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N-Trifluoromethylthio-dibenzenesulfonimide: A Shelf-Stable, Broadly Applicable Electrophilic Trifluoromethylthiolating Reagent

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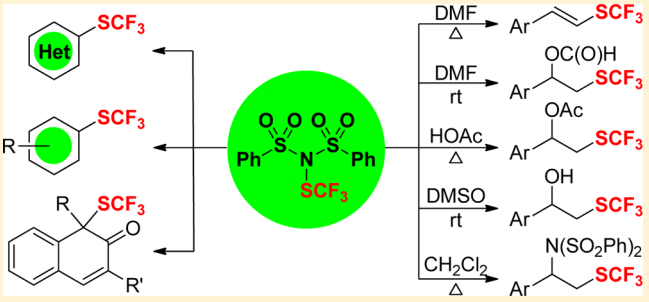
Supporting Information

ABSTRACT: The super electrophilicity of a shelf-stable, easily prepared trifluoromethylthiolating reagent *N*-trifluoromethylthio-dibenzenesulfonimide **7** was demonstrated. Consistent with the theoretical prediction, **7** exhibits reactivity remarkably higher than that of other known electrophilic trifluoromethylthiolating reagents. In the absence of any additive, **7** reacted with a wide range of electron-rich arenes and activated heteroarenes under mild conditions. Likewise, reactions of **7** with styrene derivatives can be fine-tuned by simply changing the reaction solvents to generate trifluoromethylthiolated styrenes or oxo-trifluoromethylthio or amino-trifluoromethylthio difunctionalized compounds in high yields.



INTRODUCTION

With a significantly high Hansch's hydrophobicity parameter (π = 1.44),[1] the electron-withdrawing trifluoromethylthio group (CF_3S-) has been considered as one of privileged fragments that are able to improve drug molecules' pharmacokinetic and physicochemical properties such as lipophilicity and metabolic stability.[2] Drugs and agrochemicals bearing a trifluoromethylthio group such as coccidiostat medicine Toltrazuril,[3] pesticide Fipronil,[4] and anorectic drug Tiflorex[5] (Figure 1) have already been on the market. Consequently, in the past several years, great effort has been intensively devoted to exploring new efficient methods for the incorporation of the trifluoromethylthio group into small molecules.[6]

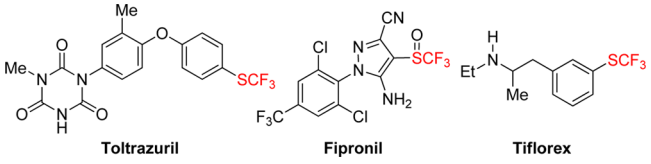


Figure 1. Drugs and agrochemicals containing a trifluoromethylthio group.

Among many strategies developed for introduction of the trifluoromethylthio group,[7,8] direct trifluoromethylthiolation using an electrophilic trifluoromethylthiolating reagent represents one of the most straightforward and promising approaches for the incorporation of the trifluoromethylthio group into small molecules.[9] In the early 1960s, the first two electrophilic trifluoromethylthiolating reagents CF_3SCl and CF_3SSCF_3 were reported.[10] Yet, the highly toxic nature of both reagents limited their practical applications.[11] Since then, a series of readily prepared, easy to handle, and stable electrophilic trifluoromethylthiolating reagents have been designed and synthesized,[12−17] allowing efficient incorporation of the trifluoromethylthio group into small molecules under mild conditions (Figure 2).

In 2013, our group discovered a general method for the preparation of a family of amide-based electrophilic trifluoromethylthiolating reagents by treating halogenated amide with $AgSCF_3$ in CH_3CN at room temperature.[17a,9b] By using this

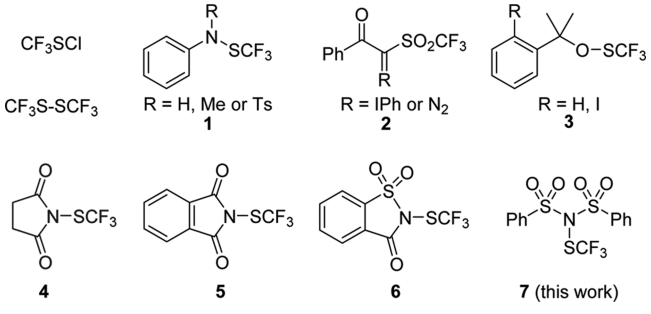


Figure 2. Electrophilic trifluoromethylthiolating reagents.

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method, we were able to efficiently synthesize *N*-trifluoromethylthiosuccinimide **4**,[15b] *N*-trifluoromethylthiophthalimide **5**,[16b] and *N*-trifluoromethylthiosaccharin **6**.[17a] We were thrilled to find that **6** is much more electrophilic than **5**, albeit the only structural difference is that one of the carbonyl groups in reagent **5** is replaced by a stronger electron-withdrawing sulfonyl group in reagent **6**. As a logical extension, we envisaged that if a compound with two sulfonyl groups such as $(PhSO_2)_2NSCF_3$ **7** could be developed, a new trifluoromethylthiolating reagent with much higher reactivity would be created.

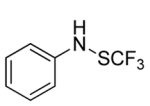
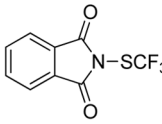
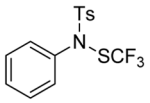
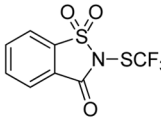
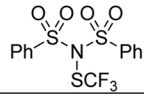
On the other hand, to quantitatively compare the electrophilicity of various trifluoromethylthiolating reagents, we established a new parameter of trifluoromethylthio cation donating ability (Tt^+DA) through density functional theory calculations. The lower the value of Tt^+DA, the higher the electrophilicity of the reagent, which fits well with the experimentally observed electrophilic reactivities of the reagents.[18] An excellent correlation has been observed between the Tt^+DAs of the reagents and the pK_a values of the corresponding amides. More specifically, the lower the pK_a of the corresponding amide, the lower Tt^+DA and the higher electrophilicity of the reagent. For example, as the amides vary from succinimide to phthalimide and saccharin, their pK_a values show a decreasing trend (10.52,[19] 10.06,[20] and 1.8[21]), as well as the Tt^+DA values of the corresponding reagents **4**–**6** (34.9, 33.0, and 17.9 kcal mol^{-1}, respectively). Following this trend and considering the pK_a of $(PhSO_2)_2NH$ (1.45),[22] we predicted that **7** would exhibit an even lower Tt^+DA value. Indeed, applying the same theoretical model to **7** gave a Tt^+DA of 9.8 kcal mol^{-1}, indicating that $(PhSO_2)_2NSCF_3$ should be much more electrophilic than **6** (Tt^+DA: 17.9 kcal mol^{-1}) and surprisingly even slightly more electrophilic than CF_3SCl (Tt^+DA: 11.1 kcal mol^{-1}).

To prove the validity of the theoretical prediction and our instinct rationale about the electrophilicity of $(PhSO_2)_2NSCF_3$, in the past two years, we have successfully synthesized $(PhSO_2)_2NSCF_3$ and systematically studied its reactivity. As described in this paper, our studies disclosed that, consistent with the theoretical prediction, **7** unprecedentedly exhibits an electrophilicity remarkably higher than that of other known electrophilic trifluoromethylthiolating reagents. In the absence of any additive, **7** reacted with a wide range of electron-rich arenes and activated heteroarenes under mild conditions to give the corresponding trifluoromethylthiolated compounds in high yields. Likewise, in the absence of any additive, reactions of **7** with styrene derivatives at 80 °C occurred smoothly to give trifluoromethylthioalkenes in high yields. In addition, when the same reaction was conducted at room temperature, a formoxy-trifluoromethylthio difunctionalized product was formed in high yields. Furthermore, the reactions can be fine-tuned to generate acetoxy-, hydroxy-, or amino-trifluoromethylthio difunctionalized compounds in high yields when different solvents are used. Finally, a dearomative trifluoromethylthiolation reaction took place for reactions of 2-naphthol derivatives with reagent **7** in the presence of a Lewis acid catalyst. Initial mechanistic studies for the reaction of formoxy-trifluoromethylthio difunctionalzation of styrene indicated that the reaction proceeded through a cation intermediate, thus supporting that reagent **7** is an excellent electrophilic trifluoromethylthiolating reagent.

RESULTS AND DISCUSSION

Tt^+DA Value of *N*-Trifluoromethylthio-dibenzenesulfonimide 7. The Tt^+DA parameter was recently proposed as a quantitative descriptor for the electrophilic trifluoromethylthiolating ability of various reagents.[18] Accordingly, we computed the Tt^+DA value of **7** using the same method described in the previous study, and the results are summarized in Table 1.

Table 1. Calculated Relative Tt^+DA Values of Electrophilic Trifluoromethylthiolating Reagents

Reagents	Tt^+DA in CH_2Cl_2 (kcal mol^{-1})	Reagents	Tt^+DA in CH_2Cl_2 (kcal mol^{-1})
 **1**	59.7[a]	 **5**	33.0[a]
 **1-Ts**	43.0[a]	 **6**	17.9[a]
CF_3SCl	11.1[a]	 **7**	9.8[b]

[a]Taken from ref 18. [b]Calculated in this study.

Notably, **7** shows the smallest Tt^+DA value (9.8 kcal mol^{-1}) among those reported *N*-SCF_3 reagents. Unexpectedly, the Tt^+DA value of **7** is even slightly smaller than that of CF_3SCl. These results suggest that, if **7** could be developed, it would be a powerful electrophilic trifluoromethylthiolating reagent.

Preparation of *N*-Trifluoromethylthio-dibenzenesulfonimide 7.[23,24] To verify the theoretical prediction, we set to synthesize **7** and test its reactivity. The preparation of **7** was relatively easy and can be accomplished in two steps starting from commercially available materials. However, the purification of this compound is a rather tedious task. Treatment of bis(phenylsulfonyl)imide with *tert*-butyl hypochlorite in methanol at room temperature for 5 min generated *N*-chlorodibenzenesulfonimide in 73% yield,[25] which was further reacted with 1.2 equiv of $AgSCF_3$ in CH_2Cl_2 for 2 h to form **7** in 89% yield, as determined by ^{19}F NMR spectroscopy (Figure 3). The

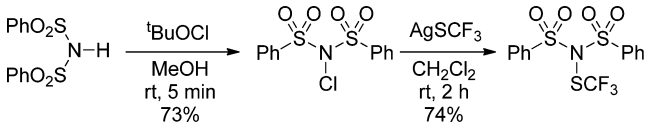


Figure 3. Preparation of *N*-trifluoromethylthio-dibenzenesulfonimide **7**.

main side product in the reaction mixture (typically 10–20% impurity) is bis(phenylsulfonyl)imide, which is difficult to remove. Initial efforts using column chromatography, recrystallization, or extraction with aqueous dilute sodium bicarbonate solution remained fruitless. After many tries, we discovered that 99% pure **7** can be obtained by multiple extractions of the oily crude mixture with petroleum ether followed by removal of petroleum ether under vacuum. The reaction can be easily scaled up to 4.0 g quantities, and compound **7** was isolated as a white solid in 74% yield. Compound **7** was characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopies and elemental analysis. The

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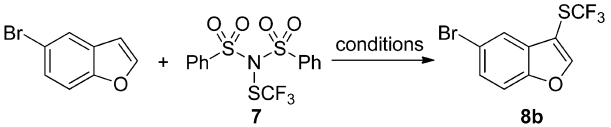
structure of compound 7 was unambiguously confirmed by X-ray analysis of its single crystals (see the Supporting Information for details).

7, a white crystalline solid, is slightly moisture sensitive but not air and light sensitive. No detectable decomposition was observed after more than three-month storage in a desiccator on shelf at ambient temperature. Compound 7 is stable in solvents such as $ClCH_2CH_2Cl$, toluene, $CHCl_3$, and CH_3CN at 80 °C for at least 24 h as determined by ^{19}F NMR spectroscopy. Compound 7 is less stable in solvents such as DMF or DMSO. It was completely decomposed after 24 h in DMF, DMSO, and acetone at room temperature or 12 h at 80 °C as determined by ^{19}F NMR spectroscopy.

Optimization of Reaction Conditions for Direct Trifluoromethylthiolation of Electron-Rich Heteroarenes. One of the most straightforward methods for the preparation of trifluoromethylthiolated arenes or heteroarenes is the Friedel–Crafts-type trifluoromethylthiolation of arenes with an electrophilic trifluoromethylthiolating reagent.[9] Typically, a Lewis acid or Brønsted acid is required to activate the trifluoromethylthiolating reagent.[16i,17a,b] For example, reactions of a variety of arenes or heteroarenes such as phenols, indoles, and pyrroles with *N*-trifluoromethylthiosaccharin **6** occurred successfully in the presence of 1.0 equiv of TMSCl or triflic acid to give the corresponding trifluoromethylthiolated arenes in high yields.[17a]

A problematic substrate of the Friedel–Crafts-type trifluoromethylthiolation reaction is benzofuran. Under the generally optimized conditions using 1.0 equiv of triflic acid as the activator, reaction of 5-bromobenzofuran with *N*-trifluoromethylthiosaccharin **6** occurred in less than 12% yield (Scheme 1, entries 1–2). With the new reagent in hand, we tested it to determine if it is electrophilic enough to react with 5-bromobenzofuran. Initially, reaction of 5-bromobenzofuran with 7 was conducted in the presence of 1.0 equiv of triflic acid in acetonitrile. It was found that the reaction occurred in less than 2% yield after 6 h at 80 °C. To our delight, the same reaction in DMF occurred smoothly to give 3-trifluoromethylthio-5-bromobenzofuran in 74% yield, as determined by ^{19}F NMR spectroscopy (Scheme 1, entries 3–4). Switching the additive from triflic acid to TMSCl led to a complete shut down of the reaction (Scheme 1, entry 5). Most strikingly, the control experiment led to the discovery that triflic acid is not required for the reaction. Reaction of 5-bromobenzofuran with 7 in DMF in the absence of triflic acid occurred in 83% yield after 6 h at 80 °C. The choice of the solvents is crucial for the conversion of the reaction. Reactions in other common solvents such as DMSO, THF, dioxane, toluene, or $ClCH_2CH_2Cl$ occurred in less than 25% yields (Scheme 1, entries 7–11). Further optimization showed that the yield increased to 90% when 2.0 equiv of reagent 7 was used (Scheme 1, entry 12). Finally, the reaction time can be shortened to 1 h without erosion of the yield (Scheme 1, entry 14). We also attempted to decrease the reaction temperature; however, the reaction conducted at 40 °C was much slower and occurred in only 62% yield after 6 h (Scheme 1, entry 13). As a comparison, no trifluoromethylthiolated product 3-trifluoromethylthio-5-bromobenzofuran was detected for the reaction of 5-bromobenzofuran with *N*-trifluoromethylthiosaccharin **6** in DMF for 1 h (Scheme 1, entry 15). These results clearly support the theoretical prediction that the electrophilicity of 7 is much higher than that of *N*-trifluoromethylthiosaccharin **6**.

Scheme 1. Optimization of Conditions for the Reaction of 5-Bromobenzofuran with Reagent 7[a,b]



7 8b

entry	reagent	solvent	additive	yield (%)[b]
1	**6**	CH_3CN	TfOH	12
2	**6**	DMF	TfOH	-
3	**7**	CH_3CN	TfOH	-
4	**7**	DMF	TfOH	74
5	**7**	DMF	TMSCl	-
6	**7**	DMF	-	83
7	**7**	DMSO	-	-
8	**7**	THF	-	25
9	**7**	dioxane	-	-
10	**7**	toluene	-	-
11	**7**	$ClCH_2CH_2Cl_2$	-	-
12	**7**	DMF	-	90[c]
13	**7**	DMF	-	62[e]
14	**7**	DMF	-	88[d]
15	**6**	DMF	-	-

[a]Reaction conditions: 5-bromobenzofuran (0.1 mmol), reagent 7 (0.15 mmol), and additive (0.1 mmol) in 0.5 mL of solvent at 80 °C for 6 h. [b]Yields were determined by ^{19}F NMR spectroscopy using trifluoromethylbenzene as the internal standard. [c]Two equivalents of reagent 7 were used. [d]Reaction was conducted for 1 h. [e]Reaction was conducted at 40 °C for 6 h.

Reaction of 7 with Electron-Rich Heteroarenes, Activated Electron-Poor Heteroarenes, and Arenes. As can be seen in the summary in Scheme 2, the reaction conditions optimized for trifluoromethylthiolation of 5-bromobenzofuran turned out to be quite efficient for trifluoromethylthiolation of a wide range of electron-rich heteroarenes and arenes. Reactions of a variety of heteroarenes such as benzofuran, benzothiophene, benzo[*d*]thiazole, imidazol(1,2-*α*)pyridines[26] bearing electron-withdrawing groups (bromide, cyano, nitro, and ester groups), and pyrroles[26] all underwent trifluoromethylthiolation in the absence of any additive in high yields (Scheme 2, **8a–g**, **8k–u**, and **8v–z**). Reactions of indoles were even faster than these heteroarenes. These reactions typically occurred in full conversion after 24 h at room temperature in CH_2Cl_2 to give the corresponding trifluoromethylthioindoles in high yields (Scheme 2, **8aa–8ae**).

Strikingly, activated electron-poor pyridine or pyrimidine with electron-donating substituent such as a methoxy group reacted with reagent 7 to give the corresponding trifluoromethylthiolated compounds in good yields under the current conditions (Scheme 2, **8h–j**). The same reactions with previously reported electrophilic trifluoromethylthiolating reagents **2–6**, however, occurred in less than 5% yields even in the presence of 1.0 equiv of a Lewis or Brønsted acid. Reaction of 2,6-dimethoxypyridine with reagent 7 proceeded smoothly to give a mixture of mono- and ditrifluoromethylthiolated products in a roughly 1:1 ratio (Scheme 2, **8h** and **8h′**). Likewise, reaction of 5-hydroquinoline with reagent 7 also generated the bis-trifluoromethylthiolated compound in 55% yield (Scheme 2, **8i**). Nevertheless, no trifluoromethylthiolated products were observed when we tried to trifluoromethylthiolate a few other heteroarenes such as 4,6-dimethylpyrimidin-

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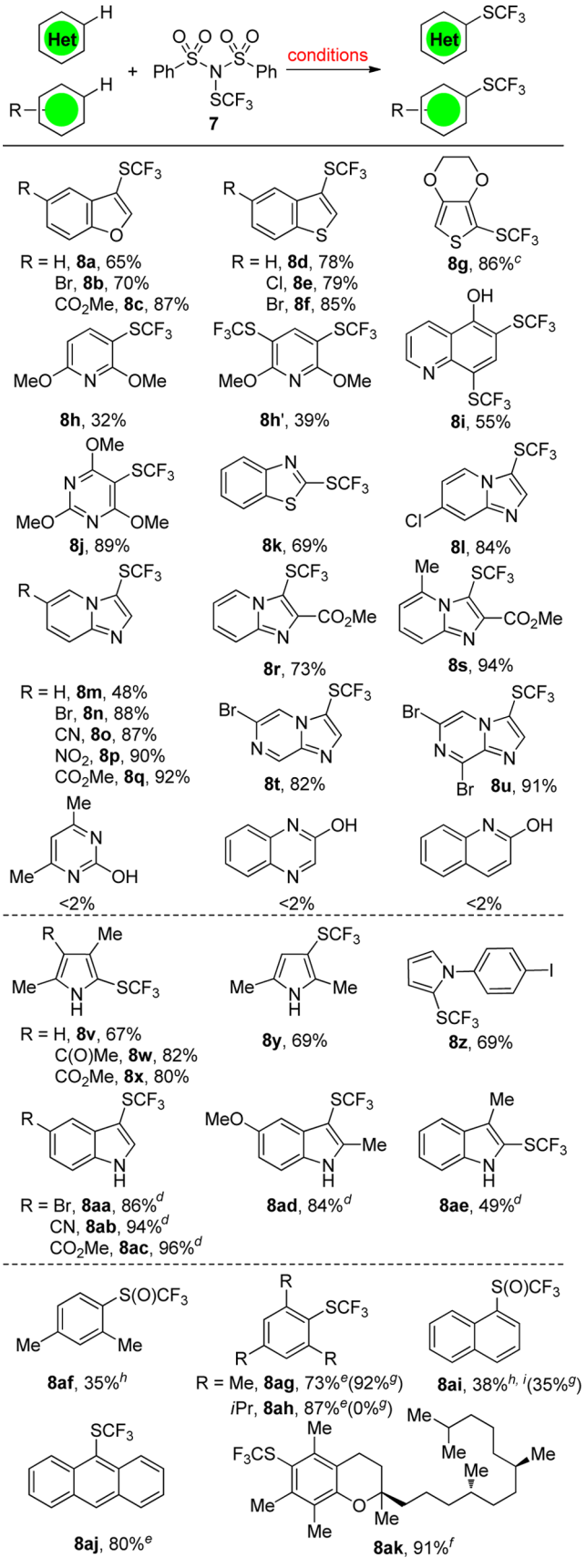
Scheme 2. Direct Trifluoromethylthiolation of Electron-Rich Heteroarenes, Activated Electron-Poor Heteroarenes, and Arenes[a,b]



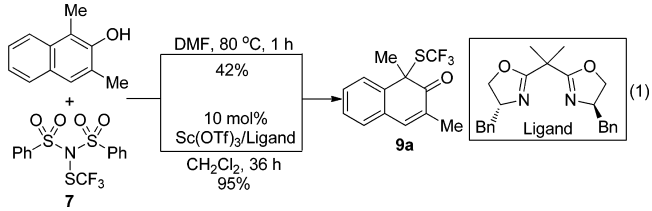
Scheme 2. continued

[a]Reaction conditions: heteroarene or arene (0.5 mmol) and reagent **7** (1.0 mmol) in DMF (2.0 mL) at 80 °C for 1 h. [b]Isolated yields. [c]Reagent **7** (1.5 equiv, 0.75 mmol) was used. [d]Indole (0.3 mmol) and reagent **7** (0.36 mmol) in CH_2Cl_2 (1.5 mL) at room temperature for 24 h. [e]Arene (1.0 mmol) and reagent **7** (0.5 mmol) in CH_2Cl_2 (2.0 mL) at 40 °C for 36 h in the presence of 1.2 equiv of triflic acid. [f]Arene (0.5 mmol) and reagent **7** (0.6 mmol) in CH_2Cl_2 (2.0 mL) at 40 °C for 36 h in the presence of 0.4 equiv of boron trifluoride etherate. [g]Arene (0.1 mmol) and reagent **7** (0.2 mmol) in DMF (0.5 mL) at 80 °C for 6 h; yield was determined by ^{19}F NMR spectroscopy using trifluoromethylbenzene as the internal standard. [h]Arene (0.8 mmol) and reagent **7** (0.4 mmol) in CH_2Cl_2 (2.0 mL) at 40 °C for 36 h in the presence of 1.2 equiv of triflic acid; the crude product was oxidized by 4.0 equiv of H_2O_2 in HOAc (2.0 mL) at 90 °C for 9 h. [i]The reaction was conducted on a 0.3 mmol scale.

2-ol, quinoxalin-2-ol, and quinolin-2-ol. Previously, trifluoromethylthiolated pyridine was accessed through reaction of in situ formed pyridyl Grignard reagent with Billard's second generation reagent **1-Ts**.[12c]

Encouraged by the excellent reactivity of reagent **7**, we next shifted our efforts to common trifluoromethylthiolate unactivated arenes, another family of problematic substrates for Friedel–Crafts-type electrophilic trifluoromethylthiolation. Interestingly, under the optimized conditions, reactions of these arenes with reagent **7** worked but were slower and required longer reaction times. For example, reactions of naphthalene and 1,3,5-trimethylbenzene in DMF occurred in 42 and 92% yields, respectively, after 6 h at 80 °C, as determined by ^{19}F NMR spectroscopy (Scheme 2, **8ag** and **8ai**). Reaction of more sterically hindered tri-isopropylbenzene, however, occurred to less than 5% conversion. Yet, in the presence 1.2 equiv of triflic acid, tri-isopropylbenzene reacted with reagent **7** to give the corresponding trifluoromethylthiolated product in 87% yield (Scheme 2, **8ah**). Similarly, a number of other common arenes were successfully trifluoromethylthiolated in good yields (Scheme 2, **8af**–**8ak**). Because the trifluoromethylthiolated arenes derived from 1,3-dimethylbenzene and naphathlene were difficult to purify, these compounds were oxidized to the corresponding sulfoxides **8af** and **8ai** (Scheme 2, **8af** and **8ai**).

Dearomative Trifluoromethylthiolation of Naphthol Derivatives. The reactions of naphthol derivatives with reagent **7** were different from those of other electron-rich arenes. For example, the formation of a new dearomative trifluoromethylthiolated product **9c** instead of the direct Friedel–Crafts-type electrophilic trifluoromethylthiolating product was observed when 1,3-dimethylnaphthol was reacted with reagent **7** in DMF at 80 °C for 1 h. The yield could not be improved by either elongating the reaction time or increasing reaction temperature. Yet, the yield of the same reaction could be significantly improved to 95% when a combination of 10 mol % $Sc(OTf)_3$ and 10 mol % of a benzyl version of the BOX ligand were used as the catalysts (eq 1) (see the Supporting



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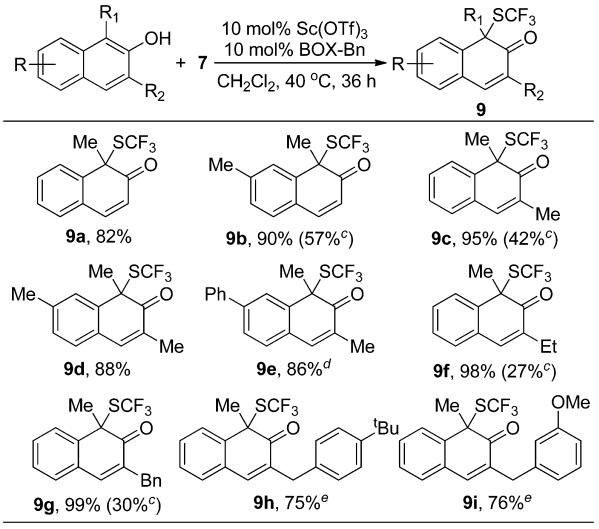
Information for details on the optimization process). Nevertheless, compound **9a** is racemic, as determined by chiral HPLC, although an optically pure Lewis acid was used as the catalyst.

As summarized in Scheme 3, a few derivatives of naphthol bearing different substituents could be successfully trifluoromethylthiolated to give the dearomative compounds in excellent yields. For example, reaction of 1-methylnaphthalen-2-ol or 1,7-dimethylnaphthalen-2-ol underwent dearomative trifluoromethylthiolation to give compounds **9a** and **9b** in 82 and 90% yields, respectively. To the best of our knowledge, the current reaction represents the first dearomative trifluoromethylthiolation reaction,[27] although much more effort is still needed to realize the asymmetric version of the reaction.

Scheme 3. Scope for Dearomative Trifluoromethylthiolation of Naphthol Derivatives with Reagent 7[a,b]

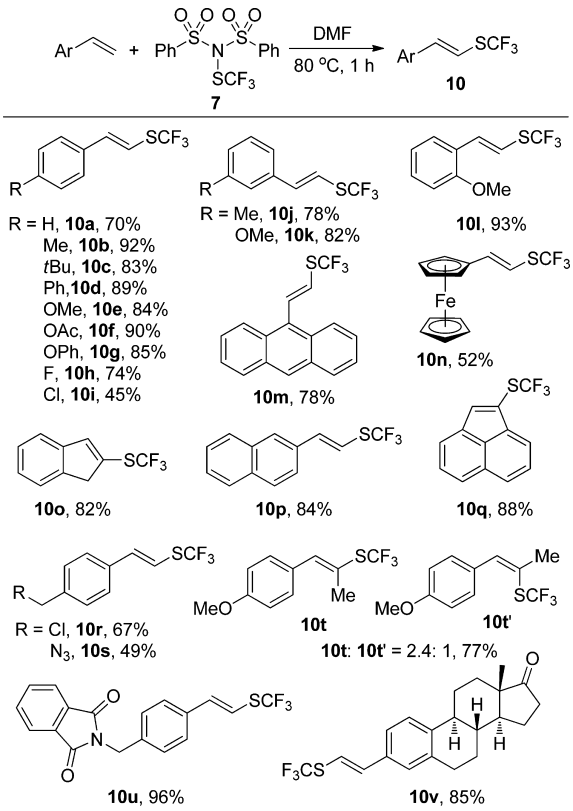


[a]Reaction conditions: naphthol derivative (0.5 mmol), reagent **7** (1.0 mmol), $Sc(OTf)_3$ (10 mol %), and BOX-Bn (10 mol %) in CH_2Cl_2 (2 mL) at 40 °C for 36 h. [b]Isolated yields. [c]Reaction of naphthol derivative (0.1 mmol) and reagent **7** (0.2 mmol) was conducted in DMF (0.5 mL) at 50 °C for 12 h, and the yield was determined by ^{19}F NMR spectroscopy using trifluoromethylbenzene as the internal standard. [d]The reaction was conducted on a 0.2 mmol scale. [e]The reactions were conducted on a 0.3 mmol scale.

Direct Trifluoromethylthiolation of Styrene Derivatives. The high reactivity of reagent **7** promotes us to study its reaction with other nucleophiles such as alkenes. We quickly discovered that reaction of styrene derivatives with reagent **7** in DMF generated trifluoromethylthiolated alkenes after 1 h at 80 °C in high yields. The discovery of such a simple and mild condition for direct trifluoromethylthiolation of alkenes is attractive. Previously, direct trifluoromethylthiolation of alkenes with an electrophilic trifluoromethylthiolating reagent was achieved by a dual photoredox/halide catalysis.[28] Other methods for the preparation of the trifluoromethylthiolated alkenes include the trifluoromethylthiolation of alkenyl iodides with $CuSCF_3$[29] or copper-catalyzed trifluoromethylthiolation of alkenyl boronic acids with an electrophilic trifluoromethylthiolating reagent.[14a,16b,e]

As summarized in Scheme 4, a variety of styrene derivatives with different substituted group can be efficiently trifluoromethylthiolated under the mild reaction conditions. In general, reaction of styrene derivatives with electron-donating groups reacted much faster than those with electron-withdrawing groups. For example, reaction of 1-methyl-4-vinylbenzene with reagent **7** afforded (*E*)-(4-methylstyryl)(trifluoromethyl)thioether **10b** in 88% yield, while reaction of methyl 4-vinylbenzoate with reagent **7** occurred in less than 10% yield, as determined by ^{19}F NMR spectroscopy. Not only did the styrene derivatives reacted highly efficiently, other aryl-substituted alkenes such as 9-vinylanthracene, vinylferrocene, 1-vinylnaphthalene, 1*H*-indene, and acenaphthylene also reacted with reagent **7** effectively to give the corresponding trifluoromethylthiolated alkenes (**10m**−**q**) in high yields. Likewise, reaction of 1,2-disubstituted styrene derivative (*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene with reagent **7** also occurred smoothly after 1 h at 80 °C to give the trifluoromethylthiolated alkene as a mixture of two isomers in a 2.4:1 ratio (Scheme 4). Because of the mild conditions of the reactions, various functional groups such as chloride, fluoride, enolizable ketone, ester, amide, alkyl chloride, and azide are compatible (Scheme 4, **10f**, **h**, **i**, **r**, **s**, **u**, and **v**). We also tried to extend the direct trifluoromethylthiolation of styrene derivatives to alkyl substituted alkenes. However, the reactions were messy under the current reaction conditions, as determined by ^{19}F NMR spectroscopy.

Scheme 4. Scope for Direct Trifluoromethylthiolation of Styrene Derivatives with Reagent 7[a]



[a]Reaction conditions: styrene derivative (0.5 mmol) and reagent **7** (1.0 mmol) in DMF (2.0 mL) at 80 °C for 1 h; isolated yields.

Preliminary Mechanistic Study of the Direct Trifluoromethylthiolating Reaction of Styrene Derivatives with Reagent 7. Experimentally, we observed that styrene derivatives with electron-donating groups reacted much faster than those with electron-withdrawing groups. In addition, the

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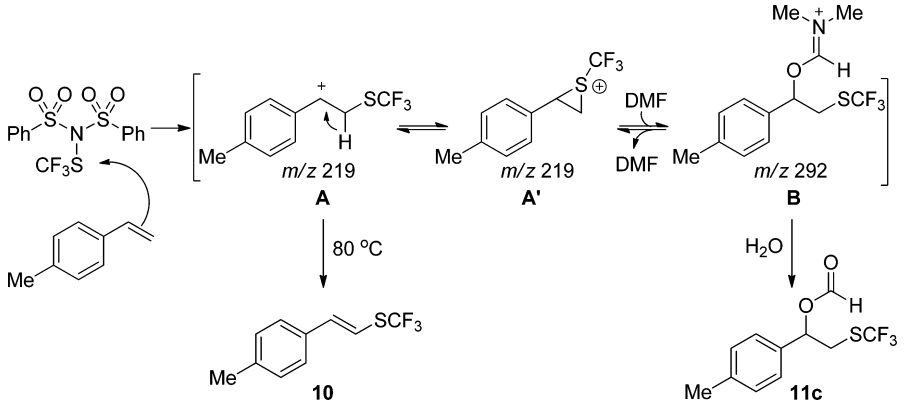

Figure 4. Proposed mechanism for direct trifluoromethylthiolation of styrene derivatives.

reaction occurred highly regioselectively to give β-trifluoromethylthio-substituted styrene derivatives. Furthermore, we also observed that reactions of alkyl-substituted alkenes with reagent **7** did occur in full conversion. Yet, a mixture that was difficult to separate and identify was generated.

On the basis of these observations, we tentatively proposed a working mechanism to explain the different rate and regioselectivity for the direct trifluoromethylthiolation of styrene derivatives, as shown in Figure 4. Initially, the electrophilic reagent **7** is attacked by styrene to form benzylic cation intermediate **A** or thiiranium intermediate **A′** followed by α-proton elimination to generate compound **10**. Because the intermediate **A** or **A′** is stabilized by the electron-donating group but destabilized by the electron-withdrawing group in the *para* position of the arenes, a faster reaction of the substrate with an electron-donating group is expected. On the other hand, the cation formed after the nucleophilic attack of an alkyl-substituted alkene undergoes elimination from two different α-protons, and the cation intermediate may also undergo cationic rearrangement, thus resulting in a mixture of different products for the reactions of alkyl-substituted alkenes.

To gain some experimental evidence about the proposed mechanism, at the beginning, we tried to monitor the reaction of 1-methyl-4-vinylbenze with reagent **7** in DMF in a NMR tube by ^{19}F NMR spectroscopy to determine if the cation intermediate can be observed. However, the main peak observed in the reaction mixture after 15 min at 80 °C was the trifluoromethylthiolated alkene product. We then monitored the reaction mixture at room temperature with the hope that the proton elimination process will be slower at this temperature. To our delight, a new peak at −41.6 ppm in ^{19}F NMR spectroscopy appeared in 75% yield. Heating the mixture at 80 °C for 1 h formed the trifluoromethylthiolated alkene in roughly 78% yield. This experiment suggests that the species with a chemical shift at −41.6 ppm is an intermediate toward the final product. To shed light on the structure of this species, we conducted an electrospray ionization tandem mass spectrometry (ESI-MS/MS) experiment. Two major peaks were detected in the ESI-MS spectrum after 1-methyl-4-vinylbenzene with reagent **7** in DMF was quickly mixed at room temperature. One signal at m/z 147 was assigned to be 2DMF·H$^+$ and the other signal at m/z 292 was assigned to be intermediate **B**: the addition of intermediate **A** or **A′** with a molecule of DMF (Figure 4). ESI-MS/MS experiments showed that DMF can be easily dissociated from intermediate **B** to form intermediate **A** or **A′** (m/z 219). Interestingly, addition of water to the reaction mixture generated 1-(*p*-tolyl)-2-(trifluoromethylthio)ethyl formate **11c** in 78% yield that was formed through hydrolysis of dimethylated carbamate ion **B**. These experiments clearly suggest intermediate **B** is derived from the attack of DMF toward intermediate **A** or **A′**. Overall, these experiments support our mechanistic assumption that the reaction proceeds through a nucleophilic attack of styrene to electrophilic trifluoromethylthiolating reagent **7**.

Direct Formoxy-, Actoxy- or Hydroxy-Trifluoromethylthiolation of Styrene Derivatives in the Absence of Activator. Compound **11c**, the hydrolysis product of intermediate **B**, can be generally regarded as a product derived from formoxy-trifluoromethylthio difunctionalization of styrene. Because 1,2-difunctionalization of alkenes represents one of the most direct, atom-economical and synthetically important transformations,[30] we studied this reaction in detail. In general, styrene derivatives with electron-donating groups reacted smoothly at room temperature after 1 h to give the corresponding formoxy-trifluoromethylthiolated compounds **11a−j** in high yields, as summarized in Scheme 5. Interestingly, other polar solvents such as acetic acid or DMSO could also react with intermediate **A or A′** to generate the corresponding actoxy- or hydroxyl-trifluoromethylthiolated products **12a−n** and **13a−j** in high yields. In these cases, cyclic alkenes also reacted with reagent **7** to give the corresponding products in high yields (Scheme 5, **12m** and **13i**). The hydroxyl-trifluoromethylthiolated products are likely derived from hydrolysis of the intermediates formed from the reaction of DMSO with intermediate **A** or **A′**.[31] Previously reported acetoxy-trifluoromethylthio difunctionalization of styrene derivatives typically required a combination of a catalytic amount of diarylselenide and stoichiometric amount of triflic acid to activate **6**[17e,23] or stoichiometric Lewis or Brønsted acid to activate Billard's reagent **1**.[12b]

Direct Amino-Trifluoromethylthiolation of Alkenes in the Absence of Activator.[32] Interestingly, when the less polar solvent CH_2Cl_2 was used, reaction of styrene derivatives with reagent **7** also occurred smoothly to give the corresponding amino-trifluoromethylthio difunctionalized products **14a−q** in synthetically useful yields, although the reactions were slow and generally required reaction in refluxed dichloromethane for 36 h. As summarized in Scheme 6, styrene derivatives with electron-donating groups reacted in high yields (Scheme 6, **14b−d**, **14g−i**), while reactions of styrene derivatives with electron-withdrawing groups occurred much slower and in much lower yields (Scheme 6, **14e** and **f**). Furthermore, cyclic alkenes or symmetric internal alkenes reacted with reagent **7** to generate the corresponding products

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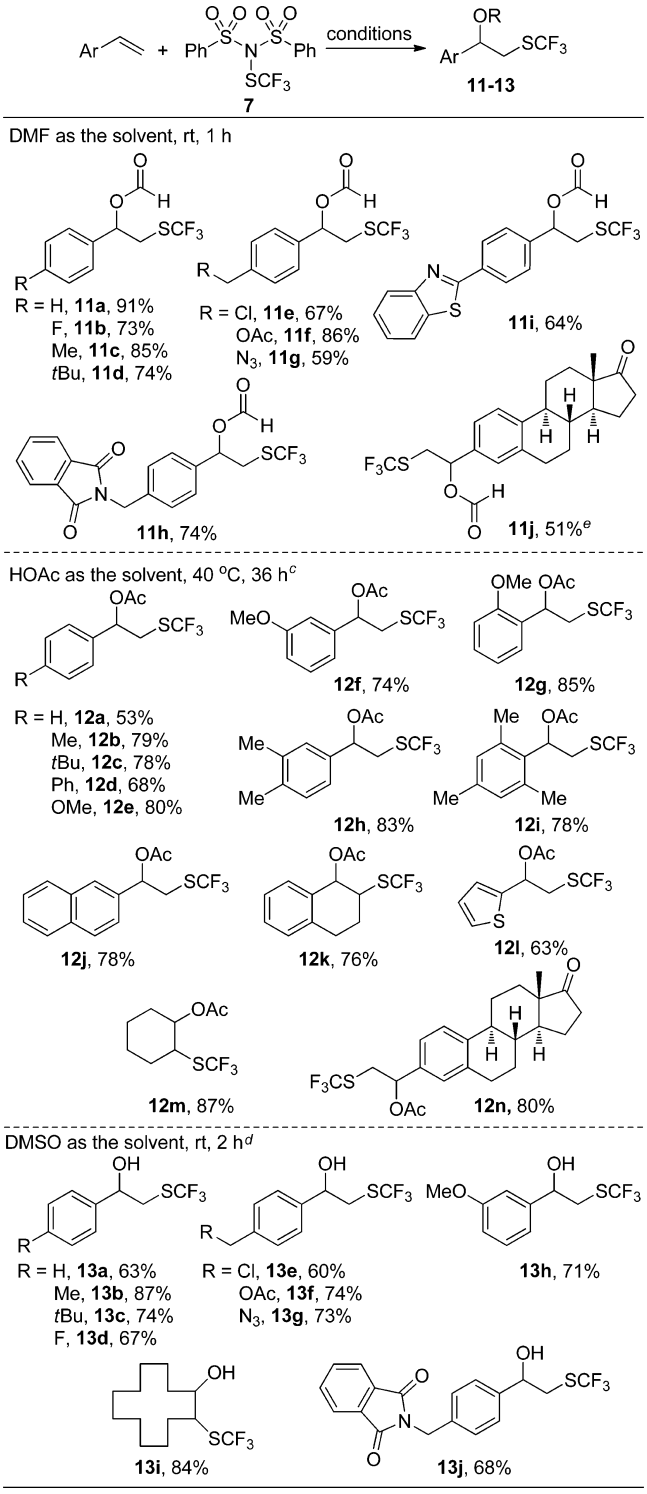
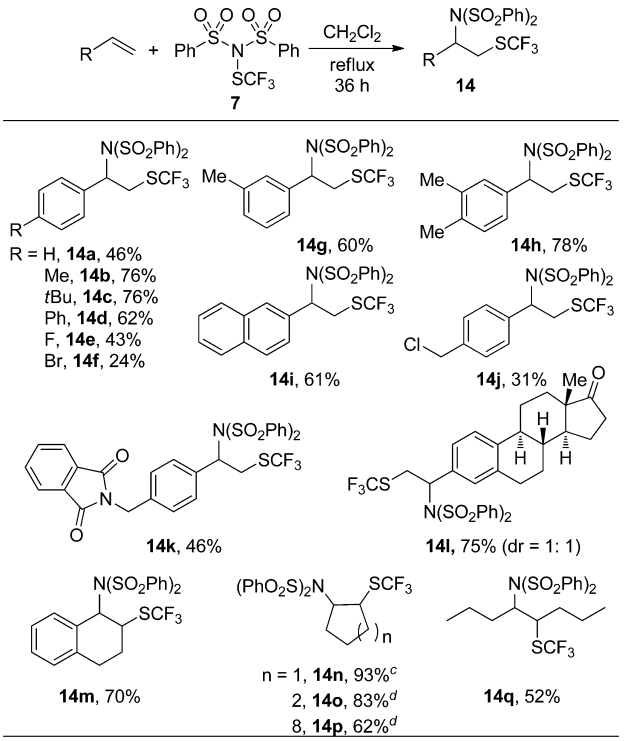
Scheme 5. Scope for Direct Formoxy-, Acetoxy-, or Hydroxy-Trifluoromethylthiolation of Styrene Derivatives in Different Solvents[a,b]



[a]Reaction conditions: alkene (0.5 mmol) and reagent 7 (1.0 mmol) in DMF (2.0 mL) at room temperature for 1 h. [b]Isolated yields. [c]The reactions were conducted in HOAc (2.0 mL) at 40 °C for 36 h. [d]The reactions were conducted in DMSO (2.0 mL) at room temperature for 2 h. [e]Alkene (0.4 mmol) was used.

as a pair of inseparable diastereomers in high yields (Scheme 6, **14n−q**).

Scheme 6. Scope for Direct Amino-Trifluoromethylthiolation of Alkenes with Reagent 7[a,b]



[a]Reaction conditions: alkene (0.5 mmol) and reagent 7 (1.0 mmol) in CH_2Cl_2 (2.0 mL) at 50 °C for 36 h. [b]Isolated yields. [c]40 °C. [d]Reagent 7 (1.5 equiv, 0.75 mmol) was used.

Reaction of Other Nucleophiles with *N*-Trifluoromethylthio-dibenzenesulfonimide 7. We also tried to extend the difunctionlization method of styrenes to other nucleophiles. However, the direct nucleophilic substitution products from the reactions of the nucleophiles such as 1*H*-indazoles, amines, thiols, or sodium benzenesulfinates with reagent **7** instead of the difunctionalization products were obtained, as summarized in Scheme 7. Furthermore, reactions of styrene and reagent **7** with other nucleophiles such as TMSCN or $TMSN_3$ in different solvents were also studied. In these cases, the reactions were messy.

Comparison of the Reactivities of *N*-Trifluoromethylthio-dibenzenesulfonimide 7 with Other Electrophilic Trifluoromethylthiolating Reagents. From the reactions of reagent **7** with heteroarenes, arenes, and styrene derivatives in different solvents, we can clearly see the power of reagent **7** as highly electrophilic trifluoromethylthiolating reagent. To gain more understanding about the electrophilicity of different electrophilic trifluoromethylthiolating reagents, we conducted a study to compare the electrophilicities of the known trifluoromethylthiolating reagents such as reagent **1** and its more powerful analogue **1-Ts**, reagents **3**, **5**, and **6**. The results for the reactions of these reagents with 5-bromobenzofuran, 4-methylstyrene, or 4-methoxystyrene under the optimization conditions developed in this paper are summarized in Scheme 8. In general, reagents **1**, **1-Ts**, and **5** showed reactivities significantly lower than that of reagent **7** because no desired trifluoromethylthiolating products were observed for reactions of these substrates with reagents **1**, **1-Ts**, and **5**. Reagents **3** and **6** did react with 4-methylstyrene, but both reactions were much slower than those with reagent **7**.

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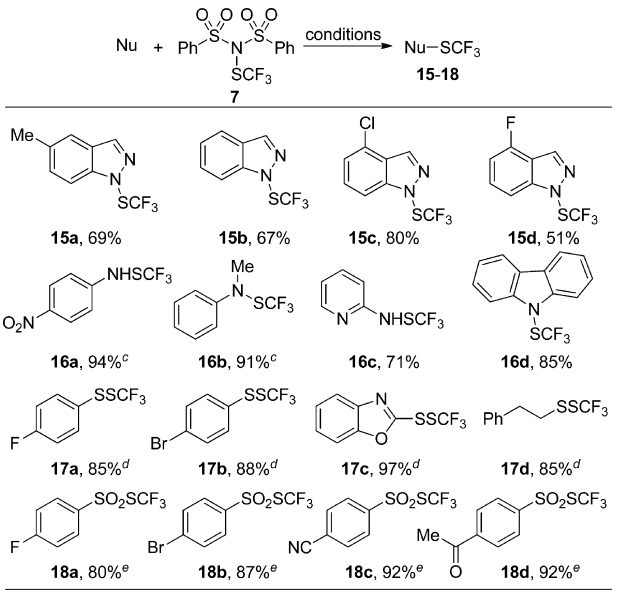
Scheme 7. Scope for Trifluoromethylthiolation of Different Nucleophiles with Reagent 7[a,b]



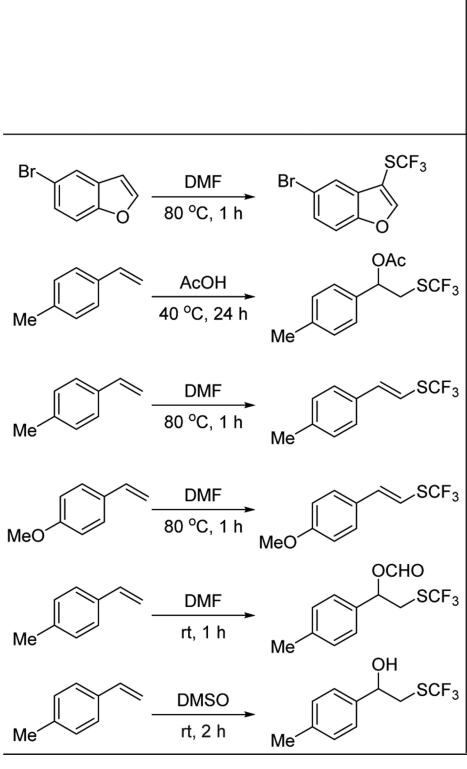
[a]Reaction conditions: indazole or amine (0.5 mmol) and reagent 7 (1.0 mmol) in DMF (2.0 mL) at 80 °C for 1 h. [b]Isolated yields. [c]Amine (0.3 mmol) and reagent 7 (0.36 mmol) in CH_2Cl_2 (1.5 mL) at room temperature for 24 h. [d]Thiol (0.3 mmol) and reagent 7 (0.33 mmol) in CH_2Cl_2 (1.5 mL) at room temperature for 12 h. [e]Sodium benzenesulfinate (0.6 mmol) and reagent 7 (0.30 mmol) in AcOH (1.5 mL) at room temperature for 12 h.

Interestingly, reagent **3** has an electrophilicity parameter much worse (Tt^+DA: 53.7 kcal mol^{-1}) than any of the other reagents (9.8−43.0 kcal mol^{-1}). Yet, the more reactive 4-methoxystyrene reacted with reagent **3** and gave the corresponding trifluoromethylthiolated alkenes in 83% yield. These results suggest that Tt^+DAs are more reliable when comparing electrophilicity of the analogue electrophilic *N*-SCF_3 reagents. Overall, these experiments clearly suggest the high electrophilicity of reagent **7** compared to that of other *N*-SCF_3 electrophilic trifluoromethylthiolating reagents.

CONCLUSION

In summary, we successfully demonstrated that the new electrophilic reagent **7** is an excellent electrophilic trifluoromethylthiolating reagent, consistent with our theoretical prediction. In the absence of any additive, reactions of **7** with a wide range of electron-rich arenes and activated heteroarenes underwent Friedel−Crafts-type electrophilic trifluoromethylthiolation under mild conditions. In the presence of a Lewis acid, reactions of 1-substituted-2-naphthol derivatives with reagent **7** occurred to give dearomative trifluoromethylthiolation products in high yields. In addition, in the absence of any additive, reactions of **7** with styrene derivatives in DMF occurred smoothly at 80 °C for 1 h to give trifluoromethylthiolated alkenes in high yields. Interestingly, the same reaction conducted at room temperature gave formoxy-trifluoromethylthio difunctionalized compounds in high yields. Furthermore, the reactions can be fine-tuned by changing the solvents to generate acetoxy- or hydroxy-trifluoromethylthio difunctionalized compounds in high yields. Likewise, when the reaction was conducted in the less polar solvent dichloromethane, an

Scheme 8. Comparison of the Reactivities of *N*-Trifluoromethylthio-dibenzenesulfonimide 7 with Other Electrophilic Trifluoromethylthiolating Reagents[a]



1	1-Ts	3	5	6	7
—	—	—	—	—	89%
—	—	—	—	21%	88%
—	—	33%	—	20%	81%
—	—	83%	—	46%	85%
—	—	—	—	—	78%
—	—	—	—	—	88%

[a]Yields were determined by ^{19}F NMR spectroscopy using trifluoromethbenzene as the internal standard.

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amino-trifluoromethylthio difunctionalization was successfully realized. Overall, as shown in this paper, the high electrophilicity of reagent 7 and the simple, mild reaction conditions of the reactions involving reagent 7 make it the choice reagent for incorporation of the trifluoromethylthio group into small molecules. Improvements to the purification process of the reagent and expansion of the scope of this reagent are underway and will be reported in the near future.

EXPERIMENTAL SECTION

General Information. All solvents were purified by standard methods. ^{1}H NMR spectra were recorded on a 500, 400, or 300 MHz spectrometer. ^{19}F NMR spectra were recorded on a 376 or 282 MHz spectrometer. ^{13}C NMR spectra were recorded on a 400 or 500 MHz spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0, and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the internal standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. All reactions were monitored by TLC or ^{19}F NMR. Flash column chromatography was carried out using 300−400 mesh silica gel at medium pressure. All reagents were received from commercial sources. Solvents were freshly dried and degassed according to the purification handbook *Purification of Laboratory Chemicals* before use.

Preparation of N-Trifluoromethylthio-dibenzenesulfonimide ***7***. To a suspension of *N*-(phenylsulfonyl)benzenesulfonamide (9.0 g, 30 mmol) in MeOH (10 mL) was added *t*BuOCl (5.0 mL) quickly. The suspension turned to a clear solution, and a large amount of white precipitate was formed after a few minutes. The precipitate was filtered and dried under high vacuum to give *N*-chloro-*N*-(phenylsulfonyl)-benzenesulfonamide as a white powder (7.3 g, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.09−8.02 (m, 4 H), 7.77−7.70 (m, 2 H), 7.63−7.56 (m, 14 H); ^{13}C NMR (126 MHz, $CDCl_3$, 293 K, TMS) δ 136.6, 135.2, 129.4, 129.3 ppm.

To a 100 mL round-bottomed flask charged with *N*-chloro-*N*-(phenylsulfonyl) benzenesulfonamide (4.0 g, 12 mmol) and $AgSCF_3$ (3.0 g, 14 mmol) was added dichloromethane (50 mL). The mixture was stirred vigorously at room temperature for 120 min and then filtered through a pad of Celite and washed with dichloromethane (50 mL). The filtrate was concentrated in vacuo to give a colorless oil. The residue was extracted with petroleum ether (50 mL × 10). The solution was combined, and the solvent was evaporated under vacuum. The colorless oil was transferred into a 50 mL round-bottomed flask using 20 mL of dichloromethane. The solvent was evaporated under vacuum. The residue was further dried under high vacuum to give **7** as a white solid (>99% purity, 3.5 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.05 (d, J = 8.1 Hz, 4 H), 7.71 (t, J = 7.4 Hz, 2 H), 7.58 (t, J = 7.7 Hz, 4 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −48.20 (s, 3 F); ^{13}C NMR (126 MHz, $CDCl_3$, 293 K, TMS) δ 138.0, 135.1, 129.3, 129.2, 127.6 (q, J = 318.8 Hz) ppm. Elemental analysis for $C_{13}H_{10}F_3NO_4S_3$ calcd C, 39.29; H, 2.54; N, 3.52; found C, 39.30; H, 2.56; N, 3.62.

General Procedure for Trifluoromethylthiolation of Electron-Rich Arenes and Heteroarenes (8a−8z). *N*-Trifluoromethylthio-dibenzenesulfonimide **7** (398 mg, 1.0 mmol) was placed into an oven-dried Schlenk tube equipped with a stirring bar under argon. Benzofuran (59 mg, 0.5 mmol) and freshly distilled DMF (2.0 mL) were added. The reaction was stirred at 80 °C for 1 h. Distilled water (10.0 mL) and ether (50.0 mL) were added, and the organic phase was separated. The organic phase was washed with distilled water (10.0 mL × 3). The organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give 3-trifluoromethylthio-benzofuran **8a** (70 mg, 65%, eluent: petroleum ether, R_f = 0.7) as a colorless liquid.

General Procedure for Trifluoromethylthiolation of Indoles (8aa−8ae). To a 25 mL oven-dried Schlenk tube charged with 5-bromo-1*H*-indole (59 mg, 0.3 mmol) were added **7** (144 mg, 0.36 mmol), and CH_2Cl_2 (1.5 mL). The mixture was stirred at room temperature for 24 h. The solvent was removed under vacuum, and the residue was purified by flask column chromatography to give 5-bromo-3-trifluoromethylthio-1*H*-indole **8aa** (80 mg, 86%, eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.2) as a white solid.

General Procedure for Trifluoromethylthiolation of Common Arenes (8ag, 8ah, and 8aj). *N*-Trifluoromethylthio-dibenzenesulfonimide **7** (199 mg, 0.5 mmol) was placed into an oven-dried Schlenk tube that was equipped with a stirring bar under argon. Mesitylene (121 mg, 1.0 mmol), triflic acid (90 mg, 0.6 mmol) and freshly distilled CH_2Cl_2 (2.0 mL) were added. The reaction was stirred at 40 °C for 36 h. The solvent was removed under vacuum and the residue was purified by flask column chromatography to give mesityltrifluoromethylthioether **8ag** (80 mg, 73%, eluent: petroleum ether, R_f = 0.8) as a colorless liquid.

General Procedure for Oxidation of Compounds 8af and 8ai. An aqueous solution (30% w/w) of H_2O_2 (1.6 mmol, 4.0 equiv) was dropped at room temperature onto a solution of the above crude sulfide in acetic acid (2.5 mL). The reaction was stirred at 90 °C for 9 h. The mixture was poured into water (10.0 mL) and extracted with diethyl ether (20 mL × 3). The gathered organic phases were washed with water (15 mL), saturated aqueous $NaHCO_3$ (15 mL × 2), and brine (15 mL) and then dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by flask column chromatography to give 2,4-dimethyl-1-(trifluoromethylsulfinyl)-benzene **8af** (32 mg, 35%, eluent: petroleum ether/ether = 10:1, R_f = 0.3) as a colorless oil

Procedure for Trifluoromethylthiolation of (*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman (8ak). *N*-Trifluoromethylthio-dibenzenesulfonimide **7** (239 mg, 0.6 mmol) was placed into an oven-dried Schlenk tube that was equipped with a stirring bar under argon. (*R*)-2,5,7,8-Tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman (207 mg, 0.5 mmol), boron trifluoride etherate (29 mg, 0.2 mmol) and freshly distilled CH_2Cl_2 (2.0 mL) were added. The reaction was stirred at 40 °C for 36 h. The solvent was removed under vacuum, and the residue was purified by flask column chromatography to give (*R*)-2,5,7,8-tetramethyl-6-(trifluoromethylthio)-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman **8ak** (233 mg, 91%, eluent: petroleum ether, R_f = 0.8) as a light yellow oil.

3-(Trifluoromethylthio)benzofuran ***8a***.[7a] The general procedure conducted with **7** (398 mg, 1.0 mmol), benzofuran (59 mg, 0.5 mmol), and DMF (2 mL) gave **8a** (70 mg, 65%) as a colorless liquid. Eluent: petroleum ether, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1 H), 7.76 (dd, J = 5.9, 2.7 Hz, 1 H), 7.61−7.53 (m, 1 H), 7.45−7.36 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.14 (s, 3 F) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 151.7 (d, J = 1.1 Hz), 129.1 (q, J = 309.8 Hz), 128.2, 125.8, 124.3, 120.2, 112.2, 103.3 (q, J = 2.8 Hz) ppm.

5-Bromo-3-(trifluoromethylthio)benzofuran ***8b***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 5-bromobenzofuran (99 mg, 0.5 mmol), and DMF (2 mL) gave **8b** (104 mg, 70%) as a colorless liquid. Eluent: petroleum ether, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1 H), 7.86 (s, 1 H), 7.50 (d, J = 8.8 Hz, 1 H), 7.43 (d, J = 8.7 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.02 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 152.8, 130.2, 129.0, 128.9 (q, J = 311.1 Hz), 123.0, 117.7, 113.7, 103.1 (q, J = 3.1 Hz) ppm. MS (EI) 296, 298. HRMS (EI) for $C_9H_4OF_3SBr$ calcd 295.9118; found 295.9115. IR (KBr) ν = 1530, 1438, 1281, 1258, 1167, 1102, 1053, 1014, 802, 694, 619 cm^{-1}.

Methyl 3-(trifluoromethylthio)benzofuran-5-carboxylate ***8c***. The general procedure conducted with **7** (398 mg, 1.0 mmol), methyl benzofuran-5-carboxylate (88 mg, 0.5 mmol), and DMF (2 mL) gave **8c** (120 mg, 87%) as a white solid. Eluent: petroleum ether/diethyl ether = 100:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1 H), 8.13 (d, J = 8.7 Hz, 1 H), 8.00 (s, 1 H), 7.59 (d, J = 8.7 Hz, 1 H), 3.93 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.97 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 158.0, 152.9, 128.9 (q, J = 311.1 Hz), 128.3, 127.6, 126.9, 122.6, 112.2, 104.3 (q, J = 3.1 Hz), 52.5 ppm. MS

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(EI) 245 (100), 276 (61.79). HRMS (EI) for $C_{11}H_7O_3F_3S$ calcd 276.0068; found 276.0072. IR (KBr) ν = 1711, 1612, 1592, 1533, 1434, 1315, 1277, 1236, 1192, 1166, 1098, 974, 771, 746, 700, 620, 424 cm^{-1}. Mp 81.1−82.0 °C.

3-(Trifluoromethylthio)benzo[b]thiophene **8d**. The general procedure conducted with **7** (398 mg, 1.0 mmol), benzo[*b*]thiophene (67 mg, 0.5 mmol), and DMF (2 mL) gave **8d** (91 mg, 78%) as a colorless liquid. Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 1 H), 7.96 (s, 1 H), 7.91−7.86 (m, 1 H), 7.51 (ddd, J = 8.1, 7.2, 1.1 Hz, 1 H), 7.47−7.41 (m, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.62 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 139.5, 138.1, 129.2 (q, J = 311.1 Hz), 125.5, 125.5, 123.0, 123.0, 115.4 (q, J = 2.1 Hz) ppm. MS (EI) 165 (100), 234 (67.60). HRMS (EI) for $C_9H_5F_3S_2$ calcd 233.9785; found 233.9779. IR (KBr) ν = 1455, 1421, 1255, 1107, 838, 754, 730, 460, 444 cm^{-1}.

5-Chloro-3-(trifluoromethylthio)benzo[b]thiophene **8e**. The general procedure conducted with **7** (398 mg, 1.0 mmol), 5-chlorobenzo[*b*]thiophene (85 mg, 0.5 mmol), and DMF (2 mL) gave **8e** (106 mg, 79%) as a white solid. Eluent: petroleum ether, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−7.96 (m, 2 H), 7.80 (d, J = 8.6 Hz, 1 H), 7.41 (dd, J = 8.6, 1.8 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.58 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 139.8, 137.7, 132.3, 129.0 (q, J = 312.1 Hz), 126.2, 124.0, 122.7, 114.9 (q, J = 2.1 Hz) ppm. MS (EI) 199 (100), 268. HRMS (EI) for $C_9H_4F_3S_2Cl$ calcd 267.9395; found 267.9397. IR (KBr) ν = 1425, 1410, 1248, 1162, 1126, 1104, 1076, 876, 843, 794, 619, 459 cm^{-1}. Mp 85.6−87.1 °C.

5-Bromo-3-(trifluoromethylthio)benzo[b]thiophene **8f**. The general procedure conducted with **7** (398 mg, 1.0 mmol), 5-bromobenzo[*b*]thiophene (107 mg, 0.5 mmol), and DMF (2 mL) gave **8f** (133 mg, 85%) as a white solid. Eluent: petroleum ether, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1 H), 8.00 (s, 1 H), 7.74 (d, J = 8.5 Hz, 1 H), 7.54 (dd, J = 8.5, 1.4 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.56 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 139.6, 138.2, 128.9 (q, J = 311.1 Hz), 128.8, 125.8, 124.3, 120.0, 114.9 (q, J = 2.1 Hz) ppm. MS (EI) 314 (100). HRMS (EI) for $C_9H_4F_3S_2Br$ calcd 311.8890; found 311.8893. IR (KBr) ν = 1582, 1423, 1404, 1161, 1129, 1103, 1067, 876, 842, 794, 615, 460 cm^{-1}. Mp 85.9−87.3 °C.

5-(Trifluoromethylthio)-2,3-dihydrothieno[3,4-b][1,4]dioxine **8g**. The general procedure conducted with **7** (398 mg, 1.0 mmol), 2,3-dihydrothieno[3,4-*b*][1,4]dioxine (71 mg, 0.5 mmol), and DMF (2 mL) gave **8g** (104 mg, 86%) as a white solid. Eluent: petroleum ether/ethyl acetate = 80:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (s, 1 H), 4.32−4.29 (m, 2 H), 4.23−4.19 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −45.11 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 141.5, 128.6 (q, J = 313.1 Hz), 108.0, 94.3 (d, J = 2.0 Hz), 65.3, 64.3 ppm. MS (EI) 173 (100), 242 (76.32). HRMS (EI) for $C_7H_5O_2F_3S_2$ calcd 241.9683; found 241.9686. IR (KBr) ν = 1573, 1491, 1450, 1418, 1371, 1248, 1196, 1142, 1108, 1068, 977, 907, 758, 750, 693, 451 cm^{-1}. Mp 68.5−69.3 °C.

2,6-Dimethoxy-3-(trifluoromethylthio)pyridine **8h**. The general procedure conducted with **7** (398 mg, 1.0 mmol), 2,6-dimethoxypyridine (70 mg, 0.5 mmol), and DMF (2 mL) gave **8h** (38 mg, 32%) as a white solid and **8h′** (65 mg, 39%) as a white solid. Eluent: petroleum ether, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 1 H), 6.36 (d, J = 8.2 Hz, 1 H), 4.01 (s, 3 H), 3.96 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.78 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 164.3, 150.2, 129.6 (q, J = 311.1 Hz), 103.1, 96.1 (d, J = 2.0 Hz), 54.4, 54.1 ppm. MS (EI) 239 (100). HRMS (EI) for $C_8H_8NO_2F_3S$ calcd 239.0228; found 239.0219. IR (KBr) ν = 1585, 1573, 1475, 1467, 1415, 1379, 1328, 1268, 1240, 1107, 1070, 1030, 1013, 812, 767, 753 cm^{-1}. Mp 38.5−39.5 °C.

2,6-Dimethoxy-3,5-bis(trifluoromethylthio)pyridine **8h′**. Eluent: petroleum ether, R_f = 0.4, pale yellow solid (65 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1 H), 4.07 (s, 6 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.76 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 159.0, 129.3 (q, J = 311.1 Hz), 98.2 (d, J = 2.1 Hz), 55.2 ppm. MS (EI) 339 (100). HRMS (EI) for $C_9H_7NO_2F_6S_2$ calcd 338.9822; found 338.9806. IR (KBr) ν = 1574, 1546, 1482, 1467, 1389, 1304, 1273, 1243, 1121, 1084, 770, 754, 434 cm^{-1}. Mp 63.2−64.2 °C.

6,8-Bis(trifluoromethylthio)quinolin-5-ol **8i**. The general procedure conducted with **7** (398 mg, 1.0 mmol), quinolin-5-ol (73 mg, 0.5 mmol), and DMF (2 mL) gave **8i** (94 mg, 55%) as a yellow orange solid. Eluent: petroleum ether/ethyl acetate = 2:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (dd, J = 4.2, 1.6 Hz, 1 H), 8.71 (dd, J = 8.4, 1.6 Hz, 1 H), 8.27 (br, 1 H), 7.58 (dd, J = 8.4, 4.3 Hz, 1 H), 7.42 (s, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.30 (s, 3 F), −42.50 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 153.6, 150.4, 144.4, 132.9, 129.7 (q, J = 311.1 Hz), 128.6 (q, J = 313.1 Hz), 122.1, 120.3, 117.5, 102.7 ppm. MS (EI) 345 (100). HRMS (EI) for $C_{11}H_5NOF_6S_2$ calcd 344.9717; found 344.9727. IR (KBr) ν = 2924, 1570, 1489, 1265, 1201, 1165, 1124, 1100, 1080, 870, 785, 498 cm^{-1}. Mp 144.5−145.5 °C.

2,4,6-Trimethoxy-5-(trifluoromethylthio)pyrimidine **8j**. The general procedure conducted with **7** (398 mg, 1.0 mmol), 2,4,6-trimethoxypyrimidine (85 mg, 0.5 mmol), and DMF (2 mL) gave **8j** (119 mg, 89%) as a white solid. Eluent: petroleum ether/ethyl acetate = 70:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.03 (s, 6 H), 4.01 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.63 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 166.0, 129.3 (q, J = 310.9 Hz), 80.9 (q, J = 1.8 Hz), 55.38, 55.35. MS (EI) 77 (100), 141 (95.23), 201 (81.81), 270 (53.94). HRMS (EI) for $C_8H_9N_2O_3F_3S$ calcd 270.0286; found 270.0278. IR (KBr) ν = 1569, 1500, 1469, 1454, 1366, 1196, 1122, 1048, 1002, 911, 797, 432 cm^{-1}. Mp 126.5−127.5 °C.

2-(Trifluoromethylthio)benzo[d]thiazole **8k**. The general procedure conducted with **7** (398 mg, 1.0 mmol), benzo[*d*]thiazole (68 mg, 0.5 mmol), and DMF (2 mL) gave **8k** (81 mg, 69%) as a brown liquid. Eluent: petroleum ether/diethyl ether = 90:1, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.1 Hz, 1 H), 7.89 (d, J = 8.0 Hz, 1 H), 7.59−7.44 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.22 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 151.9 (q, J = 3.1 Hz), 138.0, 128.3 (q, J = 312.1 Hz), 127.1, 126.8, 124.3, 121.4 ppm. MS (EI) 235 (100). HRMS (EI) for $C_8H_4NF_3S_2$ calcd 234.9737; found 234.9730. IR (KBr) ν = 2926, 1456, 1312, 1150, 1108, 1077, 991, 758, 727 cm^{-1}.

7-Chloro-3-(trifluoromethylthio)imidazo[1,2-a]pyridine **8l**. The general procedure conducted with **7** (398 mg, 1.0 mmol), 7-chloroimidazo[1,2-*a*]pyridine (77 mg, 0.5 mmol), and DMF (2 mL) gave **8l** (106 mg, 84%) as a white solid. Eluent: petroleum ether/ethyl acetate = 4:1, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 7.3 Hz, 1 H), 7.96 (s, 1 H), 7.74−7.63 (m, 1 H), 6.99 (dd, J = 7.3, 1.9 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −44.24 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 145.8, 134.2, 128.0 (q, J = 314.1 Hz), 124.7, 117.4, 115.7, 103.9 ppm. MS (EI) 183 (100), 185 (37.11), 252 (35.51), 254 (12.43). HRMS (EI) for $C_8H_4N_2F_3SCl$ calcd 251.9736; found 251.9733. IR (KBr) ν = 3097, 1628, 1511, 1296, 1170, 1143, 1129, 1100, 887, 855, 794, 641, 504, 468, 420 cm^{-1}. Mp 91.3−92.2 °C.

3-(Trifluoromethylthio)imidazo[1,2-a]pyridine **8m**. The general procedure conducted with **7** (398 mg, 1.0 mmol), imidazo[1,2-*a*]pyridine (59 mg, 0.5 mmol), and DMF (2 mL) gave **8m** (52 mg, 48%) as a white solid. Eluent: petroleum ether/ethyl acetate = 2:1, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 6.2 Hz, 1 H), 7.99 (d, J = 3.3 Hz, 1 H), 7.78−7.61 (m, 1 H), 7.45−7.33 (m, 1 H), 7.01 (t, J = 6.6 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −44.42 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 145.1, 128.2 (q, J = 314.1 Hz), 127.2, 124.4, 118.5, 114.0, 103.2 (q, J = 2.1 Hz) ppm. MS (EI) 149 (100), 218 (53.94). HRMS (EI) for $C_8H_5N_2F_3S$ calcd 218.0126; found 218.0124. IR (KBr) ν = 1633, 1495, 1337, 1298, 1112, 1024, 760, 747, 634, 486, 432 cm^{-1}.

6-Bromo-3-(trifluoromethylthio)imidazo[1,2-a]pyridine **8n**. The general procedure conducted with **7** (398 mg, 1.0 mmol), 6-bromoimidazo[1,2-*a*]pyridine (99 mg, 0.5 mmol), and DMF (2 mL) gave **8n** (131 mg, 88%) as a pale yellow solid. Eluent: petroleum ether/ethyl acetate = 4:1, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1 H), 7.95 (s, 1 H), 7.56 (d, J = 9.5 Hz, 1 H), 7.40 (dd, J = 9.5, 1.5 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −44.09 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 145.4, 130.7, 128.0 (q, J = 315.1 Hz), 124.6, 119.0, 109.1, 103.9 ppm. MS (EI) 229 (100), 227 (96.94), 296 (38.91), 298 (37.08). HRMS (EI) for $C_8H_4N_2F_3SBr$ calcd 295.9231; found 295.9232. IR (KBr) ν = 3091, 2362, 1508, 1490,

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1408, 1317, 1154, 1132, 1111, 806, 706, 634, 502, 465, 418 cm^{-1}. Mp 78.5−79.3 °C.

3-(Trifluoromethylthio)imidazo[1,2-a]pyridine-6-carbonitrile ***8o***. The general procedure conducted with **7** (398 mg, 1.0 mmol), imidazo[1,2-*a*]pyridine-6-carbonitrile (72 mg, 0.5 mmol), and DMF (2 mL) gave **8o** (105 mg, 87%) as a white solid. Eluent: petroleum ether/ethyl acetate = 4:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1 H), 8.14 (s, 1 H), 7.81 (d, J = 9.3 Hz, 1 H), 7.51 (dd, J = 9.3, 1.5 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.59 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 146.9, 130.5, 127.9 (q, J = 315.1 Hz), 127.2, 119.7, 115.9, 105.9 (d, J = 3.1 Hz) ppm. MS (EI) 174 (100), 243 (41.63). HRMS (EI) for $C_9H_4N_3F_3S$ calcd 243.0078; found 243.0076. IR (KBr) ν = 3027, 2237, 1628, 1529, 1504, 1426, 1323, 1297, 1181, 1153, 1138, 1105, 932, 749, 608, 429 cm^{-1}. Mp 129.1−129.9 °C.

6-Nitro-3-(trifluoromethylthio)imidazo[1,2-a]pyridine ***8p***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 6-nitroimidazo[1,2-*a*]pyridine (82 mg, 0.5 mmol), and DMF (2 mL) gave **8p** (120 mg, 90%) as a yellow green solid. Eluent: petroleum ether/ethyl acetate = 4:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, J = 1.4 Hz, 1 H), 8.19−8.10 (m, 2 H), 7.79 (d, J = 9.8 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.61 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 147.9, 138.6, 127.8 (q, J = 315.1 Hz), 124.3, 121.4, 118.4, 107.3 ppm. MS (EI) 194 (100), 263 (44.33). HRMS (EI) for $C_8H_4N_3O_2F_3S$ calcd 262.9976; found 262.9974. IR (KBr) ν = 3031, 1635, 1551, 1519, 1506, 1357, 1320, 1288, 1164, 1134, 1091, 836, 755, 730, 635, 422 cm^{-1}. Mp 111.3−112.0 °C.

Methyl 3-(Trifluoromethylthio)imidazo[1,2-a]pyridine-6-carboxylate ***8q***. The general procedure conducted with **7** (398 mg, 1.0 mmol), methyl imidazo[1,2-*a*]pyridine-6-carboxylate (88 mg, 0.5 mmol), and DMF (2 mL) gave **8q** (127 mg, 92%) as a white solid. Eluent: petroleum ether/ethyl acetate = 3:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1 H), 8.14−7.95 (m, 1 H), 7.85 (d, J = 8.6 Hz, 1 H), 7.63 (d, J = 9.4 Hz, 1 H), 3.91 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −44.23 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 149.6, 146.5, 128.1, 127.9 (q, J = 315.1 Hz), 126.8, 118.1, 117.8, 105.0 (d, J = 2.1 Hz), 52.7 ppm. MS (EI) 207 (100), 276 (32.69). HRMS (EI) for $C_{10}H_7N_2O_2F_3S$ calcd 276.0180; found 276.0184. IR (KBr) ν = 3037, 2958, 2847, 2358, 1716, 1632, 1436, 1297, 1214, 1168, 1157, 1120, 852, 770, 632, 523, 430 cm^{-1}. Mp 125.1−125.6 °C.

Ethyl 3-(Trifluoromethylthio)imidazo[1,2-a]pyridine-2-carboxylate ***8r***. The general procedure conducted with **7** (398 mg, 1.0 mmol), ethyl imidazo[1,2-*a*]pyridine-2-carboxylate (95 mg, 0.5 mmol), and DMF (2 mL) gave **8r** (105 mg, 73%) as a white solid. Eluent: petroleum ether/ethyl acetate = 3:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 6.9 Hz, 1 H), 7.75 (d, J = 9.1 Hz, 1 H), 7.47−7.38 (m, 1 H), 7.07 (t, J = 6.9 Hz, 1 H), 4.46 (q, J = 7.1 Hz, 2 H), 1.40 (t, J = 7.1 Hz, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.79 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 147.4, 143.6, 128.6, 128.2 (q, J = 315.1 Hz), 124.7, 119.3, 115.3, 106.6 (d, J = 2.1 Hz), 61.7, 14.2 ppm. MS (EI) 221 (100), 290 (44.24). HRMS (EI) for $C_{11}H_9N_2O_2F_3S$ calcd 290.0337; found 290.0340. IR (KBr) ν = 2990, 1732, 1634, 1505, 1225, 1156, 1112, 1064, 771, 752, 648 cm^{-1}. Mp 71.9−72.8 °C.

Ethyl 5-Methyl-3-(trifluoromethylthio)imidazo[1,2-a]pyridine-2-carboxylate ***8s***. The general procedure conducted with **7** (398 mg, 1.0 mmol), ethyl 5-methylimidazo[1,2-*a*]pyridine-2-carboxylate (102 mg, 0.5 mmol), and DMF (2 mL) gave **8s** (143 mg, 94%) as a light yellow oil. Eluent: petroleum ether/ethyl acetate = 4:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 9.0 Hz, 1 H), 7.28 (dd, J = 8.9, 7.2 Hz, 1 H), 6.72 (d, J = 7.0 Hz, 1 H), 4.44 (d, J = 7.1 Hz, 2 H), 2.98 (s, 3 H), 1.38 (t, J = 7.1 Hz, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −44.92 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 148.9, 145.2, 138.8, 128.6, 127.9 (q, J = 315.1 Hz), 117.8, 117.4, 106.6 (d, J = 2.1 Hz), 61.7, 22.0, 14.2 ppm. MS (EI) 189 (100), 235 (31.74), 304 (27.03). HRMS (EI) for $C_{12}H_{11}N_2O_2F_3S$ calcd 304.0493; found 304.0486. IR (KBr) ν = 2984, 1728, 1638, 1512, 1218, 1152, 1133, 1110, 1082, 1039, 787, 743 cm^{-1}.

6-Bromo-3-(trifluoromethylthio)imidazo[1,2-a]pyrazine ***8t***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 6-bromoimidazo[1,2-*a*]pyrazine (99 mg, 0.5 mmol), and DMF (2 mL) gave **8t** (122 mg, 82%) as a light yellow oil. Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J = 1.3 Hz, 1 H), 8.52 (d, J = 1.1 Hz, 1 H), 8.11 (s, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.94 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 143.4, 143.0, 127.8 (q, J = 315.1 Hz), 125.2, 118.2, 106.4 ppm. MS (EI) 230 (100), 228 (98.04), 297 (23.70), 299 (23.26). HRMS (EI) for $C_7H_3N_3F_3SBr$ calcd 296.9183; found 296.9180. IR (KBr) ν = 3034, 3009, 1597, 1482, 1440, 1317, 1174, 1151, 1110, 1079, 894, 727, 646, 459, 431 cm^{-1}. Mp 106.6−107.1 °C.

6,8-Dibromo-3-(trifluoromethylthio)imidazo[1,2-a]pyrazine ***8u***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 6,8-dibromoimidazo[1,2-*a*]pyrazine (139 mg, 0.5 mmol), and DMF (2 mL) gave **8u** (170 mg, 91%) as a pale solid. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1 H), 8.13 (s, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.62 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 141.5, 134.7, 127.7 (q, J = 315.1 Hz), 122.5, 118.0, 108.9 (d, J = 2.1 Hz) ppm. MS (EI) 69 (100), 308 (70.88), 377 (17.02). HRMS (EI) for $C_7H_2N_3F_3SBr_2$ calcd 374.8288; found 374.8279. IR (KBr) ν = 3118, 1586, 1478, 1456, 1428, 1313, 1236, 1163, 1112, 1094, 913, 858, 753, 649, 534, 462 cm^{-1}. Mp 119.8−120.6 °C.

3,5-Dimethyl-2-(trifluoromethylthio)-1H-pyrrole ***8v***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 2,4-dimethyl-1*H*-pyrrole (48 mg, 0.5 mmol), and DMF (2 mL) gave **8v** (65 mg, 67%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 200:1, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1 H), 5.88 (d, J = 2.7 Hz, 1 H), 2.25 (s, 3 H), 2.15 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −45.57 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.2, 131.7, 128.8 (q, J = 314.1 Hz), 110.4, 102.8 (d, J = 2.1 Hz), 13.4, 11.6 ppm. MS (EI) 126 (100), 195. HRMS (EI) for $C_7H_8NF_3S$ calcd 195.0330; found 195.0334. IR (KBr) ν = 3276, 2924, 2853, 1675, 1559, 1261, 1114, 844, 801 cm^{-1}.

1-(2,4-Dimethyl-5-(trifluoromethylthio)-1H-pyrrol-3-yl)ethanone ***8w***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-(2,4-dimethyl-1*H*-pyrrol-3-yl)ethanone (69 mg, 0.5 mmol), and DMF (2 mL) gave **8w** (97 mg, 82%) as a white solid. Eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 12.02 (s, 1 H), 2.44 (s, 3 H), 2.35 (s, 3 H), 2.39 (s, 3 H); ^{19}F NMR (376 MHz, $(CD_3)_2SO$) δ −44.53 (s, 3 F); ^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 193.6, 139.7, 131.6, 128.6 (q, J = 313.1 Hz), 122.0, 103.2 (d, J = 2.2 Hz), 30.7, 14.5, 12.4 ppm. MS (EI) 168 (100), 237. HRMS (EI) for $C_9H_{10}NOF_3S$ calcd 237.0435; found 237.0428. IR (KBr) ν = 3176, 3106, 3047, 2999, 1622, 1473, 1447, 1435, 1417, 1403, 1117, 953 cm^{-1}. Mp 172.3−173.1 °C.

Ethyl 2,4-Dimethyl-5-(trifluoromethylthio)-1H-pyrrole-3-carboxylate ***8x***. The general procedure conducted with **7** (398 mg, 1.0 mmol), ethyl 2,4-dimethyl-1*H*-pyrrole-3-carboxylate (84 mg, 0.5 mmol), and DMF (2 mL) gave **8x** (106 mg, 80%) as a white solid. Eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.7. ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 12.01 (s, 1 H), 4.16 (q, J = 7.1 Hz, 2 H), 2.41 (s, 3 H), 2.25 (s, 3 H), 1.25 (t, J = 7.1 Hz, 3 H); ^{19}F NMR (376 MHz, $(CD_3)_2SO$) δ −44.71 (s, 3 F); ^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 164.2, 140.3, 132.2, 128.6 (q, J = 313.1 Hz), 112.0, 103.0 (d, J = 2.2 Hz), 58.8, 14.2, 13.5, 11.6 ppm. MS (EI) 152 (100), 267. HRMS (EI) for $C_{10}H_{12}NO_2F_3S$ calcd 267.0541; found 267.0543. IR (KBr) ν = 3300, 2995, 1672, 1485, 1448, 1433, 1325, 1266, 1133, 1076, 786, 727 cm^{-1}. Mp 148.3−149.1 °C.

2,5-Dimethyl-3-(trifluoromethylthio)-1H-pyrrole ***8y***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 2,5-dimethyl-1*H*-pyrrole (48 mg, 0.5 mmol), and DMF (2 mL) gave **8y** (67 mg, 69%) as a yellow liquid. Eluent: petroleum ether/ethyl acetate = 90:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1 H), 5.97 (s, 1 H), 2.32 (s, 3 H), 2.22 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −45.50 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5, 129.9 (q, J = 310.1 Hz), 126.8, 112.7, 97.9 (d, J = 2.1 Hz), 13.0, 11.3 ppm. MS (EI) 126 (100), 195 (50.97). HRMS (EI) for $C_7H_8NF_3S$ calcd 195.0330; found 195.0332. IR (KBr) ν = 3386, 2926, 1591, 1407, 1115, 1077, 638, 544 cm^{-1}.

1-(4-Iodophenyl)-2-(trifluoromethylthio)-1H-pyrrole ***8z***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-(4-

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iodophenyl)-1*H*-pyrrole (135 mg, 0.5 mmol), and DMF (2 mL) gave **8z** (127 mg, 69%) as a white solid. Eluent: petroleum ether, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.6 Hz, 2 H), 7.13−7.04 (m, 3 H), 6.86 (dd, J = 3.8, 1.7 Hz, 1 H), 6.43−6.36 (m, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −45.24 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.3, 128.9, 128.7, 128.1 (q, J = 313.1 Hz), 124.6, 110.6, 93.5 ppm. MS (EI) 173 (100), 369 (23.05). HRMS (EI) for $C_{11}H_7NF_3SI$ calcd 368.9296; found 368.9293. IR (KBr) ν = 2962, 1507, 1487, 1436, 1323, 1260, 1144, 1105, 1009, 826, 730 cm^{-1}. Mp 48.5−49.5 °C.

5-Bromo-3-(trifluoromethylthio)-1H-indole **8aa**.[14g] The general procedure conducted with **7** (144 mg, 0.36 mmol), 5-bromo-1*H*-indole (59 mg, 0.3 mmol), and CH_2Cl_2 (1.5 mL) gave **8aa** (80 mg, 86%) as a white solid. Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.2. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.61 (s, 1 H), 7.93 (s, 1 H), 7.53 (d, J = 2.7 Hz, 1 H), 7.37 (dd, J = 8.6, 1.8 Hz, 1 H), 7.27 (d, J = 5.7 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −44.52 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 134.8, 134.0, 131.3, 129.4 (q, J = 311.1 Hz), 126.7, 122.1, 115.3, 113.3, 95.5 (q, J = 2.5 Hz) ppm.

3-(Trifluoromethylthio)-1H-indole-5-carbonitrile **8ab**.[14g] The general procedure conducted with **7** (144 mg, 0.36 mmol), 1*H*-indole-5-carbonitrile (43 mg, 0.3 mmol), and CH_2Cl_2 (1.5 mL) gave **8ab** (91 mg, 94%) as a white solid. Eluent: petroleum ether/ethyl acetate = 5:1, R_f = 0.3. ^{1}H NMR (400 MHz, d-DMSO, 293 K, TMS) δ 12.44 (s, 1 H), 8.07 (d, J = 2.7 Hz, 1 H), 7.97 (s, 1 H), 7.60 (d, J = 8.4 Hz, 1 H), 7.50 (dd, J = 8.5, 1.3 Hz, 1 H); ^{19}F NMR (376 MHz, d-DMSO) δ −44.21(s, 3 F); ^{13}C NMR (101 MHz, d-DMSO, 293 K, TMS) δ 138.3, 137.8, 129.2 (q, J = 311.1 Hz), 128.9, 125.4, 123.4, 119.9, 114.1, 103.5, 92.7 (q, J = 2.1 Hz) ppm.

Methyl 3-(Trifluoromethylthio)-1H-indole-5-carboxylate **8ac**.[14g] The general procedure conducted with **7** (144 mg, 0.36 mmol), methyl 1*H*-indole-5-carboxylate (53 mg, 0.3 mmol), and CH_2Cl_2 (1.5 mL) gave **8ac** (80 mg, 96%) as a white solid. Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.3. ^{1}H NMR (400 MHz, d-DMSO, 293 K, TMS) δ 12.25 (s, 1 H), 8.20 (s, 1 H), 7.99 (s, 1 H), 7.76 (dd, J = 8.6, 1.1 Hz, 1 H), 7.51 (d, J = 8.6 Hz, 1 H), 3.77 (s, 3 H); ^{19}F NMR (376 MHz, d-DMSO) δ −44.28 (s, 3 F); ^{13}C NMR (126 MHz, d-DMSO, 293 K, TMS) δ 166.8, 139.1, 137.0, 129.3 (q, J = 311.2 Hz), 128.7, 123.4, 122.6, 120.3, 112.8, 92.9 (q, J = 2.8 Hz), 51.9 ppm.

5-Methoxy-2-methyl-3-(trifluoromethylthio)-1H-indole **8ad**.[14g] The general procedure conducted with **7** (144 mg, 0.36 mmol), 5-methoxy-2-methyl-1*H*-indole (49 mg, 0.3 mmol), and CH_2Cl_2 (1.5 mL) gave **8ad** (66 mg, 84%) as a yellow solid. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.36 (s, 1 H), 7.18 (d, J = 8.7 Hz, 2 H), 6.87 (dd, J = 8.7, 2.4 Hz, 1 H), 3.91 (s, 3 H), 2.53 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −44.52 (s, 3 F). ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 155.5, 144.3, 131.6, 130.03, 129.99 (q, J = 312.1 Hz), 112.6, 111.8, 100.8, 92.2 (q, J = 2.0 Hz), 56.0, 12.2 ppm.

3-Methyl-2-(trifluoromethylthio)-1H-indole **8ae**.[14g] The general procedure conducted with **7** (144 mg, 0.36 mmol), 3-methyl-1*H*-indole (40 mg, 0.3 mmol), and CH_2Cl_2 (1.5 mL) gave **8ae** (34 mg, 49%) as a white solid. Eluent: petroleum ether/ethyl acetate = 50:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.12 (s, 1 H), 7.63 (d, J = 8.0 Hz, 1 H), 7.40−7.28 (m, 2 H), 7.19 (dd, J = 7.7, 7.0 Hz, 1 H), 2.47 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.10 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 137.5, 128.9 (q, J = 313.1 Hz), 128.1, 124.9, 123.8, 120.19, 120.15, 113.2 (q, J = 2.3 Hz), 111.3, 9.6 ppm.

2,4-Dimethyl-1-(trifluoromethylsulfinyl)benzene **8af**. The general procedure conducted with **7** (144 mg, 0.4 mmol), m-xylene (64 mg, 0.8 mmol), triflic acid (72 mg, 0.48 mmol), and CH_2Cl_2 (2.0 mL). The target compound was further oxidized by H_2O_2 (55 mg, 1.6 mmol) to give **8af** (32 mg, 35%) as a colorless oil. Eluent: petroleum ether/ether = 10:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.88 (d, J = 8.1 Hz, 1 H), 7.27 (d, J = 8.3 Hz, 1 H), 7.11 (s, 1 H), 2.42 (s, 3 H), 2.39 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.95 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 144.2, 138.0, 132.2, 131.2 (d, J = 1.1 Hz), 128.3, 126.1, 125.4 (q, J = 337.4 Hz), 21.5, 18.3 (d, J = 1.5 Hz) ppm. MS (EI) 153 (100), 222. HRMS (EI) for $C_9H_9OF_3S$ calcd 222.0326; found 222.0331. IR (KBr) ν = 2927, 1604, 1234, 1181, 1136, 1083, 818, 627, 465 cm^{-1}.

Mesityltrifluoromethylthioether **8ag**.[33] The general procedure conducted with **7** (199 mg, 0.5 mmol), mesitylene (121 mg, 1.0 mmol), triflic acid (90 mg, 0.6 mmol), and CH_2Cl_2 (2.0 mL) gave **8ag** (80 mg, 73%) as a colorless liquid. Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.00 (s, 2 H), 2.53 (s, 6 H), 2.30 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.99 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 145.4, 141.5, 130.3 (q, J = 311.1 Hz), 129.7, 120.2 (d, J = 1.6 Hz), 22.2, 21.3 ppm.

(Trifluoromethyl)(2,4,6-triisopropylphenyl)thioether **8ah**. The general procedure conducted with **7** (199 mg, 0.5 mmol), 1,3,5-triisopropylbenzene (205 mg, 1.0 mmol), triflic acid (90 mg, 0.6 mmol), and CH_2Cl_2 (2.0 mL) gave **8ah** (132 mg, 87%) as a colorless liquid. Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.12 (s, 2 H), 4.01−3.85 (m, 2 H), 3.01−2.87 (m, 1 H), 1.29 (d, J = 6.9 Hz, 6 H), 1.25 (d, J = 6.3 Hz, 12 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.75 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 155.2, 152.7, 129.8 (q, J = 311.1 Hz), 122.7, 118.0 (q, J = 1.5 Hz), 34.6, 31.8, 23.9 ppm. MS (EI) 290 (100), 305. HRMS (EI) for $C_{16}H_{23}F_3S$ calcd 304.1473; found 304.1478. IR (KBr) ν = 2930, 2872, 1598, 1464, 1364, 1152, 1110, 1065, 1035, 879 cm^{-1}.

1-(Trifluoromethylsulfinyl)naphthalene **8ai**. The general procedure conducted with **7** (60 mg, 0.3 mmol), naphthalene (77 mg, 0.6 mmol), triflic acid (54 mg, 0.36 mmol), and CH_2Cl_2 (1.5 mL). The target compound was further oxidized by H_2O_2 (41 mg, 1.2 mmol) to give **8ai** (28 mg, 38%) as a yellow oil. Eluent: petroleum ether/ether = 10:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.30 (d, J = 7.3 Hz, 1 H), 8.13 (d, J = 8.0 Hz, 2 H), 7.98 (d, J = 8.2 Hz, 1 H), 7.72 (t, J = 7.7 Hz, 1 H), 7.64 (p, J = 6.8 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −72.88 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 134.1, 133.7, 131.6, 130.6, 129.2, 128.3, 127.3, 126.3, 125.5, 125.4 (q, J = 338.4 Hz), 122.0 (d, J = 1.3 Hz) ppm. MS (EI) 175 (100), 244. HRMS (EI) for $C_{11}H_7OF_3S$ calcd 244.0170; found 244.0172. IR (KBr) ν = 2926, 1506, 1262, 1181, 1145, 1130, 1079, 801, 768, 470, 452 cm^{-1}.

Anthracen-9-yl-trifluoromethylthioether **8aj**. The general procedure conducted with **7** (199 mg, 0.5 mmol), anthracene (179 mg, 1.0 mmol), triflic acid (90 mg, 0.6 mmol), and CH_2Cl_2 (2.0 mL) gave **8aj** (112 mg, 80%) as a yellow green solid. Eluent: petroleum ether, R_f = 0.9. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.87 (d, J = 8.9 Hz, 2 H), 8.64 (s, 1 H), 8.04 (d, J = 8.4 Hz, 2 H), 7.78−7.62 (m, 2 H), 7.55 (dd, J = 11.2, 3.8 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.28 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 136.3, 132.6, 131.9, 129.9 (q, J = 313.1 Hz), 129.0, 128.0, 126.6, 125.8, 117.2 ppm. MS (EI) 210 (100), 279. HRMS (EI) for $C_{15}H_9F_3S$ calcd 278.0377; found 278.0373. IR (KBr) ν = 3049, 1439, 1309, 1266, 1165, 1100, 938, 899, 777, 730, 605 cm^{-1}. Mp 148.8−149.3 °C.

(R)-2,5,7,8-Tetramethyl-6-(trifluoromethylthio)-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman **8ak**. The general procedure conducted with **7** (239 mg, 0.6 mmol), (*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman (0.5 mmol), boron trifluoride etherate (0.2 mmol), and CH_2Cl_2 (2.0 mL) gave **8ak** (233 mg, 91%) as a light yellow oil. Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 2.63 (t, J = 6.7 Hz, 2 H), 2.52 (s, 3 H), 2.48 (s, 3 H), 2.14 (s, 3 H), 1.82 (qt, J = 13.4, 6.8 Hz, 2 H), 1.65−1.18 (m, 18 H), 1.15−1.06 (m, 6 H), 0.88−0.84 (m, 12 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.36 (s, 3 F); ^{13}C NMR (126 MHz, $CDCl_3$, 293 K, TMS) δ 154.3, 142.2, 141.7, 130.4 (q, J = 309.8 Hz), 124.1, 118.5, 113.7 (q, J = 1.5 Hz), 76.0, 39.6, 37.7−37.4 (m), 33.0−32.8 (m), 31.21, 31.16, 28.2, 24.99, 24.98, 22.9, 22.8, 21.6, 21.2, 19.9−19.7 (m), 19.3, 18.5, 12.8 ppm. MS (EI) 249 (100), 514. HRMS (EI) for $C_{30}H_{49}OF_3S$ calcd 514.3456; found 514.3460. IR (KBr) ν = 2927, 2868, 1559, 1458, 1379, 1306, 1147, 1107 cm^{-1}.

General Procedure for Dearomative Trifluoromethylthiolation of Naphthol Derivatives. **7** (398 mg, 1.0 mmol), $Sc(OTf)_3$ (25 mg, 0.05 mmol), BOX-Bn (19 mg, 0.05 mmol), and 1-methylnaphthalen-2-ol (79 mg, 0.5 mmol) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under argon. Freshly

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distilled CH_2Cl_2 (2.0 mL) was added, and the reaction was stirred at 40 °C for 36 h. The solvent was removed under vacuum, and the residue was purified by flask column chromatography to give 1-methyl-1-(trifluoromethylthio)naphthalen-2(1*H*)-one (105 mg, 82%, eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.4) as a light yellow liquid.

1-Methyl-1-(trifluoromethylthio)naphthalen-2(1H)-one **9a**. The general procedure conducted with **7** (398 mg, 1.0 mmol), $Sc(OTf)_3$ (25 mg, 0.05 mmol), BOX-Bn (19 mg, 0.05 mmol), 1-methylnaphthalen-2-ol (79 mg, 0.5 mmol), and CH_2Cl_2 (2.0 mL) gave **9a** (105 mg, 82%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.9 Hz, 1 H), 7.49−7.44 (m, 2 H), 7.40−7.32 (m, 2 H), 6.30 (d, J = 9.9 Hz, 1 H), 1.79 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.34 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 144.8, 141.5, 130.6, 129.9, 129.3, 129.3 (q, J = 309.8 Hz), 128.9, 128.8, 124.2, 56.5, 26.7 ppm. MS (EI) 128 (100), 157 (75.89), 189 (56.37), 230 (25.01), 258 (22.91). HRMS (EI) for $C_{12}H_9OF_3S$ calcd 258.0326; found 258.0322. IR (KBr) ν = 1675, 1567, 1240, 1108, 1060, 832, 757 cm^{-1}.

1,7-Dimethyl-1-(trifluoromethylthio)naphthalen-2(1H)-one **9b**. The general procedure conducted with **7** (398 mg, 1.0 mmol), $Sc(OTf)_3$ (25 mg, 0.05 mmol), BOX-Bn (19 mg, 0.05 mmol), 1,7-dimethylnaphthalen-2-ol (87 mg, 0.5 mmol), and CH_2Cl_2 (2.0 mL) gave **9b** (122 mg, 90%) as a yellow liquid. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1 H), 7.41 (d, J = 9.9 Hz, 1 H), 7.23 (d, J = 7.7 Hz, 1 H), 7.17 (d, J = 7.7 Hz, 1 H), 6.24 (d, J = 9.9 Hz, 1 H), 2.42 (s, 3 H), 1.79 (s, 4 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.32 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 144.7, 141.4, 141.2, 129.9, 129.58, 129.57, 129.3 (q, J = 310.2 Hz), 126.8, 123.3, 56.6, 26.6, 21.8 ppm. MS (EI) 171 (100), 203 (49.83), 244 (16.56), 272 (33.96). HRMS (EI) for $C_{13}H_{11}OF_3S$ calcd 272.0483; found 272.0478. IR (KBr) ν = 1673, 1608, 1559, 1236, 1112, 1061, 844, 756, 472 cm^{-1}.

1,3-Dimethyl-1-(trifluoromethylthio)naphthalen-2(1H)-one **9c**. The general procedure conducted with **7** (398 mg, 1.0 mmol), $Sc(OTf)_3$ (25 mg, 0.05 mmol), BOX-Bn (19 mg, 0.05 mmol), 1,3-dimethylnaphthalen-2-ol (87 mg, 0.5 mmol), and CH_2Cl_2 (2.0 mL) gave **9c** (129 mg, 95%) as a yellow liquid. Eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.7 Hz, 1 H), 7.39 (td, J = 7.6, 1.3 Hz, 1 H), 7.36−7.31 (m, 1 H), 7.26 (d, J = 11.7 Hz, 2 H), 2.06 (s, 3 H), 1.83 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.32 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 140.8, 140.2, 132.3, 120.0, 129.5 (q, J = 310.3 Hz), 129.4, 129.0, 128.8, 128.5, 56.2, 25.9, 16.3 ppm. MS (EI) 171 (100), 272 (30.41). HRMS (EI) for $C_{13}H_{11}OF_3S$ calcd 272.0483; found 272.0486. IR (KBr) ν = 1671, 1635, 1444, 1260, 1112, 1064, 960, 757, 478 cm^{-1}.

1,3,7-Trimethyl-1-(trifluoromethylthio)naphthalen-2(1H)-one **9d**. The general procedure conducted with **7** (398 mg, 1.0 mmol), $Sc(OTf)_3$ (25 mg, 0.05 mmol), BOX-Bn (19 mg, 0.05 mmol), 1,3,7-trimethylnaphthalen-2-ol (94 mg, 0.5 mmol), and CH_2Cl_2 (2.0 mL) gave **9d** (125 mg, 88%) as a yellow liquid. Eluent: petroleum ether/ethyl acetate = 30:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 0.5 Hz, 1 H), 7.22 (d, J = 0.8 Hz, 1 H), 7.18−7.12 (m, 2 H), 2.40 (s, 3 H), 2.05 (d, J = 1.3 Hz, 3 H), 1.83 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.30 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 140.8, 140.2, 139.8, 131.3, 129.6, 129.5 (q, J = 310.4 Hz), 129.2, 129.0, 127.5, 56.2, 25.8, 21.7, 16.3 ppm. MS (EI) 185 (100), 286 (35.35). HRMS (EI) for $C_{14}H_{13}OF_3S$ calcd 286.0639; found 286.0644. IR (KBr) ν = 2954, 2924, 1670, 1635, 1608, 1447, 1379, 1263, 1108, 1062, 961, 819, 755, 477 cm^{-1}.

1,3-Dimethyl-7-phenyl-1-(trifluoromethylthio)naphthalen-2(1H)-one **9e**. The general procedure conducted with **7** (160 mg, 0.4 mmol), $Sc(OTf)_3$ (10 mg, 0.02 mmol), BOX-Bn (8 mg, 0.02 mmol), 1,3-dimethyl-7-phenylnaphthalen-2-ol (50 mg, 0.2 mmol), and CH_2Cl_2 (1.0 mL) gave **9e** (60 mg, 87%) as a yellow liquid. Eluent: petroleum ether/ethyl acetate = 30:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 1.6 Hz, 1 H), 7.63 (dd, J = 5.2, 3.3 Hz, 2 H), 7.58 (dd, J = 7.9, 1.8 Hz, 1 H), 7.52−7.46 (m, 2 H), 7.44−7.38 (m, 1 H), 7.35 (d, J = 7.9 Hz, 1 H), 7.31 (s, 1 H), 2.10 (d, J = 1.3 Hz, 3 H), 1.89 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.18 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 142.4, 140.9, 140.5, 140.1, 132.2, 129.5 (q, J = 310.3 Hz), 129.5, 129.1, 129.0, 128.2, 127.5, 127.4, 127.3, 56.5, 26.3, 16.4 ppm. MS (EI) 247 (100), 348 (32.68). HRMS (EI) for $C_{19}H_{15}OF_3S$ calcd 348.0796; found 348.0801. IR (KBr) ν = 2965, 2924, 1670, 1605, 1484, 1446, 1260, 1111, 1065, 962, 764, 756, 697 cm^{-1}.

3-Ethyl-1-methyl-1-(trifluoromethylthio)naphthalen-2(1H)-one **9f**. The general procedure conducted with **7** (398 mg, 1.0 mmol), $Sc(OTf)_3$ (25 mg, 0.05 mmol), BOX-Bn (19 mg, 0.05 mmol), 3-ethyl-1-methylnaphthalen-2-ol (94 mg, 0.5 mmol), and CH_2Cl_2 (2.0 mL) gave **9f** (144 mg, 95%) as a yellow liquid. Eluent: petroleum ether/ethyl acetate = 12:1, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 7.7, 0.6 Hz, 1 H), 7.40 (td, J = 7.5, 1.7 Hz, 1 H), 7.34 (td, J = 7.4, 1.4 Hz, 1 H), 7.30 (dd, J = 7.4, 1.5 Hz, 1 H), 7.20 (s, 1 H), 2.58−2.39 (m, 2 H), 1.83 (s, 3 H), 1.17 (t, J = 7.5 Hz, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.14 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 140.1, 139.2, 137.7, 130.1, 129.5 (q, J = 310.4 Hz), 129.4, 129.2, 128.8, 128.5, 56.4, 25.9, 22.9, 12.5 ppm. MS (EI) 185 (100), 286 (27.01). HRMS (EI) for $C_{14}H_{13}OF_3S$ calcd 286.0639; found 286.0630. IR (KBr) ν = 1670, 1635, 1381, 1256, 1112, 1065, 915, 757 cm^{-1}.

3-Benzyl-1-methyl-1-(trifluoromethylthio)naphthalen-2(1H)-one **9g**. The general procedure conducted with **7** (398 mg, 1.0 mmol), $Sc(OTf)_3$ (25 mg, 0.05 mmol), BOX-Bn (19 mg, 0.05 mmol), 3-benzyl-1-methylnaphthalen-2-ol (125 mg, 0.5 mmol), and CH_2Cl_2 (2.0 mL) gave **9g** (172 mg, 95%) as a yellow liquid. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.8 Hz, 1 H), 7.41 (td, J = 7.7, 1.4 Hz, 1 H), 7.38−7.30 (m, 2 H), 7.29 (s, 1 H), 7.29−7.24 (m, 2 H), 7.22 (dd, J = 7.6, 1.1 Hz, 1 H), 7.03 (s, 1 H), 3.89−3.73 (m, 2 H), 1.85 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.08 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 141.1, 140.2, 138.5, 135.7, 129.8, 129.7, 129.51, 129.47, 129.42 (q, J = 310.5 Hz), 128.8, 128.7, 128.5, 126.6, 56.6, 35.6, 26.0 ppm. MS (EI) 247 (100), 348 (0.71). HRMS (EI) for $C_{19}H_{15}OF_3S$ calcd 348.0796; found 348.0783. IR (KBr) ν = 1670, 1494, 1381, 1112, 1074, 756, 738 cm^{-1}.

3-(4-(tert-Butyl)benzyl)-1-methyl-1-(trifluoromethylthio)-naphthalen-2(1H)-one **9h**. The general procedure conducted with **7** (240 mg, 0.6 mmol), $Sc(OTf)_3$ (15 mg, 0.03 mmol), BOX-Bn (12 mg, 0.03 mmol), 3-(4-(*tert*-butyl)benzyl)-1-methylnaphthalen-2-ol (92 mg, 0.3 mmol), and CH_2Cl_2 (1.5 mL) gave **9h** (91 mg, 75%) as a yellow oil. Eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.8 Hz, 1 H), 7.43−7.35 (m, 3 H), 7.32 (td, J = 7.5, 1.2 Hz, 1 H), 7.27−7.18 (m, 3 H), 7.05 (s, 1 H), 3.89−3.65 (m, 2 H), 1.86 (s, 3 H), 1.34 (s, 9 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.09 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 149.4, 141.0, 140.1, 135.8, 135.4, 129.9, 129.7, 129.5, 129.4 (q, J = 310.4 Hz), 129.1, 128.8, 128.5, 125.6, 56.5, 35.1, 34.5, 31.5, 25.9 ppm. MS (EI) 303 (100), 404 (0.67). HRMS (EI) for $C_{23}H_{23}OF_3S$ calcd 404.1422; found 404.1413. IR (KBr) ν = 2936, 1670, 1634, 1508, 1114, 1066, 1019, 756, 569 cm^{-1}.

3-(3-Methoxybenzyl)-1-methyl-1-(trifluoromethylthio)-naphthalen-2(1H)-one **9i**. The general procedure conducted with **7** (240 mg, 0.6 mmol), $Sc(OTf)_3$ (15 mg, 0.03 mmol), BOX-Bn (12 mg, 0.03 mmol), 3-(3-methoxybenzyl)-1-methylnaphthalen-2-ol (84 mg, 0.3 mmol), and CH_2Cl_2 (1.5 mL) gave **9h** (86 mg, 76%) as a yellow oil. Eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.8 Hz, 1 H), 7.40 (td, J = 7.7, 1.3 Hz, 1 H), 7.32 (td, J = 7.5, 1.1 Hz, 1 H), 7.28−7.20 (m, 2 H), 7.04 (s, 1 H), 6.86 (d, J = 7.7 Hz, 1 H), 6.84−6.78 (m, 2 H), 3.88−3.68 (m, 2 H), 3.80 (s, 3 H), 1.85 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.09 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 159.9, 141.3, 140.16, 140.13, 135.4, 129.8, 129.73, 129.65, 129.5, 129.4 (q, J = 310.4 Hz), 128.8, 128.5, 121.8, 115.0, 112.0, 56.6, 55.2, 35.6, 26.1 ppm. MS (EI) 277 (100), 378 (4,74). HRMS (EI) for $C_{20}H_{17}O_2F_3S$ calcd 378.0901; found 378.0893. IR (KBr) ν = 1670, 1600, 1489, 1258, 1111, 1051, 756, 733 cm^{-1}.

General Procedure for Direct Trifluoromethylthiolation of Styrene Derivatives. **7** (398 mg, 1.0 mmol) was placed into an oven-dried Schlenk tube equipped with a stirring bar under argon. Styrene (52 mg, 0.5 mmol) and freshly distilled DMF (2.0 mL) were added. The reaction was stirred at 80 °C for 1 h. Distilled water (10.0 mL) and ether (50.0 mL) were added, and the organic phase was separated.

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The organic phase was washed with distilled water (10.0 mL × 3). The organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give (*E*)-styryl(trifluoromethyl)thioether (71 mg, 70%, 0.5 mmol, eluent: petroleum ether, R_f = 0.7) as a colorless liquid.

(E)-Styryl(trifluoromethyl)thioether ***10a***. The general procedure conducted with **7** (398 mg, 1.0 mmol), styrene (52 mg, 0.5 mmol), and DMF (2 mL) gave **10a** (71 mg, 70%) as a colorless liquid. Eluent: petroleum ether, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.30 (m, 5 H), 7.02 (d, J = 15.3 Hz, 1 H), 6.76 (d, J = 15.3 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.79 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 135.2, 129.8 (q, J = 309.1 Hz), 129.3, 129.0, 127.0, 118.6 (q, J = 3.0 Hz) ppm. MS (EI) 135 (100), 204. HRMS (EI) for $C_9H_7F_3S$ calcd 204.0211; found 204.0226. IR (KBr) ν = 2916, 2849, 1023 cm^{-1}.

(E)-(4-Methylstyryl)(trifluoromethyl)thioether ***10b***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-methyl-4-vinylbenzene (59 mg, 0.5 mmol), and DMF (2 mL) gave **10b** (96 mg, 92%) as a colorless liquid. Eluent: petroleum ether, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.0 Hz, 2 H), 7.19 (d, J = 8.0 Hz, 2 H), 7.00 (d, J = 15.3 Hz, 1 H), 6.69 (d, J = 15.3 Hz, 1 H), 2.38 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.95 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9 (d, J = 1.1 Hz), 139.6, 132.5, 129.8 (q, J = 309.1 Hz), 129.7, 127.0, 110.4 (q, J = 3.0 Hz), 21.4 ppm. MS (EI) 218 (100). HRMS (EI) for $C_{10}H_9F_3S$ calcd 218.0377; found 218.0372. IR (KBr) ν = 2924, 1511, 1109, 957, 787, 755 cm^{-1}.

(E)-(4-(tert-Butyl)styryl)(trifluoromethyl)thioether ***10c***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-(*tert*-butyl)-4-vinylbenzene (80 mg, 0.5 mmol), and DMF (2 mL) gave **10c** (108 mg, 83%) as a colorless liquid. Eluent: petroleum ether, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.5 Hz, 2 H), 7.37 (d, J = 8.5 Hz, 2 H), 7.04 (t, J = 15.2 Hz, 1 H), 6.72 (t, J = 15.2 Hz, 1 H), 1.36 (s, 9 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.95 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 141.9, 132.5, 129.8 (q, J = 309.1 Hz), 126.8, 126.0, 110.6 (q, J = 3.0 Hz), 34.9, 31.3 ppm. MS (EI) 245 (100), 260. HRMS (EI) for $C_{13}H_{15}F_3S$ calcd 260.0847; found 260.0849. IR (KBr) ν = 2965, 1158, 1112, 800, 551 cm^{-1}.

(E)-(2-([1,1′-Biphenyl]-4-yl)vinyl)(trifluoromethyl)thioether ***10d***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-(*tert*-butyl)-4-vinylbenzene (90 mg, 0.5 mmol), and DMF (2 mL) gave **10d** (124 mg, 89%) as a white solid. Eluent: petroleum ether, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 8.3, 1.5 Hz, 4 H), 7.47 (dd, J = 10.8, 4.6 Hz, 4 H), 7.42−7.36 (m, 1 H), 7.06 (d, J = 15.3 Hz, 1 H), 6.80 (d, J = 15.3 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.74 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 140.9, 140.4, 134.2, 129.8 (q, J = 309.1 Hz), 129.0, 127.9, 127.7, 127.4, 127.1, 111.8 (q, J = 3.1 Hz) ppm. MS (EI) 280 (100). HRMS (EI) for $C_{15}H_{11}F_3S$ calcd 280.0534; found 280.0535. IR (KBr) ν = 3034, 1487, 1407, 1175, 1103, 961, 760, 720, 689, 474 cm^{-1}. Mp 102.8−103.5 °C.

(E)-(4-Methoxystyryl)(trifluoromethyl)thioether ***10e***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-methoxy-4-vinylbenzene (67 mg, 0.5 mmol), and DMF (2 mL) gave **10e** (100 mg, 86%) as a colorless liquid. Eluent: petroleum ether, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.6 Hz, 2 H), 6.99 (d, J = 15.2 Hz, 1 H), 6.89 (d, J = 8.8 Hz, 2 H), 6.58 (d, J = 15.2 Hz, 1 H), 3.83 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.17 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 142.3, 129.8 (q, J = 309.1 Hz), 128.5, 128.0, 114.4, 108.6 (q, J = 3.0 Hz), 55.5 ppm. MS (EI) 234 (100). HRMS (EI) for $C_{10}H_9F_3OS$ calcd 234.0326; found 234.0329. IR (KBr) ν = 2959, 1607, 1512, 1465, 1305, 1258, 1240, 1108, 1034, 959, 837, 796, 754 cm^{-1}.

(E)-4-(2-(Trifluoromethylthio)vinyl)phenyl acetate ***10f***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 4-vinylphenyl acetate (81 mg, 0.5 mmol), and DMF (2 mL) gave **10f** (118 mg, 90%) as a white solid. Eluent: petroleum ether/ethyl acetate = 30:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.5 Hz, 2 H), 7.10 (d, J = 8.6 Hz, 2 H), 6.98 (d, J = 15.3 Hz, 1 H), 6.70 (d, J = 15.3 Hz, 1 H), 2.31 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.97 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 151.4, 140.2, 133.0, 129.7 (q, J = 309.1 Hz), 128.0, 122.2, 112.1 (q, J = 3.0 Hz), 21.2 ppm. MS (EI) 220 (100), 262. HRMS (EI) for $C_{11}H_9F_3O_2S$ calcd 262.0275; found 262.0269. IR (KBr) ν = 3053, 1770, 1598, 1506, 1373, 1219, 1195, 1167, 1113, 1013, 946, 911, 807, 755, 522 cm^{-1}. Mp 48.9−49.8 °C.

(E)-(4-Phenoxystyryl)(trifluoromethyl)thioether ***10g***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-phenoxy-4-vinylbenzene (99 mg, 0.5 mmol), and DMF (2 mL) gave **10g** (126 mg, 85%) as a yellow oil. Eluent: petroleum ether, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.35 (m, 4 H), 7.18 (ddd, J = 8.5, 2.1, 1.1 Hz, 1 H), 7.11−6.97 (m, 5 H), 6.66 (d, J = 15.3 Hz, 1 H); ^{19}F (376 MHz, $CDCl_3$) δ −42.93 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 156.6, 141.3, 130.1, 130.0, 129.8 (q, J = 309.1 Hz), 128.5, 124.0, 119.5, 118.8, 110.2 (q, J = 3.1 Hz) ppm. MS (EI) 134 (100), 296 (26.44). HRMS (EI) for $C_{15}H_{11}OF_3S$ calcd 296.0483; found 296.0478. IR (KBr) ν = 3041, 1589, 1505, 1488, 1242, 1202, 1111, 958, 874, 755, 692, 514 cm^{-1}.

(E)-(4-Fluorostyryl)(trifluoromethyl)thioether ***10h***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-fluoro-4-vinylbenzene (61 mg, 0.5 mmol), and DMF (2 mL) gave **10h** (82 mg, 74%) as a light yellow liquid. Eluent: petroleum ether, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 8.7, 5.3 Hz, 2 H), 7.06 (t, J = 8.6 Hz, 2 H), 6.97 (d, J = 15.3 Hz, 1 H), 6.66 (d, J = 15.3 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.85 (s, 3 F), −111.50 (m, 1 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (d, J = 250.5 Hz), 140.2, 131.5 (d, J = 17.2 Hz), 129.7 (q, J = 309.1 Hz), 128.7 (d, J = 9.1 Hz), 116.1 (d, J = 22.2 Hz), 111.6 (hpt, J = 3.0 Hz) ppm. MS (EI) 222 (100). HRMS (EI) for $C_9H_6F_4S$ calcd 222.0126; found 222.0122. IR (KBr) ν = 2924, 2853, 1664, 1505, 1457, 1375, 1160, 1113, 800, 753 cm^{-1}.

(E)-(4-Chlorostyryl)(trifluoromethyl)thioether ***10i***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-chloro-4-vinylbenzene (70 mg, 0.5 mmol), and DMF (2 mL) gave **10i** (53 mg, 45%) as a light yellow liquid. Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.29 (m, 4 H), 6.94 (d, J = 15.4 Hz, 1 H), 6.73 (d, J = 15.4 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.67 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 135.2, 133.7, 129.6 (q, J = 309.1 Hz), 129.2, 128.1, 112.8 (q, J = 3.1 Hz) ppm. MS (EI) 134 (100), 169 (40.05), 238 (74.71). HRMS (EI) for $C_9H_6ClF_3S$ calcd 237.9831; found 237.9826. IR (KBr) ν = 2959, 2925, 2854, 1490, 1161, 1110, 1013, 955, 794, 757 cm^{-1}.

(E)-(3-Methylstyryl)(trifluoromethyl)thioether ***10j***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-methyl-3-vinylbenzene (59 mg, 0.5 mmol), and DMF (2 mL) gave **10j** (85 mg, 78%) as a light yellow liquid. Eluent: petroleum ether, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, J = 7.4 Hz, 1 H), 7.18 (d, J = 10.3 Hz, 2 H), 7.14 (d, J = 7.4 Hz, 1 H), 6.96 (d, J = 15.3 Hz, 1 H), 6.70 (d, J = 15.3 Hz, 1 H), 2.35 (s, 3 H); ^{19}F (376 MHz, $CDCl_3$) δ −42.84 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 138.7, 135.2, 130.2, 129.8 (q, J = 308.0 Hz), 128.9, 127.6, 124.2, 111.5 (q, J = 3.1 Hz), 21.5 ppm. MS (EI) 149 (100), 218 (66.88). HRMS (EI) for $C_{10}H_9F_3S$ calcd 218.0377; found 218.0372. IR (KBr) ν = 3044, 2923, 1259, 1152, 1111, 945, 770, 756, 688, 436 cm^{-1}.

(E)-(3-Methoxystyryl)(trifluoromethyl)thioether ***10k***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-methoxy-3-vinylbenzene (67 mg, 0.5 mmol), and DMF (2 mL) gave **10k** (96 mg, 82%) as a light yellow liquid. Eluent: petroleum ether, R_f = 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 7.9 Hz, 1 H), 7.03−6.94 (m, 2 H), 6.92 (s, 1H), 6.91−6.86 (m, 1 H), 6.74 (d, J = 15.3 Hz, 1 H), 3.84 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.75 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 141.1, 136.6, 130.0, 129.8 (q, J = 309.1 Hz), 119.6, 115.0, 112.3, 112.2, 55.4 ppm. MS (EI) 165 (100), 234 (98.93). HRMS (EI) for $C_{10}H_9OF_3S$ calcd 234.0326; found 234.0330. IR (KBr) ν = 2960, 2837, 1607, 1576, 1290, 1269, 1225, 1050, 952, 771, 756, 685 cm^{-1}.

(E)-(2-Methoxystyryl)(trifluoromethyl)thioether ***10l***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-methoxy-2-vinylbenzene (67 mg, 0.5 mmol), and DMF (2 mL) gave **10l** (108 mg, 93%) as a colorless liquid. Eluent: petroleum ether, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 7.6, 1.4 Hz, 1 H), 7.35−7.24 (m, 2 H), 6.96 (td, J = 7.5, 0.6 Hz, 1 H), 6.90 (d, J = 8.3 Hz, 1 H), 6.84 (d, J = 15.4 Hz, 1 H), 3.88 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.92 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 137.0, 130.4,

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129.9 (q, J = 309.1 Hz), 128.1, 124.2, 120.9, 112.4 (q, J = 3.1 Hz), 111.2, 55.6 ppm. MS (EI) 234 (100). HRMS (EI) for $C_{10}H_9F_3OS$ calcd 234.0326; found 234.0327. IR (KBr) ν = 2964, 1599, 1487, 1465, 1437, 1251, 1108, 1051, 1028, 959, 750 cm^{-1}.

(E)-(2-(Anthracen-9-yl)vinyl)(trifluoromethyl)thioether ***10m***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 9-vinylanthracene (103 mg, 0.5 mmol), and DMF (2 mL) gave **10m** (118 mg, 78%) as a yellow green solid. Eluent: petroleum ether, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1 H), 8.17 (d, J = 8.4 Hz, 2 H), 8.01 (d, J = 7.7 Hz, 2 H), 7.82 (d, J = 15.6 Hz, 1 H), 7.57−7.48 (m, 4 H), 6.68 (d, J = 15.6 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.12 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 131.4, 129.9 (q, J = 309.1 Hz), 129.8, 129.5, 128.9, 128.0, 126.4, 125.5, 125.2, 120.1 (q, J = 3.1 Hz) ppm. MS (EI) 203 (100), 234 (42.07), 304 (48.38). HRMS (EI) for $C_{17}H_{11}F_3S$ calcd 304.0534; found 304.0529. IR (KBr) ν = 3045, 1663, 1592, 1442, 1347, 1162, 1112, 957, 776, 734, 700, 539 cm^{-1}. Mp 68.2−69.4 °C.

(E)-Ferroceneyl-(trifluoromethyl)thioether ***10n***. The general procedure conducted with **7** (398 mg, 1.0 mmol), vinylferrocene (106 mg, 0.5 mmol), and DMF (2 mL) gave **10n** (81 mg, 52%) as a red brown liquid. Eluent: petroleum ether, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, J = 14.9 Hz, 1 H), 6.26 (d, J = 14.9 Hz, 1 H), 4.43 (s, 2 H), 4.35 (s, 2 H), 4.17 (s, 5 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −43.64 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 129.4 (q, J = 309.1 Hz), 105.7 (q, J = 3.1 Hz), 79.9, 70.1, 69.6, 67.7 ppm. MS (EI) 312 (100). HRMS (EI) for $C_{13}H_{11}F_3SFe$ calcd 309.9930; found 309.9933. IR (KBr) ν = 1597, 1251, 1154, 1108, 1043, 1028, 1001, 817, 754, 499 cm^{-1}.

(1H-Inden-2-yl)(trifluoromethyl)thioether ***10o***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1*H*-indene (58 mg, 0.5 mmol), and DMF (2 mL) gave **10o** (88 mg, 82%) as a yellow liquid. Eluent: petroleum ether, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.46 (m, 1 H), 7.46−7.41 (m, 1 H), 7.39−7.27 (m, 2 H), 7.27−7.25 (m, 1 H), 3.69 (s, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.51 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 143.1, 141.9, 129.5 (q, J = 310.1 Hz), 128.9 (q, J = 2.1 Hz), 127.0, 126.5, 123.8, 121.8, 44.2 (d, J = 1.1 Hz) ppm. MS (EI) 115 (100), 147 (52.34), 216 (82.18). HRMS (EI) for $C_{10}H_7F_3S$ calcd 216.0221; found 216.0214. IR (KBr) ν = 1393, 1108, 753, 714, 417 cm^{-1}.

(E)-(2-(Naphthalen-2-yl)vinyl)(trifluoromethyl)thioether ***10p***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 2-vinylnaphthalene (78 mg, 0.5 mmol), and DMF (2 mL) gave **10p** (106 mg, 84%) as a white solid. Eluent: petroleum ether, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.79 (m, 3 H), 7.77 (s, 1 H), 7.57 (dd, J = 8.6, 1.2 Hz, 1 H), 7.55−7.46 (m, 2 H), 7.16 (d, J = 15.3 Hz, 1 H), 6.86 (d, J = 15.3 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.70 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 133.7, 133.5, 132.6, 129.8 (q, J = 309.1 Hz), 128.8, 128.4, 127.9, 127.7, 126.93, 126.85, 123.2, 112.0 (q, J = 3.0 Hz) ppm. MS (EI) 185 (100), 254. HRMS (EI) for $C_{13}H_9F_3S$ calcd 254.0377; found 254.0385. IR (KBr) ν = 3057, 1507, 1166, 1107, 957, 864, 803, 748, 481, 472 cm^{-1}. Mp 83.9−84.9 °C.

Acenaphthylen-1-yl(trifluoromethyl)thioether ***10q***. The general procedure conducted with **7** (398 mg, 1.0 mmol), acenaphthylene (76 mg, 0.5 mmol), and DMF (2 mL) gave **10q** (110 mg, 88%) as a yellow liquid. Eluent: petroleum ether R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.89 (m, 3 H), 7.79 (d, J = 6.9 Hz, 1 H), 7.66 (t, J = 7.6 Hz, 1 H), 7.61 (t, J = 7.5 Hz, 1 H), 7.55 (s, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.85 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 138.9, 137.1, 129.4 (q, J = 311.1 Hz), 129.3, 128.63, 128.58, 128.24, 128.19, 128.08, 126.1, 124.3, 123.6 (d, J = 3.1 Hz) ppm. MS (EI) 183 (100), 252 (57.08). HRMS (EI) for $C_{13}H_7F_3S$ calcd 252.0221; found 252.0219. IR (KBr) ν = 1728, 1425, 1191, 1111, 815, 769, 756 cm^{-1}.

(E)-(4-(Chloromethyl)styryl)(trifluoromethyl)thioether ***10r***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-(chloromethyl)-4-vinylbenzene (77 mg, 0.5 mmol), and DMF (2 mL) gave **10r** (83 mg, 67%) as a light yellow liquid. Eluent: petroleum ether, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 4 H), 6.99 (d, J = 15.3 Hz, 1 H), 6.77 (d, J = 15.3 Hz, 1 H), 4.59 (s, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.66 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 138.5, 135.3, 129.7 (q, J = 309.1 Hz), 129.2, 127.2, 112.8 (q, J = 3.1 Hz), 45.8 ppm. MS (EI) 217 (100), 252 (42.54). HRMS (EI) for $C_{10}H_8ClF_3S$ calcd 251.9987; found 251.9982. IR (KBr) ν = 1266, 1241, 1109, 959, 944, 773, 732, 676 cm^{-1}.

(E)-(4-(Azidomethyl)styryl)(trifluoromethyl)thioether ***10s***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-(azidomethyl)-4-vinylbenzene (80 mg, 0.5 mmol), and DMF (2 mL) gave **10s** (63 mg, 49%) as a yellow liquid. Eluent: petroleum ether, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.2 Hz, 2 H), 7.32 (d, J = 8.2 Hz, 2 H), 6.99 (d, J = 15.4 Hz, 1 H), 6.77 (d, J = 15.4 Hz, 1 H), 4.35 (s, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.69 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 136.5, 135.2, 129.7 (q, J = 309.1 Hz), 128.8, 127.4, 112.7 (q, J = 3.1 Hz), 54.5 ppm. MS (EI) 217 (100), 231 (23.18), 259 (27.59). HRMS (EI) for $C_{10}H_8N_3F_3S$ calcd 259.0391; found 259.0397. IR (KBr) ν = 2926, 2100, 1511, 1258, 1109, 958, 796, 770, 756 cm^{-1}.

(1-(4-Methoxyphenyl)prop-1-en-2-yl)(trifluoromethyl)thioether ***10t*** *and* ***10t′***. The general procedure conducted with **7** (398 mg, 1.0 mmol), (*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene (75 mg, 0.5 mmol), and DMF (2 mL) gave **10t** and **10t′** (95 mg, 77%) as a light yellow liquid. Eluent: petroleum ether, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.6 Hz, 1 H), 7.25 (d, J = 8.6 Hz, 2.58 H), 7.07 (s, 1.14 H), 6.90 (d, J = 8.8 Hz, 2.94 H), 6.86 (d, J = 7.3 Hz, 1.05 H), 3.82 (s, 3.83 H), 3.81 (s, 1.59 H), 2.33 (s, 3.78 H), 2.31 (s, 1.57 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.44 (s, 1.26 F), −41.28 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 159.5, 142.59, 142.58, 137.79, 137.77, 130.8, 130.6, 130.5 (q, J = 309.1 Hz), 130.0 (q, J = 309.6 Hz), 114.0, 113.8, 55.43, 55.38, 27.10, 27.08, 22.23, 22.22 ppm. MS (EI) 164, 179, 268. HRMS (EI) for $C_{11}H_{11}OF_3S$ calcd 248.0483; found 248.0488, 248.0479. IR (KBr) ν = 2959, 2839, 1607, 1510, 1297, 1254, 1178, 1120, 1082, 1035, 824 cm^{-1}.

(E)-2-(4-(2-((Trifluoromethyl)thio)vinyl)benzyl)isoindoline-1,3-dione ***10u***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 2-(4-vinylbenzyl)isoindoline-1,3-dione (132 mg, 0.5 mmol), and DMF (2 mL) gave 174 mg (96%) of **10u** (174 mg, 96%) as a white solid. Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, J = 5.5, 3.0 Hz, 2 H), 7.70 (dd, J = 5.4, 3.1 Hz, 2 H), 7.42 (d, J = 8.2 Hz, 2 H), 7.33 (d, J = 8.2 Hz, 2 H), 6.94 (d, J = 15.3 Hz, 1 H), 6.69 (d, J = 15.3 Hz, 1 H), 4.83 (s, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.75 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 140.5, 137.4, 134.7, 134.2, 132.1, 129.6 (q, J = 309.1 Hz), 129.2, 127.2, 123.5, 112.2 (q, J = 3.1 Hz), 41.3 ppm. MS (EI) 147 (100), 160 (68.09), 363 (20). HRMS (EI) for $C_{18}H_{12}NO_2F_3S$ calcd 363.0541; found 363.0536. IR (KBr) ν = 3032, 1769, 1706, 1428, 1396, 1146, 1109, 953, 714, 531 cm^{-1}. Mp 120.5−121.2 °C.

(8R,9S,13S,14S)-13-Methyl-3-((E)-2-((trifluoromethyl)thio)vinyl)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17-(14H)-one ***10v***. The general procedure conducted with **7** (398 mg, 1.0 mmol), (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (141 mg, 0.5 mmol), and DMF (2 mL) gave 160 mg (85%) of **10v** (160 mg, 85%) as a light yellow oil. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.2 Hz, 1 H), 7.23−7.16 (m, 1 H), 7.14 (s, 1 H), 6.96 (d, J = 15.3 Hz, 1 H), 6.68 (d, J = 15.3 Hz, 1 H), 2.93 (dd, J = 8.7, 4.0 Hz, 2 H), 2.52 (dd, J = 18.7, 8.7 Hz, 1 H), 2.42 (dt, J = 6.6, 4.2 Hz, 1 H), 2.30 (dt, J = 10.7, 4.3 Hz, 1 H), 2.23−1.92 (m, 4 H), 1.80−1.37 (m, 7 H), 0.92 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −42.90 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.8, 141.6, 141.4, 137.2, 132.8, 129.7 (q, J = 309.1 Hz), 127.5, 126.0, 124.4, 110.7 (q, J = 2.1 Hz), 50.6, 48.0, 44.6, 38.1, 35.9, 31.6, 29.4, 26.5, 25.8, 21.7, 13.9 ppm. MS (EI) 380 (100). HRMS (EI) for $C_{21}H_{23}OF_3S$ calcd 380.1422; found 380.1419. IR (KBr) ν = 2931, 2863, 1739, 1111, 960, 808, 780, 755 cm^{-1}.

General Procedure for Direct Formoxy-Trifluoromethylthiolation of Styrene Derivatives in DMF. *N*-Trifluoromethylthiodibenzenesulfonimide **7** (398 mg, 1.0 mmol) was placed into an oven-dried Schlenk tube equipped with a stirring bar under argon. Styrene (52 mg, 0.5 mmol) and freshly distilled DMF (2.0 mL) were added. The reaction was stirred at room temperature for 1 h. Distilled water (10.0 mL) and ether (50.0 mL) were added, and the organic phase was

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separated. The organic phase was washed with distilled water (10.0 mL × 3). The organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give 1-phenyl-2-(trifluoromethylthio)-ethyl formate **11a** (100 mg, 91%). Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.6.

1-Phenyl-2-(trifluoromethylthio)ethyl formate ***11a***. The general procedure conducted with **7** (398 mg, 1.0 mmol), styrene (52 mg, 0.5 mmol), and DMF (2 mL) gave **11a** (100 mg, 91%) as a yellow liquid. Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1 H), 7.49−7.30 (m, 5 H), 6.06 (dd, J = 8.5, 5.0 Hz, 1 H), 3.38 (dd, J = 14.3, 8.5 Hz, 1 H), 3.27 (dd, J = 14.3, 5.0 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.16 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 137.4, 130.8 (q, J = 308.1 Hz), 129.3, 129.0, 126.6, 73.9, 35.2 (d, J = 2.0 Hz) ppm. MS (EI) 135 (100), 250 (2.29). HRMS (EI) for $C_{10}H_9O_2F_3S$ calcd 250.0275; found 250.0274. IR (KBr) ν = 1732, 1456, 1157, 1112, 969, 757, 725, 698, 524 cm^{-1}.

1-(4-Fluorophenyl)-2-(trifluoromethylthio)ethyl formate ***11b***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-fluoro-4-vinylbenzene (61 mg, 0.5 mmol), and DMF (2 mL) gave **11b** (98 mg, 73%) as a yellow liquid. Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1 H), 7.42−7.31 (m, 2 H), 7.15−7.00 (m, 2 H), 6.02 (dd, J = 8.3, 5.3 Hz, 1 H), 3.36 (dd, J = 14.4, 8.3 Hz, 1 H), 3.23 (dd, J = 14.4, 5.2 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.14 (s, 3 F), −112.02 (m, 1 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, J = 248.5 Hz), 159.6, 133.3 (d, J = 3.3 Hz), 130.7 (q, J = 308.1 Hz), 128.7 (d, J = 8.4 Hz), 116.1 (d, J = 21.8 Hz), 73.2, 35.1 ppm. MS (EI) 125 (100), 153 (95.78). HRMS (EI) for $C_{10}H_8O_2F_4S$ calcd 268.0181; found 268.0175. IR (KBr) ν = 1732, 1608, 1513, 1229, 1154, 1112, 838, 757, 564, 531 cm^{-1}.

1-(p-Tolyl)-2-(trifluoromethylthio)ethyl formate ***11c***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-methyl-4-vinylbenzene (59 mg, 0.5 mmol), and DMF (2 mL) gave **11c** (112 mg, 85%) as a colorless liquid. Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1 H), 7.26 (d, J = 8.1 Hz, 2 H), 7.20 (d, J = 8.1 Hz, 2 H), 6.02 (dd, J = 8.4, 5.2 Hz, 1 H), 3.37 (dd, J = 14.3, 8.5 Hz, 1 H), 3.24 (dd, J = 14.3, 5.1 Hz, 1 H), 2.36 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.16 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 130.8 (q, J = 308.1 Hz), 139.3, 134.5, 129.7, 126.6, 73.9, 35.1 (d, J = 2.0 Hz), 21.4 ppm. MS (EI) 121 (100), 149 (93.10), 264 (11.94). HRMS (EI) for $C_{11}H_{11}O_2F_3S$ calcd 264.0432; found 264.0444. IR (KBr) ν = 2929, 1732, 1616, 1516, 1242, 1156, 1112, 1021, 967, 819, 756, 525 cm^{-1}.

1-(4-(tert-Butyl)phenyl)-2-(trifluoromethylthio)ethyl formate ***11d***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-(*tert*-butyl)-4-vinylbenzene (80 mg, 0.5 mmol), and DMF (2 mL) gave **11d** (113 mg, 74%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1 H), 7.48−7.39 (m, 2 H), 7.36−7.29 (m, 2 H), 6.06 (dd, J = 8.7, 4.9 Hz, 1 H), 3.39 (dd, J = 14.3, 8.8 Hz, 1 H), 3.27 (dd, J = 14.3, 4.9 Hz, 1 H), 1.33 (s, 9 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.16 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 152.4, 134.4, 130.9 (q, J = 308.1 Hz), 126.4, 126.0, 73.8, 35.1 (d, J = 1.9 Hz), 34.8, 31.4 ppm. MS (EI) 163 (100), 191 (64.01), 306 (5.16). HRMS (EI) for $C_{14}H_{17}O_2F_3S$ calcd 306.0901; found 306.0911. IR (KBr) ν = 2965, 1732, 1507, 1367, 1158, 1114, 968, 832, 757, 576 cm^{-1}.

1-(4-(Chloromethyl)phenyl)-2-(trifluoromethylthio)ethyl formate ***11e***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-(chloromethyl)-4-vinylbenzene (77 mg, 0.5 mmol), and DMF (2 mL) gave **11e** (100 mg, 67%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1 H), 7.46−7.40 (m, 2 H), 7.39−7.33 (m, 2 H), 6.05 (dd, J = 8.4, 5.0 Hz, 1 H), 4.58 (s, 2 H), 3.36 (dd, J = 14.4, 8.5 Hz, 1 H), 3.25 (dd, J = 14.4, 5.0 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.12 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 138.6, 137.6, 130.7 (q, J = 308.1 Hz), 129.2, 127.1, 73.5, 45.6, 35.1 (d, J = 2.0 Hz) ppm. MS (EI) 155 (100), 183 (82.25), 298 (3.98). HRMS (EI) for $C_{11}H_{10}O_2F_3SCl$ calcd 298.0042; found 298.0038. IR (KBr) ν = 1731, 1268, 1158, 1115, 972, 838, 756, 720, 679 cm^{-1}.

4-(1-(Formyloxy)-2-(trifluoromethylthio)ethyl)benzyl acetate ***11f***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 4-vinylbenzyl acetate (89 mg, 0.5 mmol), and DMF (2 mL) gave **11f** (138 mg, 86%) as a colorless liquid. Eluent: petroleum ether/ethyl acetate = 5:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1 H), 7.46−7.31 (m, 4 H), 6.04 (dd, J = 8.4, 5.1 Hz, 1 H), 5.10 (s, 2 H), 3.36 (dd, J = 14.4, 8.5 Hz, 1 H), 3.24 (dd, J = 14.4, 5.0 Hz, 1 H), 2.10 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.15 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 159.6, 137.4, 137.2, 130.7 (q, J = 308.1 Hz), 128.8, 126.9, 73.6, 65.8, 35.1 (d, J = 2.0 Hz), 21.1 ppm. MS (EI) 119 (100), 179 (90.17), 207 (86.37), 322 (0.36). HRMS (EI) for $C_{13}H_{13}O_4F_3S$ calcd 322.0487; found 322.0500. IR (KBr) ν = 1732, 1381, 1231, 1158, 1115, 1031, 969, 757 cm^{-1}.

1-(4-(Azidomethyl)phenyl)-2-(trifluoromethylthio)ethyl formate ***11g***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-(azidomethyl)-4-vinylbenzene (80 mg, 0.5 mmol), and DMF (2 mL) gave **11g** (90 mg, 59%) as a yellow liquid. Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1 H), 7.43−7.37 (m, 2 H), 7.35 (d, J = 8.3 Hz, 2 H), 6.05 (dd, J = 8.4, 5.1 Hz, 1 H), 4.36 (s, 2 H), 3.37 (dd, J = 14.4, 8.4 Hz, 1 H), 3.25 (dd, J = 14.4, 5.1 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.12 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 137.5, 136.7, 130.7 (q, J = 308.1 Hz), 128.8, 127.2, 73.5, 54.4, 35.1 (d, J = 1.9 Hz) ppm. MS (EI) 190 (100), 305 (5.29). HRMS (EI) for $C_{11}H_{10}N_3O_2F_3S$ calcd 305.0446; found 305.0445.

1-(4-((1,3-Dioxoisoindolin-2-yl)methyl)phenyl)-2-(trifluoromethylthio)ethyl formate ***11h***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 2-(4-vinylbenzyl)isoindoline-1,3-dione (132 mg, 0.5 mmol), and DMF (2 mL) gave **11h** (150 mg, 74%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 8:1, R_f = 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1 H), 7.84 (dd, J = 5.5, 3.0 Hz, 2 H), 7.71 (dd, J = 5.4, 3.1 Hz, 2 H), 7.46 (d, J = 8.2 Hz, 2 H), 7.31 (d, J = 8.2 Hz, 2 H), 6.00 (dd, J = 8.5, 5.0 Hz, 1 H), 4.83 (s, 2 H), 3.31 (dd, J = 14.4, 8.6 Hz, 1 H), 3.20 (dd, J = 14.4, 4.9 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.15 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 159.6, 137.5, 137.1, 134.2, 132.2, 130.7 (q, J = 308.1 Hz), 129.3, 127.0, 123.5, 73.6, 41.3, 35.1 (d, J = 1.9 Hz) ppm. MS (EI) 160 (100), 262 (89.70), 294 (59.68), 409 (0.68). HRMS (EI) for $C_{19}H_{14}NO_4F_3S$ calcd 409.0596; found 409.0604. IR (KBr) ν = 2941, 1770, 1716, 1429, 1395, 1348, 1155, 1112, 939, 716 cm^{-1}.

1-(4-(Benzo[d]thiazol-2-yl)phenyl)-2-(trifluoromethylthio)ethyl formate ***11i***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 2-(4-vinylphenyl)benzo[*d*]thiazole (119 mg, 0.5 mmol), and DMF (2 mL) gave **11i** (123 mg, 64%) as a white solid. Eluent: petroleum ether/ethyl acetate = 5:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1 H), 8.14−8.11 (m, 2 H), 8.09 (d, J = 8.1 Hz, 1 H), 7.96−7.87 (m, 1 H), 7.53−7.49 (m, 3 H), 7.45−7.36 (m, 1 H), 6.11 (dd, J = 8.2, 5.1 Hz, 1 H), 3.40 (dd, J = 14.5, 8.3 Hz, 1 H), 3.30 (dd, J = 14.5, 5.1 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.05 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 159.6, 154.2, 140.0, 135.2, 134.5, 130.7 (q, J = 308.1 Hz), 128.2, 127.3, 126.6, 125.6, 123.5, 121.8, 73.4, 35.0 (d, J = 1.9 Hz) ppm. MS (EI) 240 (100), 268 (23.09), 383 (37.33). HRMS (EI) for $C_{17}H_{12}NO_2F_3S_2$ calcd 383.0262; found 383.0273. IR (KBr) ν = 2954, 2925, 1705, 1483, 1314, 1164, 1104, 964, 831, 757, 730, 559 cm^{-1}. Mp 92.8−93.8 °C.

1-((8R,9S,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-2-(trifluoromethylthio)ethyl Formate ***11j***. The general procedure conducted with **7** (319 mg, 0.8 mmol), (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*] phenanthren-17-(14*H*)-one (113 mg, 0.4 mmol), and DMF (1.6 mL) gave **11j** (87 mg, 51%) as a yellow oil. Eluent: petroleum ether/ethyl acetate = 5:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1 H), 7.31 (d, J = 8.1 Hz, 1 H), 7.14 (d, J = 8.1 Hz, 1 H), 7.09 (s, 1 H), 5.99 (dd, J = 8.6, 4.9 Hz, 1 H), 3.36 (dd, J = 14.3, 8.7 Hz, 1 H), 3.24 (dd, J = 14.3, 4.9 Hz, 1 H), 2.96−2.89 (m, 2 H), 2.51 (dd, J = 18.7, 8.6 Hz, 1 H), 2.46−2.37 (m, 1 H), 2.30 (td, J = 10.6, 4.1 Hz, 1 H), 2.16 (dd, J = 18.4, 9.4 Hz, 1 H), 2.12−1.93 (m, 3 H), 1.67−1.39 (m, 6 H), 0.91 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.13 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 141.1, 137.4, 134.9 (d, J = 1.8 Hz), 130.8 (q, J = 308.1 Hz),

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127.3, 127.2, 126.1, 123.9, 73.8 (d, J = 7.4 Hz), 50.6, 48.0, 44.5 (d, J = 1.1 Hz), 38.1 (d, J = 2.9 Hz), 35.9, 35.1, 31.7, 29.5 (d, J = 4.3 Hz), 26.5, 25.8 (d, J = 1.5 Hz), 21.7, 13.9 ppm. MS (EI) 283 (100), 311 (51.07), 426 (7.86). HRMS (EI) for $C_{22}H_{25}O_3F_3S$ calcd 426.1477; found 426.1483. IR (KBr) ν = 2933, 2862, 1734, 1157, 1115, 910, 736 cm^{-1}.

General Procedure for Actoxy-Trifluoromethylthiolation of Alkenes in Acetic Acid. 7 (299 mg, 0.75 mmol) was placed into an oven-dried Schlenk tube equipped with a stirring bar under argon. Styrene (52 mg, 0.5 mmol) and AcOH (2.0 mL) were added. The reaction was stirred at 40 °C for 36 h. Ether (50.0 mL) was added, and the organic phase was washed with saturated bicarbonate (10.0 mL × 3) and distilled water (10.0 mL). The organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give 1-phenyl-2-(trifluoromethylthio)ethyl acetate **12a** (70 mg, 53%, eluent: petroleum ether/ethyl acetate = 40:1, R_f = 0.5).

1-Phenyl-2-(trifluoromethylthio)ethyl Acetate ***12a***. The general procedure conducted with **7** (398 mg, 1.0 mmol), styrene (52 mg, 0.5 mmol), and AcOH (2 mL) gave **12a** (70 mg, 53%) as a yellow green liquid. Eluent: petroleum ether/ethyl acetate = 40:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.26 (m, 5 H), 5.95 (dd, J = 8.4, 4.9 Hz, 1 H), 3.34 (dd, J = 14.2, 8.4 Hz, 1 H), 3.24 (dd, J = 14.2, 4.9 Hz, 1 H), 2.12 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.20 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 138.1, 130.8 (q, J = 308.1 Hz), 128.98, 128.92, 126.6, 74.0, 35.4 (q, J = 2.1 Hz), 21.0 ppm. MS (EI) 107 (100), 135 (19.14), 149 (94.68); HRMS (EI) for $C_{11}H_{11}O_2F_3S$ calcd 264.0432; found 264.0430. IR (KBr) ν = 1750, 1373, 1229, 1152, 1115, 1058, 1023, 756, 698 cm^{-1}.

1-(p-Tolyl)-2-(trifluoromethylthio)ethyl Acetate ***12b***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-methyl-4-vinylbenzene (59 mg, 0.5 mmol), and AcOH (2 mL) gave **12b** (110 mg, 79%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 40:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 7.9 Hz, 2 H), 7.19 (d, J = 7.9 Hz, 2 H), 5.91 (dd, J = 8.1 Hz, 5.2 Hz, 1 H), 3.34 (dd, J = 14.0 Hz, 8.4 Hz, 1 H), 3.22 (dd, J = 14.1 Hz, 5.0 Hz, 1 H), 2.35 (s, 3 H), 2.10 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.19 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 138.9, 135.2, 130.9 (q, J = 308.1 Hz), 129.6, 126.6, 73.9, 35.3 (q, J = 2.1 Hz), 21.3, 21.0 ppm. MS (EI) 121 (100), 163 (48.03), 176 (15.09), 219 (5.62), 278 (1.70). HRMS (EI) for $C_{12}H_{13}O_2F_3S$ calcd 278.0588; found 278.0585. IR (KBr) ν = 2960, 1749, 1517, 1373, 1229, 1153, 1115, 1019, 974, 815, 525 cm^{-1}.

1-(4-(tert-Butyl)phenyl)-2-(trifluoromethylthio)ethyl Acetate ***12c***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-(*tert*-butyl)-4-vinylbenzene (81 mg, 0.5 mmol), and AcOH (2 mL) gave **12c** (124 mg, 78%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 40:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 Hz, 2 H), 7.30 (d, J = 8.0 Hz, 2 H), 5.94 (dd, J = 8.2, 4.9 Hz, 1 H), 3.35 (dd, J = 14.0, 8.7 Hz, 1 H), 3.24 (dd, J = 14.1, 4.7 Hz, 1 H), 2.11 (s, 3 H), 1.33 (s, 9 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.20 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 152.0, 130.9 (q, J = 308.1 Hz), 135.1, 126.3, 125.8, 73.9, 35.3 (q, J = 2.1 Hz), 34.8, 31.4, 21.0 ppm. MS (EI) 163 (100), 205 (28.21), 218 (10.03), 320 (1.17). HRMS (EI) for $C_{15}H_{19}O_2F_3S$ calcd 320.1058; found 320.1063. IR (KBr) ν = 2965, 2907, 2871, 1750, 1372, 1228, 1154, 1115, 1060, 1024, 830, 757, 572 cm^{-1}.

1-([1,1′-Biphenyl]-4-yl)-2-(trifluoromethylthio)ethyl Acetate ***12d***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 4-vinyl-1,1′-biphenyl (91 mg, 0.5 mmol), and AcOH (2 mL) gave **12d** (115 mg, 68%) as a yellow green liquid. Eluent: petroleum ether/ethyl acetate = 40:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.56 (m, 4 H), 7.49−7.43 (m, 4 H), 7.42−7.34 (m, 1 H), 6.01 (dd, J = 8.4, 4.9 Hz, 1 H), 3.40 (dd, J = 14.2, 8.5 Hz, 1 H), 3.29 (dd, J = 14.2, 5.0 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.07 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 142.0, 140.5, 137.0, 130.9 (q, J = 306.4 Hz), 129.0, 127.72, 127.66, 127.2, 127.0, 73.8, 35.3 (q, J = 2.1 Hz), 21.0 ppm. MS (EI) 183 (183), 225 (19.14), 238 (14.73), 340 (9.83); HRMS (EI) for $C_{17}H_{15}O_2F_3S$ calcd 340.0745; found 340.0750. IR (KBr) ν = 3031, 1750, 1488, 1372, 1228, 1152, 1116, 1060, 756, 698 cm^{-1}.

1-(4-Methoxyphenyl)-2-(trifluoromethylthio)ethyl Acetate ***12e***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-methoxy-4-vinylbenzene (67 mg, 0.5 mmol), and AcOH (2 mL) gave **12e** (118 mg, 80%) as a yellow green liquid. Eluent: petroleum ether/ethyl acetate = 40:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.7 Hz, 2 H), 6.90 (d, J = 8.7 Hz, 2 H), 5.89 (dd, J = 8.4, 5.2 Hz, 1 H), 3.81 (s, 3 H), 3.34 (dd, J = 14.0, 8.4 Hz, 1 H), 3.20 (dd, J = 14.0, 5.2 Hz, 1 H), 2.09 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.18 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 160.1, 130.9 (q, J = 308.1 Hz), 130.2, 128.1, 114.3, 73.7, 55.4, 35.3 (q, J = 2.1 Hz), 21.1 ppm. MS (EI) 137 (100), 179 (25.84), 294 (8.08); HRMS (EI) for $C_{12}H_{13}O_3F_3S$ calcd 294.0538; found 294.0534. IR (KBr) ν = 1747, 1612, 1516, 1373, 1231, 1177, 1152, 1115, 1032, 831 cm^{-1}.

1-(3-Methoxyphenyl)-2-(trifluoromethylthio)ethyl Acetate ***12f***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-methoxy-3-vinylbenzene (67 mg, 0.5 mmol), and AcOH (2 mL) gave **12f** (114 mg, 78%) as a colorless liquid. Eluent: petroleum ether/ethyl acetate = 40:1, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 8.0 Hz, 1 H), 6.99−6.82 (m, 3 H), 5.91 (dd, J = 8.4, 4.9 Hz, 1 H), 3.82 (s, 3 H), 3.32 (dd, J = 14.2, 8.4 Hz, 1 H), 3.23 (dd, J = 14.2, 4.9 Hz, 1 H), 2.12 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.20 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.83, 159.97, 139.69, 130.84 (q, J = 307.04 Hz), 130.02, 118.68, 114.09, 112.35, 73.86, 55.34, 35.34 (q, J = 2.1 Hz), 20.92 ppm. MS (EI)137 (100), 179 (39.67), 294 (32.77) ; HRMS (EI) for $C_{12}H_{13}O_3F_3S$ calcd 294.0538; found 294.0531. IR (KBr) ν = 1750, 1603, 1588, 1373, 1228, 1153, 1115, 1045, 783, 756 cm^{-1}.

1-(2-Methoxyphenyl)-2-(trifluoromethylthio)ethyl Acetate ***12g***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-methoxy-2-vinylbenzene (67 mg, 0.5 mmol), and AcOH (2 mL) gave **12g** (125 mg, 85%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 40:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 8.2 Hz, 2 H), 6.98 (t, J = 7.4 Hz, 1 H), 6.90 (d, J = 8.1 Hz, 1 H), 6.35 (dd, J = 8.3, 3.5 Hz, 1 H), 3.86 (s, 3 H), 3.40 (dd, J = 14.2, 3.6 Hz, 1 H), 3.22 (dd, J = 14.2, 8.3 Hz, 1 H), 2.16 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.22 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 156.1, 131.0 (q, J = 307.04 Hz), 129.6, 126.5, 126.2, 120.7, 110.7, 69.3, 55.5, 34.2 (d, J = 2.1 Hz), 20.9 ppm. MS (EI) 137 (100), 179 (35.70), 294 (10.21); HRMS (EI) for $C_{12}H_{13}O_3F_3S$ calcd 294.0538; found 294.0534. IR (KBr) ν = 1752, 1603, 1493, 1373, 1229, 1150, 1116, 1048, 1029, 756 cm^{-1}.

1-(3,4-Dimethylphenyl)-2-(trifluoromethylthio)ethyl Acetate ***12h***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1,2-dimethyl-4-vinylbenzene (67 mg, 0.5 mmol), and AcOH (2 mL) gave **12h** (121 mg, 83%) as a colorless oil. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 7.7 Hz, 1 H), 7.12 (s, 1 H), 7.09 (d, J = 7.7 Hz, 1 H), 5.88 (dd, J = 8.3, 5.1 Hz, 1 H), 3.34 (dd, J = 14.0, 8.6 Hz, 1 H), 3.21 (dd, J = 14.1, 4.9 Hz, 1 H), 2.28 (s, 3 H), 2.26 (s, 3 H), 2.11 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.19 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 137.6, 137.3, 135.6, 130.9 (q, J = 308.1 Hz), 130.2, 127.9, 124.0, 74.0, 35.3 (q, J = 1.8 Hz), 21.1, 19.9, 19.6 ppm. MS (EI) 135 (100), 177 (30.14), 190 (11.68), 292 (0.60); HRMS (EI) for $C_{13}H_{15}O_2F_3S$ calcd 292.0745; found 292.0744. IR (KBr) ν = 2944, 1748, 1372, 1228, 1152, 1115, 1023, 821, 756 cm^{-1}.

1-Mesityl-2-(trifluoromethylthio)ethyl Acetate ***12i***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1,3,5-trimethyl-2-vinylbenzene (74 mg, 0.5 mmol), and AcOH (2 mL) gave **12i** (119 mg, 78%) as a yellow liquid. Eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 2 H), 6.32 (dd, J = 10.3, 4.6 Hz, 1 H), 3.52 (dd, 14.5, 10.4 Hz, 1 H), 3.20 (dd, J = 14.5, 4.6 Hz, 1 H), 2.44 (s, 6 H), 2.25 (s, 3 H), 20.9 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.21 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 138.4, 136.7, 131.0 (q, J = 308.1 Hz), 131.0, 130.4, 32.7, 20.9, 20.8, 20.6 ppm. MS (EI) 149 (100), 191, 306 (1.04); HRMS (EI) for $C_{14}H_{17}O_2F_3S$ calcd 306.0901; found 306.0904. IR (KBr) ν = 2923, 1747, 1612, 1375, 1249, 1227, 1154, 1115, 1065, 1020, 852, 757 cm^{-1}.

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1-(Naphthalen-2-yl)-2-(trifluoromethylthio)ethyl Acetate ***12j***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 2-vinylnaphthalene (78 mg, 0.5 mmol), and AcOH (2 mL) gave **12j** (122 mg, 78%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 40:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.82 (m, 4 H), 7.56−7.49 (m, 2 H), 7.46 (dd, J = 8.5, 1.7 Hz, 1 H), 6.13 (dd, J = 8.4, 5.0 Hz, 1 H), 3.45 (dd, J = 14.2, 8.4 Hz, 1 H), 3.33 (d, J = 14.2, 5.0 Hz, 1 H), 2.16 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.06 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 135.4, 133.5, 133.2, 130.9 (q, J = 308.1 Hz), 129.0, 128.2, 127.9, 126.7, 126.7, 126.2, 123.7, 74.2, 35.3 (q, J = 2.1 Hz), 21.0 ppm. MS (EI) 157 (100), 199 (22.25), 314 (25.41); HRMS (EI) for $C_{15}H_{13}O_2F_3S$ calcd 314.0588; found 314.0594. IR (KBr) ν = 3059, 1747, 1371, 1228, 1114, 1060, 1024, 819, 755, 478 cm^{-1}.

2-(Trifluoromethylthio)-1,2,3,4-tetrahydronaphthalen-1-yl Acetate ***12k***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1,2-dihydronaphthalene (65 mg, 0.5 mmol), and AcOH (2 mL) gave **12k** (109 mg, 76%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 30:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.18 (m, 3 H), 7.15 (d, J = 7.5 Hz, 1 H), 6.06 (d, J 5.1 Hz, 1 H), 3.79 (dd, J = 8.2, 6.7 Hz, 1 H), 2.96 (t, J = 6.4 Hz, 2 H), 2.52 (dt, J = 11.4, 7.2 Hz, 1 H), 2.23−2.07 (m, 4 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −39.53 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 136.2, 131.9, 131.0 (q, J = 308.1 Hz), 130.2, 129.07, 129.05, 126.9, 71.7, 44.2, 25.9, 25.7, 21.2 ppm. MS (EI) 129 (100), 146 (81.84), 188 (34.45), 230 (5.85); HRMS (EI) for $C_{11}H_9F_3S$ [M − OAc]$^+$ 230.0377; found 230.0379. IR (KBr) ν = 2931, 1744, 1371, 1228, 1151, 1119, 1024, 961, 755 cm^{-1}.

1-(Thiophen-2-yl)-2-(trifluoromethylthio)ethyl Acetate ***12l***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 2-vinylthiophene (55 mg, 0.5 mmol), and AcOH (2 mL) gave **12l** (85 mg, 63%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 4.9 Hz, 1 H), 7.11 (s, 1 H), 7.00 (d, J = 1.3 Hz, 1 H), 6.23 (t, J = 6.3 Hz, 1 H), 3.42 (dd, J = 13.9, 8.3 Hz, 1 H), 3.32 (dd, J = 14.1, 4.8 Hz, 1 H), 2.10 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.18 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 140.5, 130.8 (q, J = 308.1 Hz), 127.1, 126.8, 126.3, 69.6, 35.4, 21.0 ppm. MS (EI) 217 (100), 234 (38.90); HMRS (EI) for $C_9H_9O_2F_3S_2$ calcd 269.9996; found 270.0001. IR (KBr) ν = 2962, 1750, 1437, 1371, 1227, 1112, 1020, 965, 834, 757, 706 cm^{-1}.

2-(Trifluoromethylthio)cyclohexyl Acetate ***12m***. The general procedure conducted with **7** (398 mg, 1.0 mmol), cyclohexene (41 mg, 0.5 mmol), and AcOH (2 mL) gave **12m** (105 mg, 87%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.72 (td, J = 9.3, 4.2 Hz, 1 H), 3.18 (td, J = 10.4, 4.2 Hz, 1 H), 2.33−2.20 (m, 1 H), 2.12−2.00 (m, 4 H), 1.80−1.66 (m, 2 H), 1.66−1.51 (m, 1 H), 1.50−1.28 (m, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −39.20 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 131.0 (q, J = 308.1 Hz), 73.6, 47.7, 32.9, 31.5, 25.2, 23.4, 21.1 ppm. MS (EI) 182, 200. HRMS (EI) for $C_7H_{11}OF_3S$ [M − Ac + H]$^+$ calcd 200.0483; found 200.0477. IR (KBr) ν = 2944, 2864, 1745, 1451, 1375, 1236, 1111, 1038, 1016, 967 cm^{-1}.

1-((8R,9S,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-2-(trifluoromethylthio)ethyl Acetate ***12n***. The general procedure conducted with **7** (398 mg, 1.0 mmol), (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17-(14*H*)-one (141 mg, 0.5 mmol), and AcOH (2 mL) gave **12n** (175 mg, 80%) as a light yellow oil. Eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.1 Hz, 1 H), 7.07 (s, 1 H), 5.87 (dd, J = 8.5, 4.8 Hz, 1H), 3.33 (dd, J = 14.0, 8.7 Hz, 1 H), 3.21 (dd, J = 14.0, 4.8 Hz, 1 H), 3.02−2.83 (m, 2 H), 2.62−2.44 (m, 1 H), 2.44- 2.36 (m, 1 H), 2.28 (dd, J = 13.7, 6.9 Hz, 1 H), 2.23−1.89 (m, 7 H), 1.76−1.36 (m, 7 H), 0.91 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.12 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 140.7, 137.23, 137.22, 135.6, 130.9 (q, J = 306.3 Hz), 127.28, 127.24, 126.0, 123.8, 77.4, 73.9, 73.9, 50.6, 48.1, 44.5, 38.1, 38.1, 36.0, 35.3, 31.7, 29.5, 29.5, 26.5, 25.8, 21.7, 21.1, 14.0 ppm. MS (EI) 283 (100), 284 (21.99), 296 (10.54), 440 (0.18); HRMS (EI) for $C_{23}H_{27}O_3F_3S$ calcd 440.1633; found 440.1636. IR (KBr) ν = 2932, 2862, 1739, 1500, 1435, 1372, 1232, 1111, 1024, 976, 823, 756, 734, 580, 446 cm^{-1}.

General Procedure for Hydroxyl-Trifluoromethylthiolation of Alkenes in DMSO. **7** (398 mg, 1.0 mmol) was placed into an oven-dried Schlenk tube equipped with a stirring bar under argon. Styrene (52 mg, 0.5 mmol) and DMSO (2.0 mL) were added. The reaction was stirred at room temperature for 2 h. Distilled water (10.0 mL) and ether (50.0 mL) were added, and the organic phase was separated. The organic phase was washed with distilled water (10.0 mL × 3). The organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give 1-phenyl-2-(trifluoromethylthio)-ethanol **13a** (70 mg, 63%, eluent: petroleum ether/ethyl acetate = 30:1, R_f = 0.2) as a light yellow liquid.

1-Phenyl-2-(trifluoromethylthio)ethanol ***13a***. The general procedure conducted with **7** (398 mg, 1.0 mmol), styrene (52 mg, 0.5 mmol), and DMSO (2 mL) gave **13a** (70 mg, 63%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 30:1, R_f = 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.31 (m, 5 H), 4.95−4.88 (m, 1 H), 3.22 (dd, J = 13.9, 4.2 Hz, 1 H), 3.14 (dd, J = 13.9, 9.0 Hz, 1 H), 2.52 (d, J = 3.2 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.94 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 131.1 (q, J = 308.1 Hz), 129.0, 128.7, 125.9, 72.9, 38.6 (d, J = 1.6 Hz) ppm. MS (EI) 107 (100), 222 (1.58). HRMS (EI) for $C_9H_9OF_3S$ calcd 222.0326; found 222.0322. IR (KBr) ν = 3384, 1494, 1455, 1115, 1057, 756, 723, 699, 525 cm^{-1}.

1-(p-Tolyl)-2-(trifluoromethylthio)ethanol ***13b***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-methyl-4-vinylbenzene (59 mg, 0.5 mmol), and DMSO (2 mL) gave **13b** (102 mg, 87%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 40:1, R_f = 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.1 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H), 4.94−4.82 (m, 1 H), 3.20 (dd, J = 13.8, 4.6 Hz, 1 H), 3.14 (dd, J = 13.8, 8.6 Hz, 1 H), 2.45 (d, J = 2.9 Hz, 1 H), 2.37 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.97 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 138.5, 131.1 (q, J = 308.1 Hz), 129.6, 125.9, 72.8, 38.5 (d, J = 1.5 Hz), 21.3 ppm. MS (EI) 121 (100). HRMS (EI) for $C_{10}H_{11}OF_3S$ calcd 236.0483; found 236.0474. IR (KBr) ν = 3382, 2925, 1515, 1151, 1116, 1059, 820, 756, 525 cm^{-1}.

1-(4-(tert-Butyl)phenyl)-2-(trifluoromethylthio)ethanol ***13c***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-(*tert*-butyl)-4-vinylbenzene (80 mg, 0.5 mmol), and DMSO (2 mL) gave **13c** (102 mg, 74%) as a white solid. Eluent: petroleum ether/ethyl acetate = 40:1, R_f = 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.37 (m, 2 H), 7.32 (m, 2 H), 4.99−4.77 (m, 1 H), 3.21 (dd, J = 13.8, 4.4 Hz, 1 H), 3.15 (dd, J = 13.9, 8.8 Hz, 1 H), 2.42 (d, J = 3.3 Hz, 1 H), 1.33 (s, 9 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.97 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 138.6, 131.2 (q, J = 308.1 Hz), 125.9, 125.7, 72.8, 38.5 (d, J = 1.5 Hz), 34.8, 31.4 ppm. MS (EI) 163 (100), 278 (1.05). HRMS (EI) for $C_{13}H_{17}OF_3S$ calcd 278.0952; found 278.0957. IR (KBr) ν = 3359, 2968, 2906, 1157, 1109, 1060, 841, 570 cm^{-1}. Mp 37.5−38.5 °C.

1-(4-Fluorophenyl)-2-(trifluoromethylthio)ethanol ***13d***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-fluoro-4-vinylbenzene (61 mg, 0.5 mmol), and DMSO (2 mL) gave **13d** (80 mg, 67%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 30:1, R_f = 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.31 (m, 2 H), 7.13−6.98 (m, 2 H), 4.97−4.76 (m, 1 H), 3.18 (dd, J = 14.0, 4.3 Hz, 1 H), 3.10 (dd, J = 14.0, 8.8 Hz, 1 H), 2.54 (d, J = 3.2 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.91 (s, 3 F), −113.40 (tt, J = 8.6, 5.3 Hz, 1 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, J = 247.1 Hz), 137.3 (d, J = 3.1 Hz), 131.0 (q, J = 308.1 Hz), 127.7 (d, J = 8.2 Hz), 115.9 (d, J = 21.6 Hz), 72.3, 38.7 (q, J = 1.3 Hz) ppm. MS (EI) 125 (100), 240 (1.53). HRMS (EI) for $C_9H_8OF_4S$ calcd 240.0232; found 240.0235. IR (KBr) ν = 3386, 1606, 1512, 1227, 1158, 1119, 1059, 839, 756, 531 cm^{-1}.

1-(4-(Chloromethyl)phenyl)-2-(trifluoromethylthio)ethanol ***13e***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-(chloromethyl)-4-vinylbenzene (77 mg, 0.5 mmol), and DMSO (2 mL) gave **13e** (80 mg, 60%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ

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7.41 (d, J = 8.1 Hz, 2 H), 7.37 (d, J = 8.1 Hz, 2 H), 5.11−4.66 (m, 1 H), 4.59 (s, 2 H), 3.20 (dd, J = 14.0, 4.1 Hz, 1 H), 3.11 (dd, J = 13.9, 9.0 Hz, 1 H), 2.58 (d, J = 2.8 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.90 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 138.0, 131.02 (q, J = 308.1 Hz), 129.2, 126.3, 72.5, 45.9, 38.6 (d, J = 1.5 Hz) ppm. MS (EI) 155 (100), 270 (1.36). HRMS (EI) for $C_{10}H_{10}OF_3SCl$ calcd 270.0093; found 270.0085. IR (KBr) ν = 3397, 1420, 1267, 1112, 1061, 814, 756, 720, 679 cm^{-1}.

4-(1-Hydroxy-2-(trifluoromethylthio)ethyl)benzyl acetate ***13f***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 4-vinylbenzyl acetate (89 mg, 0.5 mmol), and DMSO (2 mL) gave **13f** (108 mg, 74%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 8:1, R_f = 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.32 (m, 4 H), 5.08 (s, 2 H), 4.97−4.83 (m, 1 H), 3.19 (dd, J = 13.9, 4.4 Hz, 1 H), 3.12 (dd, J = 13.9, 8.7 Hz, 1 H), 2.85 (d, J = 3.2 Hz, 1 H), 2.09 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.97 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 141.7, 136.4, 131.1 (q, J = 308.1 Hz), 128.7, 126.2, 72.6, 66.0, 38.5 (d, J = 1.5 Hz), 21.1 ppm. MS (EI) 179 (100), 294 (0.44). HRMS (EI) for $C_{12}H_{13}O_3F_3S$ calcd 294.0531; found 294.0532. IR (KBr) ν = 3447, 1740, 1382, 1239, 1116, 1066, 824, 756 cm^{-1}.

1-(4-(Azidomethyl)phenyl)-2-(trifluoromethylthio)ethanol ***13g***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-(azidomethyl)-4-vinylbenzene (80 mg, 0.5 mmol), and DMSO (2 mL) gave **13g** (101 mg, 73%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.2 Hz, 2 H), 7.33 (d, J = 8.2 Hz, 2 H), 4.92 (dd, J = 8.8, 3.9 Hz, 1 H), 4.34 (s, 2 H), 3.20 (dd, J = 14.0, 4.2 Hz, 1 H), 3.11 (dd, J = 14.0, 8.9 Hz, 1 H), 2.68 (s, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.90 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 135.9, 131.0 (q, J = 308.1 Hz), 128.7, 126.4, 72.5, 54.5, 38.6 (d, J = 0.8 Hz) ppm. MS (EI) 162 (100), 277 (0.71). HRMS (EI) for $C_{10}H_{10}N_3OF_3S$ calcd 277.0497; found 277.0496. IR (KBr) ν = 3408, 2102, 1420, 1342, 1247, 1115, 1062, 756 cm^{-1}.

1-(3-Methoxyphenyl)-2-(trifluoromethylthio)ethanol ***13h***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-methoxy-3-vinylbenzene (67 mg, 0.5 mmol), and DMSO (2 mL) gave **13h** (89 mg, 71%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 30:1, R_f = 0.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.26 (m, 1 H), 6.95−6.92 (m, 2 H), 6.90−6.84 (m, 1 H), 4.88 (dd, J = 8.8, 4.1 Hz, 1 H), 3.82 (s, 3 H), 3.21 (dd, J = 13.9, 4.2 Hz, 1 H), 3.13 (dd, J = 13.9, 8.9 Hz, 1 H), 2.54 (s, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.97 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 143.3, 131.1 (q, J = 306.2 Hz), 130.0, 118.2, 114.1, 111.5, 72.8, 55.4, 38.6 (q, J = 1.6 Hz) ppm. MS (EI) 137 (100), 252 (19.87). HRMS (EI) for $C_{10}H_{11}O_2F_3S$ calcd 252.0432; found 252.0427. IR (KBr) ν = 3423, 1602, 1587, 1490, 1286, 1262, 1150, 1116, 1048, 785, 696 cm^{-1}.

2-(Trifluoromethylthio)cyclododecanol ***13i***. The general procedure conducted with **7** (398 mg, 1.0 mmol), cyclododecene (84 mg, 0.5 mmol), and DMSO (2 mL) gave **13i** (119 mg, 84%) as a white solid. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (br, 0.25 H), 3.95 (s, 1 H), 3.38 (dt, J = 8.9, 4.5 Hz, 1.21 H), 2.11−1.85 (m, 3.75 H), 1.82−1.62 (m, 1.87 H), 1.62−1.25 (m, 22.29 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ-39.46 (s, 3 F), −39.73 (s, 0.69 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.6 (q, J = 306.0 Hz), 68.8, 48.8, 32.1, 32.0, 24.8, 24.7, 23.6, 23.2, 23.0, 22.7, 22.3, 22.2, 21.8, 21.4, 21.1 ppm. MS (EI) 215 (100), 266 (10.63). HRMS (EI) for $C_{13}H_{23}OF_3S$ calcd 284.1422; found 284.1419. IR (KBr) ν = 3383, 2939, 2864, 1470, 1447, 1145, 1108, 1004, 754, 456 cm^{-1}.

2-(4-(1-Hydroxy-2-(trifluoromethylthio)ethyl)benzyl)isoindoline-1,3-dione ***13j***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 2-(4-vinylbenzyl)isoindoline-1,3-dione (132 mg, 0.5 mmol), and DMSO (2 mL) gave **13j** (129 mg, 68%) as a white solid. Eluent: petroleum ether/ethyl acetate = 4:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.77 (m, 2 H), 7.74−7.65 (m, 2 H), 7.40 (d, J = 8.2 Hz, 2 H), 7.30 (d, J = 8.2 Hz, 2 H), 4.87 (dt, J = 8.2, 4.0 Hz, 1 H), 4.80 (s, 2 H), 3.14 (dd, J = 13.9, 4.5 Hz, 1 H), 3.08 (dd, J = 13.8, 8.6 Hz, 1 H), 2.87 (d, J = 3.5 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −40.99 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 141.4, 136.7, 134.2, 132.1, 131.1 (q, J = 308.1 Hz), 129.1, 126.3, 123.5, 72.6, 41.3, 38.5 (d, J = 1.4 Hz) ppm. MS (EI) 266 (100). HRMS (EI) for $C_{18}H_{12}NO_2F_3S$ calcd 363.0541; found 363.0539. IR (KBr) ν = 3435, 1768, 1723, 1698, 1432, 1392, 1148, 1104, 1070, 939, 755, 713, 624, 531 cm^{-1}. Mp 89.5−90.5 °C.

General Procedure for Direct Amino-Trifluoromethylthiolation of Alkenes in CH_2Cl_2. **7** (398 mg, 1.0 mmol) was placed into an oven-dried Schlenk tube equipped with a stirring bar under argon. Styrene (52 mg, 0.5 mmol) and freshly distilled CH_2Cl_2 (2.0 mL) were added. The reaction was stirred at 50 °C for 36 h. The solvent was removed under vacuum, and the residue was purified by flask column chromatography to give *N*-(1-phenyl-2-(trifluoromethylthio)ethyl)-*N*-(phenylsulfonyl)benzenesulfonamide **14a** (114 mg, 46%, eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.6).

N-(1-Phenyl-2-(trifluoromethylthio)ethyl)-N-(phenylsulfonyl)-benzenesulfonamide ***14a***. The general procedure conducted with **7** (398 mg, 1.0 mmol), styrene (52 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14a** (114 mg, 46%) as a white solid. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.27 (m, 15 H), 5.77 (dd, J = 11.5, 4.5 Hz, 1 H), 4.28−4.10 (m, 1 H), 3.11 (dd, J = 14.3, 4.5 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.16 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 134.0, 133.1, 130.6 (q, J = 308.1 Hz), 129.8, 129.1, 129.0, 128.7, 128.3, 63.4, 30.6 (d, J = 2.1 Hz) ppm. MS (DART POS) 519 (M + NH_4), 523.9 (M + Na), 539.8 (M+K); HRMS (DART POS) for $C_{21}H_{22}O_4N_2F_3S_3$ calcd 519.0688; found 519.0679. IR (KBr) ν = 3067, 3005, 1448, 1381, 1363, 1352, 1182, 1168, 1146, 1112, 953, 873, 577, 548 cm^{-1}. Mp 129.4−130.5 °C.

N-(Phenylsulfonyl)-N-(1-(p-tolyl)-2-(trifluoromethylthio)ethyl)-benzenesulfonamide ***14b***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-methyl-4-vinylbenzene (59 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14b** (194 mg, 76%) as a white solid. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.33 (m, 10 H), 7.30 (d, J = 8.1 Hz, 2 H), 7.12 (d, J = 8.1 Hz, 2 H), 5.75 (dd, J = 11.6, 4.5 Hz, 1 H), 4.16 (dd, J = 13.5, 12.4 Hz, 1 H), 3.11 (dd, J = 14.2, 4.5 Hz, 1 H), 2.38 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.17 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 139.1, 133.9, 130.6 (q, J = 308.1 Hz), 130.0, 129.8, 129.3, 128.9, 128.3, 63.3, 30.7 (d, J = 2.1 Hz), 21.2 ppm. MS (DART POS) 533 (M + NH_4), 553.9 (M + K); HRMS (DART POS) for $C_{22}H_{24}O_4N_2F_3S_3$ (M + NH_4) calcd 533.0845; found 533.0836. IR (KBr) ν = 3066, 2924, 1448, 1385, 1360, 1344, 1173, 1118, 1082, 813, 720, 685, 578, 554 cm^{-1}. Mp 121.1−122.0 °C.

N-(1-(4-(tert-Butyl)phenyl)-2-(trifluoromethylthio)ethyl)-N-(phenylsulfonyl)benzenesulfonamide ***14c***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-(*tert*-butyl)-4-vinylbenzene (81 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14c** (212 mg, 76%) as a white solid. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13−7.05 (m, 14 H), 5.77 (dd, J = 11.5, 4.6 Hz, 1 H), 4.18 (dd, J = 13.7, 12.1 Hz, 1 H), 3.13 (dd, J = 14.2, 4.6 Hz, 1 H), 1.37 (s, 9 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.19 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 140.2, 133.9, 130.7 (q, J = 308.1 Hz), 130.0, 129.5, 128.9, 128.4, 125.6, 63.3, 34.8, 31.5, 30.8 (q, J = 2.1 Hz) ppm. MS (DART POS) 575.0 (M + NH_4), 580.0 (M + Na), 595.9 (M + K); HRMS (DART POS) for $C_{25}H_{30}O_4N_2F_3S_3$ (M+K) calcd 596.0613; found 595.0992. IR (KBr) ν = 3064, 2965, 2870, 1450, 1385, 1362, 1350, 1173, 1115, 1052, 825, 754, 719, 684, 578, 552 cm^{-1}. Mp 107.5−108.5 °C.

N-(1-([1,1′-Biphenyl]-4-yl)-2-(trifluoromethylthio)ethyl)-N-(phenylsulfonyl)benzenesulfonamide ***14d***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 4-vinyl-1,1′-biphenyl (91 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14d** (171 mg, 62%) as a white solid. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30−7.09 (m, 19 H), 5.85 (d, J = 11.5, 4.5 Hz), 4.28−4.16 (m, 1 H), 3.17 (dd, J = 14.3, 4.5 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.08 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 140.3, 140.1, 134.0, 132.0, 130.6 (q, J = 308.1 Hz), 130.3, 129.1, 129.0, 128.4, 128.0, 127.3, 127.2, 63.2, 30.7 (q, J = 2.1 Hz) ppm. MS (DART POS) 600.0 (M + Na), 615.9 (M + K); HRMS (DART POS) for $C_{27}H_{26}O_4N_2F_3S_3$ (M + NH_4) calcd 595.1001; found 595.0992. IR

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(KBr) ν = 3067, 2962, 1447, 1381, 1364, 1173, 1111, 1085, 775, 753, 607, 578, 524 cm^{-1}. Mp 129.9−130.6 °C.

N-(1-(4-Fluorophenyl)-2-(trifluoromethylthio)ethyl)-N-(phenylsulfonyl)benzenesulfonamide ***14e***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-fluoro-4-vinylbenzene (61 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14e** (111 mg, 43%) as a white solid. Eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.4. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02−7.08 (m, 12 H), 7.01 (t, J = 8.5 Hz, 2 H), 5.72 (dd, J = 11.5, 4.4 Hz, 1 H), 4.21−4.03 (m, 1 H), 3.11 (dd, J = 14.3, 4.5 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.10 (s, 3 F), −111.95−112.27 (m, 1 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, J = 250.5 Hz), 139.9, 134.1, 131.8 (d, J = 8.1 Hz), 130.5 (q, J = 308.1 Hz), 129.1, 129.0 (d, J = 4.1 Hz), 128.2, 115.6, 62.8, 30.8 (q, J = 2.1 Hz) ppm. MS (DART POS) 537.0 (M + NH_4), 541.9 (M + Na), 557.9 (M + K); HRMS (DART POS) for $C_{21}H_{21}O_4N_2F_4S_3$ (M+NH_4) calcd 537.0594; found 537.0589. IR (KBr) ν = 3071, 2959, 1605, 1513, 1385, 1359, 1233, 1172, 1120, 839, 769, 720, 685, 579, 552, 534 cm^{-1}. Mp 89.2−90.0 °C.

N-(1-(4-Bromophenyl)-2-(trifluoromethylthio)ethyl)-N-(phenylsulfonyl)benzenesulfonamide ***14f***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-bromo-4-vinylbenzene (92 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14f** (68 mg, 24%) as a white solid. Eluent: petroleum ether/ethyl acetate = 30:1, R_f = 0.6. ^1H NMR (400 MHz, $CDCl_3$) δ 8.15−6.97 (m, 14 H), 5.70 (dd, J = 11.5, 4.4 Hz, 1 H), 4.17−4.03 (m, 1 H), 3.09 (dd, J = 14.4, 4.5 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.05 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 134.1, 132.2, 131.8, 131.5, 130.5 (q, J = 308.1 Hz), 129.1, 128.3, 123.4, 62.7, 30.6 (d, J = 2.1 Hz) ppm. MS (DART POS) 596.8 (M + NH_4), 601.8 (M + Na), 617.7 (M+K); HRMS (DART POS) for $C_{21}H_{21}O_4N_2BrF_3S_3$ (M + NH_4) calcd 596.9793; found 596.9786. IR (KBr) ν = 3062, 2960, 2924, 2853, 1492, 1450, 1377, 1331, 1164, 1104, 1072, 955, 815, 751, 681, 576, 544 cm^{-1}. Mp 98.6−99.8 °C.

N-(Phenylsulfonyl)-N-(1-(m-tolyl)-2-(trifluoromethylthio)ethyl)-benzenesulfonamide ***14g***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-methyl-3-vinylbenzene (59 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14g** (153 mg, 60%) as a colorless oil. Eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.6. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95−7.27 (m, 10 H), 7.22 (t, J = 8.5 Hz, 2 H), 7.15 (d, J = 6.5 Hz, 2 H), 5.75 (dd, J = 11.5, 4.4 Hz, 1 H), 4.21−4.10 (m, 1 H), 3.10 (dd, J = 14.3, 4.5 Hz, 1 H), 2.24 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.20 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 138.5, 133.9, 132.8, 130.8, 130.6 (q, J = 308.1 Hz), 129.8, 128.9, 128.5, 128.4, 126.5, 63.4, 30.7, 21.4 ppm. MS (DART POS) 537.8 (M + Na), 554.0 (M + K); HRMS (DART POS) for $C_{22}H_{24}O_4N_2F_3S_3$ (M + NH_4) calcd 533.0845; found 533.0834. IR (KBr) ν = 3066, 2962, 2932, 1608, 1448, 1383, 1361, 1169, 1112, 837, 959, 875, 754, 720, 685, 616, 578, 548 cm^{-1}.

N-(1-(3,4-Dimethylphenyl)-2-(trifluoromethylthio)ethyl)-N-(phenylsulfonyl)benzenesulfonamide ***14h***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1,2-dimethyl-4-vinylbenzene (67 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14h** (206 mg, 78%) as a colorless oil. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.5. ^1H NMR (400 MHz, $CDCl_3$) δ 8.00−7.15 (m, 10 H), 7.17−6.98 (m, 3 H), 5.76 (dd, J = 11.5, 4.4 Hz, 1 H), 4.22−4.03 (m, 1 H), 3.11 (dd, J = 14.2, 4.4 Hz, 1 H), 2.27 (s, 3 H), 2.13 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.20 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 137.7, 130.7 (q, J = 308.1 Hz), 137.0, 133.8, 131.3, 130.2, 129.7, 128.8, 128.3, 126.8, 63.3, 30.7, 19.7, 19.6 ppm. MS (DART POS) 547.1 (M + NH_4), 551.9 (M + Na), 567.8 (M + K); HRMS (DART POS) for $C_{23}H_{26}O_4N_2F_3S_3$ (M+NH_4) calcd 547.1001; found 547.0991. IR (KBr) ν = 3066, 2973, 2922, 2863, 1583, 1506, 1479,1448, 1382, 1104, 988, 960, 872, 818, 753, 685, 613, 576, 549 cm^{-1}.

N-(1-(Naphthalen-2-yl)-2-(trifluoromethylthio)ethyl)-N-(phenylsulfonyl)benzenesulfonamide ***14i***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 2-vinylnaphthalene (78 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14i** (168 mg, 61%) as a white solid. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.5. ^1H NMR (400 MHz, $CDCl_3$) δ 8.46−6.55 (m, 17 H), 5.99 (dd, J = 11.5, 4.5 Hz, 1 H), 4.43−4.24 (m, 1 H), 3.25 (dd, J = 14.3, 4.5 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.09 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 133.9, 133.3, 132.8, 130.6 (q, J = 308.1 Hz), 130.2, 129.1, 128.9, 128.5, 128.4, 128.3, 127.6, 127.2, 127.0, 126.7, 63.5, 30.8 ppm. MS (DART POS) 569.0 (M + NH_4), 573.8 (M + Na), 589.8 (M + K); HRMS (DART POS) for $C_{25}H_{24}O_4N_2F_3S_3$ (M+NH_4) calcd 569.0848; found 569.0840. IR (KBr) ν = 3065, 2974, 1448, 1371, 1355, 1168, 1139, 1115, 1080, 829, 810, 747, 717, 682, 587, 568, 548 cm^{-1}. Mp 132.6−133.5 °C.

N-(1-(4-(Chloromethyl)phenyl)-2-(trifluoromethylthio)ethyl)-N-(phenylsulfonyl)benzenesulfonamide ***14j***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1-(chloromethyl)-4-vinylbenzene (77 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14j** (85 mg, 31%) as a pale yellow solid. Eluent: petroleum ether/ethyl acetate = 30:1, R_f = 0.4. ^1H NMR (400 MHz, $CDCl_3$) δ 7.99−7.06 (m, 14 H), 5.76 (dd, J = 11.6, 4.4 Hz, 1 H), 4.60 (s, 2 H), 4.24−4.08 (m, 1 H), 3.10 (dd, J = 14.4, 4.4 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.08 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 138.7, 134.1, 133.3, 130.5 (q, J = 308.1 Hz), 130.3, 129.1, 129.0, 128.3, 63.0, 45.6, 30.6 ppm. MS (DART POS) 566.9 (M + NH_4), 571.9 (M + Na), 587.8 (M + K); HRMS (DART POS) for $C_{22}H_{23}O_4N_2ClF_3S_3$ (M +NH_4) calcd 567.0455; found 567.0448. IR (KBr) ν = 3069, 3011, 2962, 1447, 1384, 1361, 1158, 1122, 872, 755, 719, 685, 583, 568, 548 cm^{-1}. Mp 111.5−112.6 °C.

N-(1-(4-((1,3-Dioxoisoindolin-2-yl)methyl)phenyl)-2-(trifluoromethylthio)ethyl)-N-(phenylsulfonyl)benzenesulfonamide ***14k***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 2-(4-vinylbenzyl)isoindoline-1,3-dione (132 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14k** (152 mg, 46%) as a white solid. Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.2. ^1H NMR (400 MHz, $CDCl_3$) δ 8.27−6.72 (m, 18 H), 5.72 (dd, J = 11.5, 4.5 Hz, 1 H), 4.98−4.79 (m, 2 H), 4.18−4.05 (m, 1 H), 3.09 (dd, J = 14.3, 4.5 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.12 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 139.9, 137.4, 134.3, 133.9, 132.5, 132.1, 130.5 (q, J = 308.1 Hz), 130.1, 129.0, 128.2, 128.1, 123.5, 63.0, 41.0, 30.6 ppm. MS (DART POS) 678 (M + NH_4), 698.9 (M + K); HRMS (DART POS) for $C_{30}H_{27}O_6N_3F_3S_3$ (M + NH_4) calcd 678.1009; found 678.0992. IR (KBr) ν = 3068, 1771, 1717, 1448, 1427, 1386, 1362, 1171, 1122, 720, 686, 576, 552 cm^{-1}. Mp 107.5−108.1 °C.

N-(1-((8R,9S,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-2-(trifluoromethylthio)ethyl)-N-(phenylsulfonyl)-benzenesulfonamide ***14l***. The general procedure conducted with **7** (398 mg, 1.0 mmol), (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17-(14*H*)-one (141 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14l** (251 mg, 75%) as a white solid. Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.2. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05−7.18 (m, 11 H), 7.13 (d, J = 8.1 Hz, 1 H), 7.00 (d, J = 10.7 Hz, 1 H), 5.77 (dd, J = 11.4, 4.3 Hz, 1 H), 4.20−4.03 (m, 1 H), 3.11 (dt, J = 14.1, 3.5 Hz, 1 H), 2.82 (dt, J = 16.6, 8.3 Hz, 1 H), 2.70−2.36 (m, 3 H), 2.30 (m, 1 H), 2.24−1.89 (m, 4 H), 1.77−1.27 (m, 6 H), 0.97 (s, 1.5 H), 0.94 (s, 1.5 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −41.16 (s, 1.5 F), −41.16 (s, 1.5 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.61, 220.57, 140.7, 140.2, 136.86, 136.85, 133.8, 130.66, 130.64, 130.02, 129.99, 128.8, 128.3, 126.6, 126.50, 125.45, 125.43, 63.1, 63.0, 50.53, 50.49, 47.97, 47.95, 44.54, 44.46, 38.2, 38.1, 35.9, 31.6, 30.6, 29.3, 29.2, 26.5, 26.4, 25.9, 25.8, 21.7, 21.6, 13.93, 13.91 ppm. MS (DART POS) 678.0 (M + H), 700 (M + Na), 715 (M + K); HRMS (DART POS) for $C_{33}H_{35}O_5NF_3S_3$ (M + H) calcd 678.1624; found 678.1604. IR (KBr) ν = 3064, 2931, 2862, 1739, 1449, 1383, 1169, 1114, 1083, 1004, 719, 685, 580, 551 cm^{-1}. Mp 127.8−128.5 °C.

N-(Phenylsulfonyl)-N-(2-(trifluoromethylthio)-1,2,3,4-tetrahydronaphthalen-1-yl)benzenesulfonamide ***14m***. The general procedure conducted with **7** (398 mg, 1.0 mmol), 1,2-dihydronaphthalene (65 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14m** (190 mg, 70%) as a white solid. Eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.6. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21−7.19 (m, 10 H), 7.18−7.11 (m, 2 H), 7.06 (d, J = 8.0 Hz, 1 H), 6.82−6.72 (m, 1 H), 5.74 (d, J = 9.5 Hz, 1 H), 4.61 (ddd, J = 13.2, 9.5, 4.0 Hz, 1 H), 3.27−3.08 (m, 1 H), 2.79 (dt, J = 16.3, 3.6 Hz, 1 H), 2.65−2.46 (m, 1 H), 2.03 (qd, J = 12.7, 3.9 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.98 (s, 3 F); ^{13}C NMR

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(101 MHz, $CDCl_3$) δ 140.1, 138.7, 133.9, 131.7, 130.5 (q, J = 308.1 Hz), 129.8, 129.5, 128.8, 128.5, 128.0, 126.6, 65.6, 47.1, 33.4, 29.4 ppm. MS (DART POS) 545.0 (M + NH_4), 565.9 (M + K); HRMS (DART POS) for $C_{23}H_{24}O_4N_2F_3S_3$ (M + NH_4) calcd 545.0845; found 545.0836. IR (KBr) ν = 3073, 2937, 2874, 2847, 1448, 1382, 1374, 1339, 1318, 1165, 1109, 1078, 892, 818, 775, 756, 716, 581, 549 cm^{-1}. Mp 113.5−114.7 °C.

N-(Phenylsulfonyl)-N-(2-(trifluoromethylthio)cyclopentyl)-benzenesulfonamide ***14n***. The general procedure conducted with **7** (398 mg, 1.0 mmol), cyclopentene (34 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14n** (216 mg, 93%) as a white solid. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.3 Hz, 4 H), 7.66 (t, J = 7.4 Hz, 2 H), 7.56 (t, J = 7.8 Hz, 4 H), 4.41−4.27 (m, 1 H), 4.18 (dd, J = 18.2, 9.1 Hz, 1 H), 2.42 (dt, J = 12.5, 6.1 Hz, 1 H), 2.17−2.05 (m, 1 H), 1.92−1.82 (m, 1 H), 1.78−1.59 (m, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −39.69 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 134.2, 130.7 (q, J = 308.1 Hz), 129.2, 128.5, 65.9, 45.8, 34.5, 29.4, 22.2 ppm. MS (DART POS) 466.0 (M + H), 483.0 (M + NH_4), 487.9 (M + Na), 503.9 (M + K); HRMS (DART POS) for $C_{18}H_{22}O_4N_2F_3S_3$ (M + NH_4) calcd 483.0688; found 483.0684. IR (KBr) ν = 3006, 2974, 2952, 2881, 1448, 1391, 1366, 1350, 1169, 1112, 1043, 859, 755, 723, 686, 578, 560, 548 cm^{-1}. Mp 63.7−64.8 °C.

N-(Phenylsulfonyl)-N-(2-(trifluoromethylthio)cyclohexyl)benzenesulfonamide ***14o***. The general procedure conducted with **7** (398 mg, 1.0 mmol), cyclohexene (41 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14o** (198 mg, 83%) as a white solid. Eluent: petroleum ether/ethyl acetate = 8:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25−7.89 (m, 4 H), 7.67 (t, J = 7.4 Hz, 2 H), 7.56 (t, J = 7.7 Hz, 4 H), 4.24 (td, J = 11.5, 4.1 Hz, 1 H), 3.76 (td, J = 11.8, 3.5 Hz, 1 H), 2.43 (d, J = 13.4 Hz, 1 H), 2.32 (qd, J = 12.6, 3.6 Hz, 1 H), 1.77−1.49 (m, 4 H), 1.40−1.08 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −37.85 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 138.0, 134.5, 133. 9, 130.7 (q, J = 309.1 Hz), 129.2, 129.0, 128.8, 128.7, 65.5, 46.9 (q, J = 1.3 Hz), 36.8, 32.6, 26.2, 25.3 ppm. MS (DART POS) 479.9 (M + H), 496.9 (M + NH_4); HRMS (DART POS) for $C_{19}H_{21}O_4NF_3S_3$ (M + H) calcd 480.0579; found 480.0575. IR (KBr) ν = 3070, 2946, 2859, 1448, 1371, 1170, 1121, 1035, 866, 685, 580, 550 cm^{-1}. Mp 163.8−164.7 °C.

N-(Phenylsulfonyl)-N-(2-((trifluoromethyl)thio)cyclododecyl)-benzenesulfonamide ***14p***. The general procedure conducted with **7** (398 mg, 1.0 mmol), cyclododecene (84 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14p** (165 mg, 62%) as a white solid. Eluent: petroleum ether/ethyl acetate = 8:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63−7.35 (m, 10 H), 4.61−3.75 (m, 2 H), 2.56−0.67 (m, 20 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −39.80 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 138.7, 134.5, 133.8, 130.7 (q, J = 308.1 Hz), 129.5, 129.2, 129.1, 128.8, 61.9, 49.7, 29.9, 27.7, 25.9, 25.7, 23.5, 23.0, 22.7, 22.5, 22.4, 18.4 ppm. MS (DART POS) 564.0 (M + H), 581.0 (M + NH_4), 586 (M + Na), 602 (M + K); HRMS (DART POS) for $C_{25}H_{36}O_4N_2F_3S_3$ (M+NH_4) calcd 581.1784; found 581.1776. IR (KBr) ν = 3075, 2933, 2906, 2857, 1451, 1374, 1167, 1138, 1112, 1089, 748, 719, 579, 549 cm^{-1}. Mp 163.1−164.2 °C.

N-(Phenylsulfonyl)-N-(5-((trifluoromethyl)thio)octan-4-yl)-benzenesulfonamide ***14q***. The general procedure conducted with **7** (398 mg, 1.0 mmol), oct-4-ene (57 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) gave **14q** (131 mg, 52%) as a white solid. Eluent: petroleum ether/ethyl acetate = 15:1, R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 7.6 Hz, 2 H), 8.10 (d, J = 7.6 Hz, 2 H), 7.72−7.62 (m, 2 H), 7.57 (t, J = 7.7 Hz, 4 H), 4.19−4.09 (m, 1 H), 3.50−3.36 (m, 1 H), 2.42−2.22 (m, 1 H), 2.07−1.89 (m, 1 H), 1.60−1.42 (m, 2 H), 1.34−1.10 (m, 2 H), 1.07−0.86 (m, 1 H), 0.73 (t, J = 7.3 Hz, 3 H), 0.62 (t, J = 7.1 Hz, 3 H), 0.42 (dd, J = 22.4, 10.5 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −37.21 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 139.1, 134.4, 134.1, 130.8 (q, J = 308.1 Hz), 129.4, 129.2, 129.1, 128.9, 68.3, 52.3, 34.1, 33.1, 20.4, 20.0, 13.6, 13.34 ppm. MS (DART POS) 509.9 (M + H), 527.0 (M + NH_4), 532.0 (M + Na), 547.9 (M + K); HRMS (DART POS) for $C_{21}H_{30}O_4N_2F_3S_3$ (M + NH_4) calcd 527.1320; found 527.1304. IR (KBr) ν = 3068, 2963, 2933, 2874, 1449, 1373, 1354, 1169, 1111, 1083, 841, 755, 720, 686, 587, 552 cm^{-1}. Mp 63.2−64.2 °C.

General Procedure A for Direct Trifluoromethylthiolation of Other Nucleophiles (15a−15d, 16c, and 16d). **7** (398 mg, 1.0 mmol) was placed into an oven-dried Schlenk tube equipped with a stirring bar under argon. 5-Methyl-1*H*-indazole (66 mg, 0.5 mmol) and freshly distilled DMF (2.0 mL) were added. The reaction was stirred at 80 °C for 1 h. Distilled water (10.0 mL) and ether (50.0 mL) were added, and the organic phase was separated. The organic phase was washed with distilled water (10.0 mL × 3). The organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give 5-methyl-1-(trifluoromethylthio)-1*H*-indazole **15a** (79 mg, 69%, eluent: petroleum ether/ether = 40:1, R_f = 0.4) as a light yellow liquid.

General Procedure B for Direct Trifluoromethylthiolation of Other Nucleophiles (16a, 16b, and 17a−17d). To a 25 mL oven-dried Schlenk tube charged with 4-nitroaniline (42 mg, 0.3 mmol) were added **7** (144 mg, 0.36 mmol) and CH_2Cl_2 (1.5 mL). The mixture was stirred at room temperature for 24 h. The solvent was removed under vacuum, and the residue was purified by flask column chromatography to give *N*-(4-nitrophenyl)-*S*-(trifluoromethyl)-thiohydroxylamine **16a** (67 mg, 94%, eluent: petroleum ether/ether = 10:1, R_f = 0.6) as a pale white solid.

General Procedure C for Direct Trifluoromethylthiolation of Other Nucleophiles (18a−18d). To a 25 mL oven-dried Schlenk tube charged with sodium 4-fluorobenzenesulfinate (110 mg, 0.6 mmol) were added **7** (120 mg, 0.3 mmol) and AcOH (1.5 mL). The mixture was stirred at room temperature for 12 h. Ether (50.0 mL) was added, and the organic phase was washed with saturated bicarbonate (10.0 mL × 3) and distilled water (10.0 mL). The organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give *S*-(trifluoromethyl) 4-fluorobenzenesulfonothioate **18a** (63 mg, 80%, eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.8) as a light yellow liquid.

5-Methyl-1-(trifluoromethylthio)-1H-indazole ***15a***. The general procedure A conducted with **7** (398 mg, 1.0 mmol), 5-methyl-1*H*-indazole (66 mg, 0.5 mmol), and DMF (2 mL) gave **15a** (79 mg, 69%) as a light yellow liquid. Eluent: petroleum ether/ether = 40:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1 H), 7.55 (d, J = 8.5 Hz, 1 H), 7.51 (s, 1 H), 7.37 (d, J = 8.5 Hz, 1 H), 2.48 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −50.20 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 140.7, 133.2, 130.7, 128.5 (q, J = 318.2 Hz), 125.8, 120.8, 110.4, 21.3 ppm. MS (EI) 132 (100), 232 (2.34). HRMS (EI) for $C_9H_7N_2F_3S$ calcd 232.0282; found 232.0287. IR (KBr) ν = 1585, 1501, 1214, 1168, 1145, 1075, 999, 953, 805, 602, 517 cm^{-1}.

6-Bromo-1-(trifluoromethylthio)-1H-indazole ***15b***. The general procedure A conducted with **7** (398 mg, 1.0 mmol), 6-bromo-1*H*-indazole (99 mg, 0.5 mmol), and DMF (2 mL) gave **15b** (110 mg, 75%) as a yellow liquid. Eluent: petroleum ether/ether = 50:1, R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 1.0 Hz, 1 H), 7.85 (s, 1 H), 7.64−7.56 (m, 1 H), 7.42 (dd, J = 8.5, 1.5 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −49.87 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 141.0, 128.3 (q, J = 318.2 Hz), 127.2, 124.3, 123.5, 122.6, 114.0 ppm. MS (EI) 196 (100), 198 (99.72), 296 (2.48), 298 (2.32). HRMS (EI) for $C_8H_4N_2F_3SBr$ calcd 295.9231; found 295.9232. IR (KBr) ν = 1617, 1345, 1174, 1132, 1075, 1040, 948, 909, 838, 781, 706, 675, 585, 421 cm^{-1}.

4-Chloro-1-(trifluoromethylthio)-1H-indazole ***15c***. The general procedure A conducted with **7** (398 mg, 1.0 mmol), 4-chloro-1*H*-indazole (77 mg, 0.5 mmol), and DMF (2 mL) gave **15c** (100 mg, 80%) as a white solid. Eluent: petroleum ether/ether = 150:1, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 1.1 Hz, 1 H), 7.56 (d, J = 8.4 Hz, 1 H), 7.50−7.40 (m, 1 H), 7.31−7.24 (m, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −49.89 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 139.4, 129.5, 128.3 (q, J = 318.2 Hz), 127.3, 124.7, 123.2, 109.4 ppm. MS (EI) 183 (100), 252 (92.43). HRMS (EI) for $C_8H_4N_2F_3SCl$ calcd 251.9736; found 251.9739. IR (KBr) ν = 3034, 1609, 1581, 1496, 1405, 1187, 1144, 1119, 1087, 920, 782, 461 cm^{-1}.

4-Fluoro-1-(trifluoromethylthio)-1H-indazole ***15d***. The general procedure A conducted with **7** (398 mg, 1.0 mmol), 4-fluoro-1*H*-indazole (68 mg, 0.5 mmol), and DMF (2 mL) gave **15d** (60 mg,

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51%) as a white solid. Eluent: petroleum ether/ether = 150:1, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1 H), 7.53−7.43 (m, 2 H), 7.00−6.92 (m, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −49.90 (s, 3 F), −117.37−117.48 (m, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6 (d, J = 254.9 Hz), 148.1 (d, J = 7.7 Hz), 137.1, 129.8 (d, J = 7.8 Hz), 128.2 (q, J = 318.2 Hz), 115.5 (d, J = 23.3 Hz), 108.1 (d, J = 18.4 Hz), 106.8 (d, J = 4.4 Hz) ppm. MS (EI) 236 (100). HRMS (EI) for $C_8H_4N_2F_4S$ calcd 236.0031; found 236.0037. IR (KBr) ν = 2929, 1632, 1592, 1507, 1409, 1366, 1188, 1119, 969, 783, 652, 460 cm^{-1}.

N-(4-Nitrophenyl)-S-(trifluoromethyl)thiohydroxylamine **16a**.[12a] The general procedure B conducted with **7** (144 mg, 0.36 mmol), 4-nitroaniline (42 mg, 0.3 mmol), and CH_2Cl_2 (1.5 mL) gave **16a** (67 mg, 94%) as a pale white solid. Eluent: petroleum ether/ether = 10:1, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 9.1 Hz, 2 H), 7.19 (d, J = 9.1 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −52.30 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 142.3, 129.1 (q, J = 318.2 Hz), 125.8, 115.0 ppm.

N-Methyl-N-phenyl-S-(trifluoromethyl)thiohydroxylamine **16b**.[17a] The general procedure B conducted with **7** (144 mg, 0.36 mmol), *N*-methylaniline (33 mg, 0.3 mmol), and CH_2Cl_2 (1.5 mL) gave **16b** (57 mg, 91%) as a colorless liquid. Eluent: petroleum ether, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, J = 7.9 Hz, 2 H), 7.27 (d, J = 8.0 Hz, 2 H), 7.00 (t, J = 7.2 Hz, 1 H), 3.53 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −50.38 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 130.5 (q, J = 323.2 Hz), 129.1, 121.3, 116.1, 46.3 ppm.

N-(Pyridin-2-yl)-S-(trifluoromethyl)thiohydroxylamine **16c**.[17a] The general procedure A conducted with **7** (398 mg, 1.0 mmol), pyridin-2-amine (47 mg, 0.5 mmol), and DMF (2 mL) gave **16c** (68 mg, 71%) as a white solid. Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 16.9 Hz, 1 H), 8.21 (dd, J = 5.0, 0.9 Hz, 1 H), 7.70−7.63 (m, 1 H), 7.31 (d, J = 8.5 Hz, 1 H), 6.92−6.85 (m, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −52.93 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 147.9, 138.9, 129.6 (q, J = 318.2 Hz), 117.1, 107.9 ppm.

9-((Trifluoromethyl)thio)-9H-carbazole **16d**. The general procedure A conducted with **7** (398 mg, 1.0 mmol), 9*H*-carbazole (84 mg, 0.5 mmol), and DMF (2 mL) gave **16d** (105 mg, 79%) as a white solid. Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−8.02 (m, 2 H), 7.79 (d, J = 8.2 Hz, 2 H), 7.60−7.52 (m, 2 H), 7.43−7.35 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −49.61 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 129.1 (q, J = 318.2 Hz), 127.0, 125.3, 122.6, 120.5, 111.2 ppm. MS (EI) 198 (100), 267 (72.85). HRMS (EI) for $C_{13}H_8NF_3S$ calcd 267.0330; found 267.0327. IR (KBr) ν = 3060, 1601, 1478, 1451, 1439, 1263, 1218, 1170, 1142, 1118, 723, 477, 459 cm^{-1}.

1-(4-Fluorophenyl)-2-(trifluoromethyl)disulfane **17a**.[17a] The general procedure B conducted with **7** (144 mg, 0.36 mmol), 4-fluorobenzenethiol (39 mg, 0.3 mmol), and CH_2Cl_2 (1.5 mL) gave **17a** (59 mg, 85%) as a yellow liquid. Eluent: petroleum ether, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.57 (m, 2 H), 7.11−7.03 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −45.82 (s, 3 F), −110.65 (tt, J = 8.4, 5.2 Hz, 1 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7 (d, J = 250.8 Hz), 134.0 (d, J = 8.9 Hz), 130.2 (d, J = 3.4 Hz), 129.4 (q, J = 315.2 Hz), 116.8 (d, J = 22.3 Hz) ppm.

1-(4-Bromophenyl)-2-(trifluoromethyl)disulfane **17b**.[17a] The general procedure B conducted with **7** (144 mg, 0.36 mmol), 4-bromobenzenethiol (57 mg, 0.3 mmol), and CH_2Cl_2 (1.5 mL) gave **17b** (77 mg, 88%) as a yellow liquid. Eluent: petroleum ether, R_f = 0.7, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.6 Hz, 2 H), 7.45 (d, J = 8.6 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −45.78 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.0, 132.7, 132.1, 129.2 (q, J = 314.2 Hz), 123.7 ppm.

2-((Trifluoromethyl)sulfinothioyl)benzo[d]oxazole **17c**.[17a] The general procedure B conducted with **7** (144 mg, 0.36 mmol), benzo[*d*]oxazole-2-thiol (46 mg, 0.3 mmol), and CH_2Cl_2 (1.5 mL) gave **17c** (73 mg, 97%) as a colorless liquid. Eluent: petroleum ether, R_f = 0.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dt, J = 6.6, 2.7 Hz, 1 H), 7.61−7.46 (m, 1 H), 7.41−7.34 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −45.64 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 152.7, 141.9, 128.4 (q, J = 314.7 Hz), 126.0, 125.3, 120.2, 110.8 ppm.

1-Phenethyl-2-(trifluoromethyl)disulfane **17d**.[17a] The general procedure B conducted with **7** (144 mg, 0.36 mmol), 2-phenylethanethiol (42 mg, 0.3 mmol), and CH_2Cl_2 (1.5 mL) gave **17d** (61 mg, 85%) as a colorless liquid. Eluent: petroleum ether, R_f = 0.7, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, J = 7.3 Hz, 2 H), 7.29 (d, J = 7.3 Hz, 2 H), 7.23 (d, J = 7.0 Hz, 1 H), 3.23−3.10 (m, 2 H), 3.11−2.99 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −46.01 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 129.7 (q, J = 313.6 Hz), 128.8, 128.7, 126.9, 41.1, 35.3 ppm.

S-(Trifluoromethyl)-4-fluorobenzenesulfonothioate **18a**.[14h] The general procedure C conducted with **7** (120 mg, 0.3 mmol), sodium 4-fluorobenzenesulfinate (110 mg, 0.6 mmol), and AcOH (1.5 mL) gave **18a** (63 mg, 80%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 20:1, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, J = 8.7, 4.8 Hz, 2 H), 7.56 (dd, J = 14.4, 5.7 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.52 (s, 3 F), −99.75--99.87 (m, 1 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6 (d, J = 259.8 Hz), 140.8 (d, J = 1.9 Hz), 131.0 (d, J = 10.1 Hz), 127.4 (q, J = 313.2 Hz), 117.2 (d, J = 23.1 Hz) ppm.

S-(Trifluoromethyl)-4-bromobenzenesulfonothioate **18b**.[14h] The general procedure C conducted with **7** (120 mg, 0.3 mmol), sodium 4-bromobenzenesulfinate (146 mg, 0.6 mmol), and AcOH (1.5 mL) gave **18b** (85 mg, 87%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 30:1, R_f = 0.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.6 Hz, 2 H), 7.76 (d, J = 8.7 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.34 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 133.1, 130.9, 129.2, 127.3 (q, J = 313.3 Hz) ppm.

S-(Trifluoromethyl)-4-cyanobenzenesulfonothioate **18c**.[14h] The general procedure C conducted with **7** (120 mg, 0.3 mmol), sodium 4-cyanobenzenesulfinate (114 mg, 0.6 mmol), and AcOH (1.5 mL) gave **18c** (74 mg, 92%) as a light yellow liquid. Eluent: petroleum ether/ethyl acetate = 30:1, R_f = 0.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.4 Hz, 2 H), 7.93 (d, J = 8.5 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.06 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 133.6, 128.3, 127.0 (q, J = 313.9 Hz), 118.9, 116.7 ppm.

S-(Trifluoromethyl) 4-acetylbenzenesulfonothioate **18d**. The general procedure C conducted with **7** (120 mg, 0.3 mmol), sodium 4-acetylbenzenesulfinate (124 mg, 0.6 mmol), and AcOH (1.5 mL) gave **18d** (79 mg, 92%) as a white solid. Eluent: petroleum ether/ethyl acetate = 10:1, R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.6 Hz, 2 H), 8.08 (d, J = 8.5 Hz, 2 H), 2.67 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −38.22 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 147.8, 141.8, 129.5, 128.1, 127.1 (q, J = 313.4 Hz), 27.0 ppm. MS (EI) 183 (100), 267 (72.85). HRMS (EI) for $C_9H_7O_3F_3S_2$ calcd 283.9789; found 283.9792. IR (KBr) ν = 1697, 1399, 1364, 1260, 1169, 1099, 1078, 834, 760, 628, 596, 551 cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01178.

Synthesis, analytic data, computational details, and NMR data of compounds **8**−**18** (PDF)

X-ray diffraction data of compound **7** (CIF)

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Notes

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