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Copper-mediated aerobic (phenylsulfonyl)difluoromethylation of arylboronic acids with difluoromethyl phenyl sulfone†

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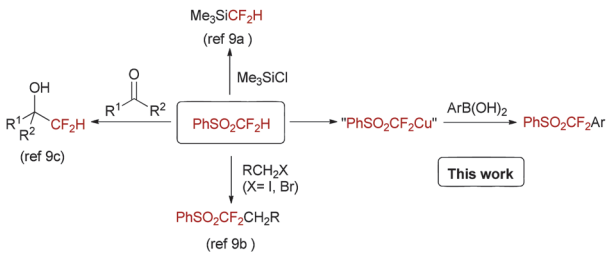
A new method for the generation of the "$PhSO_2CF_2Cu$" species from readily available difluoromethyl phenyl sulfone ($PhSO_2CF_2H$) has been developed. The "$PhSO_2CF_2Cu$" reagent can be applied in (phenylsulfonyl)difluoromethylation of arylboronic acids, which affords a convenient approach to introducing the $PhSO_2CF_2$ group into aromatics.

Fluorinated organic compounds have attracted extensive attention in recent years due to their widespread applications in pharmaceuticals, agrochemicals, and functional materials.[1,2] Among them, aromatic compounds containing the difluoromethylene (CF_2) group are of high importance, since the CF_2 moiety is known to be isosteric to the oxygen atom.[3] Hence, it is of great interest to develop new methods for the selective introduction of CF_2 group(s) onto aromatic rings. In this context, the transition-metal-assisted cross-coupling reactions represent one of the most straightforward strategies for the incorporation of CF_2 into arenes,[4–6] among which, copper-mediated difluoroalkylation has significant advantages due to its high efficiency and the relatively low cost of copper.[7]

Selective (phenylsulfonyl)difluoromethylation reactions have been systematically studied in recent years,[8] since the $PhSO_2CF_2$ group can be readily transformed into difluoromethyl (CF_2H),[9] difluoromethylene ($-CF_2-$),[10] and difluoromethylidene ($=CF_2$)[11] functionalities. Difluoromethyl phenyl sulfone ($PhSO_2CF_2H$),[9,12] a useful nucleophilic (phenylsulfonyl)difluoromethylation agent, has been investigated extensively, partially owing to its simple preparative procedure (Scheme 1). However, the introduction of (phenylsulfonyl)difluoromethyl group into sp^2 carbons *via* a transition-metal-assisted protocol is rare.[13] To the best of our knowledge, there is no report on the transition-metal-mediated (phenylsulfonyl)difluoromethylation with $PhSO_2CF_2H$.



Scheme 1 Application of difluoromethyl phenyl sulfone.

Recently, a new method has been developed for the formation of "$CuCF_3$"[14a] and "CuC_2F_5".[14b] We envisioned that the "$PhSO_2CF_2Cu$" species could be generated from $PhSO_2CF_2H$. Previously, we reported the "$PhSO_2CF_2Cu$" species generated from $PhSO_2CF_2SiMe_3$, and its (phenylsulfonyl)difluoromethylation of alkynyl halides.[15] However, due to the lower stability of "$PhSO_2CF_2Cu$" than "$CuCF_3$", the cross-coupling reaction of aryl iodides with "$PhSO_2CF_2Cu$" failed, because the oxidative addition process usually requires high temperature and/or long reaction time. Thus, we envisioned that the synthesis of (phenylsulfonyl)difluoromethylated arenes can be achieved *via* the copper-mediated oxidative cross-coupling reaction of arylboronic acids with $PhSO_2CF_2H$ under mild conditions. Although copper-mediated oxidative trifluoromethylation of arylboronic acids *via* "$CuCF_3$" intermediate has been well documented,[16] the oxidative *gem*-difluoromethylenation of arylboronic acids has received less attention,[17] probably because of the low stability of the "RCF_2Cu" intermediate. Herein, we wish to disclose an efficient method for preparation of the "$PhSO_2CF_2Cu$" species generated from $PhSO_2CF_2H$, and its application in (phenylsulfonyl)difluoromethylation of arylboronic acids.

It is well known that the hydrogen atom of the CF_2H group in $PhSO_2CF_2H$ (**1**) is rather acidic, and a common base such as sodium methoxide or even aqueous sodium hydroxide can deprotonate it in an equilibrium mode to generate $PhSO_2CF_2^-$.[9b,10,12] At the onset of our investigation, sodium methoxide was employed as the base. Into the mixture of CuCl (0.2 mmol) and MeONa (2 equiv.)

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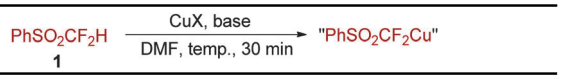
Table 1 Screening of formation of "$PhSO_2CF_2Cu$"[a]



Entry	CuX	Base (equiv.)	Temp. (°C)	Yield[b] (%)
1	CuCl	MeONa (2.0)	rt	34
2	CuCl	MeONa (2.0)	0	45
3	CuCl	^{t}BuONa (2.0)	0	56
4	CuCl	^{t}BuONa (2.0)	−20	64
5	CuCl	^{t}BuOK (2.0)	−20	62
6	CuCl	^{t}BuONa (1.2)	−20	56
7	CuCl	^{t}BuONa (2.4)	−20	36
8	CuI	^{t}BuONa (2.0)	−20	63
9	CuSCN	^{t}BuONa (2.0)	−20	57
10[c]	CuCl	^{t}BuONa (2.0)	−20	62
11[d]	CuCl	^{t}BuONa (2.0)	−20	74
12[e]	CuCl	^{t}BuONa (2.0)	−20	88
13[f]	**CuCl**	**^{t}BuONa (2.0)**	**−20**	**96**
14[g]	CuCl	^{t}BuONa (2.0)	−20	94

[a] Reaction conditions: **1** (0.2 mmol), CuX (0.2 mmol), DMF (1 mL). [b] Yields were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. [c] NMP was used as the solvent. [d] **1** (0.24 mmol) was used. [e] **1** (0.28 mmol) was used. "$[(PhSO_2CF_2)_2Cu]^-$" (11%, ^{19}F NMR) was produced. [f] **1** (0.32 mmol) was used. "$[(PhSO_2CF_2)_2Cu]^-$" (29%, ^{19}F NMR) was produced. [g] Reaction conditions: **1** (0.8 mmol), CuCl (0.5 mmol), DMF (2 mL).

in DMF at room temperature, reagent **1** was added dropwise at the same temperature for 30 min under an argon atmosphere. To our delight, "$PhSO_2CF_2Cu$" (δ = −92.0 ppm) was formed in 34% yield as determined by ^{19}F NMR spectroscopy (Table 1, entry 1). The low yield of "$PhSO_2CF_2Cu$" generated from **1** was probably due to two reasons: first of all, the use of 2MeONa–CuCl did give small quantities of "$PhSO_2CF_2Cu$" under the conditions. Second, the "$PhSO_2CF_2Cu$" species possesses low thermal stability at this temperature.[15] As was expected, when the reaction was carried out at 0 °C (Table 1, entry 2), the yield of "$PhSO_2CF_2Cu$" was increased to 45%. Therefore, it seems that an appropriate base is critical for the generation of "$PhSO_2CF_2Cu$". The results obtained under various reaction conditions are listed in Table 1. With the consideration in mind, we attempted the reaction using other bases such as ^{t}BuONa at a lower temperature (−20 °C); as a result, the yield of "$PhSO_2CF_2Cu$" was increased to 64% (Table 1, entry 4). However, when ^{t}BuOK was used, it was found that some side reactions occurred, even though this copper species was formed in a moderate yield (Table 1, entry 5). In addition, the reaction had to be carried out by using 2 equiv. of ^{t}BuONa, which was necessary to obtain "$PhSO_2CF_2Cu$" in good yields. As stated in our previous report,[18] the "$CuCF_3$" species can be generated from $PhSO_2CF_3$ or $PhSOCF_3$ *via* treatment of CuCl and 2 equiv. of ^{t}BuOK. It is noteworthy that no formation of "$CuCF_2H$" was detected when $PhSO_2CF_2H$ or $PhSOCF_2H$ was employed under the same conditions. These results also proved that cleavage of the CF_2–H bond is much easier than the S–CF_2H bond in $PhSO_2CF_2H$. Furthermore, the use of CuI or CuSCN failed to improve the yield of "$PhSO_2CF_2Cu$" (Table 1, entries 8 and 9). For solvent screening, it was found that NMP was inferior to DMF (Table 1, entry 10).

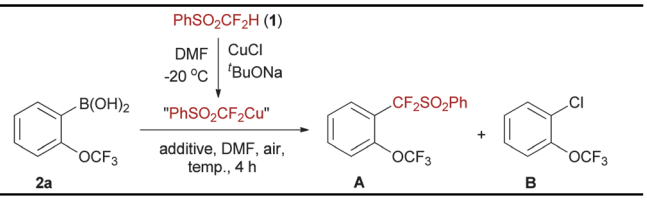
To improve the yield of "$PhSO_2CF_2Cu$", we increased the loading of **1** under the optimized conditions. When the amount of **1** was increased to 1.2 equiv., the yield was correspondingly enhanced to 74% (Table 1, entry 11). It is noteworthy that a slight excess of **1** results in a new species (−96.3 ppm in ^{19}F NMR spectroscopy), which is assigned as "$[(PhSO_2CF_2)_2Cu]^-$" on the basis of our experimental results and the literature data.[15] Consequently, when 1.6 equiv. of **1** was used, the total yield of the "$PhSO_2CF_2Cu$" species was increased to 97% (Table 1, entry 13), with 66% contribution from "$PhSO_2CF_2Cu$" (−92.1 ppm in ^{19}F NMR spectroscopy) and 29% from "$[(PhSO_2CF_2)_2Cu]^-$" (−96.3 ppm in ^{19}F NMR spectroscopy) (see ESI,† Section 2 for details). It is noted that "$[(PhSO_2CF_2)_2Cu]^-$" possesses lower thermal stability than "$PhSO_2CF_2Cu$", and the former species can be transformed into the latter species at room temperature (see ESI,† Section 3 for details).

Next, we examined the stability of "$PhSO_2CF_2Cu$" under various conditions. Unlike previously reported the "$CuCF_3$" species generated from phenyl trifluoromethyl sulfoxide,[18] the "$PhSO_2CF_2Cu$" species generated from $PhSO_2CF_2H$ was gradually decomposed at rt and decomposed completely after 4 h. Furthermore, the yield of "$PhSO_2CF_2Cu$" decreased from 80% to 46% at −12 °C after 24 h under an argon atmosphere. Interestingly, it was found that the addition of 18-crown-6 could stabilize the "$PhSO_2CF_2Cu$" species, which was decreased to 65% after 24 h at −12 °C and to 58% after 60 h under the same conditions (see ESI,† Section 4 for details). According to previous reports[19] and our experiment, we reasoned that the addition of 18-crown-6, with a strong affinity for metal cations (Na^+ in this case), would diminish the electrophilicity of Na^+, thereby decreasing the decomposition of "$PhSO_2CF_2Cu$".

With the efficient method for the generating of the "$PhSO_2CF_2Cu$" species from $PhSO_2CF_2H$ in hand (Table 1, entry 13), we further employed this copper species for the (phenylsulfonyl)difluoromethylation of various arylboronic acids (Table 2). Initially, we attempted the reaction of arylboronic acid (**2a**) with the "$PhSO_2CF_2Cu$" species generated from $PhSO_2CF_2H$ at 0 °C under an air atmosphere. However, only 16% yield of the (phenylsulfonyl)-difluoromethylated product was detected, and the aryl chloride (**B**) as a main byproduct was formed in the case of CuCl (Table 2, entry 1). When the reaction was carried out at rt, to our delight, the product was obtained in 67% yield after 4 h, but the byproduct **B** was still generated (Table 2, entry 2). Using a copper source without a halide counterion, such as CuOTf, did not generate the analogous byproduct, while the formation of "$PhSO_2CF_2Cu$" was inhibited. To overcome this hurdle, various additives were further screened, which enable the improvement of the desired product yield and/or reduce the generation of byproduct **B**. The addition of 1,10-phenanthroline, as a ligand for coordination of Cu to stabilize "$PhSO_2CF_2Cu$", failed to give the product (Table 2, entry 3). As previously reported,[16a,c] K_3PO_4 can improve the desired product yield, but does not fit our reaction system. Fortunately, when a portion of $AgNO_3$ was added to the reaction mixture, the product yield was increased to 72% (Table 2, entry 5).

Silver nitrate ($AgNO_3$) was used to trap the chloride ions, thus diminishing the generation of aryl chloride **B** (Table 2, entries 2, 5 and 6). Furthermore, a spot of $Cu(OAc)_2{\cdot}H_2O$ was found to be favorable for the generation of the (phenylsulfonyl)difluoromethylated product (Table 2, entry 7). Consequently, a mixture

Table 2 Optimization of reaction conditions[a]



Entry	Additive (equiv.)	Temp.	Yield[b] of **A** (**B**) (%)
1	—	0 °C	16 (28)
2	—	rt	67 (18)
3	1,10-Phen (1.0)	rt	0 (0)
4	K_3PO_4 (1.0)	rt	68 (18)
5	$AgNO_3$ (0.5)	rt	72 (15)
6	$AgNO_3$ (1.0)	rt	73 (10)
7	$AgNO_3$ (0.5) + $Cu(OAc)_2{\cdot}H_2O$ (0.2)	rt	75 (7)
8[c]	$AgNO_3$ (0.6) + $Cu(OAc)_2{\cdot}H_2O$ (0.3)	rt	80 (7)
9[d]	$AgNO_3$ (0.6) + $Cu(OAc)_2{\cdot}H_2O$ (0.3)	rt	0 (—)

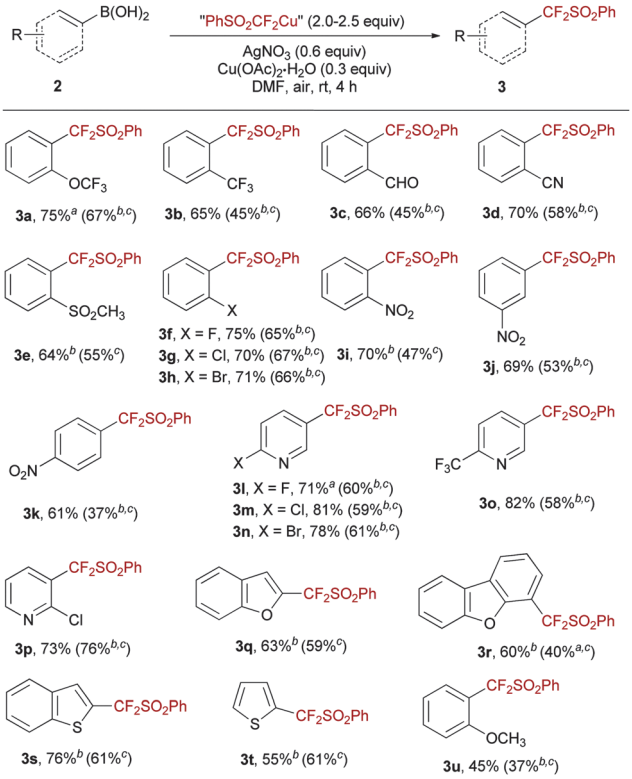
[a] Reaction conditions: **2a** (0.2 mmol), "$PhSO_2CF_2Cu$" (2.0–2.5 equiv.), DMF (2 mL). [b] Yields were determined by ^{19}F NMR using $PhCF_3$ as an internal standard. [c] The reaction was conducted with 0.4 mmol of **2a** for 6 h. [d] The reaction was conducted under argon atmosphere.

of $AgNO_3$ (0.6 equiv.) and $Cu(OAc)_2{\cdot}H_2O$ (0.3 equiv.) was selected as the optimum additive for the (phenylsulfonyl)difluoromethylation of arylboronic acid **2a** with "$PhSO_2CF_2Cu$" generated from $PhSO_2CF_2H$.

Having identified the optimum reaction conditions, we further explored the scope and the limitations of the (phenylsulfonyl)difluoromethylation of arylboronic acids with "$PhSO_2CF_2Cu$" generated from $PhSO_2CF_2H$ (Scheme 2). The (phenylsulfonyl)difluoromethylation can tolerate various substituents at the *ortho*-position such as trifluoromethoxy, trifluoromethyl, formyl, nitrile, sulfonyl, halides (–F, –Cl, –Br), nitro, and methoxyl, affording the desired products in moderate to good yields (Scheme 2, **3a–3i**, **3u**). The reaction afforded slightly low yields with *meta*- and *para*-substituted arylboronic acids (Scheme 2, **3j–3k**). Generally, the electron-deficient substrates provide superior yields to electron-rich substrates. In addition, this transformation was also applicable to various *N*-, *O*-, and *S*-containing heterocyclic arylboronic acids, and the (phenylsulfonyl)difluoromethylated heteroarenes were obtained in good yields (Scheme 2, **3l–3t**). It is worth noting that some products can be obtained in good yields without the aid of additives (Scheme 2, **3e**, **3i**, **3q–3t**).

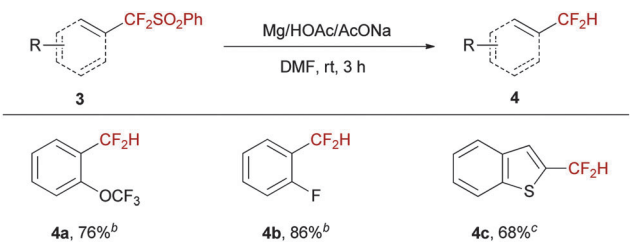
Regarding the reaction mechanism, we envisioned that the present copper-mediated (phenylsulfonyl)difluoromethylation reaction proceeds through a similar reaction mechanism to the previously reported $CuCF_3$-mediated coupling reaction with arylboronic acids.[16a,b,f] The pregenerated "$PhSO_2CF_2Cu(I)$" species is firstly oxidized to Cu(III) species, followed by transmetallation with an arylboronic acid. The formed "$PhSO_2CF_2Cu(III)Ar$" species undergoes reductive elimination to give the coupling product **3**.[16f] Based on our experimental data, it can be concluded that oxygen (O_2) is a crucial oxidant in our coupling reaction (Table 2, entries 2 and 9). The presence of $AgNO_3$ and $Cu(OAc)_2{\cdot}H_2O$ is also beneficial to the O_2-involved oxidative coupling process.

To demonstrate the synthetic applications of the (phenylsulfonyl)difluoromethylated heteroarenes (**3**), reductive desulfonylation[20] of **3** with Mg^0/HOAc/NaOAc could give difluoromethyl arenes (**4**) in good yields. Some representative results are summarized in Scheme 3.



Scheme 2 The substrate scope of arylboronic acids. Reaction conditions: $ArB(OH)_2$ (0.2 mmol), "$PhSO_2CF_2Cu$" (2.0–2.5 equiv.), $AgNO_3$ (0.6 equiv.), $Cu(OAc)_2{\cdot}H_2O$ (0.3 equiv.), DMF (2 mL). Yields were of isolated products. [a] The reaction were conducted in 0.4 mmol of arylboronic acides in DMF (4 mL) for 6 h. [b] No addition of $AgNO_3$ and $Cu(OAc)_2{\cdot}H_2O$. [c] Yields were determined by ^{19}F NMR using $PhCF_3$ as an internal standard.

In summary, we have developed an efficient method for the generation of "$PhSO_2CF_2Cu$" with readily available difluoromethyl phenyl sulfone. The "$PhSO_2CF_2Cu$" species was applied in the reaction of (phenylsulfonyl)difluoromethylation of arylboronic acids under mild conditions. The reaction can tolerate formyl, nitrile, sulfonyl, halides, nitro, and various *N*-, *O*-, and *S*-containing heterocycles, affording (phenylsulfonyl)difluoromethylated products in moderate to good yields. Furthermore, the reductive desulfonylation



Scheme 3 Synthesis of difluoromethylated aromatics by reductive desulfonylation. Reaction conditions: **3** (0.2 mmol), Mg (3 mmol), HOAc/NaOAc (1 : 1) (1.5 mL), and DMF (2 mL). [b] Yields were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. [c] The yield was of isolated product.

of some (phenylsulfonyl)difluoromethylated products with Mg^0/HOAc/NaOAc gave difluoromethyl arenes in good yields. It is also worth noting that the active copper species is confirmed for the first time involving the oxidative *gem*-difluoromethylenation of arylboronic acids.

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