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VIP S-(Trifluoromethyl)Benzothioate (TFBT): A KF-Based Reagent for Nucleophilic Trifluoromethylthiolation

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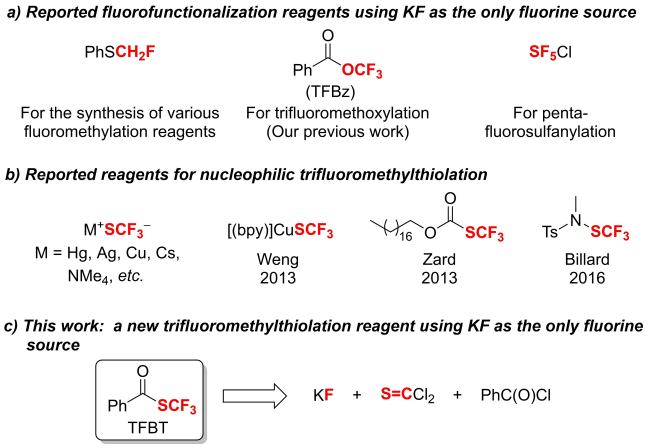
Abstract: *S*-(Trifluoromethyl)benzothioate (TFBT) has been developed as an inexpensive, bench-stable, and user-friendly trifluoromethylthiolation reagent, which can be easily synthesized by using KF as the only fluorine source. By using TFBT, trifluoromethylthiolates with various counterions can be readily obtained. The synthetic application of TFBT was demonstrated by trifluoromethylthiolation-halogenation of arynes, bis(trifluoromethylthiolation)–halogenation of 1,2-benzdiynes, nucleophilic substitution of alkyl halides, deoxytrifluoromethylthiolation of alcohols, and cross-coupling with aryl and vinyl boronic acids.

Fluorine-containing groups are significant structural motifs and have found widespread applications in pharmaceuticals, agrochemicals and materials.[1] Due to the scarcity of naturally occurring organofluorine compounds, various reagents have been exploited for the direct introduction of carbon- and heteroatom-linked fluorine-containing groups into organic molecules.[2,3] However, most of the reagents are prepared with corrosive HF, environmentally hazardous fluorinated gases or expensive metal fluorides such as AgF.[3] Until now, few of the reagents have been developed by using safe and inexpensive KF as the only fluorine source (Scheme 1a). Monofluoromethyl phenyl sulfide ($PhSCH_2F$), synthesized form KF and $PhSCH_2Cl$, has been used to prepare various monofluoromethylation reagents.[4] In 2018, our group reported the synthesis of trifluoromethyl benzoate (TFBz) from KF, triphosgene and benzoyl bromide and demonstrated the versatility of TFBz as a nucleophilic trifluoromethoxylation reagent.[5] Very recently, the groups of Togni and Qing developed KF-based synthesis of pentafluorosulfanylation reagent SF_5Cl.[6]

As one of representative fluorine-containing functional groups, trifluoromethylthio group (SCF_3) possesses important potentials in drug design because of its stability, electronegativity and lipophilicity.[7] Although various direct trifluoromethylthiolation methods have been developed in recent years,[8] their corresponding fluorine sources are still relatively limited and suffer from high cost. For instance, nucleophilic trifluoromethylthiolation (Scheme 1b) was initially achieved with unstable or water sensitive $MSCF_3$[9] (M=Hg, Ag, Cu, Cs, NMe_4, etc) that were synthesized by using cost-ineffective metal fluorides or Ruppert-Prakash reagent ($TMSCF_3$) as the fluorine source. In 2013, Weng and co-workers reported the use of [(bpy)$CuSCF_3$] as an air-stable nucleophilic trifluoromethylthiolation reagent, which was obtained from bipyridine (bpy), CuF_2, sulfur powder and $TMSCF_3$.[10] In the same year, Zard and co-workers demonstrated the synthesis of trifluoromethyl thiocarbonate from xanthate and trifluoroacetic anhydride (TFAA), which could release SCF_3^- under the combined action of KF and tetrahydropyrrole.[11] In 2016, Billard and co-workers employed trifluoromethanesulfenamide (BB23, synthesized from $TMSCF_3$ and DAST) as a SCF_3 source under the activation of iodide anion.[12]

To address the practicability issue of present nucleophilic trifluoromethylthiolation, we envisioned the development of a new bench-stable and user-friendly trifluoromethylthiolation reagent that can be easily prepared using KF as the only



Scheme 1. The development of a new trifluoromethylthiolation reagent by using KF as the only fluorine source.

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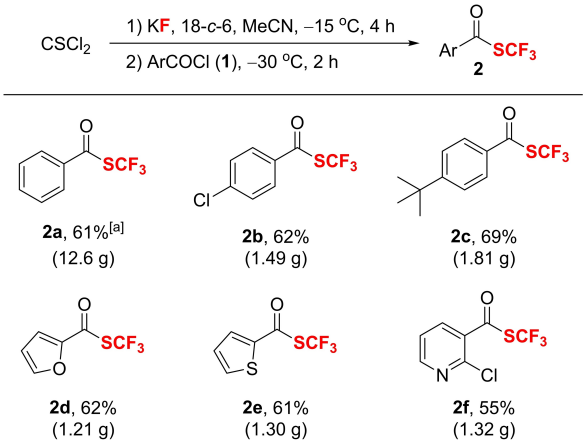
fluorine source. Inspired by our previously developed nucleophilic trifluoromethoxylation reagent TFBz,[5] we planned to synthesize *S*-(trifluoromethyl) benzothioate (TFBT, **2a**) from KF, thiophosgene ($S{=}CCl_2$) and benzoyl chloride (Scheme 1c) by the in-situ formation of CF_3S^- species. Previously, TFBT was prepared from trifluoromethylthiolation reactions with expensive CF_3S-containing reagents,[9b,13] and TFBT has never been reported as a CF_3S^- precursor. Herein, we wish to disclose our recent success in the synthesis of TFBT from KF, $S{=}CCl_2$ and PhCOCl (through consecutive triple fluorinations, followed by benzoylation) and its application in trifluoromethylthiolation of various electrophiles.

Our investigation began with the preparation of TFBT (**2a**) from the commercially available $S{=}CCl_2$, KF and a benzoyl halide (Scheme 2). Previously, nucleophilic trifluoromethylthiolation with the combination of $S{=}CCl_2$ and KF was found to be problematic due to the decomposition of CF_3SK (even at 0 °C) and the formation of side products.[14] With these in mind, we added 18-crown-6 to stabilize the CF_3SK formed in situ and used highly reactive benzoyl bromide as the electrophilic trap. Initial attempt in THF gave the desired product **2a** in 59% isolated yield (see Table S1, entry 5 in the Supporting Information); however, the reproducibility of the reaction under such conditions was poor due to uncontrolled competitive pathways that could lead to benzoyl fluoride, $S{=}C(CF_3S)_2$ and CF_3SSCF_3 (observed by ^{19}F NMR). To suppress these undesired side reactions, we changed the solvent to MeCN and replaced the electrophilic species with benzoyl chloride **1a**, and the reaction could give **2a** in 47% yield at an elevated temperature for chlorine/fluorine exchange reaction of $S{=}CCl_2$ (Table S2, entry 2). After further optimization (Table S2, entries 3–6), we established the standard reaction conditions. As shown in Scheme 2, the reaction on 100-mmol scale could afford TFBT (**2a**) as a stable liquid in 61% isolated yield. In addition, *S*-(trifluoromethyl) thioesters with different substituents on the phenyl group (**1b–c**) or different heteroaryl groups (**1d–f**) could be produced from the corresponding acyl chlorides in 55–69% yields (Scheme 2).

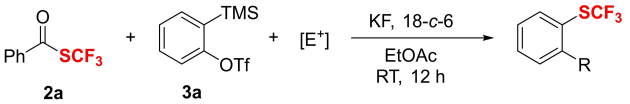
With TFBT (**2a**) in hand, we investigated its synthetic power as a nucleophilic trifluoromethylthiolation reagent. Arynes, as highly reactive electrophiles, were used as probes to test the release of CF_3S^- from TFBT. In our previous work, the trifluoromethylthiolation-iodination of arynes was performed with $AgSCF_3$.[15] To assess the necessity of silver, we tried the vicinal difunctionalization of arynes under transition metal-free conditions (Table 1). The reaction was carried out by simply mixing **2a**, *o*-trimethylsilylaryl triflate (**3**, the precursor of benzyne), an electrophilic halogenation reagent, and KF/18-crown-6 in ethyl acetate (EtOAc) and stirring the mixture at room temperature. Although the use of NIS or I_2 as the electrophile afforded the desired product in low yields (Table 1, entries 1 and 2), both alkynyl iodides and perfluoroalkyl iodides were found to be efficient electrophilic iodination reagents (Table 1, entries 3–5). Of note is that normal perfluoroalkyl iodides such as nC_4F_9I, which was shown to be of low electrophilicity towards aryl silver species,[15] possessed comparable reactivity to alkynyl iodides such as 1-iodophenylacetylene in trapping the aryl anion in the absence of silver. This result indicates that the current TFBT-mediated trifluoromethylthiolation of arynes generates more reactive *o*-SCF_3 aryl anion intermediates than the *o*-SCF_3 aryl-Ag intermediates in previously known $AgSCF_3$-mediated method.[15] The screening of solvent showed that acetonitrile and THF are inferior to EtOAc in iodination reaction (Table 1, entries 6–8). In addition, the in situ formed *o*-(trifluoromethylthio)aryl anion could also be trapped by other electrophilic halogenation reagents such as 1-bromophenylacetylene and bromopentafluorobenzene, providing the trifluoromethylthiolation–bromination product in moderate yields (Table 1, entries 9 and 10).

Next, we explored the scope of this trifluoromethylthiolation-halogenation with TFBT (**2a**) and structurally diverse aryne precursors (Scheme 3). For iodination, nC_4F_9I was chosen as the electrophile to demonstrate the unique



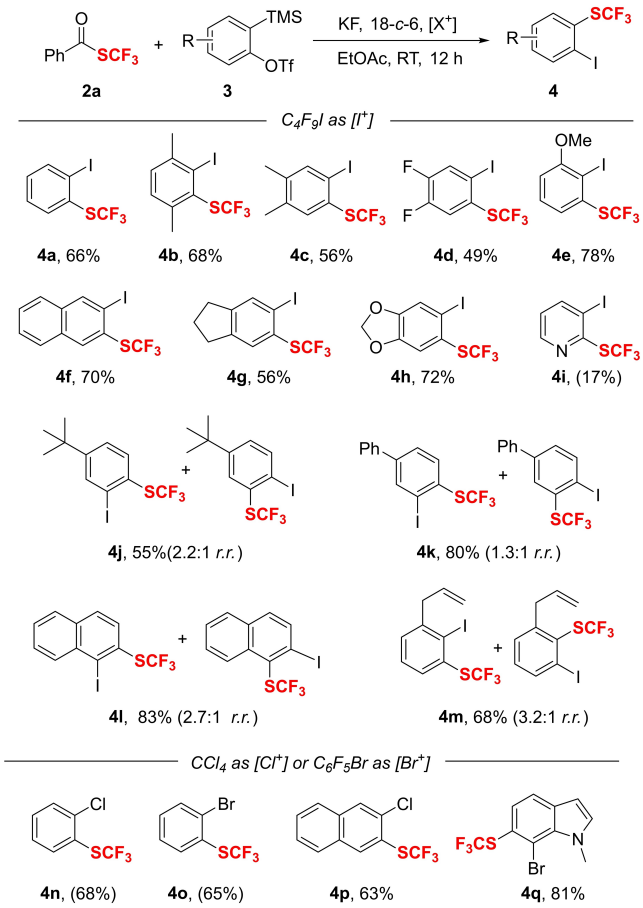
Scheme 2. Preparation of *S*-(trifluoromethyl) thioesters **2**. Reaction conditions: $CSCl_2$ (1.2 equiv), KF (4.0 equiv), 18-*c*-6 (1.2 equiv), MeCN (30.0 mL), stirred at −15 °C for 4 h; then cooled to −30 °C, **1** (10.0 mmol, 1.0 equiv) added, and the mixture stirred for another 2 h. Yields of the isolated products are shown. [a] Performed on 100-mmol scale.

Table 1. Screening of the reaction conditions.



Entry[a]	[E⁺]	Solvent	R	Yield [%][b]
1	NIS	EtOAc	I	0
2	I_2	EtOAc	I	14
3	Ph–≡–I	EtOAc	I	72
4	n-C_4F_9I	EtOAc	I	67
5	n-$C_6F_{13}I$	EtOAc	I	66
6	n-$C_6F_{13}I$	MeCN	I	53
7	Ph–≡–I	MeCN	I	63
8	Ph–≡–I	THF	I	59
9	Ph–≡–Br	EtOAc	Br	53
10	C_6F_5Br	EtOAc	Br	56

[a] Reaction conditions: **3a** (0.1 mmol, 1.0 equiv), **2a** (3.0 equiv), KF (4.5 equiv), 18-*c*-6 (4.5 equiv), [E⁺] (4.0 equiv), EtOAc (1.0 mL), room temperature, 12 h. [b] Yield was determined by ^{19}F NMR analysis of the crude reaction mixture with C_6F_6 as internal standard.



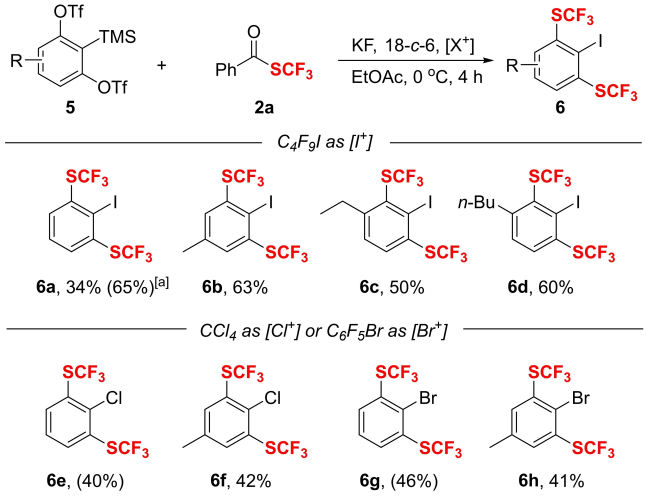
Scheme 3. Scope of difunctionalization of arynes. Reactions were performed on a 0.3 mmol scale. Reaction conditions: **3** (1.0 equiv), **2a** (3.0 equiv), KF (4.5 equiv), 18-*c*-6 (4.5 equiv), [X$^+$] (X=I, Br, Cl, 4.0 equiv), EtOAc (3.0 mL) room temperature, 12 h. For a list of the structures of **3**, see the Supporting Information. Yields of the isolated products are shown. Yields were determined by ^{19}F NMR spectroscopy with C_6F_6 as internal standard; the ratio of isomers is shown in parentheses. *r.r.*: regioisomer ratio.

reactivity of *o*-(trifluoromethylthio)aryl anions under transition metal-free conditions. Both *o*- and *m*-substituted precursors smoothly underwent trifluoromethoxylation–iodination to give the corresponding products in moderate to good yields (**4b**–**h**, **4j**–**m**). Functionalities including fluorine, acetal, methoxy and allyl group are well tolerated (**4d**–**f**, **4h** and **4m**). In the case of the pyridyne precursor **3i**, the low yield probably arises from the competitive consumption of pyridyne by the nucleophilic nitrogen atom of the pyridyne ring (**4i**). For asymmetrical arynes, the regioselectivity is related to both steric effect and electronic effect of their substituents, as is demonstrated by the high selectivity in the reaction of 3-methoxy aryne (**4e**) and moderate to poor selectivity in the reaction of other arynes (**4j**–**m**). When CCl_4 or C_6F_5Br was used instead of *n*-C_4F_9I, the trifluoromethylthiolation-chlorination/bromination product could be obtained in good yields (**4n**–**q**).

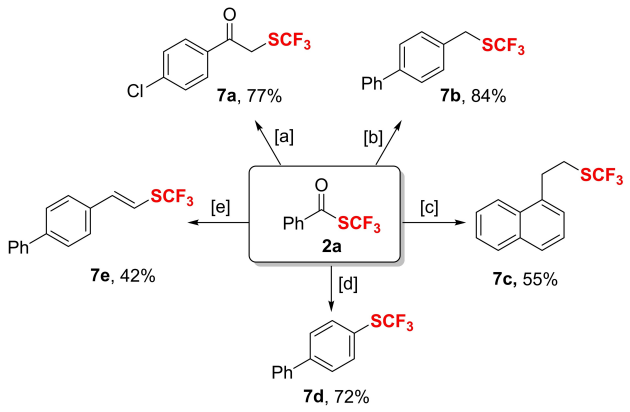
Inspired by above successful difunctionalization, we investigated the reaction between TFBT (**2a**) and 1,2-benzdiyne precursor **5a** (Table S3).[16] Although the intermediate was unstable, the trifunctionalization product with two trifluoromethylthio groups *ortho* to iodide could be detected in 65% yield when the reaction was carried out at 0 °C with 3 Å molecular sieve (MS) as an additive (Table S3, entry 12). With the optimized reaction conditions in hand, we examined the scope of 1,2-benzdiyne precursors and electrophilic halogenation reagents (Scheme 4). The 1,2-benzdiyne precursors bearing different substituents could undergo the bis(trifluoromethylthiolation)–iodination process to afford desired products in 50–65% yield (**6a**–**d**). However, owing to the electron withdrawing effect of SCF_3, the *ortho*-ditrifluoromethylthio aryl anion intermediates exhibit weaker nucleophilicity, which leads to the decline of yields (**6e**–**h**).

To further demonstrate the synthetic application of reagent TFBT (**2a**), we applied it to several other trifluoromethylthiolation processes (Scheme 5). In the presence of AgF and KI,[17] the bromide of α-bromoketone or 4-bromoethylbiphenyl could be substituted by SCF_3 to afford trifluoromethylthiolation products in good yields (**7a**, **7b**). Furthermore, we used **2a**/KF (instead of $AgSCF_3$)[18] and realized the deoxytrifluoromethylthiolation of 2-naphthaleneethanol (**7c**). Finally, reagent **2a** could be used in the oxidative trifluoromethylthiolation of aryl or vinyl boronic acid[19] under promotion of copper to provide the corresponding cross-coupling products (**7d**, **7e**).

In summary, we have developed *S*-(trifluoromethyl) benzothioate (TFBT) as a bench-stable and user-friendly nucleophilic trifluoromethylthiolation reagent. This reagent was synthesized by using KF as the only fluorine source, and can readily release SCF_3^- with various counterions. 1,2-Trifluoromethylthiolation-halogenation of arynes and 1,3-bis(trifluoromethylthiolation)-2-halogenation of 1,2-benzdiynes provide a useful synthetic tool for the one-pot synthesis of trifluoromethylthiolated aryl halides that are suitable for further elaboration.



Scheme 4. Scope of trifunctionalization of arynes. Reactions were performed on a 0.3 mmol scale. Reaction conditions: **2a** (1.0 equiv), **5** (0.75 equiv), [X$^+$] (X=I, Br, Cl, 1.5 equiv), KF (2.0 equiv), 18-*c*-6 (2.0 equiv), 3 Å molecular sieve (10 mg), EtOAc (4.0 mL), 0 °C, 4 h. For a list of the structures of **5**, see the Supporting Information. Yields of the isolated products determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as internal standard are shown in parentheses. [a] 1.5 mmol scale.



Scheme 5. Versatile trifluoromethylthiolations with reagent **2a**. Yields of the isolated products are shown. See the Supporting Information for more details. [a] α-Bromo-*p*-chloroacetophenone (0.3 mmol, 1.0 equiv), **2a** (2.0 equiv), AgF (2.0 equiv), KI (2.0 equiv), MeCN (3.0 mL), RT, overnight. [b] 4-Bromomethyl biphenyl (0.3 mmol, 1.0 equiv), **2a** (2.0 equiv), AgF (2.0 equiv), KI (2.0 equiv), MeCN (3.0 mL), RT, overnight. [c] 2-Naphthylethanol (0.3 mmol, 1.0 equiv), **2a** (4.0 equiv), KF (6.0 equiv), 18-*c*-6 (6.0 equiv), nBu$_4$NI (4.0 equiv), PhMe (3.0 mL), 80 °C, 8 h. [d] *p*-Phenylphenylboronic acid (0.3 mmol, 1.0 equiv), **2a** (2.0 equiv), Me$_4$NF (1.9 equiv), Cu(OTf)$_2$ (1.0 equiv), dtbpy (1.0 equiv), Cs_2CO_3 (1.2 equiv), THF (9.0 mL), air, RT, overnight. [e] *Trans*-2-(4-biphenyl)vinylboronic acid (0.3 mmol, 1.0 equiv), **2a** (1.5 equiv), Me$_4$NF (1.5 equiv), Cu(OTf)$_2$ (1.0 equiv), dtbpy (1.0 equiv), Cs_2CO_3 (1.25 equiv), THF (10.0 mL), air, RT, overnight.

Other trifluoromethylthiolation reactions, including nucleophilic substitution of alkyl halides, deoxytrifluoromethylthiolation of alcohols, and cross-coupling with aryl and vinyl boronic acids, can also be achieved by using TFBT as the reagent.

Experimental Section

A typical procedure for preparing *S*-(trifluoromethyl) thioester (2a in Scheme 2): Under the protection of nitrogen, potassium fluoride (23.2 g, 400 mmol, 4.0 equiv), 18-*c*-6 (31.8 g, 120 mmol, 1.2 equiv) and acetonitrile (200 mL) were added to a dry Schlenk tube. After cooling to −15 °C, thiophosgene (9.2 mL, 120 mmol, 1.2 equiv) was added, and the mixture was vigorously stirred for 4 h. Then, the temperature was cooled to −30 °C and benzoyl chloride (11.6 mL, 100 mmol, 1.0 equiv) added. After stirring for another 2 h, the reaction was quenched by water, raised to room temperature, and extracted with ether (3×100 mL). The organic phases were combined, washed with water and saturated brine, and dried with anhydrous Na_2SO_4. After filtration, the solution was concentrated by evaporation and the residue was distilled under reduced pressure (8 Torr, 70–80 °C) to provide **2a** as a yellow liquid (12.6 g, 61 %).

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: aryne · multifunctionalization · potassium fluoride · *S*-(trifluoromethyl)benzothioate · trifluoromethylthiolation

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