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Copper-catalyzed Trifluoromethylation of Aryl- and Vinylboronic Acids with Generation of CF₃-radicals

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Yang Li, Lipeng Wu, Helfried Neumann, and Matthias Beller*

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The selective trifluoromethylation of aryl- and vinylboronic acids proceeds smoothly with CF₃SO₂Na (Langlois reagent) in the presence of copper catalysts and *t*-BuOOH. Thereby, the 10 method relies both on transition metal catalysis and selective radical reactions. Advantageously, the protocol can be performed at room temperature under air atmosphere and avoid the issue of poor regioselectivity

Trifluoromethylated aryl and heteroaryl compounds represent an 15 important structural motif in pharmaceuticals, agrochemicals, and advanced organic materials.¹ Due to the increasing interest on this class of compounds, the development of new methodologies for generation C-CF₃ bonds has attracted significant attention in recent years.² More specifically, two major approaches for the 20 formation of these bonds have emerged in the last decade: On the one hand, transition metal catalyzed or metal-mediated trifluoromethylation reactions are applied using prefunctionalized substrates such as aryl halides,³ arylboron compounds,⁴ arenes substituted with directing groups,⁵ or ²⁵ heteroarenes.⁶ Clearly, the major advantage of this approach is the control of the specific regioselectivity. Unfortunately, these transformations always involve relatively expensive trifluoromethylsilanes, such as Ruppert's reagent (TMSCF₃)^{3a-}

- ^{b,3g,3h,3j,3k,3m,4a-b,4f,5b,6} or TESCF₃^{3c,3d} to generate a CF₃ synthon ³⁰ (Eq 1), and *S*-(trifluoromethyl) thiophenium salts,^{3f,4d,4e,5} Togni's reagent^{4c,4i} to generate a CF₃⁺ intermediate (Eq 2). A second synthetic approach takes advantage of highly reactive CF₃ radicals.⁷ For examples, the groups of MacMillan^{7c} and Baran^{7d} demonstrated elegantly the direct trifluoromethylation of arenes
- ³⁵ and heterocycles. They used either visible light or *t*-BuOOH (TBHP) to initiate CF₃ radical formation from CF₃SO₂Cl or the Langlois reagent (CF₃SO₂Na).^{7a,8} The latter reactions proceed under mild conditions, albeit with poor regioselectivity (Eq 3). Inspired by these results, we envisioned to bring together the
- ⁴⁰ advantages of both strategies by combining transition metal catalysis with the high reactivity of CF₃ radicals. Probably, in such an approach the regioselectivity might be controlled by transition metal catalysis, while the CF₃ radical is generated under mild reaction conditions from less expensive reagents.
- ⁴⁵ Notably, during our work Sanford and co-workers reported an approach towards this direction using the CuOAc-catalyzed trifluoromethylation with CF₃I using visible light at 60°C (Eq 4).⁹

Herein, we report copper-catalyzed trifluoromethylations of aryl and vinyl boronic acids with in situ generated CF₃-radicals from ⁵⁰ the reaction of TBHP and CF₃SO₂Na at room temperature with

the mixture of water and DCM as solvents.

	1. TM catalyzed or mediated trifluoromethylation:							
	Ar - R	+	CF3-	[TM]	ArCF ₃	(Eq. 1)		
	Ar - R	+	${\rm CF_3}^+$	[I M]	ArCF ₃	(Eq. 2)		
55	R = H, X, B(OH) ₂ and its derivatives							
	2. Radical trifluoromethylation:			photoredox catalysis				
	Ar=H +	. Cł	-3SO ⁵ H	or t-BuOOH	ArCF ₃	(Eq. 3)		
	R' = CI, N	la						
	Cooperation of TM catalysis with radical trifluoromethylation:							
60	ArB(OH)2 +	CF ₃ I	catalysis cat. [Cu]	ArCF ₃	(Eq. 4)		
	This work:	rk:		DMF, 60 °C				
	RB(OH)	2 +	CF ₃ SO ₂ Na	t-BuOOH cat. [Cu]	RCF ₃	(Eq. 5)		
	R = Ar, v	vinyl		DCM/H ₂ O, rt				

Scheme 1 Strategies for the formation of C-CF₃ bonds.

At the start of our investigations, 4-methoxyphenyl-boronic acid (1a) was selected as a substrate for selective trifluoromethylation. Obviously, there are two major problems in this model reaction: The first issue is the competition of the direct 70 radical reaction with the arene compared to the small amount of in situ formed aryl metal species. The second issue is to avoid oxidation of the arylboronic acid.¹⁰ To overcome these problems, different metal catalysts including Pd,3d,3m,5,6a,11 and Cu complexes^{3a-3c, 3e-31,3n,4,6b} were tested. In addition, an extensive 75 variation of reaction parameters, e.g. ligands, solvents, temperature, additives, etc. were performed. To our delight, the desired product 4a was obtained in decent yield (53%) using simple Cu(OAc)₂ as catalyst in a mixture of DCM and water as solvent at rt (Table 1, entry 1). Noteworthy, without Cu(OAc)₂ so less than 5% of product was detected (Table 1, entry 2). Cu(I)OAc and other copper catalysts exhibited lower efficiency than Cu(OAc)₂ (Table 1, entries 3-8). Under slightly acidic reaction conditions the chemoselectivity of this transformation is increased. Hence, using 2.5 equiv of NH₄Cl promoted a higher ⁸⁵ yield of **4a** (Table 1, entries 1, 9 and 10). Notably, the function of the ligand (2,4,6-collidine) to the metal is important to this reaction, too (Table 1, entries 11-15). In the absence of 2,4,6collidine, the reaction yield was decreased sharply to only 22% (Table 1, entry 11). Increasing the amount of the

trifluoromethylation reagent (NaSO₂CF₃) improved the yield to 64% (Table 1, entries 1, 16 to 17) and raising the ratio of TBHP to NaSO₂CF₃ led to a slightly higher efficiency (Table 1, entry 18). Finally, addition of 0.24 equiv of imidazole as an additive ⁵ gave the desired product in a 74% yield (Table 1, entry 19).

Table 1Copper-catalyzedtrifluoromethylation of 4methoxyphenylboronic acid: Variation of reaction conditions^a

MeO{	B(OH) ₂ + 0	CF3SO2Na +	TBHP	20 mol% 2,4,6-coll DCM, H	[Cu] idine H₂O → MeO→	CF3
	1a	2	3	rt, air, i	6 h	4a
Entry	[Cu]	CF ₃ SO ₂ Na (equiv)	TBHP ^b (equiv)	NH ₄ Cl (equiv)	2,4,6-collidine (equiv)	Yield(%) ^c
1	Cu(OAc) ₂	5.0	10.0	2.5	2.0	53
2	—	5.0	10.0	2.5	2.0	<5
3	CuOAc	5.0	10.0	2.5	2.0	40
4	Cu(CF ₃ CO ₂) _{2*} H ₂ O	5.0	10.0	2.5	2.0	44
5	CuBr	5.0	10.0	2.5	2.0	40
6	Cul	5.0	10.0	2.5	2.0	38
7	Cu(CH ₃ CN) ₄ BF ₄	5.0	10.0	2.5	2.0	36
8	Cu(CH ₃ CN) ₄ OTf	5.0	10.0	2.5	2.0	44
9	Cu(OAc) ₂	5.0	10.0	3.0	2.0	36
10	Cu(OAc) ₂	5.0	10.0	2.0	2.0	39
11	Cu(OAc) ₂	5.0	10.0	2.5	—	22
12	Cu(OAc) ₂	5.0	10.0	2.5	1.0	46
13	Cu(OAc) ₂	5.0	10.0	2.5	1.5	49
14	Cu(OAc) ₂	5.0	10.0	2.5	2.5	49
15	Cu(OAc) ₂	5.0	10.0	2.5	3.0	28
16	Cu(OAc) ₂	6.0	12.0	2.5	2.0	55
17	Cu(OAc) ₂	7.0	14.0	2.5	2.0	64
18	Cu(OAc) ₂	7.0	16.1	2.5	2.0	66
19	Cu(OAc) ₂	7.0	16.1	2.5	2.0	74 <i>ª</i>
^a All the reactions were performed on 0.25 mmol scale in DCM (4 mL) and H ₂ O (1.5 mL).						
"TBHP (tert-butyl hydroperoxide) was used as 70% solution in water. CGC yield is shown						
and dodecane was used as internal standard. a 0.24 equiv of imidazole was added.						

With the optimized reaction conditions in hand, the substrate 25 scope was investigated. Arylboronic acids with electron-donating substituents (methoxy, methyl, 3,4-methylenedioxy) underwent trifluoromethylation in good yields (Table 2, 4a, 74% yield, 4b, 66% yield, 4c, 61%). Classic hydroxyl protecting groups (Bn and TBS) are well-tolerated in this reaction (Table 2, 4d, 73% yield, 30 4e, 69% yield). Notably, methylthio and N,N-dimethylamino substituents survive under the mild reaction conditions, albeit in modest yields (Table 2, 4f, 47% yield, 4g, 39% yield). We observed that steric hindrance in ortho position to the boryl group decreased the reaction efficiency somewhat (Table 2, 4h, 4i).

- Decreasing of substrates' electron density induced some 35 lower reaction efficiency (Table 2, 4j-4o). Halide-substituted starting materials represent especially interesting substrates because of further functionalization of trifluoromethylated arenes. Hence, we were pleased to find that the reactions of 4-
- 40 iodophenylboronic acid as well as the corresponding bromides and chlorides worked reasonably well when increasing the amount of Cu(OAc)₂ (Table 2, 4m-4o). Some typical examples of heteroaromatic substrates were also investigated. In fact, the arylboronate derived from benzofuran underwent the reaction
- ⁴⁵ with good yield (Table 2, 4p) and the corresponding boronic acid derived from an indole derivative also gave an acceptable yield (Table 2, 4q). Then, 6-bromohexylboronic acid was selected as an example to investigate the activity of the alkylboronic acids. However, no desired product was observed in this case.
- Conjugated aromatic systems with trifluoromethyl 50 substituents such as β -trifluoromethylstyrene derivatives have found wide use in Organic Light Emitting Diodes (OLEDs) and they are of general interest for other applications as advanced materials.¹² Hence, we were pleased to find that our novel
- ⁵⁵ protocol can be also applied to vinylboronic acids.¹³

View Article Online Table 2 Substrate scope of the Cu-catalyzed trifluoromethylation of arylboronic acids^{a†}



^a All the reactions were performed on 0.25 mmol scale in DCM (4 mL) and H₂O (1.5 mL) with CF₃SO₂Na (7 equiv) and TBHP (16.1 equiv). ^b GC yield was reported as the average of two runs. ^c ¹⁹F NMR yield was reported. ^d Isolated yield was reported. ^e 6 mL of DCM was used. ^f 40 mol% of Cu(OAc)2 and 48 mol% of imidazole was used. gPotassium benzofuran-2-trifluoroborate was used as STM

Compared with the trifluoromethylation of arylboronic acids, the 60 vinylboronic acids are less sensitive towards the influence of substituents (Table 3, 6a-6g). Even with strong electronwithdrawing substituents (6f, 6g), the trifluoromethylation proceeded smoothly with good yields. It should be noted that the trifluoromethylation occurred highly selective and no (Z) isomer 65 was observed during this protocol.^{4c,4d,13e,13f,14}. Next, (Z)potassium styryltrifluoroborate was selected as a representative of Z-alkenylboronic acid derivatives for stereoselectivity studies. Contrary to the (E)-vinylboronic acids, the (Z)-isomer gave a mixture of regioisomers with a ratio of E:Z = 1 : 0.7. The 70 formation of this mixture is attributed to higher stability of the (E)-isomer.

Table 3 T	rifluoromethyl	lation of	vinylboro	nic a	cids ^a
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Ar ->>> B(OH) ₂ + CF ₃ SO ₂ Na + TBHP 5				Cu(OAc) ₂ imidazole 2,4,6-collidir NH4Cl (2 DCM, H ₂ O	(20 mo%) (24 mol%) he (2 equiv) 5 equiv) 5 equiv) 5 rt, air, 6 h	► Ar ∕ CF3 6		
CF ₃ OMe	CF3	CF3	CF3 Ph	CF ₃ CI	CF ₃ F	CF3 CF3	CF ₃	
^a All the reactions were performed on 0.25 mmol scale in DCM (4 mL) and H ₂ O (1.5 mL) with CF ₃ SO ₂ Na (^c /c ₂ -public dimensional dimensionada dimensionada dimensionada								

Based on our observations, we propose the reaction 75 mechanism as shown in Scheme 2. On the one hand, transmetallation of the arylboronic acid takes place with the active Cu(II) species (7) to give the aryl copper(II) complex (8). On the other hand, the CF₃ radical is generated from the reaction 80 of TBHP with NaSO₂CF₃. Reaction of both active species should afford the arylcopper(III)CF₃ intermediate (9) (path A).¹⁵

The desired product is obtained by reductive elimination of intermediate 9 which also releases the Cu(I) complex (10). Finally, 10 is re-oxidized to the active Cu(II) catalyst (7) to close

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Scheme 2 Proposed reaction mechanism

the catalytic cycle. Another mechanistic pathway which we can not exclude at this point is the reaction of the Cu(II) complex 7 ¹⁵ with CF₃ radicals to generate the aryl copper(III) complex 11.^{6b} Subsequent transmetallation with the aryl- or vinylboronic acid will lead again to intermediate 9 (path B).

In summary, this communication reports a convenient Cucatalyzed trifluoromethylation of aryl- and vinylboronic acids

- 20 using less expensive and stable CF₃SO₂Na as CF₃ source. Although a large quantity of TBHP was used, synthetic applications are not limited because of the very low cost. The protocol is robust and the reactions work in water and DCM under air atmosphere at room temperature. Notably, the presented
- 25 methodology makes use of cooperative transition metal catalysis and CF₃ radical formation. Furthermore, it suggests a new orientation in organic transformations.9,16

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- Leibniz-Institut für Katalyse e.V. an der Universität Rostock; Albert 30 Einstein Str. 29a,18059 Rostock, Germany; E-mail Matthias.Beller@catalysis.de
- † Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b00000x/
- 35 † The corresponding boronic ester of substrate 11 (2-(biphenyl-4-yl)-5,5dimethyl-1.3.2-dioxaborinane) was selected as a sample to detect the other by-products or the remaining STM because of the practicable dectection. In the same reaction condition as 11, product 41 was obtained in 22% yield (GC yield) accompanying with 53% STM. (GC yield).
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