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Copper(II)-catalyzed trifluoromethylation of iodoarenes using Chen's reagent†

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The introduction of a trifluoromethyl group to organic molecules is significant for modern drug discovery; thus practical routes towards catalytic trifluoromethylation are highly desired. Herein, we report the efficient copper(II)-catalyzed nucleophilic trifluoromethylation of various aryl and heteroaryl iodides using methyl fluorosulfonyldifluoroacetate ($FO_2SCF_2CO_2Me$, Chen's reagent). The use of $CuCl_2$ instead of CuI resulted in a significant improvement in the original Chen's methodology; specifically, catalytic amounts (10 to 15%) of $CuCl_2$ were used instead of Cu(I) salts for the generation of $CuCF_3$ species. The improved trifluoromethylation converts aryl and heteroaryl iodides into the corresponding CF_3-containing molecules with multiple functional groups in moderate to high yields. Moreover, a mechanism was proposed for this new catalytic system.

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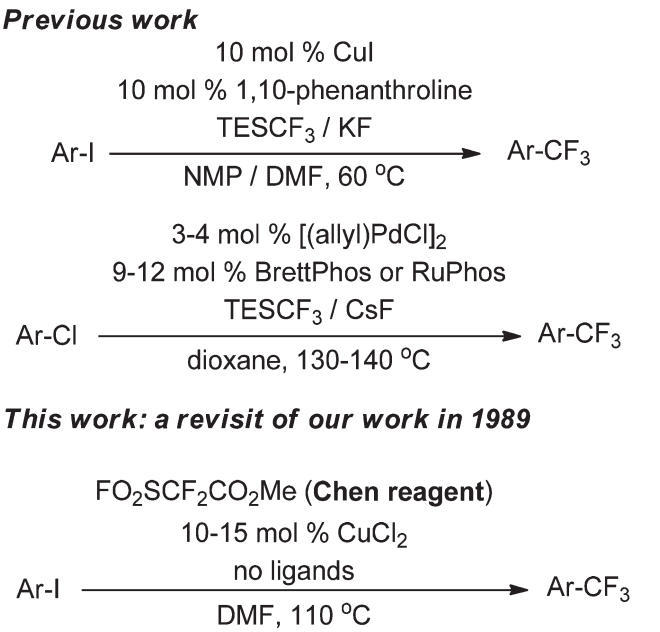
Introduction

Fluorine plays a unique role in chemical transformations, pharmaceutical effects, and physical properties; as a result, a variety of trifluoromethylated aromatics have been developed for potent drugs such as Prozac.[1–3] Many strategies have been applied for the trifluoromethylation of aryl and heteroaryl compounds, including radical trifluoromethylation, electrophilic trifluoromethylation, and nucleophilic trifluoromethylation.[4–15] Among them, CF_3Cu complexes are generally prepared or generated *in situ* to ensure efficient trifluormethylation.[16–20] However, copper-mediated trifluoromethylation reactions of haloarenes usually require stoichiometric or excess amounts of copper species to obtain good yields of trifluoromethylated products. As such, catalytic trifluoromethylation reactions are in high demand and represent a significant challenge in organic chemistry.

In 1989, Chen first reported the catalytic trifluoromethylation of aryl, alkenyl, and benzyl halides using methyl fluorosulfonyldifluoroacetate ($FO_2SCF_2CO_2Me$, Chen's reagent).[20] Today, this approach is well-recognized as Chen's methodology.[16,18a,21–24] Besides this example, catalytic trifluoromethylation was not reported until 2009 (Scheme 1).[8,25–31] In 2009, Amii reported a catalytic trifluoromethylation reaction using Cu(I)-diamine complexes and CF_3SiEt_3.[25a] In 2010, Buchwald achieved the Pd-catalyzed trifluoromethylation of aryl chlorides using a phosphine ligand such as BrettPhos or RuPhos.[30] Mechanistically,



Scheme 1 Nucleophilic trifluoromethylations.

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"ligandless" reactions facilitate the reactivity of "$CuCF_3$" and thus promote the oxidative addition of "$CuCF_3$" to aryl halides.[32] However, catalysis without nitrogen or phosphine ligands has not been extensively studied.

Chen's reagent is a commercially available and easy to handle liquid for the trifluoromethylation of haloarenes; it exhibits good functional group compatibility and a versatile trifluoromethylation ability. This cost-effective reagent is amenable for the trifluoromethylation of a wide variety of bioactive compounds. However, even in the pioneering work, copper species were often used in stoichiometric or excess amounts in academic research and industrial applications.[21,22] Chen's reagent is also used as a difluorocarbene reagent or a precursor for a difluoromethyl radical ($^{\bullet}CF_2CO_2Me$).[23] Moreover, a series of related reagents have been developed for trifluoromethylation.[18a,24] In some cases, Chen's reagent was claimed to be better than the Ruppert–Prakash reagent ($TMSCF_3$), $CF_3B(OMe)_3K$, and CF_3CO_2Na.[22a] Trifluoromethylation using Chen's reagent can also be induced by zero valence copper, as disclosed in Chen's early research.[21a] Owing to recent green requirements in transition metal catalysis, we revisited the initial publication in 1989, and found an improved catalytic trifluoromethylation, which we believe will benefit the future discovery of new medicines and agrochemicals.

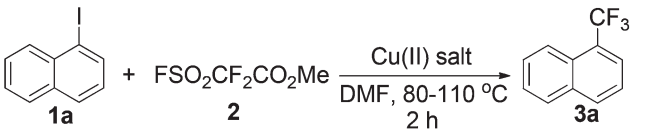
Results and discussion

Among most examples described in the previous work published in 1989, excess aryl iodides were typically required, which hindered the separation of the starting materials from final products when the modifying molecules were structurally complex.[20] Therefore, it is desired to use organic halides as limiting reagents.

To begin, we screened the reaction conditions using 1-iodonaphthalene (**1a**) as a model substrate and limiting reagent, and reacted it with Chen's reagent (**2**) in the presence of 10 mol% $CuCl_2$ in DMF at 110 °C (Table 1). The 88% yield of the trifluoromethylated aromatic (**3a**) was inspiring (Table 1, entry 1). Next, we compared the effects of several copper(II) salts, namely $CuBr_2$, $Cu(OAc)_2$, and $Cu(OH)_2$, which give the desired products in 84%, 86%, and 86% yields, respectively (Table 1, entries 2–4). However, CuO and CuF_2 did not give the desired product (Table 1, entries 5 and 6). When the amount of $CuCl_2$ was reduced to 5 mol%, the product yield decreased to 67% (Table 1, entry 7). The reduction of **2** to 2.0 equivalents or 1.5 equivalents gave the product in 80% and 73% yields (Table 1, entries 8 and 9). Finally, reaction temperatures of 100, 90, and 80 °C resulted in moderate to good yields (55 to 83%) of the products (Table 1, entries 10–12). The yield was 83% at 120 °C (Table 1, entry 13).

Next, we explored the scope of the copper(II)-catalyzed nucleophilic trifluoromethylation of aromatic and heteroaromatic iodides (Table 2). Electron-deficient aryl iodides exhibited good reactivity and the products (**3e–3m**, **3p**, and **3q**) were

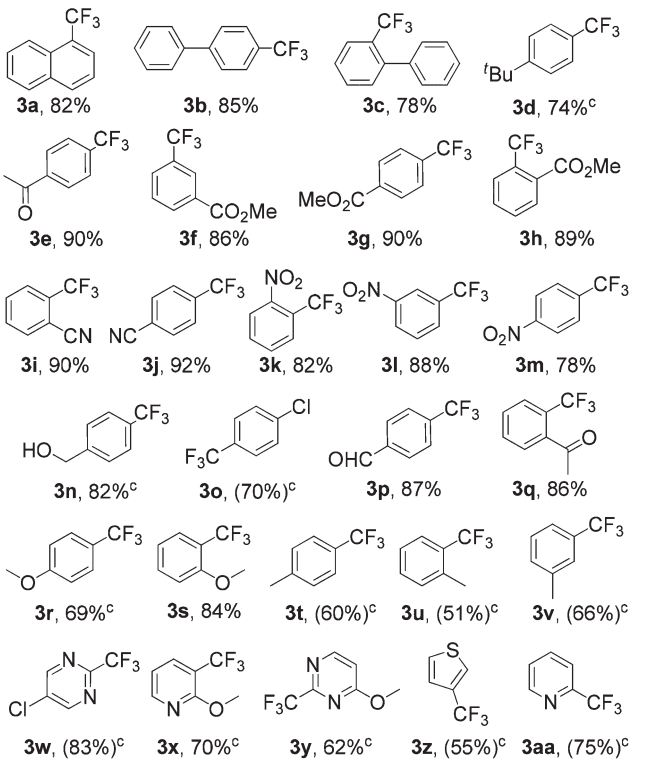
Table 1 Optimization of trifluoromethylation catalyzed by Cu(II) salts[a]



Entry	[Cu]	[Cu] mol%	**2** (equiv.)	Temp. (°C)	Yield[b] (%)
1	$CuCl_2$	10	2.5	110	88[c](82)[d]
2	$CuBr_2$	10	2.5	110	84[c]
3	$Cu(OAc)_2$	10	2.5	110	86[c]
4	$Cu(OH)_2$	10	2.5	110	86[c]
5	CuO	10	2.5	110	0
6	CuF_2	10	2.5	110	0
7	$CuCl_2$	5	2.5	110	67
8	$CuCl_2$	10	2.0	110	80
9	$CuCl_2$	10	1.5	110	73
10	$CuCl_2$	10	2.5	100	83
11	$CuCl_2$	10	2.5	90	72
12	$CuCl_2$	10	2.5	80	55
13	$CuCl_2$	10	2.5	120	83

[a] Reaction conditions: 1-Iodonaphthalene (**1a**, 0.5 mmol), copper salt (as indicated), **2** (as indicated), at the indicated reaction temperatures in DMF (1.5 mL) under a nitrogen atmosphere for 2 h. [b] The yields were determined by the ^{19}F NMR analysis of crude reaction mixtures using benzotrifluoride as the internal standard. [c] **1a** was completely consumed. [d] Isolated yields.

Table 2 Substrate scope of copper(II)-catalyzed trifluoromethylation[a,b]



[a] Reaction conditions: Iodides (0.5 mmol), **2** (2.5 equiv.) and $CuCl_2$ (10 mol%) at 110 °C in DMF (1.5 mL) under a nitrogen atmosphere for 2 h. [b] Isolated yields (^{19}F NMR yields). [c] Reaction conditions: Iodides (0.5 mmol), **2** (3 equiv.), and $CuCl_2$ (15 mol%), at 110 °C in DMF (1.5 mL) under a nitrogen atmosphere for 2 h.

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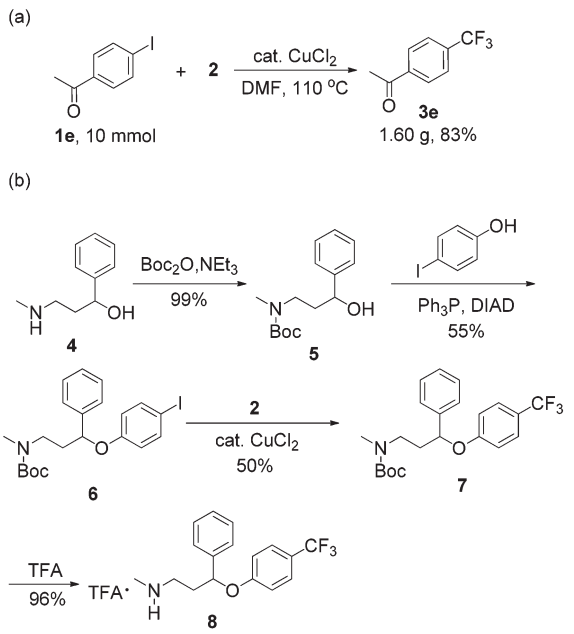
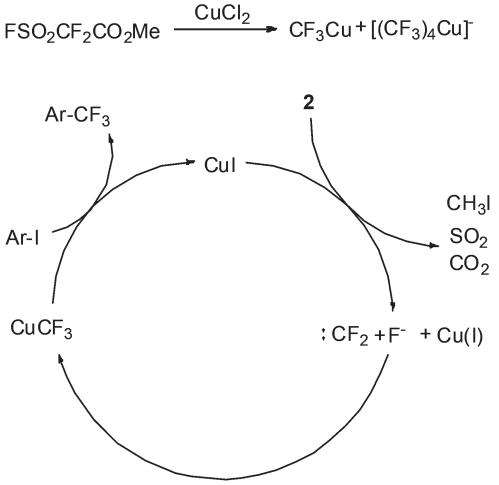
obtained in 78–92% yields. While some electron-neutral (**3a–3c**) and electron-rich substrates (**3s**) gave the corresponding products in 78–85% yields, aryl and heteroaryl substrates required slightly greater amounts of the catalyst (15 mol% of $CuCl_2$) and 3 equivalents of **2** for a good conversion. Thus, **3d**, **3n**, **3o**, **3r**, **3t**, and **3v** were obtained in 51 to 82% yields. An *ortho* effect was observed upon comparing *o*-methoxy and *p*-methoxy aryl iodides (**3r** *vs.* **3s**). A range of functional groups, including nitro, halogen, aldehyde, ether, ester, ketone, cyano, and hydroxyl moieties, were tolerated in this transformation. Notably, halogen, aldehyde, ketone, ester, and hydroxyl groups can provide a complementary platform for further transformations. Additionally, heteroaryl iodides (5-chloro-2-iodopyrimidine, 3-iodo-2-methoxypyridine, 2-iodo-4-methoxypyrimidine, 3-iodothiophene, and 2-iodopyridine) were all suitable substrates, giving the desired trifluoromethylated products (**3w–3aa**) in moderate to good yields (55–83%).

In order to demonstrate the potential synthetic utility of this reaction, a large-scale experiment was performed, which produced **3e** in 83% yield (Scheme 2a). This methodology could be used to produce biologically active molecules such as Prozac (Scheme 2b).

To gain further insights into the Cu(II)-catalyzed trifluoromethylation reaction, the decomposition of **2** and its reaction with $CuCl_2$ were studied using ^{19}F NMR spectroscopy (see the ESI†). When $CuCl_2$ was mixed with **2** in a 0.2 : 1 ratio in DMF, two signals at −28.9 ppm and −34.1 ppm were detected within 5 min. According to the literature,[33,34] the signals at −28.9 ppm and −34.1 ppm were assigned "$CuCF_3$" and "$[Cu(CF_3)_4]^-$," respectively. Based on these findings, we proposed a mechanism for the Cu(II) catalyzed trifluoromethylation (Scheme 3). First, $CuCl_2$ reacts with **2** in DMF giving Cu(I)



Scheme 2 Application of Cu(II)-catalyzed trifluoromethylation.



Scheme 3 Proposed mechanism of Cu(II)-catalyzed trifluoromethylation with Chen's reagent.

("$CuCF_3$") and Cu(III) ($[Cu(CF_3)_4]^-$) species. The "ligandless" $CuCF_3$ generated *in situ* reacts with haloarenes to provide the desired trifluoromethylated products and generates CuI, which acts as the catalyst for the reaction. By using a catalytic amount of CuI, the yield of trifluoromethylation was 86% (for **3a**). When KCl and Bu_4NCl were added as an additive to the reaction mixture under the CuI catalyzed conditions, the yields decreased to 48% and 72%, respectively. These experiments imply that the CuI instead of chlorides is the true catalyst for the reaction.

Conclusion

The efficient copper(II)-catalyzed nucleophilic trifluoromethylation of aryl and heteroaryl iodides was achieved in the presence of Chen's reagent. 10–15 mol% Cu(II) chloride allowed the conversion of various aryl and heteroaryl iodides into the corresponding trifluoromethyl-containing products in moderate to high yields. The reaction was applicable to both electron-deficient and electron-rich arenes, as well as heteroarenes, and a broad range of functional groups was tolerated. The power of Chen's methodology was highlighted, and this work will reinforce the synthesis of functional molecules bearing CF_3 moieties.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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