

# Controllable Double Difluoromethylene Insertions into S–Cu Bonds: (Arylthio)tetrafluoroethylation of Aryl Iodides with $\text{TMSCF}_2\text{Br}$

Shitao Pan, Qiqiang Xie, Xiu Wang, Rumin Huang, Yuhao Lu, Chuanfa Ni, and Jinbo Hu\*

**Abstract:** A new method of constructing “ $\text{ArSCF}_2\text{CF}_2\text{Cu}$ ” from  $\text{ArSCu}$  and  $\text{TMSCF}_2\text{Br}$  (TMS = trimethylsilyl) has been developed. The cross-coupling reactions of the obtained “ $\text{ArSCF}_2\text{CF}_2\text{Cu}$ ” with diverse aryl iodides ( $\text{Ar'I}$ ) provide an efficient access to  $\text{Ar'CF}_2\text{CF}_2\text{SAr}$ . Mechanistic studies demonstrate that the “ $\text{ArSCF}_2\text{CF}_2\text{Cu}$ ” species were generated through controllable double difluoromethylene insertions into  $\text{ArS-Cu}$  bonds rather than the 1,2-addition of  $\text{ArSCu}$  to tetrafluoroethylene.

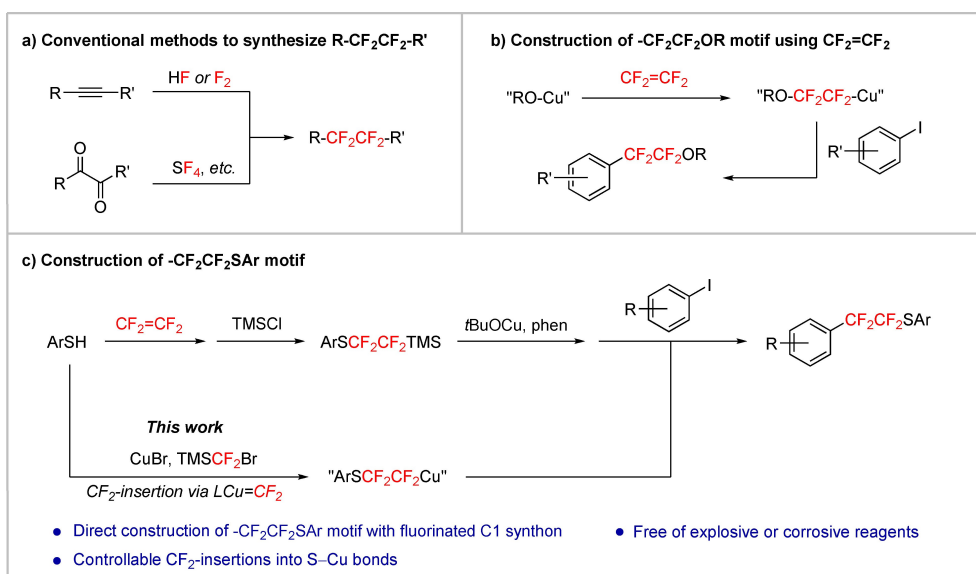
It is widely realized that selective incorporation of fluorine-containing moieties into organic molecules has become a routine and powerful strategy in the development of new pharmaceuticals and functional materials, owing to the unique properties that fluorine can bring about. At present, several fluorine-containing motifs have been intensively studied, such as trifluoromethyl,<sup>[1]</sup> difluoromethyl,<sup>[2]</sup> and pentafluoroethyl groups.<sup>[3]</sup> Among these fluorinated functionalities, the tetrafluoroethylene motif ( $-\text{CF}_2\text{CF}_2-$ ) has attracted considerable attention due to its special applications in liquid crystal materials,<sup>[4]</sup> pharmaceuticals,<sup>[5a]</sup> and agrochemicals.<sup>[5b–e]</sup> Nowadays, the traditional methods to synthesize tetrafluoroethylene-bridged molecules include: 1) deoxofluorination of 1,2-dicarbonyl compounds using  $\text{SF}_4$  or its analogues,<sup>[6]</sup> and 2) perfluorination of C–C triple bonds<sup>[7]</sup> (Scheme 1a). However, the fluorination of 1,2-dicarbonyl compounds or C–C triple bonds can not be applicable to synthesize the heteroatom-containing tetrafluoroethylene motif, such as  $\text{ArOCF}_2\text{CF}_2\text{Ar}$ <sup>[8,9]</sup> or  $\text{ArSCF}_2\text{CF}_2\text{Ar}$ ,<sup>[10,11]</sup> which are commonly synthesized directly or indirectly from ozone-depleting substances (ODS) such as  $\text{BrCF}_2\text{CF}_2\text{Br}$  and  $\text{ICF}_2\text{CF}_2\text{I}$ . Notably, Ogoshi and co-workers have succeeded in the synthesis of  $\text{ArOCF}_2\text{CF}_2\text{Ar}$  using tetrafluoroethylene ( $\text{CF}_2=\text{CF}_2$ ). The migratory insertion of  $\text{CF}_2=\text{CF}_2$  into  $\text{RO-Cu}$  bonds resulted in the formation of “ $\text{ROCF}_2\text{CF}_2\text{Cu}$ ”, which could be converted to a broad range of valuable products (Scheme 1b),<sup>[12]</sup> and similar transformation was also reported by our group in 2017.<sup>[3k]</sup> Unfortunately, they

found that the migratory insertion of  $\text{CF}_2=\text{CF}_2$  into  $\text{ArS-Cu}$  bond was in low efficiency, and instead,  $\text{ArSCF}_2\text{CF}_2\text{Ar}$  was synthesized through four steps (including three separation steps) using  $\text{CF}_2=\text{CF}_2$  (Scheme 1c).<sup>[10]</sup> Thus, it is not convenient to prepare  $\text{ArOCF}_2\text{CF}_2\text{Ar}$  or  $\text{ArSCF}_2\text{CF}_2\text{Ar}$  in common laboratories, which restrains the exploration of their physicochemical properties and applications to a certain degree. Furthermore, given the known applications of  $\text{ArOCF}_2\text{CF}_2\text{Ar}$  motif as the core skeleton in insecticides<sup>[5a,8d]</sup> and lubricants,<sup>[8e]</sup> it is desirable to develop new synthetic methods for the synthesis of its analogous motif  $\text{ArSCF}_2\text{CF}_2\text{Ar}$ .

In alignment with our continuing efforts in controllable fluorocarbon chain elongation reactions using  $\text{TMSCF}_3$  or  $\text{TMSCF}_2\text{Br}$  (TMS = trimethylsilyl) as the fluorinated C1 synthon (difluorocarbene precursor),<sup>[3k–n,13]</sup> herein we report a new method for the formation of “ $\text{ArSCF}_2\text{CF}_2\text{Cu}$ ” species from  $\text{ArSCu}$ <sup>[22]</sup> and  $\text{TMSCF}_2\text{Br}$ . Unlike our previous work on the controllable  $\text{CF}_2$ -insertions into C–Cu bonds of fluoroalkyl- and fluoroarylcopper species,<sup>[3m,n,13a,b]</sup> this work represents a unique example of controllable  $\text{CF}_2$ -insertions into S–Cu bonds. Furthermore, the cross-coupling reactions between “ $\text{ArSCF}_2\text{CF}_2\text{Cu}$ ” and aryl/heteroaryl iodides proved to be a robust synthetic method for the preparation of  $\text{ArSCF}_2\text{CF}_2\text{Ar}$ .

We set out to explore the reaction by using  $\text{PhSCu}$ <sup>[22]</sup> as the substrate. Surprisingly, no desired product was observed when  $\text{CuCF}_3$  was used as the copper difluorocarbene source (for details, see Supporting Information), which was probably due to the mismatched transmetalation between stable  $\text{PhSCu}$  and highly reactive “ $\text{F-Cu=CF}_2$ ”.<sup>[3m,13a,14a]</sup> This result indicates the limitation of the conventional method originally reported by Burton and co-workers,<sup>[14]</sup> through which the fluorinated carbon chains are constructed using  $\text{CuCF}_3$  as the copper difluorocarbene source. Thus, another commonly-used difluorocarbene source (bromodifluoromethyl)trimethylsilane ( $\text{TMSCF}_2\text{Br}$ )<sup>[15,16]</sup> was chosen owing to its different reactivity compared with  $\text{CuCF}_3$  (Table 1).<sup>[13b]</sup> Gratifyingly, the desired product “ $\text{PhSCF}_2\text{CF}_2\text{Cu}$ ” (**1**) could be formed in 58 % yield (along with “ $\text{PhSCF}_2\text{CF}_2\text{CF}_2\text{Cu}$ ” (**2**) in 16 % yield) when mixing  $\text{CuCl}$ ,  $\text{PhSH}$ , 1,10-phenanthroline (phen),  $\text{NaH}$ , 18-crown-6 (18-c-6) and  $\text{TMSCF}_2\text{Br}$  in *N*-methylpyrrolidinone (NMP) (entry 1). It was noteworthy that  $(\text{PhS})_3\text{CH}$  was generated in the reaction mixture (detected by GC-MS), which strongly supported the involvement of difluorocarbene in the reaction. Encouraged by this result, the influence of different copper(I) salts was examined subsequently (entries 2–4). The counter anions of copper salts only exhibited slight influence on the yields of **1**

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**Scheme 1.** Synthetic methods for the construction of tetrafluoroethylene-bridged structures. TMS = trimethylsilyl.

**Table 1:** Survey of reaction conditions of controllable CF<sub>2</sub>-insertions into PhS-Cu bond.<sup>[a]</sup>

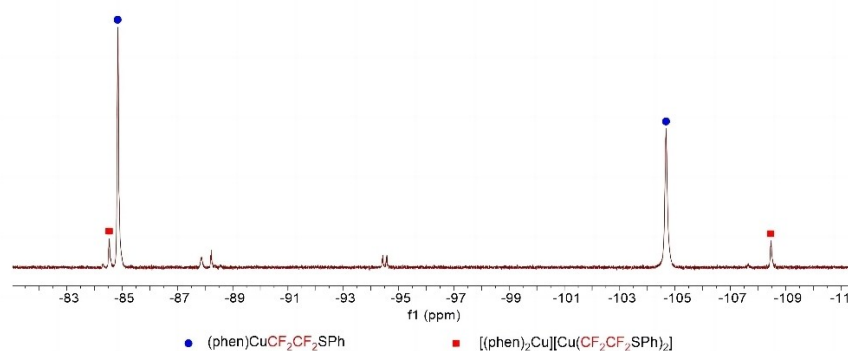
Entry	CuX	Solvent	TMSCF <sub>2</sub> Br (mmol)	"PhS(CF <sub>2</sub> ) <sub>2</sub> Cu" + "PhS(CF <sub>2</sub> ) <sub>3</sub> Cu"	
				1 (%)	2 (%)
1	CuCl	NMP	0.40	58	16
2	CuBr	NMP	0.40	57	12
3	CuI	NMP	0.40	58	12
4	CuOAc	NMP	0.40	57	14
5	CuBr	THF	0.40	35	9
6	CuBr	DMF	0.40	53	13
7 <sup>[b]</sup>	CuBr	NMP	0.40	64	9
8 <sup>[b]</sup>	CuBr	NMP	0.36	63	6
9 <sup>[c]</sup>	CuBr	NMP	0.36	65	5
10 <sup>[c,d]</sup>	CuBr	NMP	0.36	36	1
11 <sup>[c,e]</sup>	CuBr	NMP	0.36	55	5
12 <sup>[c,f]</sup>	CuBr	NMP	0.36	40	6
13 <sup>[c,g]</sup>	CuBr	NMP	0.36	53	7
14 <sup>[c,h]</sup>	CuBr	NMP	0.36	39	4

[a] Conditions: PhSH (0.60 mmol), CuX/phen (0.20 mmol), 18-c-6 (0.60 mmol), NaH (0.60 mmol), solvent (2.0 mL). The yields of **1** and **2** were calculated using  $n(\text{TMSCF}_2\text{Br})/2$  and  $n(\text{TMSCF}_2\text{Br})/3$ , respectively, as theoretical yields. Yields were determined by <sup>19</sup>F NMR with PhCF<sub>3</sub> as the internal standard. In all cases, the molar ratio CuX/phen = 1:1. [b] CuBr/phen (0.24 mmol) were used. [c] CuBr/phen (0.26 mmol) were used. [d] TMEDA was used instead of phen. [e] BINAP was used instead of phen. [f] LiH was used instead of NaH. [g] No phen was used. [h] No 18-c-6 was used. Phen = 1,10-phenanthroline; 18-c-6 = 18-crown-6; NMP = *N*-methylpyrrolidinone; THF = tetrahydrofuran; DMF = *N,N*-dimethylformamide.

and **2** when NMP was used as the solvent. Eventually, CuBr was selected as the copper source (entry 2). As for the solvent, tetrahydrofuran (THF) was a poor solvent for this reaction (entry 5), while *N,N*-dimethylformamide (DMF) proved to be a good solvent (entry 6), which was consistent with the previous reports.<sup>[3m,n,13a,b]</sup> Taking the yields of **1** and

**2** into account, we selected NMP as the solvent in the following study. The yields of **1** increased (with the formation of **2** being diminished) when adding more CuBr to the reaction (entries 2 and 7). Evidently, reducing the amount of TMSCF<sub>2</sub>Br to 0.36 mmol resulted in a lower yield of **2** (entry 8). Therefore, it could be concluded that the loadings of both CuBr and TMSCF<sub>2</sub>Br are crucial to the reaction.

Careful screening of the equivalences of CuBr and TMSCF<sub>2</sub>Br (for details, see Supporting Information) resulted in 65 % yield of **1**, along with 5 % yield of **2** (Table 1, entry 9). Next, the influence of ligands was examined. Both TMEDA (tetramethylethylenediamine) and BINAP [(2*R*,3*S*)-2,2'-bis(diphenylphosphono)-1,1'-binaphthyl] led to the lower yields of **1**, implying the advantage of phen as ligand (entries 10–11). The use of base LiH (instead of NaH) resulted in the yield decrease of **1**, indicating the counter ion effect of Li<sup>+</sup> (entry 12). It was found that the removal of either 18-c-6 or phen from the reaction mixture was also detrimental to the reaction (entries 13 and 14). We envisioned that the reaction intermediate might be stabilized by phen (entry 13), and the solubility of the in situ generated PhSM (M=Cu or Na) could be increased notably with the assistance of 18-c-6 (entry 14). Having optimized the reaction conditions of the controllable CF<sub>2</sub>-insertions into PhSCu, the product "PhSCF<sub>2</sub>CF<sub>2</sub>Cu" could be obtained successfully and its <sup>19</sup>F NMR spectrum was shown in Scheme 2 (for details, see Supporting Information). It is obvious that "PhSCF<sub>2</sub>CF<sub>2</sub>Cu" exists in the solution with two forms, which is similar to its analogue "PhOCF<sub>2</sub>CF<sub>2</sub>Cu" reported by Ogoshi and co-workers.<sup>[12]</sup> Therefore, the structures of these two forms were assigned according to those of "PhOCF<sub>2</sub>CF<sub>2</sub>Cu".<sup>[12]</sup> To remove the excessive PhS<sup>-</sup> in the reaction mixture that is detrimental to the transformation of **1**, C<sub>6</sub>F<sub>6</sub> was added as the scavenger of PhS<sup>-</sup>



**Scheme 2.**  $^{19}\text{F}$  NMR spectrum of “PhSCF<sub>2</sub>CF<sub>2</sub>Cu” species.

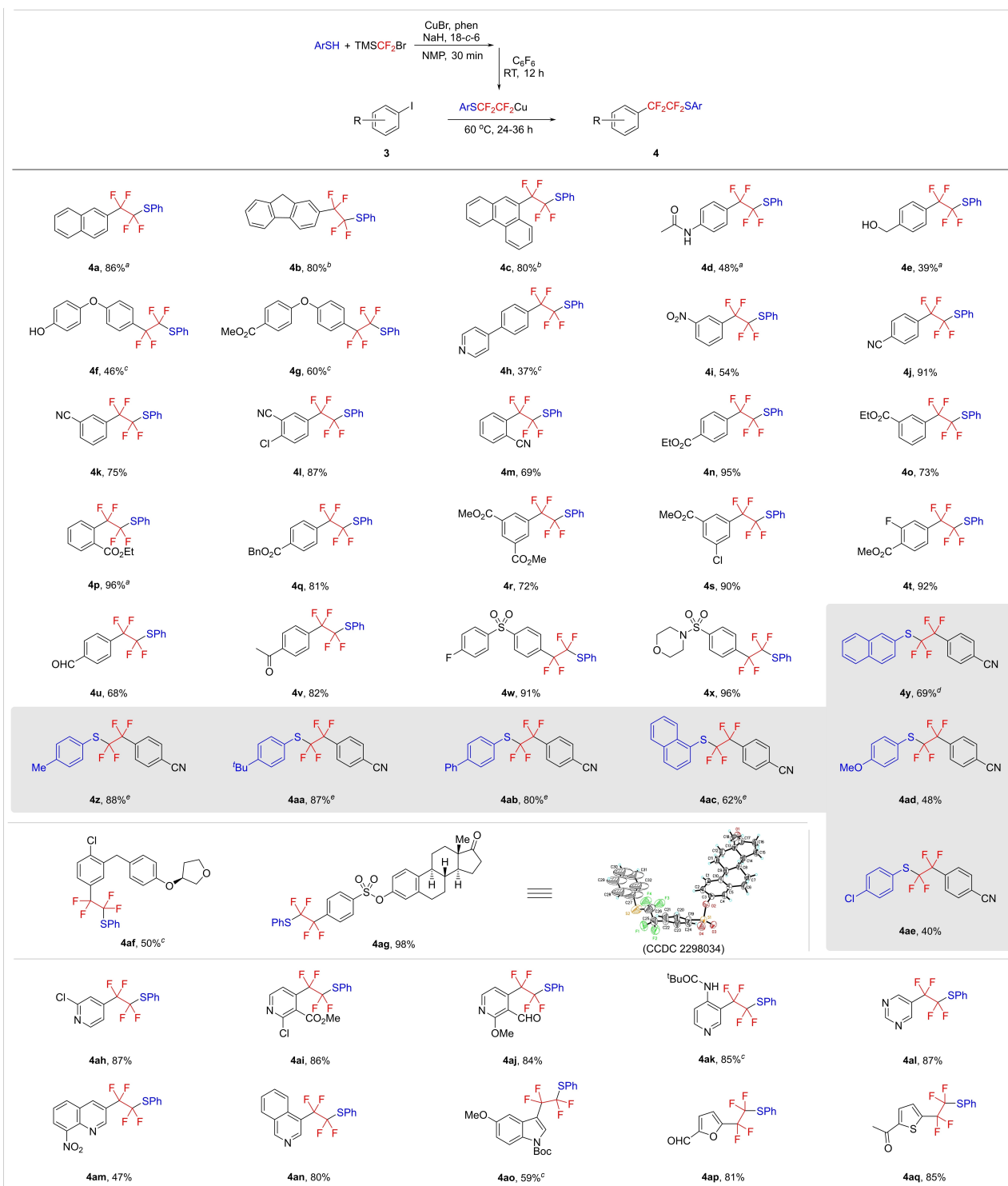
after the completion of the reaction (for details, see Supporting Information).

Having the optimized conditions for the preparation TMSCF<sub>2</sub>Br-derived “PhSCF<sub>2</sub>CF<sub>2</sub>Cu” in hand, we next examined its cross-coupling with the aryl iodides. The results are shown in Scheme 3. The reactions with various aryl iodides proceeded smoothly to give desired products in moderate to excellent yields with high selectivity of double/triple difluoromethylene insertions (up to 40:1). Functional groups such as cyano (**4j–4m**, **4y–4ae**), acetyl (**4g**, **4n–4t**, **4ai** and **4ao**), halogens (**4l**, **4s**, **4t**, **4w**, **4ae**, **4af**, **4ah** and **4ai**), acyl (**4u**, **4v**, **4ag**, **4aj**, **4ap** and **4aq**) and sulfonamide (**4x**) were all compatible with the standard reaction conditions. It is noteworthy that the mild reaction conditions rendered the good tolerance of substrates with commonly reactive functional groups, such as hydroxyl (**4e**, **4f**) and amino groups (**4d** and **4ak**). The electronic effect was obviously observed in this reaction. For the electron-poor aryl iodides, they could be consumed in the reaction within 24 h and the desired products were delivered in excellent yields. In contrast, the reactions with electron-rich aryl iodides required higher loading of **1** and prolonged reaction time to deliver moderate yields of desired products (**4f–4h**). Moreover, it is noteworthy that the yields of the cross-coupling reactions between electron-rich aryl iodides and “PhSCF<sub>2</sub>CF<sub>2</sub>Cu” could be improved significantly with the extra addition of CuBr (**4a–4e**). To our surprise, the reactions with nitro-substituted aryl iodides provided products **4i** and **4am** only in low yields. In addition, the steric effect seemed to have only a small influence on the chemical outcome of the reaction (**4n–4p**). Even the *ortho*-substituted aryl iodides (**4m** and **4p**) could serve as good substrates in this cross-coupling reaction. Importantly, this controllable double difluoromethylene insertions reaction still proceeded well when changing the parent thiophenol to other substituted thiophenols, thus affording the corresponding cross-coupling products in moderate to excellent yields, respectively (**4y–4ae**). Moreover, this synthetic protocol was effective for the late-stage (aryltio)tetrafluoroethylation of relatively complex molecule or pharmaceutical intermediate, affording the corresponding products in good yields (**4af** and **4ag**). It is noteworthy that the structure of **4ag** was confirmed by single-crystal X-ray diffraction.<sup>[17]</sup> To further

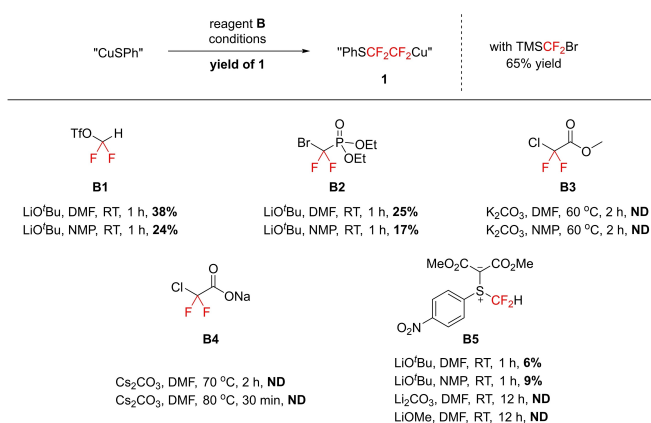
demonstrate the generality of this method, the heteroaryl iodides were also examined. To our delight, the desired products could be obtained in moderate to excellent yields, and the different functional groups substituted on the pyridine ring had little effect on the coupling reaction (**4ah–4ak**). Various *N*-containing heterocycles, including pyrimidine (**4al**), quinoline (**4am**), *iso*-quinoline (**4an**) and indole (**4ao**), all showed good compatibility with this copper-mediated (aryltio)tetrafluoroethylation reaction. The *O*- and *S*-containing heterocycles were also amenable to this reaction (**4ap** and **4aq**).

Having achieved the cross-coupling reactions between **1** and aryl/heteroaryl iodides successfully, next we examined the scaled synthesis and other synthetic applications of this method (for details, see Supporting Information). The reaction with **3ag** was scaled to 1.0 mmol, and the desired product **4ag** was obtained in 95 % yield (only with a slight decrease of the yield; see Scheme S1a). Furthermore, the halogenation of “PhSCF<sub>2</sub>CF<sub>2</sub>Cu” was also carried out. As expected, the reaction between NBS and “PhSCF<sub>2</sub>CF<sub>2</sub>Cu” proceeded smoothly to afford the desired brominated product PhSCF<sub>2</sub>CF<sub>2</sub>Br (**5**) in 90 % yield (Scheme S1b). It should be noted that BrCF<sub>2</sub>CF<sub>2</sub>Br, an ozone-depleting substance, always participated in the synthesis of products **5** and its analogues.<sup>[9,11,18]</sup> Therefore, this method could serve as an environmentally more friendly alternative method for the synthesis of **5** and its analogues. In addition, when subjected to the oxidation conditions using NaIO<sub>4</sub>/RuCl<sub>3</sub>,<sup>[19]</sup> **4j** could be easily converted into sulfone **6**, a useful reagent commonly used in organic transformations,<sup>[20]</sup> in 91 % yield (Scheme S1c).

To gain more insights into this selective double difluoromethylene insertions into ArS–Cu bonds, we set out to investigate the reaction mechanism. First of all, the difluoromethylene insertion reactions using other difluorocarbene reagents **B1–B5** were screened (Scheme 4). Under the previously reported standard reaction conditions for their activation to release difluorocarbene,<sup>[21]</sup> the desired product **1** could be detected only in low yields with other difluorocarbene precursors. However, on the other hand, it is noteworthy that the generation of **1** (although in low yields; see Scheme 4) strongly suggests the involvement of difluorocarbene species in this double difluoromethylene



**Scheme 3.** Copper-mediated (aryltio)tetrafluoroethylation of aryl/heteroaryl iodides with ArSH and TMSCF<sub>2</sub>Br. Reaction conditions: **3** (0.20 mmol, 1.0 equiv.), CuBr (1.04 mmol, 5.2 equiv.), TMSCF<sub>2</sub>Br (1.44 mmol, 7.2 equiv.), ArSH (2.40 mmol, 12.0 equiv.), phen (1.04 mmol, 5.2 equiv.), 18-c-6 (2.40 mmol, 12.0 equiv.), NaH (2.40 mmol, 12.0 equiv.), C<sub>6</sub>F<sub>6</sub> (2.40 mmol, 12.0 equiv.), NMP (8.0 mL). Isolated yields were given. [a] **3** (0.20 mmol), CuBr (1.56 mmol), TMSCF<sub>2</sub>Br (2.16 mmol), PhSH (3.60 mmol), phen (1.56 mmol), 18-c-6 (3.60 mmol), NaH (3.60 mmol), C<sub>6</sub>F<sub>6</sub> (3.60 mmol), NMP (12.0 mL) were used. CuBr (1.04 mmol) was added with **3**. [b] **3** (0.20 mmol), CuBr (1.56 mmol), TMSCF<sub>2</sub>Br (2.16 mmol), PhSH (3.60 mmol), phen (1.56 mmol), 18-c-6 (3.60 mmol), NaH (3.60 mmol), C<sub>6</sub>F<sub>6</sub> (3.60 mmol), NMP (12.0 mL) were used. CuBr (3.12 mmol) was added with **3**. [c] **3** (0.20 mmol), CuBr (1.56 mmol), TMSCF<sub>2</sub>Br (2.16 mmol), PhSH (3.60 mmol), phen (1.56 mmol), 18-c-6 (3.60 mmol), NaH (3.60 mmol), C<sub>6</sub>F<sub>6</sub> (3.60 mmol), NMP (12.0 mL) were used. [d] **3** (0.20 mmol), CuBr (1.04 mmol), TMSCF<sub>2</sub>Br (1.20 mmol), 2-naphthalenethiol (2.40 mmol), phen (1.04 mmol), 18-c-6 (2.40 mmol), NaH (2.40 mmol), C<sub>6</sub>F<sub>6</sub> (2.40 mmol), NMP (8.0 mL) were used. [e] **3** (0.20 mmol), CuBr (1.04 mmol), TMSCF<sub>2</sub>Br (1.32 mmol), ArSH (2.40 mmol), phen (1.04 mmol), 18-c-6 (2.40 mmol), NaH (2.40 mmol), C<sub>6</sub>F<sub>6</sub> (2.40 mmol), NMP (8.0 mL) were used. TMSCF<sub>2</sub>Br = (bromodifluoromethyl)trimethylsilane, 18-c-6 = 18-crown-6, phen = 1,10-phenanthroline, NMP = 1-methyl-2-pyrrolidinone.



**Scheme 4.** The reactions between other difluorocarbene reagents and PhSCu.

insertions reaction. Therefore, two possible pathways of the generation of “PhSCF<sub>2</sub>CF<sub>2</sub>Cu” were proposed: 1) the insertion of CF<sub>2</sub>=CF<sub>2</sub> (generated in situ through the dimerization of difluorocarbene) into PhS–Cu bond, and 2) the stepwise CF<sub>2</sub>-insertions into PhS–Cu bond via copper difluorocarbene intermediates (Scheme 5a).

At first, we examined the possibility of the insertion of CF<sub>2</sub>=CF<sub>2</sub> into PhS–Cu bond. The CF<sub>2</sub>=CF<sub>2</sub> gas (prepared from  $\text{TMSCF}_3$ <sup>[3k]</sup>) was introduced into the reaction tube containing PhSCu (prepared using standard reaction procedure), and the reaction mixture was stirred at room temperature for 3 h (Scheme 5b). We found that the “PhSCF<sub>2</sub>CF<sub>2</sub>Cu” species was not observed in the reaction mixture, but PhSCF<sub>2</sub>CF<sub>2</sub>H was formed in 45% yield (Scheme 5b). Next, we determined the stability of **1**. The different amounts of water were added into the solution of pre-prepared **1**. After stirring the mixture for 3 h at room temperature, the yields of **1** were detected by <sup>19</sup>F NMR (for details, see Supporting Informations). “PhSCF<sub>2</sub>CF<sub>2</sub>Cu” remained in high yield and only a slight decomposition was

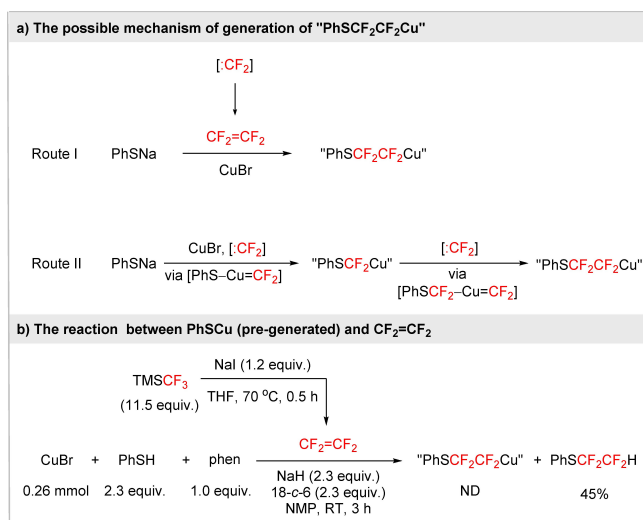
observed. Thus, PhSCF<sub>2</sub>CF<sub>2</sub>H in the reaction mixture should mainly come from the protonation of PhSCF<sub>2</sub>CF<sub>2</sub><sup>−</sup>, which was generated from the direct nucleophilic addition to CF<sub>2</sub>=CF<sub>2</sub> by thiophenoxide anion (PhS<sup>−</sup>), rather than the protonation of **1**. Therefore, it could also be concluded that PhSCF<sub>2</sub>CF<sub>2</sub><sup>−</sup> was difficult to be captured by cuprous salt to generate PhSCF<sub>2</sub>CF<sub>2</sub>Cu (**1**). Our results indicate that the generation of “PhSCF<sub>2</sub>CF<sub>2</sub>Cu” from the addition of thiophenoxide anion (PhS<sup>−</sup>) to CF<sub>2</sub>=CF<sub>2</sub> in the presence of cuprous salt is in low efficiency, which is consistent with the previous report by Ogoshi and co-workers.<sup>[10]</sup> Therefore, the proposed first pathway (Scheme 5a, Route I) can be ruled out. Moreover, the single CF<sub>2</sub>-insertion product, “PhSCF<sub>2</sub>Cu”, was considered as the important intermediate. Unexpectedly, during our whole process of optimizations, “PhSCF<sub>2</sub>Cu” was not observed, and only PhSCF<sub>2</sub>H was detected as the by-product.

On the basis of these experimental results, the possible reaction pathway of the controllable double CF<sub>2</sub>-insertions into a ArS–Cu bond was proposed as follows: at first, ArSCu was prepared through the system of CuBr/ArSH/NaH/phen/18-c-6 in NMP along with the generation of ArSNa. After the addition of TMSCF<sub>2</sub>Br, “ArSCF<sub>2</sub>Cu” was generated from the CF<sub>2</sub>-insertion into ArS–Cu bond via a copper difluorocarbene intermediate (generated from TMSCF<sub>2</sub>Br).<sup>[3m,13a–b,14]</sup> Subsequently, as the experimental results suggested, the second CF<sub>2</sub>-insertion into “ArSCF<sub>2</sub>Cu” (via another copper difluorocarbene intermediate) occurred rapidly to provide “ArSCF<sub>2</sub>CF<sub>2</sub>Cu” (Scheme 5a, Route II).

In conclusion, we have developed a general synthetic protocol to construct “ArSCF<sub>2</sub>CF<sub>2</sub>Cu” species using TMSCF<sub>2</sub>Br as the C1 synthon in both high yield and high selectivity. The cross-coupling reaction between “ArSCF<sub>2</sub>CF<sub>2</sub>Cu” and aryl/heteroaryl iodides provided the desired products in moderate to excellent yields. Diverse synthetic applications of “ArSCF<sub>2</sub>CF<sub>2</sub>Cu” species were also presented, such as halogenation (to give ArSCF<sub>2</sub>CF<sub>2</sub>Br) and oxidation (to give sulfones). Moreover, the mechanistic investigation indicated that “ArSCF<sub>2</sub>CF<sub>2</sub>Cu” was generated by the stepwise CF<sub>2</sub>-insertions into ArS–Cu bond rather than the addition of ArSCu into CF<sub>2</sub>=CF<sub>2</sub>. These results showcase the synthetic power of our controllable fluorocarbon chain elongation (CFCE) strategy<sup>[13e]</sup> with TMSCF<sub>2</sub>Br reagent to construct valuable fluorinated motifs, and further studies in this direction are underway in our laboratory.

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**Scheme 5.** Proposed reaction mechanism. ND = not detected.

## 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:** Difluorocarbene · copper carbene · C–S bond · homologation · (aryltio)tetrafluoroethylation · fluoroalkylcopper

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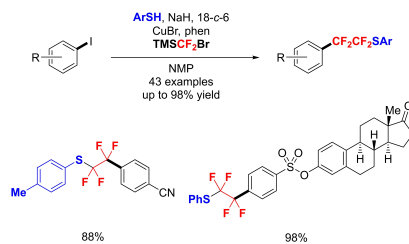
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## Communications

## Fluorine Chemistry

S. Pan, Q. Xie, X. Wang, R. Huang, Y. Lu,  
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Controllable Double Difluoromethylene  
Insertions into S–Cu Bonds:  
(Arylthio)tetrafluoroethylation of Aryl I-  
dides with  $\text{TMSCF}_2\text{Br}$



Controllable double difluoromethylene insertions into S–Cu bonds have been developed with  $\text{TMSCF}_2\text{Br}$  reagent, which provides a general synthetic protocol to construct  $\text{ArSCF}_2\text{CF}_2\text{Cu}$  intermediates as well as the  $\text{ArSCF}_2\text{CF}_2\text{Ar}'$  products.