, 2 H), 7.33 (d, *J* = 8.4 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -43.5 (s, 3 F) ppm.

((4-Bromophenyl)ethynyl)(trifluoromethyl)sulfane 7b.[14] Light yellow liquid (55.4 mg, 66%). Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K, TMS) δ 7.49 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -40.6 (s, 3 F) ppm;

4-(((Trifluoromethyl)thio)ethynyl)benzonitrile 7c.[5] Light yellow liquid (32.0 mg, 47%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.65 (d, *J* = 8.4 Hz, 2 H), 7.56 (d, *J* = 8.4 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -42.9 (s, 3 F) ppm. MS (EI): *m/z* (%) 227， 158 (100), 114, 93, 69.

((4-Methoxyphenyl)ethynyl)(trifluoromethyl)sulfane 7d.[14] Colorless liquid (48.7 mg, 70%). Eluent: ethyl acetate/petroleum ether = 1/100, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.46 (d, *J* = 8.8 Hz, 2 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 3.83 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -44.1 (s, 3 F) ppm.

((4-*tert*-Butylphenyl)ethynyl)(trifluoromethyl)sulfane 7e.[14] Light yellow liquid (66.6 mg, 86%). Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K, TMS) δ 7.48 (d, *J* = 7.5 Hz, 2 H), 7.40 (d, *J* = 8.7 Hz, 2 H), 1.34 (s, 9 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -44.3 (s, 3 F) ppm.

((4-Pentylphenyl)ethynyl)(trifluoromethyl)sulfane 7f.[14] Light yellow liquid (75.1 mg, 92%). Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K, TMS) δ 7.44 (d, *J* = 7.8 Hz, 2 H), 7.18 (d, *J* = 8.1 Hz, 2 H), 2.64 (t, *J* = 7.5 Hz, 2 H), 1.66-1.61 (m, 2 H), 1.35-1.31 (m, 4 H), 0.92 (t, *J* = 6.6 Hz, 3 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -44.3 (s, 3 F) ppm.

((4-Nitrophenyl)ethynyl)(trifluoromethyl)sulfane 7g.[1] Light yellow liquid (53.4 mg, 72%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.23 (d, *J* = 9.2 Hz, 2 H), 7.63 (d, *J* = 9.2 Hz, 2 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -42.8 (s, 3 F) ppm.

((3-Fluorophenyl)ethynyl)(trifluoromethyl)sulfane 7h.[1] Light yellow liquid (42.2 mg, 64%). Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.35-7.25 (m, 2 H), 7.18 (d, *J* = 9.2 Hz, 1 H), 7.12-7.07 (m, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -43.4 (s, 3 F), -112.3 (m, 1 F) ppm.

3-((Trifluoromethylthio)ethynyl)thiophene 7i.[14] Colorless liquid (34.2 mg, 55%). Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.64-7.63 (m, 1 H), 7.31-7.30 (m, 1 H), 7.19-7.17 (m, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -43.5 (s, 3 F) ppm.

(6-Iodohex-1-yn-1-yl)(trifluoromethyl)sulfane 7j. Light yellow liquid (33.2 mg, 36%). Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 3.21 (t, *J* = 6.8 Hz, 2 H), 2.44 (t, *J* = 7.2 Hz, 2 H), 1.95-1.90 (m, 2 H), 1.73-7.67 (m, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -44.2 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 128.6 (q, *J* = 312.1 Hz), 103.0, 58.1 (q, *J* = 4.3 Hz), 32.4, 28.9, 19.3, 5.8

ppm. IR (KBr): ν = 2945, 2865, 2204, 1429, 1327, 1288, 1260, 1212, 1158, 1107, 758, 735 cm^{-1}. MS (EI): *m/z* (%) 308, 261, 159, 139, 79 (100), 70. HRMS: Calcd for $C_7H_8F_3SI$: 307.9344; Found: 307.9340.

General procedure for electrophilic trifluoromethylthiolation of indoles with reagent 1c.

Camphorsulfonic acid (CSA) (6.9 mg, 0.03 mmol), indole (0.30 mmol) and reagent **1c** (77.9 mg, 0.33 mmol) were placed into an oven-dried sealed bomb equipped with a stirring bar under Ar. Under a positive flow of argon, 1.5 mL of freshly distilled 1,2-dichloroethane was added. The reaction was stirred at 40 ^oC and monitored by ^{19}F NMR spectroscopy until the disappearance of the electrophilic trifluoromethylthiolating reagent **1c** (typically 48 h). 15 mL of brine and 10 mL of CH_2Cl_2 was added and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The product was purified by flash chromatography on silica gel.

5-Bromo-3-((trifluoromethyl)thio)-1*H*-indole 8a.[8] Yellow liquid (30.1 mg, 40%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.62 (s, 1 H), 7.93 (s, 1 H), 7.54 (s, 1 H), 7.38 (d, *J* = 8.8 Hz, 1 H), 7.29 (d, *J* = 8.8 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.5 (s, 3 F) ppm.

3-((Trifluoromethyl)thio)-1*H*-indole-5-carbonitrile 8b.[8] Yellow solid (16.6 mg, 23%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^1H NMR (400 MHz, DMSO-d_6, 293 K, TMS) δ 12.54 (s, 1 H), 8.19 (d, *J* = 6.4 Hz, 1 H), 8.09 (s, 1 H), 7.69

(d, J = 8.8 Hz, 1 H), 7.60 (dd, J = 8.8, 1.2 Hz, 1 H); ^{19}F NMR (376 MHz, DMSO-d_6) δ -44.1 (s, 3 F) ppm.

2-Methyl-3-((trifluoromethyl)thio)-1*H*-indole 8c.[8] White solid (47.9 mg, 69%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.35 (s, 1 H), 7.72 (d, J = 8.0 Hz, 1 H), 7.34-7.29 (m, 1 H), 7.24-7.19 (m, 2 H), 2.58 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.9 (s, 3 F) ppm.

Methyl 3-((trifluoromethyl)thio)-1*H*-indole-5-carboxylate 8d.[8] White solid (28.9 mg, 35%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^{1}H NMR (400 MHz, DMSO-d_6, 293 K, TMS) δ 12.36 (s, 1 H), 8.28 (s, 1 H), 8.09 (s, 1 H), 7.84 (dd, J = 8.4, 1.6 Hz, 1 H), 7.59 (d, J = 8.8 Hz, 1 H), 3.85 (s, 3 H) ppm; ^{19}F NMR (376 MHz, DMSO-d_6) δ -44.2 (s, 3 F) ppm.

2,5-Dimethyl-3-((trifluoromethyl)thio)-1*H*-indole 8e.[8] White solid (69.8 mg, 95%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.22 (s, 1 H), 7.50 (s, 1 H), 7.20 (d, J = 8.4 Hz, 1 H), 7.05 (d, J = 8.0 Hz, 1 H), 2.56 (s, 3 H), 2.49 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.5 (s, 3 F) ppm.

3-Methyl-2-((trifluoromethyl)thio)-1*H*-indole 8f.[8] White solid (29.8 mg, 43%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.13 (s, 1 H), 7.63 (d, J = 8.4 Hz, 1 H), 7.38-7.31 (m, 2 H), 7.17 (t, J = 7.2 Hz, 1 H), 2.47 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.0 (s, 3 F) ppm.

1-Methyl-3-((trifluoromethyl)thio)-1*H*-indole 8g.[8] White solid (65.2 mg, 94%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$,

293 K, TMS) δ 7.83 (d, J = 7.6 Hz, 1 H), 7.39-7.31 (m, 4 H), 3.82 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.9 (s, 3 F) ppm.

General procedure for electrophilic α-trifluoromethylthiolation of β-keto esters with reagent 1c.

β-keto esters (0.3 mmol, 1.0 equiv), DMAP (40.3 mg, 0.33 mmol, 1.1 equiv), and reagent **1c** (106.3 mg, 0.6 mmol, 2.0 equiv) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. The tube was quickly sealed with a rubber stopper and 1.5 mL of freshly distilled CH_2Cl_2 was added. The reaction was stirred at room temperature and monitored by ^{19}F NMR spectroscopy until the disappearance of **1c** (typically 12 h). 25 mL of distilled water and 10 mL of CH_2Cl_2 was added and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (5 x 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The product was purified by flash chromatography on silica gel.

General procedure for electrophilic α-trifluoromethylthiolation of oxindoles with reagent 1c.

Oxindoles (0.30 mmol, 1.0 equiv), DMAP (40.3 mg, 0.33 mmol, 1.1 equiv), and reagent **1c** (106.3 mg, 0.45 mmol, 1.5 equiv) were placed into an oven-dried Schlenk tube that is equipped with a stirring bar under Ar. The tube was quickly sealed with a rubber stopper and 2.5 mL of freshly distilled CH_2Cl_2 was added. The reaction was stirred at room temperature and monitored by ^{19}F NMR spectroscopy until the disappearance of **1c** (typically 12 h). 25 mL of distilled water and 10 mL of CH_2Cl_2

was added and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (5 x 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The product was purified by flash chromatography on silica gel.

Methyl 6-methyl-1-oxo-2-((trifluoromethyl)thio)-2,3-dihydro-1*H*-indene-2-carboxylate 9a. Light yellow liquid (86.6 mg, 95% yield). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.61 (s, 1 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 7.41 (d, *J* = 8.0 Hz, 1 H), 4.13 (d, *J* = 17.6 Hz, 1 H), 3.78 (s, 3 H), 3.60 (d, *J* = 17.6 Hz, 1 H), 2.42 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -37.3 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 195.0, 167.6, 149.3, 138.9, 138.1, 133.2, 130.0 (q, *J* = 309.9 Hz), 126.1, 125.4, 63.9, 54.4, 40.2, 21.2 ppm. IR (KBr): ν = 2958, 1745, 725, 1618, 1587, 1495, 1435, 1281, 1252, 1154, 1112, 1027, 864, 758 cm^{-1}. MS (EI): *m/z* (%) 304, 245, 203, 171 (100), 69, 51, 39. HRMS: Calcd for $C_{13}H_{11}SO_3F_3$: 304.0370; Found: 304.0379.ppm.

Adamantan-1-yl 5-fluoro-1-oxo-2-((trifluoromethyl)thio)-2,3-dihydro-1*H*-indene-2-carboxylate 9b.[1] Light yellow liquid (116.9 mg, 91% yield). Eluent: ethyl acetate/ petroleum ether = 1/10, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.49-7.37 (m, 3 H), 4.00 (d, *J* = 17.6 Hz, 1 H), 3.58 (d, *J* = 17.6 Hz, 1 H), 2.14 (s, 3 H), 2.02 (s, 6 H), 1.61 (s, 6 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.9 (s, 3 F), -112.7 (m, 1 F) ppm.

Methyl 5,6-dimethoxy-1-oxo-2-((trifluoromethyl)thio)-2,3-dihydro-1*H*-indene-2-carboxylate 9c.[1] White solid (94.6 mg, 90% yield). Eluent: ethyl acetate/petroleum

ether = 1/10, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.17 (s, 1 H), 6.90 (s, 1 H), 4.08 (d, *J* = 17.6 Hz, 1 H), 3.98 (s, 3 H), 3.88 (s, 3 H), 3.77 (s, 3 H), 3.55 (d, *J* = 17.6 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -37.5 (s, 3 F) ppm.

Adamantan-1-yl 5-methoxy-1-oxo-2-((trifluoromethyl)thio)-1,2,3,4-tetrahydro naphthalene-2-carboxylateoxylate 9d.[2] White solid (111.7 mg, 82% yield). Eluent: ethyl acetate/petroleum ether = 1/5, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.58 (d, *J* = 8.0 Hz, 1 H), 7.29 (t, *J* = 8.8 Hz, 1 H), 7.04 (d, *J* = 8.0 Hz, 1 H), 3.87 (s, 3 H), 3.10-2.94 (m, 3 H), 2.47-2.39 (m, 1 H), 2.11 (s, 3 H), 2.01-1.93 (m, 6 H), 1.59 (s, 6 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.6 (s, 3F) ppm.

Adamantanyl 8-methoxy-1-oxo-2-((trifluoromethyl)thio)-1,2,3,4-tetrahydro naphthalene-2-carboxylate 9e.[2] White solid (114.2 mg, 85% yield). Eluent: ethyl acetate/petroleum ether = 1/5, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.47 (d, *J* = 2.8 Hz, 1 H), 7.15 (d, *J* = 8.4, 1 H), 7.10 (dd, *J* = 8.4, 2.8 Hz, 1 H), 3.83 (s, 3 H), 3.21-3.12 (m, 1 H), 3.07 - 2.96 (m, 2 H), 2.49-2.48 (m, 1 H), 2.13 (s, 3 H), 2.12 (s, 6 H), 1.61 (s, 6 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -35.5 (s, 3 F) ppm.

***tert*-Butyl 3-methyl-2-oxo-3-((trifluoromethyl)thio)indoline-1-carboxylate 9f.**[2] Light yellow liquid (78.1 mg, 75%). Eluant: ethyl acetate/petroleum ether = 1/10, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.61 (s, 1 H), 7.89 (d, *J* = 8.4 Hz, 1 H), 7.41 (d, *J* = 7.6 Hz, 1 H), 7.37 (td, *J* = 8.0 Hz, 0.8 Hz 1 H), 7.23 (t, *J* = 7.6 Hz, 1 H), 1.74 (s, 3 H), 1.64 (s, 9 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.4 (s, 3 F) ppm.

***tert*-Butyl 2-oxo-3-phenyl-3-((trifluoromethyl)thio)indoline-1-carboxylate 9g.** Light yellow liquid (101.9 mg, 83%). Eluant: ethyl acetate/petroleum ether = 1/10, R_f

= 0.7. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.98 (d, *J* = 8.0 Hz, 1 H), 7.58-7.52 (m, 3 H), 7.47 (t, *J* = 7.2 Hz, 1 H), 7.37-7.31 (m, 4 H), 1.63 (s, 9 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.8 (s, 3 F) ppm.

***tert*-Butyl 5-chloro-2-oxo-3-phenyl-3-((trifluoromethyl)thio)indoline-1-carboxyl -ate 9h.** White solid (107.7 mg, 81%). Eluant: ethyl acetate/petroleum ether = 1/10 (R_f = 0.7). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.07 (d, *J* = 1.6 Hz, 1 H), 7.50-7.48 (m, 3 H), 7.38-7.31 (m, 4 H), 1.62 (s, 9 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.7 (s, 3 F) ppm.

***tert*-Butyl 5-bromo-2-oxo-3-phenyl-3-((trifluoromethyl)thio)indoline-1-carboxyl -ate 9i.** Colorless liquid (124.2 mg, 85%). Eluant: ethyl acetate/petroleum ether = 1/10, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.89 (d, *J* = 8.8 Hz, 1 H), 7.69 (d, *J* = 1.9 Hz, 1 H), 7.58 (dd, *J* = 8.8, 2.0 Hz, 1 H), 7.50 (dd, *J* = 5.0, 2.0 Hz, 2 H), 7.46-7.34 (m, 3 H), 1.60 (s, 9 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.7 (s, 3 F) ppm.

***tert*-Butyl 3-(4-fluorophenyl)-2-oxo-3-((trifluoromethyl)thio)indoline-1-carboxyl -ate 9j.** Colorless liquid (115.3 mg, 90%). Eluant: ethyl acetate/petroleum ether = 1/10, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.98 (dd, *J* = 8.2, 4.8 Hz, 1 H), 7.53-7.51 (m, 2 H), 7.40-7.38 (m, 3 H), 7.28-7.28 (s, 1 H), 7.17 (t, *J* = 8.8, 2.4 Hz, 1 H), 1.62 (s, 9 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.7 (s, 3 F), -116.4 (m, 1 F) ppm.

***tert*-Butyl 3-(4-fluorophenyl)-2-oxo-3-((trifluoromethyl)thio)indoline-1-carboxyl -ate 9k.** Light yellow liquid (116.6 mg, 91%). Eluant: ethyl acetate/petroleum ether =

1/10, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.98 (d, *J* = 8.0 Hz, 1 H), 7.57- 7.52 (m, 3 H), 7.49-7.45 (m, 1 H), 7.34 (t, *J* = 8.0 Hz, 1 H), 7.05 (t, *J* = 8.0 Hz, 2 H), 1.62 (s, 9 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.9 (s, 3 F), -111.6 (m, 1 F) ppm.

***tert*-Butyl 3-(4-methoxyphenyl)-2-oxo-3-((trifluoromethyl)thio)indoline-1-carboxylate 9l.** Colorless liquid (117.2 mg, 89%). Eluant: ethyl acetate/petroleum ether = 1/10, R_f = 0.7. ^{11}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.96 (d, *J* = 8.4 Hz, 1 H), 7.58 (d, *J* = 8.0 Hz, 1 H), 7.47-7.32 (m, 3 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 6.87 (d, *J* = 6.8 Hz, 2 H), 3.78 (s, 3 H), 1.62 (s, 9 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.0 (s, 3 F) ppm.

General procedure for electrophilic trifluoromethylthiolation of sodium sulfinates with reagent 1c.

Sodium sulfinates (0.75 mmol) and reagent **1c** (118.2 mg, 0.5 mmol) were placed into an oven-dried sealed bomb equipped with a stirring bar under Ar. Under a positive flow of argon, 2.5 mL of AcOH was added. The reaction was stirred at room temperature and monitored by ^{19}F NMR spectroscopy until the disappearance of the electrophilic trifluoromethylthiolating reagent **1c** (typically 12 h). 15 mL of brine and 30 mL of Et_2O was added and the organic phase was separated. The aqueous phase was extracted with water (3 × 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The product was purified by flash chromatography on silica gel.

***S*-(Trifluoromethyl) benzenesulfonothioate 10a.** Colorless liquid (115.0 mg, 95%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$,

293 K, TMS) δ 8.01 (d, *J* = 8.0 Hz, 2 H), 7.71(t, *J* = 7.6 Hz, 1 H), 7.61 (t, *J* = 7.9 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.40 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 144.7, 135.4, 129.8, 127.7, 127.5 (q, *J* = 313.6 Hz) ppm. IR (KBr): ν = 3071, 1582, 1477, 1449, 1363, 1162, 1100, 1072, 753, 682, 589, 556, 538 cm^{-1}. MS (EI): *m/z* (%) 242, 141, 77 (100), 69, 51, 39. HRMS: Calcd for $C_7H_5S_2O_2F_3$: 241.9683; Found: 241.9681.

***S*-(trifluoromethyl) 4-methoxybenzenesulfonothioate 10b.** Colorless liquid (117.8 mg, 87%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.92 (d, *J* = 8.8 Hz, 2 H), 7.03 (d, *J* = 9.2 Hz, 2 H), 3.91 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.70 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 165.1, 136.2, 130.5, 127.7 (q, *J* = 312.9 Hz), 114.9, 56.1 ppm. IR (KBr): ν = 2948, 2847, 1593, 1577, 1496, 1463, 1359, 1315, 1270, 1154, 1104, 1074, 1025, 835, 802, 660, 626, 582, 556, 534 cm^{-1}. MS (EI): *m/z* (%) 272, 247, 219, 171 (100), 155, 123, 107, 92, 77, 63, 50, 38. HRMS: Calcd for $C_8H_7S_2O_3F_3$: 271.9789; Found: 271.9791.

***S*-(trifluoromethyl) 4-iodobenzenesulfonothioate 10c.** Colorless liquid (161.9 mg, 88%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.98 (d, *J* = 8.8 Hz, 2 H), 7.69 (d, *J* = 8.8 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.3 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 144.4, 139.2, 128.9, 127.3 (q, *J* = 315.7 Hz), 103.8 ppm. IR (KBr): ν = 1565, 1387, 1363, 1274, 1170, 1096, 1071, 1054, 1006, 817, 729, 623, 595, 548 cm^{-1}. MS (EI): *m/z* (%) 368, 267 (100), 203, 127, 93, 76, 69, 50. HRMS: Calcd for $IC_7H_4S_2O_2F_3$:

367.8650; Found: 367.8647.

***S*-(trifluoromethyl) 3-chlorobenzenesulfonothioate 10d.** Colorless liquid (124.2 mg, 90%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.98 (s, 1 H), 7.90 (d, *J* = 8.0 Hz, 1 H) , 7.70 (d, *J* = 8.0 Hz, 1 H), 7.57 (t, *J* = 8.0 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.2 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 146.1, 136.1, 135.5, 132.0, 131.1, 127.3 (q, *J* = 313.6 Hz), 125.9 ppm. IR (KBr): ν = 3093, 1578, 1462, 1413, 1367, 1166, 1124, 1095, 1072, 792, 761, 673, 599, 564, 539, 507 cm^{-1}. MS (EI): *m/z* (%) 276, 248, 203, 175, 111 (100), 75, 69, 50. HRMS: Calcd for $ClC_7H_4S_2O_2F_3$: 275.9293; Found: 275.9295.

***S*-(trifluoromethyl) 4-nitrobenzenesulfonothioate 10e.** Colorless liquid (71.7 mg, 50%). Eluent: ethyl acetate/petroleum ether = 1/3, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.47 (d, *J* = 8.8 Hz, 2 H), 7.21 (d, *J* = 8.8 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -37.9 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 151.4, 149.5, 129.3, 127.1 (q, *J* = 314.2 Hz), 125.1 ppm. IR (KBr): ν = 3109, 3070, 2874, 1608, 1537, 1403, 1348, 1313, 1163, 1096, 1070, 1012, 965, 854, 761, 745, 734, 624, 599, 552 cm^{-1}. MS (EI): *m/z* (%) 287, 271, 228, 186 (100), 122, 92, 76, 69, 50. HRMS: Calcd for $NC_7H_4S_2O_4F_3$: 286.9534; Found: 286.9537.

***S*-(trifluoromethyl) 4-bromobenzenesulfonothioate 10f.** Colorless liquid (145.5 mg, 91%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.86 (d, *J* = 8.4 Hz, 2 H), 7.76 (d, *J* = 8.4 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.1 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 143.7, 133.2, 131.0, 129.2, 127.3 (q, *J* = 313.5 Hz) ppm. IR (KBr): ν = 1571, 1470,

1392, 1366, 280, 1170, 1100, 1073, 1009, 761, 739, 624, 598, 553 cm^{-1}. MS (EI): *m/z* (%) 322, 282, 219 (100), 155, 108, 75, 69, 50. HRMS: Calcd for $C_7H_4O_2F_3S_2Br$: 319.8788; Found: 319.8784.

***S*-(trifluoromethyl) 4-fluorobenzenesulfonothioate 10g.** Colorless liquid (120.9 mg, 93%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.06-8.02 (m, 2 H), 7.31-7.26 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.4 (s, 3 F), -99.77 (m, 1 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 166.6 (d, *J* = 260.0 Hz), 140.8, 131.0 (d, *J* = 9.6 Hz), 127.4 (q, *J* = 315.6 Hz), 117.3 (d, *J* = 23.6 Hz) ppm. IR (KBr): ν = 1589, 1492, 1409, 1366, 1295, 1246, 1155, 1101, 1072, 841, 816, 761, 658, 582, 556, 520 cm^{-1}. MS (EI): *m/z* (%) 259.9, 207, 159 (100), 95, 75, 69, 50. HRMS: Calcd for $C_7H_4O_2F_4S_2$: 259.9589; Found: 259.9588.

***S*-(trifluoromethyl) 4-cyanobenzenesulfonothioate 10h**. Colorless liquid (113.5 mg, 85%). Eluent: ethyl acetate/petroleum ether = 1/5, R_f = 0.8. ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.12 (d, *J* = 8.8 Hz, 2 H), 7.93 (d, *J* = 8.8 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.1 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 148.0, 133.6, 128.4, 127.0 (q, *J* = 314.9 Hz), 118.9, 116.8 ppm. IR (KBr): ν = 3114, 3071, 3041, 2237, 1398, 1369, 1357, 1307, 1292, 1185, 1154, 1099, 1068, 1016, 968, 837, 795, 762, 714, 627, 576, 559, 537, 498 cm^{-1}. MS (EI): *m/z* (%) 267, 228, 166, 102 (100), 75, 69, 50. HRMS: Calcd for $C_8H_4O_2F_3S_2N$: 266.9636; Found: 266.9632.

***S*-(trifluoromethyl) pyridine-3-sulfonothioate 10i.** Colorless liquid (103.3 mg, 85%). Eluent: ethyl acetate/petroleum ether = 1/10, R_f = 0.8. ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 9.18 (s, 1 H), 8.93 (d, *J* = 8.0 Hz, 1 H), 8.26 (d, *J* = 8.0 Hz, 1

H), 7.58 (t, J = 8.0 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.3 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 155.4, 148.4, 141.6, 135.4, 127.2 (q, J = 313.6 Hz), 124.4 ppm. IR (KBr): ν = 1574, 1565, 1418, 1367, 1170, 1106, 1082, 1033, 1016, 761, 739, 696, 618, 596, 557, 541 cm^{-1}. MS (EI): *m/z* (%) 242.9, 142 (100), 78, 69, 51. HRMS: Calcd for $C_6H_4O_2F_3S_2N$: 242.9636; Found: 242.9631.

***S*-(trifluoromethyl) 3-methylquinoline-8-sulfonothioate 10j.** White solid (149.3 mg, 97%). Mp: 133-134 ^{o}C. Eluent: ethyl acetate/petroleum ether = 1/5, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.95 (d, J = 2.4 Hz, 1 H), 8.35 (dd, J = 8.0, 1.6 Hz, 1 H), 8.09 (dd, J = 8.0, 1.6 Hz, 1 H), 8.05 (s, 1 H), 7.62 (t, J = 8.0 Hz, 1 H), 2.56 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -38.3 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 153.7, 141.2, 140.3, 135.4, 135.2, 133.1, 129.6, 129.2, 128.0 (q, J = 313.6 Hz), 125.3, 18.8 ppm. IR (KBr): ν = 1574, 1565, 1418, 1367, 1170, 1106, 1082, 1033, 1016, 761, 739, 696, 618, 596, 557, 541 cm^{-1}. MS (EI): *m/z* (%) 307, 243, 138, 206, 174, 142 (100), 115, 89, 77, 69, 51. HRMS: Calcd for $C_{11}H_9O_2F_3S_2N$ (M+H) : 308.0021; Found: 308.0023.

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Associated Content

Supporting Information. NMR spectra of all products and cif file of single crystal **10j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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