

Copper-Promoted Trifluoromethylation of Primary and Secondary Alkylboronic Acids**

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The introduction of a CF₃ group to an organic molecule can significantly modify its biological properties by increasing its lipophilicity and metabolic stability.^[1] Accordingly, the development of new methods to form the C–CF₃ bond has attracted considerable interest in synthetic organic chemistry.^[2] While earlier studies in this field focused on stoichiometric trifluoromethylation methods,^[3] recent attention has been turned to transition-metal-catalyzed trifluoromethylation reactions, which usually are carried out under milder conditions and exhibit improved yields, selectivity, and functional-group tolerance.^[4] Until now great success has been achieved with regards to Pd-^[5–7] or Cu-mediated^[8,9] trifluoromethylation of various sp²- and sp-hybridized carbon centers. In some recent studies breakthroughs have also been made for the catalytic trifluoromethylation reactions at allylic sp³-hybridized carbon centers.^[10] Nonetheless, it remains a more difficult challenge to use transition metals to promote trifluoromethylation at nonactivated sp³-hybridized carbon centers.

Herein, we report an unprecedented Cu-promoted trifluoromethylation reaction of primary and secondary alkylboronic acids with the Ruppert–Prakash reagent^[11] (TMSCF₃). This work was inspired by our recent finding of a rather general and robust approach for the preparation of primary and secondary alkylboronic acid derivatives from aliphatic halides and pseudohalides.^[12] Notably, compounds bearing a CF₃ group on their alkyl chains are interesting candidates in the design of bioactive molecules, but methods for the incorporation of CF₃ into aliphatic skeletons remain rare.^[13–15] It is therefore our goal to extend the scope of the Cu-promoted reaction to develop a general approach for the construction of C_{sp}–CF₃ bonds. Furthermore, it should be pointed out that the use of alkylboronic acids in catalytic C–C

cross-coupling reactions has been relatively less studied owing to their poor transmetalation reactivity. Although there has been some success with Pd catalysts,^[16] no cross-coupling of alkylboronic acids has ever been reported for Cu chemistry. Thus, the present finding also provides a rare example for the Cu-promoted cross-coupling reaction of alkylboronic acids.

Our study began by examining the cross-coupling of a primary alkylboronic acid (**1a**) with the Ruppert–Prakash reagent. Initially we tested previous reaction conditions (catalyst = CuOTf·0.5C₆H₆, ligand = 1,10-phenanthroline, oxidant = Ag₂CO₃) developed for Cu-mediated trifluoromethylation of arylboronic acids (Table 1, entry 1).^[8c] Although the desired product (**2a**) could be detected, its yield was very low (16%). To improve the reaction, we examined the effect of using different Cu salts. CuI gives a similar result to CuOTf·0.5C₆H₆, whereas the other Cu salts such as [Cu(MeCN)₄]BF₄ and CuTc only afford a trace amount of product (entries 2–4). As CuI is much less expensive and more air stable than CuOTf·0.5C₆H₆, we used CuI in our subsequent investigations. For the ligand, our study shows that the use of phenanthrolines bearing electron-donating substituents can increase the yield (entries 5–7). The often more powerful *N*-heterocyclic carbene ligand (**L5**) in Cu chemistry, however, fails to promote this reaction (entry 8). In addition, the use of the less-rigid bipyridine ligand (**L6**) results in a lower yield (entry 9).

By using the best ligand (**L3**) identified from the above experiments, we next examined the effects of using different oxidants. Most of the Ag salts that we investigated (i.e. Ag₂O, AgOAc, AgOTFA, AgOTf) gave poor results (entries 10–13), but pleasingly when AgBF₄ was used a modest yield of 50% was achieved (entry 14). Furthermore, the use of other oxidants including 1,4-benzoquinone and Cu(OAc)₂ also resulted in poor yields (entries 15–16). With AgBF₄ as oxidant, we examined the effect of inorganic bases on the reaction. The reactions in the presence of K₂CO₃, Cs₂CO₃, and *t*BuOK gave lower yields than that in the presence of K₃PO₄ (entries 17–19), whereas when KF was used the yield was increased to 68% (entry 20). To further improve the yield, we increased the loading of CuI to 50 mol% (entry 21) and obtained a good yield of the desired product (88%). Finally, we only detected a trace amount of **2a** from the reaction in the absence of CuI (entry 21). This control experiment confirms the catalytic role of Cu in the trifluoromethylation process.

With the optimized reaction conditions established, we examined the trifluoromethylation of a number of primary alkylboronic acids to test the scope of the reaction (Scheme 1). These alkylboronic acids were prepared from the corresponding alkyl halides or tosylates by using our

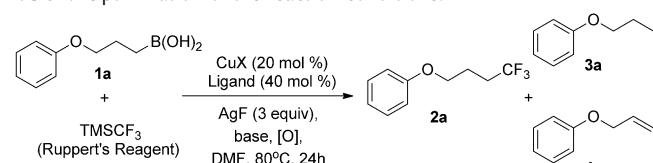
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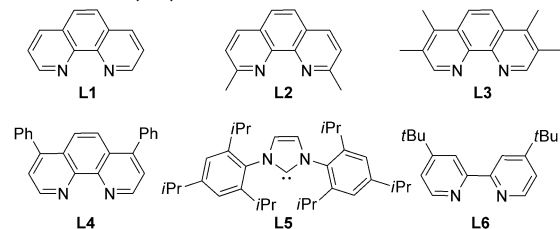
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Table 1: Optimization of the reaction conditions.^[a]



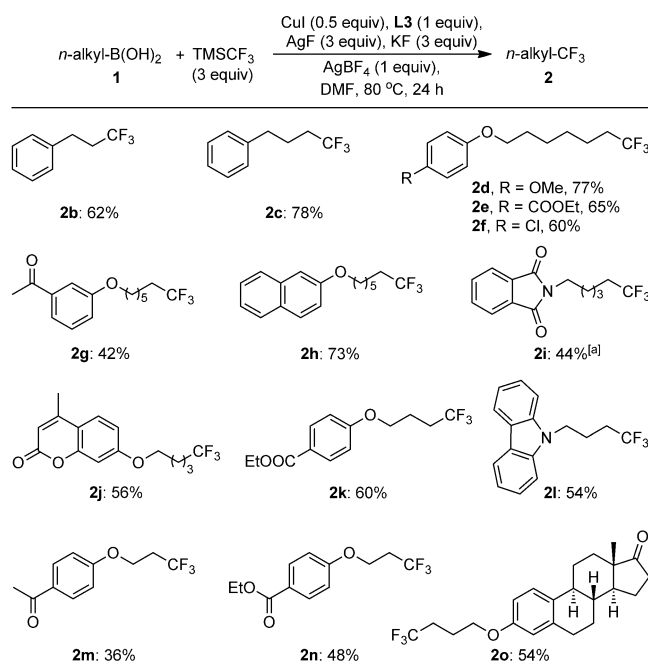
Entry	CuX	Ligand	[O]	Base	Yield of 2a (3a/4a) [%] ^[b]
1	CuOTf·0.5C ₆ H ₆	L1	Ag ₂ CO ₃	K ₃ PO ₄	16 (25:8)
2	[Cu(MeCN) ₄]BF ₄	L1	Ag ₂ CO ₃	K ₃ PO ₄	trace (32:18)
3	CuTc	L1	Ag ₂ CO ₃	K ₃ PO ₄	trace (22:20)
4	CuI	L1	Ag ₂ CO ₃	K ₃ PO ₄	15 (14:9)
5	CuI	L2	Ag ₂ CO ₃	K ₃ PO ₄	trace (8:5)
6	CuI	L3	Ag ₂ CO ₃	K ₃ PO ₄	26 (24:11)
7	CuI	L4	Ag ₂ CO ₃	K ₃ PO ₄	18 (25:9)
8	CuI	L5	Ag ₂ CO ₃	K ₃ PO ₄	trace (6:4)
9	CuI	L6	Ag ₂ CO ₃	K ₃ PO ₄	14 (16:10)
10	CuI	L3	Ag ₂ O	K ₃ PO ₄	trace (16:5)
11	CuI	L3	AgOAc	K ₃ PO ₄	trace (4:6)
12	CuI	L3	AgOTFA	K ₃ PO ₄	8 (7:3)
13	CuI	L3	AgOTf	K ₃ PO ₄	16 (10:6)
14	CuI	L3	AgBF ₄	K ₃ PO ₄	50 (9:5)
15	CuI	L3	BQ	K ₃ PO ₄	trace (—)
16	CuI	L3	Cu(OAc) ₂	K ₃ PO ₄	12 (5:—)
17	CuI	L3	AgBF ₄	K ₂ CO ₃	38 (8:3)
18	CuI	L3	AgBF ₄	Cs ₂ CO ₃	25 (6:2)
19	CuI	L3	AgBF ₄	<i>t</i> BuOK	8 (17:8)
20	CuI	L3	AgBF ₄	KF	68 (5:2)
21 ^c	CuI	L3	AgBF ₄	KF	88 (4:1) [78] ^[d]
22	—	L3	AgBF ₄	KF	trace (6:—)

[a] Reaction conditions: **1a** (0.1 mmol), TMSCF₃ (0.3 mmol), [Cu] (20% mol), ligand (0.4 equiv), [O] (1 equiv), base (3 equiv), AgF (3 equiv), 80°C, 24 h. [b] Yields were determined by GC analysis (average of two runs). [c] This reaction was conducted with 50 mol % of CuI and 1 equiv of **L3**. [d] The yield of the isolated product is given in the square parentheses. BQ = 1,4-benzoquinone, CuTc = (thiophene-2-carbonyloxy)copper, OTFA = trifluoroacetate, Tf = trifluoromethanesulfonyl, TMS = trimethylsilyl.



previously developed Cu-catalyzed borylation method.^[12] The new reaction tolerates a number of functional groups including ether, ester, ketone, amide, and amine. The yields of the desired products are modest to good. A coumarin derivative (**2j**) was successfully trifluoromethylated in 56% yield by this Cu-promoted approach. Furthermore, we also used the new method to prepare a trifluoromethylated derivative of a bioactive molecule (**2o**; an estrone derivative) in 54% yield.

After primary alkylboronic acids were successfully trifluoromethylated, we turned our attention to more-challenging substrates, namely, secondary alkylboronic acids. The above CuI protocol is not optimal for the trifluoromethylation of secondary alkylboronic acids as under those con-

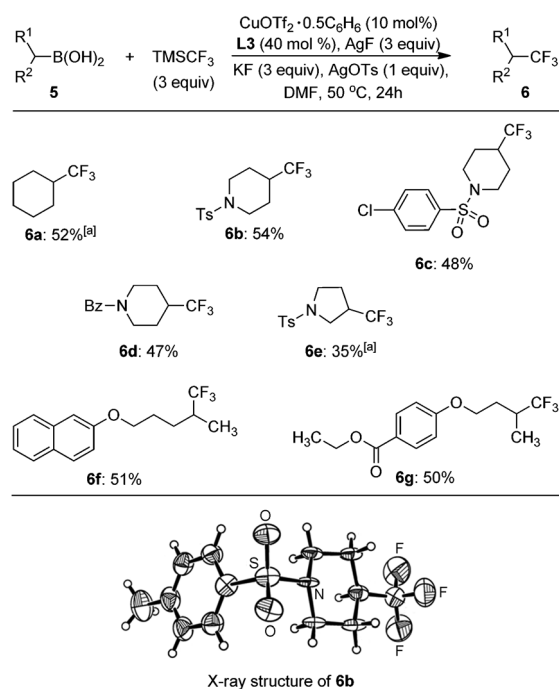


Scheme 1. Scope of Cu-promoted trifluoromethylation of primary alkylboronic acids. Reactions were carried out at 80°C for 24 h on a 0.2 mmol scale. Yields of the isolated products are shown. [a] This reaction was conducted with 25 mol % of CuOTf·0.5C₆H₆. DMF = *N,N*-dimethylformamide.

ditions the yield for the reaction of cyclohexylboronic acid is lower than 10%. A careful analysis of the reaction reveals the formation of protonated (i.e. cyclohexane) and β-H elimination (i.e. cyclohexene) products in significant quantities. To overcome this problem we returned to using CuOTf·0.5C₆H₆. We also screened a variety of oxidants and found that AgOTf is the most effective. With cyclohexylboronic acid as the substrate, the optimal yield of the desired product (**6a**) is 52%. However, cyclohexane and cyclohexene are still produced as by-products and increasing the catalyst loading or temperature does not improve the yield. We expect that rational design of the ligand may solve the selectivity problem with regards to protonation and β-H elimination. We decided to leave this challenge to our ensuing studies because the present yields (albeit being modest) are already practical for the incorporation of CF₃ at secondary sp³-hybridized carbon centers.

To examine the scope of the trifluoromethylation reaction of secondary sp³-hybridized carbon centers, we prepared a number of secondary alkylboronic acids from the corresponding secondary alkyl halides or tosylates by using the Cu-catalyzed borylation method (Scheme 2).^[12] Our results show that both acyclic and cyclic secondary alkylboronic acids can be successfully trifluoromethylated. Importantly, *N*-protected piperidines and pyrrolidines are well-tolerated in the transformation. The structure of compound **6b** was confirmed by X-ray analysis.

To summarize, we have developed an unprecedented Cu-promoted trifluoromethylation reaction of primary and secondary alkylboronic acids with TMSCF₃. This transforma-



Scheme 2. Scope of Cu-promoted trifluoromethylation of secondary alkylboronic acids. Reactions were carried out at 50 °C for 24 h on a 0.2 mmol scale. Yields of the isolated products are shown. The X-ray crystal structure of **6b** is shown with the thermal ellipsoids set at 45% probability.^[17] [a] Yield was determined by ¹⁹F NMR spectroscopy using CF₃Ph as the internal standard. Bz = benzoyl, Ts = *p*-toluenesulfonyl.

tion extends the concept and scope of the recently popularized transition-metal-mediated trifluoromethylation reactions, which mostly occur at the sp²- and sp-hybridized carbon centers. It also represents one of the first examples of Cu-catalyzed C–C cross-coupling reactions of alkylboronic acid derivatives. Many synthetically relevant functional groups including ester, amide, ether, amine, and ketone can be tolerated in the reaction. Both cyclic and acyclic alkanes can be successfully trifluoromethylated by this new method. Our next challenge is to optimize the ligands to improve the reaction yield or, more ambitiously, to induce stereocontrol in the trifluoromethylation of sp³-hybridized carbon centers.

Experimental Section

A typical procedure for Cu-promoted trifluoromethylation of primary alkylboronic acids (**1a** in Table 1): In a glove box, KF (34.8 mg, 0.6 mmol), AgF (76.2 mg, 0.6 mmol), and AgBF₄ (38.8 mg, 0.2 mmol) were added to a sealed tube equipped with a stirring bar. The tube was capped with a septum and removed from the glove box. After **1a** (36 mg, 0.2 mmol), CuI (19 mg, 0.1 mmol), and **L3** (47.2 mg, 0.2 mmol) were added, the vessel was evacuated and filled with argon (three times). DMF (1 mL) and TMS-CF₃ (89 mg, 0.6 mmol) were added sequentially by syringe under an argon atmosphere. After addition of all substrates, the reaction mixture was stirred for 24 h at 80 °C. Then water was added to the mixture at room temperature. The resulting mixture was extracted with ethyl acetate three times, and the combined organic phase was washed with water and brine and then dried over MgSO₄. After filtration and evaporation of the solvent, the crude mixture was purified by column chromatography on silica gel

with petroleum ether/ethyl acetate (100:1) to give the target product **2a** (31.8 mg, 78% yield).

A typical procedure for Cu-promoted trifluoromethylation of secondary alkylboronic acid (**3b** in Scheme 2): In a glove box, KF (38.8 mg, 0.6 mmol), AgF (76.2 mg, 0.6 mmol), and [Cu(OTf)₂·C₆H₆] (10 mg, 0.02 mmol) were added to a sealed tube equipped with a stirring bar. The tube was capped with a septum and removed from the glove box. After **3b** (56.6 mg, 0.2 mmol), AgOTs (55.8 mg, 0.2 mmol), and **L3** (9.5 mg, 0.08 mmol) were added, the vessel was evacuated and filled with argon (three times). DMF (1 mL) and TMS-CF₃ (89 mg, 0.6 mmol) were added sequentially by syringe under an argon atmosphere. After addition of all substrates, the reaction mixture was stirred for 24 h at 50 °C. Then water was added to the mixture at room temperature. The resulting mixture was extracted by ethyl acetate three times, and the combined organic phase was washed with water and brine and then dried over MgSO₄. After filtration and evaporation of the solvent, the crude mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) to give the target products **4b** (33 mg, 54% yield).

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- [17] CCDC 900254 (**6b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.