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Synthetic Methods

Triphenylphosphine-Mediated Deoxygenative Reduction of CF_3SO_2Na and Its Application for Trifluoromethylthiolation of Aryl Iodides

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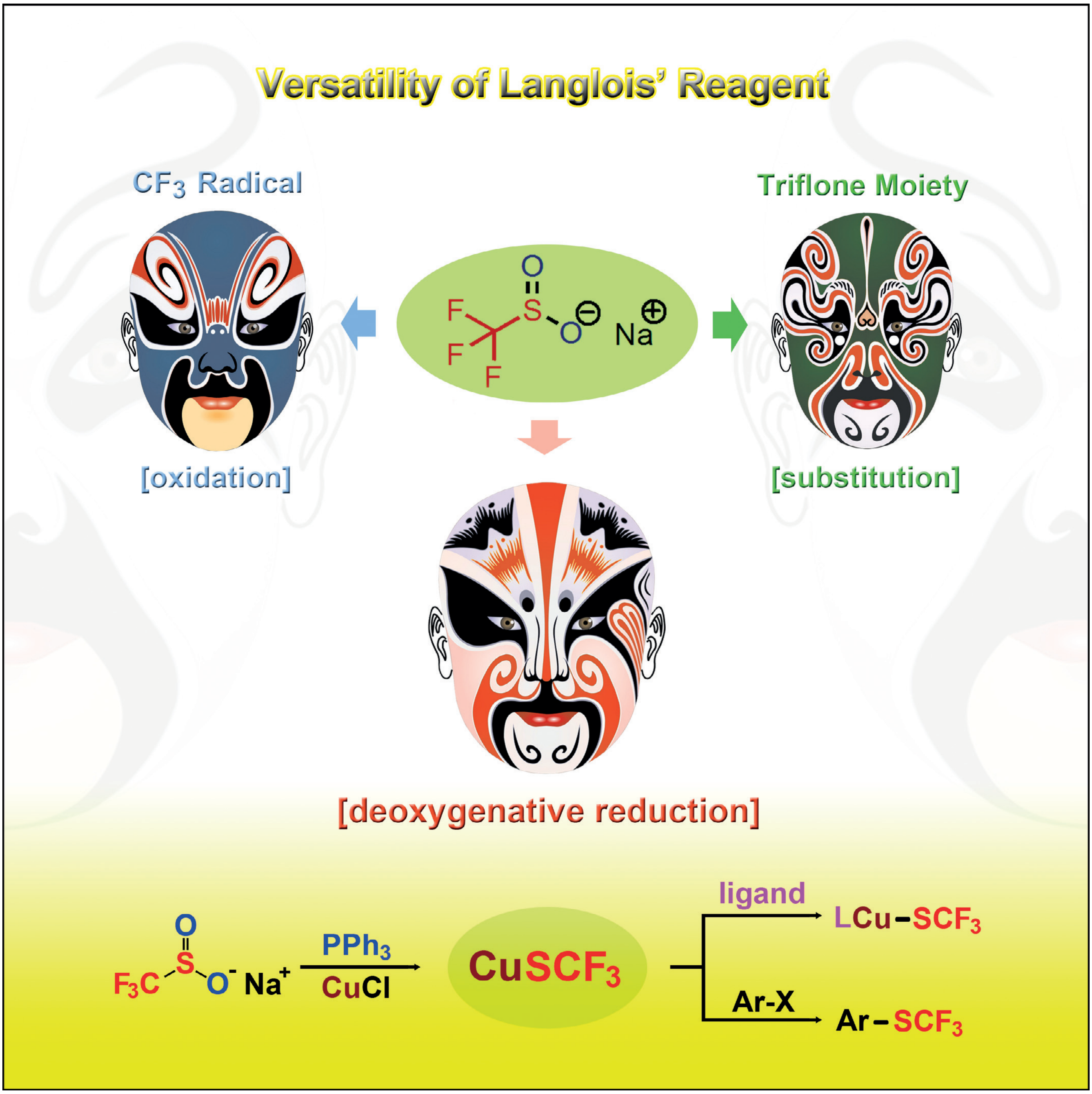


Abstract: We report herein a practical method for taming Langlois' reagent CF_3SO_2Na to generate $CuSCF_3$ by a triphenylphospine-mediated deoxygenative reduction process. This chemistry highlights a novel utilization of the inherent CF_3S skeleton of Langlois' reagent as a CF_3S feedstock under mild conditions. The $CuSCF_3$ intermediate generated by this protocol can react with a wide array of supporting ligands to furnish several air-stable $[LCu(SCF_3)]$ complexes as valuable trifluoromethylthiolating agents. In addition, the $CuSCF_3$ intermediate can be directly employed for the trifluoromethylthiolation of (hetero)aryl iodides with operational simplicity and atomic efficiency.

The incorporation of fluorine-containing groups into bioactive molecules has become a valuable tactic for modifying and discovering new drugs.[1] The highly lipophilic and electron-withdrawing SCF_3 moiety[2] is highly prized within the family of fluorine-containing substituents in this field, exemplified by several commercial products, such as Toltrazuril and Tiflorex. Various approaches for the direct installment of a SCF_3 moiety have been reported and represent more attractive approaches to $RSCF_3$ products than traditionally indirect methods (halogen–fluorine exchange, trifluoromethylation of sulfur-containing precursors, and so forth).[3] Diverse electrophilic trifluoromethylthiolating reagents[4] have recently been developed that have greatly enriched the "SCF_3" toolbox (Figure 1). The Pd/Ni-catalyzed[5,6] or Cu-mediated[7] trifluoromethylthiolation of aryl halides with $MSCF_3$ nucleophiles ($AgSCF_3$, Me_4NSCF_3, $[(bpy)Cu^I(SCF_3)]$), as well as oxidative trifluoromethylthiolation[8] also provide elegant access to $RSCF_3$ molecules. Additionally, several impressive trifluoromethylthiolation reactions were established using the combination of external sulfur sources and trifluoromethylating reagents, such as $FSO_2CF_2CO_2Me$, $TMSCF_3$, and CF_3CO_2Na.[9] However, despite the great progress on all the aforementioned direct trifluoromethylthiolation methods, there are still serious practical limitations in the field. For instance, the use of precious metals, expensive ligands, and electrophilic/nucleophilic trifluoromethylthiolating reagents are all concerns for developing scale-up processes.

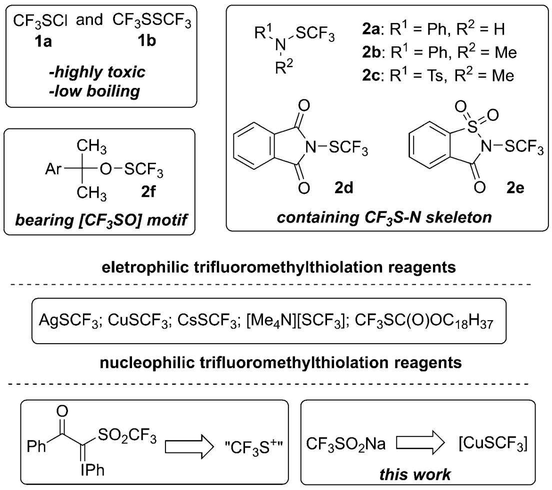
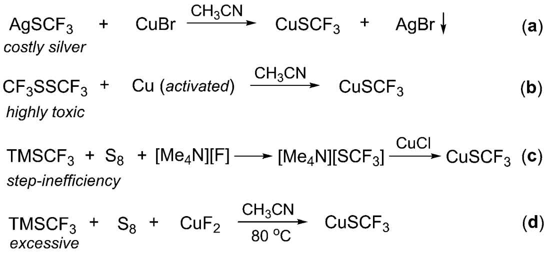
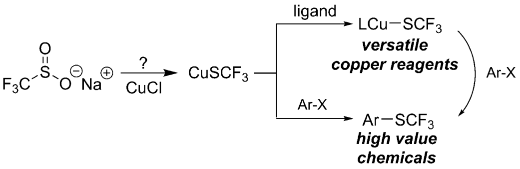


Figure 1. Toolbox of trifluoromethylthiolating reagents.

In this context, it is an ongoing quest to develop cheaper, milder, and more convenient methods for the synthesis of organic trifluoromethyl sulfides.[3] Copper–SCF_3 complexes,[7,10] in many regards, are attractive reagents for converting aryl halides into the corresponding aryl trifluoromethyl sulfides ($ArSCF_3$). However, the classic reported methods for preparations of $CuSCF_3$ still have several shortcomings that lie in steps inefficiency or use of expensive $AgSCF_3$ and toxic CF_3SSCF_3 as starting materials (Scheme 1a–c).[10] Recently, Weng et al. reported the generation of $CuSCF_3$ by utilizing CuF_2, elemental sulfur, and $TMSCF_3$ combination strategy (Scheme 1d).[7c] Nevertheless, this protocol still depends on excessive addition of $TMSCF_3$ and a redox event converting Cu^{II} to Cu^I. To address these drawbacks, we sought to develop a synthetic strategy that could generate $CuSCF_3$ from a commercially available and inexpensive reagent. The Langlois' reagent (CF_3SO_2Na) could conceivably generate SCF_3 without any additional sulfur sources (Scheme 2), although it is known to act as a trifluoromethyl radical source under oxidative conditions.[11] With the inspiration from Shibata's report on using trifluromethanesulfonyl hypervalent iodonium ylide (featuring an inherent CF_3SO_2 moiety



Scheme 1. Classic methods for the preparation of $CuSCF_3$.



Scheme 2. Reaction development considerations for the use of CF_3SO_2Na to generate $CuSCF_3$.

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and a neighboring ylide group) as an effective trifluoromethylthiolation reagent,[12] we were excited about the possibility to exploit the simpler reagent CF_3SO_2Na for the synthesis of $CuSCF_3$ under appropriate deoxygenative conditions in the absence of external sulfur sources.

Table 1. Comparison of deoxygenation reagents for CF_3SO_2Na.[a]

$$CF_3SO_2Na + \underset{\mathbf{3}}{PR_3} \xrightarrow[N_2,\ RT]{CH_3CN} CF_3SSCF_3 + O{=}PR_3$$

Entry	PR_3	Yield of CF_3SSCF_3[b]
1	Ph_3P (**3a**)	27 %
2	Ph_2PMe (**3b**)	22 %
3	$PhPMe_2$ (**3c**)	20 %
4	PMe_3 (**3d**)	13 %
5	PBu_3 (**3e**)	18 %
6	$P(NEt_2)_3$ (**3f**)	None[c]
7	Zinc powder	None[c]

[a] Yield was determined by ^{19}F NMR spectroscopy of the crude product mixture using $PhCF_3$ as internal standard; PR_3 (1.5 equiv). [b] The moderate yield could be caused by the volatile properties of CF_3SSCF_3. [c] No conversion of CF_3SO_2Na and no formation of CF_3SSCF_3.

Table 2. Optimization of synthesis of $CuSCF_3$ from CF_3SO_2Na.[a]

$$CF_3SO_2Na + \text{reductant} + \begin{matrix}\text{copper}\\ \text{source}\end{matrix} \xrightarrow[N_2,\ RT,\ 12\ h]{\text{solvent (1 mL)}} CuSCF_3$$

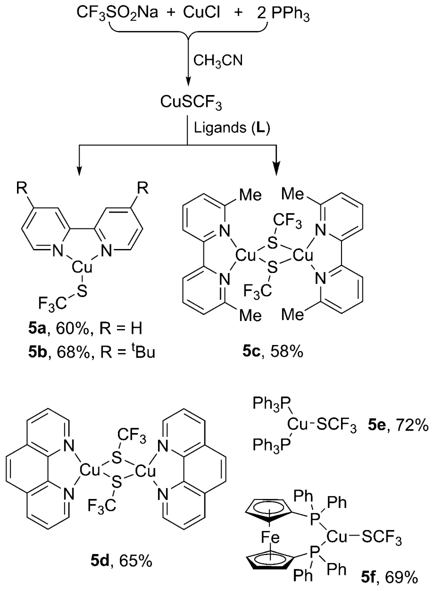
Entry	Reductant	Copper Source	Solvent	Yield[b]
1	Ph_3P (**3a**)	Cu powder[c]	CH_3CN	trace
2	Ph_3P (**3a**)	CuCl	CH_3CN	70 %
3	Ph_3P[d] (**3a**)	CuCl	CH_3CN	83 %
4	$MePPh_2$[d] (**3b**)	CuCl	CH_3CN	79 %
5	Me_2PPh[d] (**3c**)	CuCl	CH_3CN	75 %
6	Me_3P[d] (**3d**)	CuCl	CH_3CN	None[e]
7	Bu_3P[d] (**3e**)	CuCl	CH_3CN	None[e]
8	Ph_3P[d] (**3a**)	CuCl	DMF	None[e]
9	Ph_3P[d] (**3a**)	CuCl	DMI	None[e]

[a] General conditions: CF_3SO_2Na (0.2 mmol, 1.0 equiv) and copper source (0.2 mmol, 1.0 equiv) were dissolved in solvent (1.0 mL), then reductant (0.4 mmol, 2.0 equiv) was added and stirred under N_2/RT. [b] Yield was determined by ^{19}F NMR spectroscopy of the crude product mixture using $PhCF_3$ as internal standard. [c] Unactivated Cu powder was utilized. [d] Reductant was added in a pre-cooled $CuCl/CF_3SO_2Na/CH_3CN$ mixture (approximately −25 °C), and then returned to RT for stirring. This addition procedure works well on a multiple-gram scale synthesis of $CuSCF_3$. [e] No conversion of CF_3SO_2Na was detected, and the coordination complexes between phosphines and CuCl was observed.

Initial studies were focused on searching for reductants capable of abstracting the oxygen atoms from CF_3SO_2Na. We found that simple phosphine compounds (Table 1; **3a**–**e**) could convert CF_3SO_2Na to CF_3SSCF_3 with moderate success, whereas hexaethylphosphorous triamide ($P(NEt_2)_3$; **3f**) and metal-based reductants, like zinc powder, were inert, even at elevated temperatures (Table 1). The ability of phosphines to extrude oxygen atoms from CF_3SO_2Na is consistent with the strong thermodynamic impetus of P=O bond formation ($\approx 544\ kJ\,mol^{-1}$).[13] With the phosphine reducing agents identified, we investigated whether this deoxygenative process could be exploited for the construction of desired $CuSCF_3$ (Table 2). Initially, copper powder was used to trap the CF_3SSCF_3 generated in situ. However, only trace amount of $CuSCF_3$ was observed, even when stirred for several days at room temperature or heated at 50–60 °C, overnight (entry 1). Gratifyingly, $CuSCF_3$ was generated in 70 % yield according to ^{19}F NMR analysis (signal at −27.5 ppm) when the copper source was CuCl (entry 2). Addition of Ph_3P to a pre-cooled $CuCl/CF_3SO_2Na$ solution in CH_3CN, and then warming to room temperature minimized side reactions and improved the yield to 83 % (entry 3). Further solvent and reducing agent screening confirmed that $CuCl/CF_3SO_2Na/Ph_3P$ combination in a 1:1:2 equivalent ratio, respectively, in acetonitrile solvent represented the optimal conditions for the efficient production of $CuSCF_3$ in terms of low cost, air stability and yield (entries 3–9). Notably, the phosphines (**3a**–**c**) bearing a phenyl ring showed good reaction efficiency in the generation of $CuSCF_3$, whereas the more electron-rich Me_3P (**3d**) and Bu_3P (**3e**) displayed sluggish reactivities (entries 6–7), and formation of the corresponding inert $[ClCu(PMe_3)_x]$ and $[ClCu(PBu_3)_x]$ species indicated by ^{31}P NMR was observed. In contrast, preformed $[ClCu(PPh_3)_2]$ (**3**)[14] reacted smoothly with CF_3SO_2Na in acetonitrile, furnishing $CuSCF_3$ in 72 % yield [Eq. (1)]. The reason why the $[ClCu(PMe_3)_x]$ and $[ClCu(PBu_3)_x]$ species show poor reactivity towards CF_3SO_2Na is still not very clear. A possible explanation could be the stronger bonding of the electron-rich trialkylphosphines (**3d** or **3e**) to the copper(I) center that prevents the dissociation of trialkylphosphines for deoxygenative reduction.

$$CF_3SO_2Na \xrightarrow[\substack{CH_3CN\\ N_2,\ RT,\ 5\ h}]{[CuCl(PPh_3)_2]} \underset{72\ \%}{CuSCF_3} + 2\ Ph_3P{=}O + NaCl\downarrow \quad (1)$$

With the optimized reaction conditions for generating $CuSCF_3$ from CF_3SO_2Na established, we sought to use this chemistry to prepare a series of air-stable, ligated, and synthetically useful trifluoromethylthiolating agents $[LCu(SCF_3)]$ (Scheme 3). Initially, 2,2′-bipyridine was selected as the supporting ligand for the preparation of $[(bpy)Cu^{I}(SCF_3)]$ (**5a**), which is a versatile trifluoromethylthiolation agent for various R–X substrates.[7c–e] Gratifyingly, **5a** was afforded as red crystals in 60 % yield. Its structure was confirmed by NMR spectroscopy, elemental analysis, and single-crystal X-ray crystallography (see the Supporting Information). Next, several related derivatives $[(dtbpy)Cu^{I}(SCF_3)]$ (**5b**),[7c] $[\{(phen)Cu^{I}(SCF_3)\}_2]$ (**5d**),[7c] and $[(Ph_3P)_2Cu^{I}(SCF_3)]$ (**5e**)[7d] were also efficiently obtained by similar procedures. When 6,6-dimethylbipyridine was employed as the chelating ligand, the dimer **5c** was obtained in 58 % yield. The dimeric structure of **5c** (Figure 2, left)[15] differs remarkably from the other reported bipyridine-based complexes **5a** and **5b**. Similarly, treatment of $CuSCF_3$ with 1,1′-bis(diphenylphosphino)ferrocene (dppf) provided $[(dppf)Cu^{I}(SCF_3)]$ (**5f**) as a yellow solid in 69 % yield, and its structure was also verified by single-crystal X-ray crystallography (Figure 2, right).[15] It is



Scheme 3. Synthesis of [LCu^I(SCF$_3$)] complexes **5a–f**.

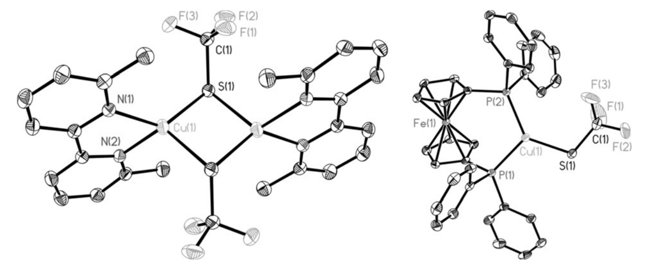
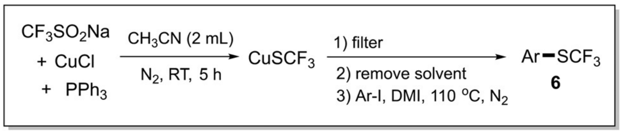


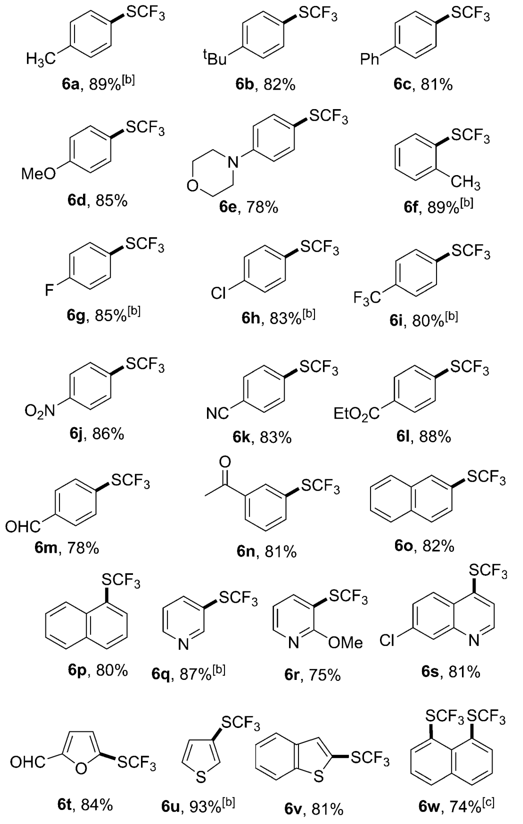
Figure 2. ORTEP diagrams of **5c** (left) and **5f** (right).

worth noting that complexes **5c** and **5f** were air-stable for several days in solid state.[7c]

In addition to the application for convenient preparation of the aforementioned [LCu(SCF$_3$)] complexes, further exploration of the ligand-free generated CuSCF$_3$ for a direct coupling with aryl halides was conducted. First, the direct coupling between aryl iodides and CuSCF$_3$ was explored (Table 3). Direct addition of iodobenzene into the solution of CuSCF$_3$ in CH$_3$CN and heating at 110 °C for 24 h afforded PhSCF$_3$ in 13 % yield, with a majority of CuSCF$_3$ (74 %) remaining unconverted. Further solvent screening indicated that 1,3-dimethyl-2-imidazolidinone (DMI) was the superior solvent for this direct coupling reaction (even compared with the known suitable solvent NMP[10a–d]), providing PhSCF$_3$ in 85 % yield (see the Supporting Information for details). A wide array of aryl iodides, including heteroaryl iodides, was then chosen for testing the efficiency of this methodology. As shown in Table 3, aryl and heteroaryl iodides bearing either electron-withdrawing or -donating substituents could be transformed into the corresponding products in high yields (74–93 %). The fluoro (**6g**), choloro (**6h**, **6s**), nitro (**6j**), cyano (**6k**), ester (**6l**), ketone (**6n**), and aldehyde (**6m**, **6t**) groups were well-tolerated under standard conditions that could provide opportunities for further elaboration. Moreover, the coupling conditions were compatible with heteroaryl iodides bearing pyridine (**6q**, **6r**), quinoline (**6s**), furan (**6t**), and thiophene (**6u**, **6v**) rings, and delivered the products with high efficiency. Notably, two CF$_3$S groups were introduced into the C1 and C8 sites of the naphthalene in a single step (**6w**), demonstrating the potential for multiple trifluoromethylthiolations of polyiodoarenes.

Table 3. Direct trifluoromethylthiolation of ArI with CuSCF$_3$ generated from CF$_3$SO$_2$Na.[a]





6a, 89%[b]
6b, 82%
6c, 81%
6d, 85%
6e, 78%
6f, 89%[b]
6g, 85%[b]
6h, 83%[b]
6i, 80%[b]
6j, 86%
6k, 83%
6l, 88%
6m, 78%
6n, 81%
6o, 82%
6p, 80%
6q, 87%[b]
6r, 75%
6s, 81%
6t, 84%
6u, 93%[b]
6v, 81%
6w, 74%[c]

[a] General conditions: In situ generated CuSCF$_3$ (ca. 0.25 mmol, remove insoluble NaCl and solvent CH$_3$CN), aryl iodide (0.2 mmol), DMI (1 mL), N$_2$, 110 °C, 24–48 h; yield of isolated products are shown unless the product is very volatile. [b] Yield was determined by ^{19}F NMR spectroscopy of the crude product mixture using PhCF$_3$ as internal standard for volatile products. [c] 1,8-Diiodonaphthalene (0.1 mmol) was added.

In summary, we have demonstrated a mild, convenient, and cost-effective method for the synthesis of CuSCF$_3$ and related air-stable [LCu^I(SCF$_3$)] by a deoxygenative reduction of Langlois' reagent. In this deoxygenative reduction process, the choice of both phosphine reductants and solvents was found to be critical for the conversion of CF$_3$SO$_2$Na. Direct coupling between the CuSCF$_3$ generated in situ with aryl iodides in DMI solvent provided an efficient and operationally-simple method for the construction of a diverse array of aryl trifluoromethyl sulfides. Further applications of this chemistry using other R_fSO_2Na derivatives and the systematic mechanistic studies are under way on our laboratory.

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Keywords: copper · cross-coupling · fluorine · organic chemistry · sulfur

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