Organic LETTERS

Letter

pubs.acs.org/OrgLett

Palladium-Catalyzed Monofluoromethylation of Arylboronic Esters with Fluoromethyl Iodide

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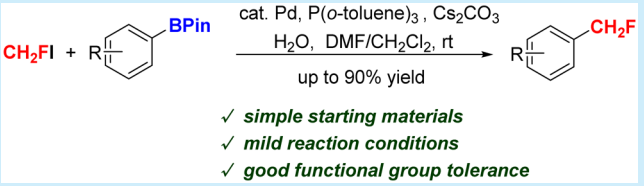
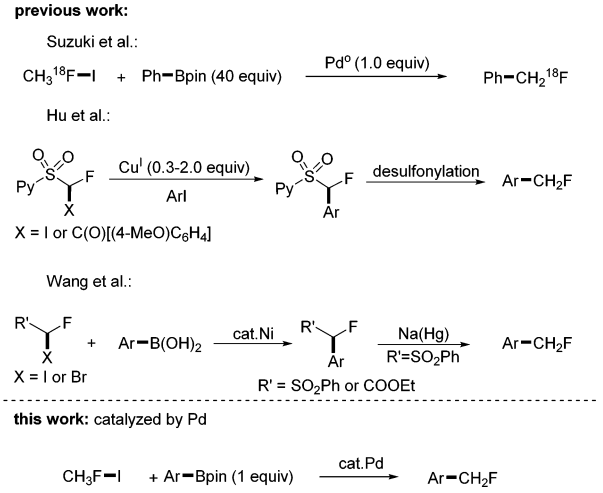
Supporting Information

ABSTRACT: The first palladium-catalyzed direct monofluoromethylation of arylboronic esters to produce monofluoromethyl arenes is reported. The reaction is typically carried out at room temperature within 4 h and has a good functional group tolerance. The monofluoromethylating agent, CH_2FI, was readily prepared via a halogen-exchange process.



Recent years have witnessed rapidly increasing demand for organofluorine compounds. Properties of organic molecules, such as lipophilicity, metabolic stability, and bioavailability, can be significantly altered by the introduction of fluorinated moieties.[1] Therefore, organofluorine compounds have become regular candidates for agrochemicals and pharmaceuticals.[2] In contrast to the prosperous progress of the transition-metal-catalyzed tri-[3] and difluoromethylation[4] of arenes during the past years, the incorporation of the monofluoromethyl (CH_2F) group into arenes has been studied to a much lesser extent.[5] Conventionally, monofluoromethyl arenes (benzylic fluorides) are prepared via nucleophilic fluorination of benzylic alcohols, their derivatives, and benzylic halides.[6] Although this well- and long-known fluorination method is efficient and convenient for the preparation of many benzylic fluorides, it is not suitable for the late-stage monofluoromethylation of complex molecules due to the limited availability of the corresponding benzylic precursors.[7] Considering that many biologically active molecules, such as afloqulone, fluticasone propionate, and the anesthetic sevofurane, contain the CH_2F group as the crucial motif,[8] the modification of complex molecules with the CH_2F group is potentially useful to improve their bioactivities. However, following Olah's report on monofluoromethylation of arenes with fluoromethanol,[9] it is only in 2009 that the Suzuki group reported the second example of direct monofluoromethylation of arenes.[10] In Suzuki's report, a large excess amount of pinacolphenylboronate (40 equiv) was treated with [^{18}F]CH_2FI as the limiting reactant using a stoichiometric amount of palladium and the yield was modest (57%, Scheme 1).[10] As an alternative, indirect monofluoromethylation of arenes assisted by removable activation groups have also appeared in recent years.[11,12] In 2013, our group reported a copper-catalyzed debenzoylative monofluoromethylation of aryl iodides using fluoromethyl 2-pyridyl sulfone reagents.[12a,b] More recently, Wang and co-workers reported the nickel-catalyzed monofluoromethylation of arylboronic acids, using fluoromethylating agents bearing either a phenylsulfonyl or ethoxycarbonyl moiety.[12c] However, the reaction conditions of the cross-coupling step were relatively harsh, and the demand for Na(Hg) amalgam for reductive desulfonylation may limit the compatibility of the substrates.[12c] Herein, we report a facile synthesis of CH_2FI and its use in the first example of palladium-catalyzed direct monofluoromethylation of the arylboronic esters.

Scheme 1. Transition-Metal-Participated Cross-Coupling Monofluoromethylation Reactions



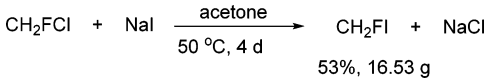
We surmised that a palladium-catalyzed monofluoromethylation using fluoromethyl iodide (CH_2FI) and boronate esters could be realized under carefully optimized reaction conditions. However, there are only a few methods to prepare CH_2FI, which use highly toxic reagents (such as HgF_2), and the purification is usually difficult.[13] We commenced our study with a halogen-exchange process (Finkelstein reaction)[14] to prepare

Received: May 10, 2015
Published: May 29, 2015

DOI: 10.1021/acs.orglett.5b01361
Org. Lett. 2015, 17, 3086–3089

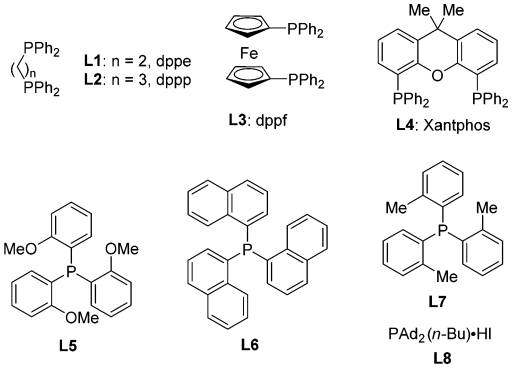
CH_2FI. We chose acetone (200 mL) as the solvent and NaI as the iodination reagent (390 mmol) to exchange the chlorine atom of CH_2FCl (195 mmol) with iodine. After purification, we obtained CH_2FI in 53% isolated yield (Scheme 2).

Scheme 2. Novel Method to Prepare CH_2FI Reagent



Having CH_2FI in hand, we chose air-stable biphenylboronic ester (**2a**) as model substrate to survey reaction conditions. In the presence of a catalytic amount of [$Pd_2(dba)_3$] (5 mol %) in DMF at 50 °C, with K_2CO_3 as the base and tris(*o*-tolyl)phosphine (**L7**, Scheme 3) as the ligand, the desired

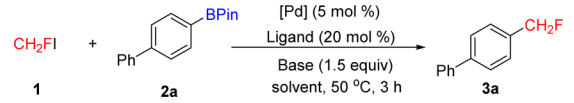
Scheme 3. Various Ligands Used in Pd-Catalyzed Cross-Coupling Reactions



monofluoromethylated product **3a** was obtained in 20% yield (Table 1, entry 1). Thereafter, a survey of bases (see Table S1 in the Supporting Information) was conducted, which indicated that Cs_2CO_3 showed better activity (Table 1, entry 2). Similar to many other Suzuki cross-coupling reactions, the addition of water plays an important role in our reaction. With 1 equiv of water added, the yield increased to 57% (Table 1, entry 4). Finally, the optimal yield of **3a** (74%) was obtained when the reaction was carried out with CH_2Cl_2 and DMF as cosolvent (Table 1, entry 6; for details of the survey of solvents, see Tables S2 in the Supporting Information).

Using the optimized reaction conditions (Table 1, entry 6) as standard, we next investigated the influence of the ligands and palladium source. The nature of the phosphine ligand has a strong influence on the reaction outcome (Table 1, entries 6–13). Flexible bidentate phosphine ligands (**L1** and **L2**) and rigid bidenate phosphine ligand dppf (**L3**)[15] were ineffective in the current reaction (Table 1, entries 7–9). XantPhos (**L4**), a bidentate phosphine ligand with a wide bite angle,[16] was found to be ineffective as well (Table 1, entry 10). The dialkylbiaryl phosphine ligands developed by Buchwald and co-workers[17] were also examined, but neither of them gave a high yield (see Table S3 in the Supporting Information). Other meta or para substituted triarylphosphine ligands gave only a trace amount of the desired product (see Table S3 in the Supporting Information), which indicates that the steric nature (rather than the electronic effect) plays an important role in this reaction. The tris(2-methoxyphenyl)phosphine (**L5**) and tri(1-naphthyl)phosphine (**L6**) performed almost as effectively as tri(*o*-tolyl)phosphine (**L7**) (Table 1, entries 6 and 11–12) .

Table 1. Survey of Reaction Conditions[a]



entry	ligand	[Pd]	base	H_2O (equiv)	yield (%)[b]
1[c]	**L7**	$Pd_2(dba)_3$	K_2CO_3	–	20
2[c]	**L7**	$Pd_2(dba)_3$	Cs_2CO_3	–	22
3[c]	**L7**	$Pd_2(dba)_3$	K_2CO_3	1.0	15
4[c]	**L7**	$Pd_2(dba)_3$	Cs_2CO_3	1.0	57
5[d]	**L7**	$Pd_2(dba)_3$	Cs_2CO_3	1.0	64
6	**L7**	$Pd_2(dba)_3$	Cs_2CO_3	1.0	74
7[e]	**L1**	$Pd_2(dba)_3$	Cs_2CO_3	1.0	0
8[e]	**L2**	$Pd_2(dba)_3$	Cs_2CO_3	1.0	0
9[e]	**L3**	$Pd_2(dba)_3$	Cs_2CO_3	1.0	0
10[e]	**L4**	$Pd_2(dba)_3$	Cs_2CO_3	1.0	0
11	**L5**	$Pd_2(dba)_3$	Cs_2CO_3	1.0	58
12	**L6**	$Pd_2(dba)_3$	Cs_2CO_3	1.0	66
13[e]	**L8**	$Pd_2(dba)_3$	Cs_2CO_3	1.0	73
14[f]	**L7**	$Pd(dppf)Cl_2$	Cs_2CO_3	1.0	68
15[f]	**L7**	$Pd(OAc)_2$	Cs_2CO_3	1.0	46
16[f]	**L7**	$Pd(PPh_3)_4$	Cs_2CO_3	1.0	39
17	**L7**	$Pd_2(dba)_3$	Cs_2CO_3	5.0	83
18[g]	**L7**	$Pd_2(dba)_3$	Cs_2CO_3	5.0	87
19[h]	**L7**	$Pd_2(dba)_3$	Cs_2CO_3	5.0	85 (83)

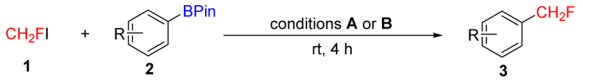
[a]Reaction conditions (unless otherwise noted): **2a** (0.15 mmol, 1.0 equiv), CH_2FI (1.1 equiv), [Pd] (5 mol %), ligand (20 mol %), base (1.5 equiv), DMF/CH_2Cl_2 = 1:1 (1 mL in total), 50 °C, 3 h. [b]Determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard, and yield within parentheses is that of the isolated product. [c]DMF (1 mL). [d]CH_2Cl_2 (1 mL). [e]Ligand (10 mol %) was used. [f]10 mol % [Pd] was used. [g]**2a** (0.15 mmol, 1.0 equiv), room temperature, 4 h. [h]**2a** (0.50 mmol, 1.0 equiv), room temperature, 4 h.

The phosphine ligand $PAd_2(n\text{-Bu})\cdot HI$ (**L8**), which was used by the Zhang group in their heteroaryldifluoromethylation reaction recently,[18] also worked well in our reaction (Table 1, entry 13). Considering the cost efficiency, we finally chose tri(*o*-tolyl)phosphine as the supporting ligand. A survey of palladium sources showed that $Pd_2(dba)_3$ was optimal, followed by $Pd(dppf)Cl_2$, giving a 68% yield (Table 1, entry 14; for details, see Table S4 in the Supporting Information). Increasing the amount of CH_2FI did not improve the product yield (see Table S8 in the Supporting Information). Adjusting the amount of added water to 5 equiv improved the yield to 83% (Table 1, entry 17; for details, see Table S5 in the Supporting Information). Finally, we decreased the reaction temperature to room temperature and prolonged the reaction time to 4 h, and the 4-fluoromethyl-1,1′-biphenyl (**3a**) was isolated in 83% yield (Table 1, entry 19).

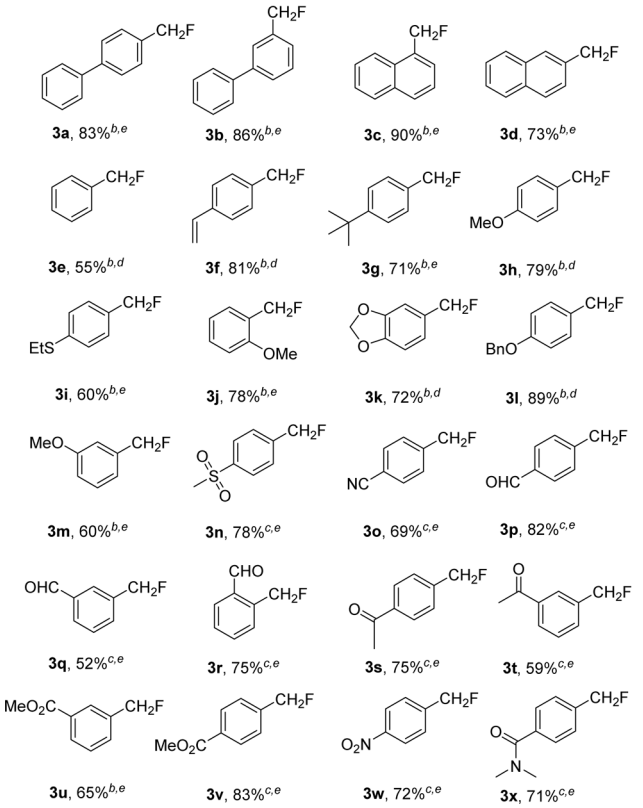
With the optimized reaction conditions (Table 1, entry 19) as standard, we examined the scope of this palladium-catalyzed monofluoromethylation of arylboronic pinacol esters (**2**). As shown in Scheme 4, both electron-neutral and electron-rich aryl boronates are compatible with this reaction, giving the corresponding products in high yields. According to the previous study,[4h] the benzylic fluorides of anisyl and phenolic substrates are not stable because of their highly electron-rich properties. During our study, we also found the electron-rich products, such as **3h** and **3l**, decomposed during the purification process. In contrast to electron-rich and electron-neutral substrates, the reactions of electron-deficient aryl boronate esters gave low yields, with the homocoupling

DOI: 10.1021/acs.orglett.5b01361
Org. Lett. 2015, 17, 3086–3089

Scheme 4. Monofluoromethylation of Arylboronate Esters[a]



A: $Pd_2(dba)_3$ (5 mol %), P(*o*-toluene)$_3$ (20 mol %), H_2O (5 equiv), Cs_2CO_3 (1.5 equiv)
B: $Pd(dppf)Cl_2$ (10 mol %), P(*o*-toluene)$_3$ (20 mol %), H_2O (5 equiv), Cs_2CO_3 (1.5 equiv)



[a]Reaction conditions (unless otherwise noted): **2** (0.5 mmol, 1.0 equiv), CH_2FI (1.1 equiv), P(*o*-toluene)$_3$ (20 mol %), Cs_2CO_3 (1.5 equiv), DMF/CH_2Cl_2 = 1:1 (3 mL in total), room temperature, 4 h. [b]For conditions A: $Pd_2(dba)_3$ (5 mol %). [c]For conditions B: $Pd(dppf)Cl_2$ (10 mol %). [d]Determined by ^{19}F NMR spectroscopy using benzotrifluoride as an internal standard. [e]Yield of the isolated product.

product being formed as major byproducts when we used $Pd_2(dba)_3$ as the catalyst. To our delight, changing the palladium catalyst from $Pd_2(dba)_3$ (5 mol %) to $Pd(dppf)Cl_2$ (10 mol %) significantly improved the product yields. Therefore, various boronic esters containing an electron-withdrawing group, such as sulfonyl (**3n**), cyano (**3o**), acetyl (**3t**), ester (**3u**), nitro (**3w**), and amides (**3x**), afforded the desired products in good yields (Scheme 4).

To demonstrate further the synthetic application of our monofluoromethylation protocol, we applied this method to the late-stage monofluoromethylation of biologically active compounds. Estrone-derived arylboronate ester was prepared in two steps from estrone by a palladium-catalyzed borylation reaction of the corresponding triflate.[19] We carried out the monofluoromethylation under the optimized reaction conditions, and 3-monofluoromethyl-3-dehydroxyestrone (**5**) was obtained in 73% yield (Scheme 5).

In conclusion, we have described a new preparation of fluoromethyl iodide (CH_2FI) and its use in the first palladium-catalyzed direct monofluoromethylation of arylboronic esters.

Scheme 5. Monofluoromethylation of Biologically Active Estrone (4)[a]

[a](a) Tf_2O (1.1 equiv), DIPEA (1.1 equiv), 87%; (b) $[Pd(dppf)Cl_2]$ (4 mol %), $(Bpin)_2$ (2.0 equiv), KOAc (3.0 equiv), 69%; (c) $[Pd_2(dba)_3]$ (5 mol %), P(*o*-toluene)$_3$ (20 mol %), CH_2FI (1.1 equiv), Cs_2CO_3 (1.5 equiv), 73%.

Under mild conditions, both electron-rich and electron-deficient arylboronic esters could be monofluoromethylated in good yields. It can be easily anticipated that aryl halides and phenols are promising substrates for borylation and subsequent monofluoromethylation reactions. We also demonstrated the late-stage monofluoromethylation of a biologically active molecule using our monofluoro-methylation protocol (Scheme 5). Considering the mild conditions of this method and the high potential of monofluoromethyl-containing compounds as biologically active agents, this protocol promises to find more applications in the life-science-related fields. Further exploitation of CH_2FI-based chemistry is underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data for products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01361.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Basic Research Program of China (2015CB931900, 2012CB821600), the National Natural Science Foundation of China (21372246, 21421002, 21402227), Shanghai City (13QH1402400 and 15XD1504400), and the Chinese Academy of Sciences.

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