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Palladium-Catalyzed Intermolecular Aryldifluoroalkylation of Alkynes

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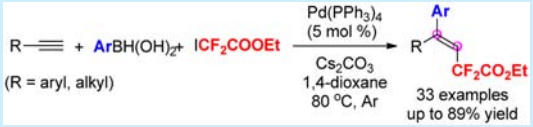
Supporting Information

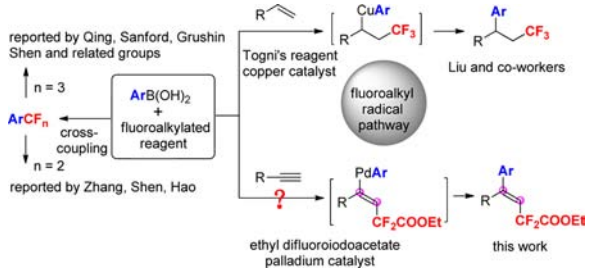
ABSTRACT: A palladium-catalyzed aryldifluoroalkylation of alkynes with ethyl difluoroiodoacetate and arylboronic acids as reaction partners is described. The alkyne difunctionalization process provides various aryldifluoroalkylated products in one pot under mild reaction conditions. A wide range of alkynes and diverse arylboronic acids are compatible with these reaction conditions. High reaction efficiency and broad substrate scope are the notable features of this transformation. Preliminary mechanistic investigations indicate that a difluoroalkyl radical addition pathway is involved in this transformation.



Because of the unique properties of fluoroalkyl groups, the synthesis of organofluorine compounds has a profound impact on the design of lead compounds in pharmaceuticals and agrochemicals.[1] Numerous methods for the incorporation of fluorine and trifluoromethyl groups have been extensively studied in the past decades.[2,3] Despite significant advances in this area, efficient and general methods for the formation of fluoroalkylated organic molecules, especially compounds containing a difluoromethyl group, have been less explored.[4,5] The CF_2 group can functionalize as an isopolar and isosteric substitute for oxygen atom.[6] Traditionally, the CF_2-containing molecules are synthesized via the reaction of aldehydes or ketones with aminosulfur trifluorides.[7] As a source of difluorinated moieties, CF_2CO_2Et is appealing not only because it is readily available, but also for its ability to be further modified into other functionalized fluoroalkyl-containing groups.[8] In this regard, various significant methods for the introduction of CF_2CO_2Et into organic molecules using a transition-metal catalyst or a visible light photocatalyst have been established.[9,10] For example, Cho and several other groups have reported the difluoroalkylation reactions of alkenes.[11] Zhang developed the difluoroalkylation of arylboronic acids with bromodifluoroacetate using a palladium catalyst and a nickel catalyst, respectively.[12] Pannecoucke and relevant groups reported an interesting generation of CF_2CO_2Et species via direct C−H functionalization.[13] However, related intermolecular difluoroalkylation reactions involving three-component coupling remains an underdeveloped process and continues to attract considerable attention from the synthetic community.

Alkynes perform irreplaceable roles in organic synthesis. Consequently, tremendous efforts based on the intermolecular difunctionalization strategy to construct *gem*-fluoroallyl units ($CF_nC{=}C$) from readily available alkynes have been established.[14] Our group is always interested in the fluoroalkylation reactions and have reported a copper-catalyzed difunctionalization of alkynes for the synthesis of β-trifluoromethylated acrylonitriles and trifluoromethyl-substituted 2*H*-azirines recently.[15] Nevertheless, most of these methodologies typically suffer from low yield of the products due to high reactivity of the vinyl radical intermediate.[16] In 2014, Hu and co-workers reported an iron-catalyzed 1,2-addition of perfluoroalkyl iodides to alkynes.[17] The strategy provides a streamlined access to perfluoroalkylated organic compounds with a wide substrate scope. However, to the best of our knowledge, the three-component aryldifluoroalkylation of alkynes by palladium catalyst has not been developed, even though cross-coupling reactions between fluoroalkylated reagents and aryl boronicacids are well established (Scheme 1).[18,19] Last year, a related copper-catalyzed intermolecular fluoroalkylarylation of alkenes was described by Liu (Scheme 1).[20] Inspired by this work, we hypothesized that the introduction of a fluoroalkyl group synchronously with an aryl group into alkynes via a 1,2-addition reaction could also be accomplished. Herein, we report a contribution toward palladium-catalyzed aryldifluoroalkylation of alkynes with the use of ethyl difluoroiodoacetate and arylboronic acids as reaction partners in one pot. The reaction

Scheme 1. Methods for Incorporation of Fluoroalkyl Groups



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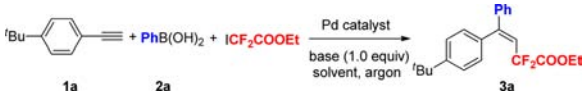
provides a straightforward way to access corresponding products and is applicable to a wide range of alkynes and organoborons.

To verify our initial hypothesis, we began our catalyst development by utilizing *tert*-butylphenylacetylene **1a**, phenylboronic acid **2a**, and ethyl difluoroiodoacetate as model substrates at 80 °C under argon. Gratifyingly, the process occurred smoothly in 1,4-dioxane with $PdCl_2(PPh_3)_2$ as a catalyst and K_2CO_3 as a base, leading to the expected aryldifluoroalkylated product **3a** in 58% yield (Table 1, entry 1). Various bases

Table 1. Optimization of the Reaction Conditions for Aryldifluoromethylation of Alkynes[a]



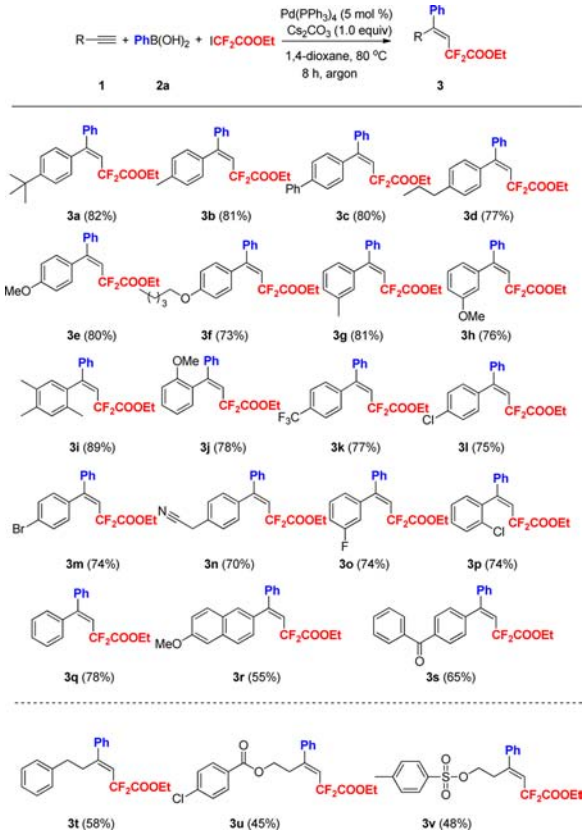
entry	catalyst[b] (mol %)	base	solvent	yield[c] (%)
1	$PdCl_2(PPh_3)_2$ (5)	K_2CO_3	1,4-dioxane	58
2	$PdCl_2(PPh_3)_2$ (5)	^tBuOK	1,4-dioxane	44
3	$PdCl_2(PPh_3)_2$ (5)	NaOAc	1,4-dioxane	8
4	$PdCl_2(PPh_3)_2$ (5)	Cs_2CO_3	1,4-dioxane	70
5	$Pd(OAc)_2$ (5)	Cs_2CO_3	1,4-dioxane	32
6	$Pd_2(dba)_3$ (5)	Cs_2CO_3	1,4-dioxane	30
7	$Pd(PPh_3)_4$ (5)	Cs_2CO_3	1,4-dioxane	82
8	$Pd(PPh_3)_4$ (5)	Cs_2CO_3	toluene	37
9	$Pd(PPh_3)_4$ (5)	Cs_2CO_3	THF	70
10	$Pd(PPh_3)_4$ (5)	Cs_2CO_3	DCE	67
11	$Pd(PPh_3)_4$ (5)	Cs_2CO_3	DMF	0
12[d]	$Pd(PPh_3)_4$ (5)	Cs_2CO_3	1,4-dioxane	70
13[e]		Cs_2CO_3	1,4-dioxane	0
14[f]	$Pd(PPh_3)_4$ (5)		1,4-dioxane	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), ethyl difluoroiodoacetate (0.3 mmol), catalyst (5 mol %), 8 h, 80 °C, under argon. [b]Number given in parentheses is mol % used. [c]Isolated yield. [d]Under air condition. [e]Without palladium catalyst. [f]Without base.

were subsequently screened, such as ^tBuOK, NaOAc, and Cs_2CO_3, among which Cs_2CO_3 was found to be the optimal one and afforded the product **3a** in 70% yield (entry 4). When the palladium catalyst was changed to $Pd(PPh_3)_4$, the yield of product **3a** could be improved to 82% (entry 7). 1,4-Dioxane still turned out to be the best choice compared to other solvents (entries 8−11). The reaction also proceeded well under an air atmosphere and gave 70% yield of the corresponding product **3a** (entry 12). Control reactions demonstrated that no desired product **3a** was observed whether the reaction was carried out in the absence of palladium catalyst or a base (entries 13 and 14).

To demonstrate the substrate scope of this reaction, a variety of alkynes were examined. As depicted in Scheme 2, high stereoselectivity with single isomers was achieved in all cases. Alkynes with various substituents on the aromatic ring were found to undergo this transformation and afforded the products **3a−v** in moderate to good yields. In general, electronic properties of substituents on the aryl group do not affect the yields of this transformation. The alkyne with a 2,4,5-trimethyl substituent on the aryl group worked pretty well and gave the corresponding product **3i** in good yield (89%). The sterically congested 2-OMe-substituted phenylacetylene was also a competent coupling partner, leading to the expected product **3j** in 78% yield. The methoxy naphthyl substrate underwent the aryldifluoroalkylation process to give product **3r** in a decreased yield. Also, a moderate yield of the product **3s** was obtained when

Scheme 2. Substrate Scope for the Aryldifluoromethylation of Alkynes[a,b]



[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), ethyl difluoroiodoacetate (0.3 mmol), $Pd(PPh_3)_4$ (5 mol %), 1,4-dioxane (1.0 mL), 8 h, 80 °C, under argon. [b]Isolated yields.

the substrate bore a benzoyl at the *para*-position. It should be mentioned that alkylalkynes underwent aryldifluoroalkylation under standard conditions, even though the yields were relatively low compared with aromatic alkyne. For example, terminal alkynes bearing a phenyl group gave the desired product **3t** in 58% yield. Products **3u** and **3v** bearing a benzoate group and a *p*-toluenesulfonyl group were obtained in 45% and 48% yields, respectively. A gram-scale reaction was also conducted, and a satisfactory yield (70%) of the product **3a** was obtained (Scheme 3).

Scheme 3. Gram-Scale Reaction

Encouraged by these results, we wished to further investigate the scope of diverse arylboronic acids (Scheme 4). Arylboronic acids that contain a range of functional groups, such as alkyl, ether, and halide, underwent the intended transformation smoothly to give the corresponding products in moderate to high yields. It was found that arylboronic acids with typical electron-withdrawing groups (such as ester or CF_3−) on the aromatic ring can be used in this transformation (**4f** and **4h**). A substrate-bearing 3,5-dichloride on the aromatic ring also

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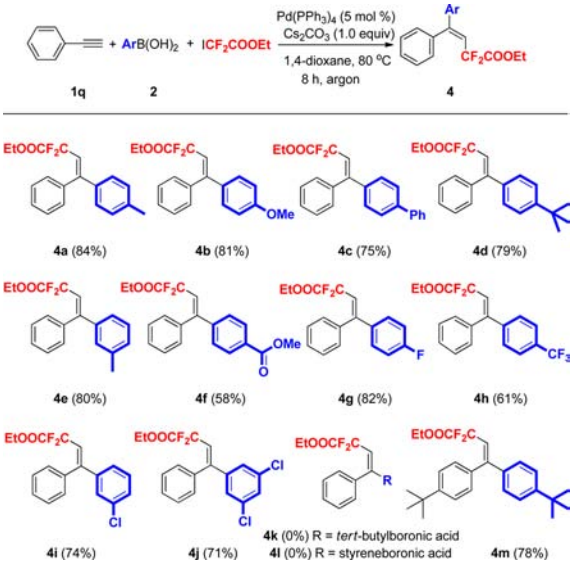
Scheme 4. Substrate Scope for the Aryldifluoromethylation of Arylboronic Acids[a,b]

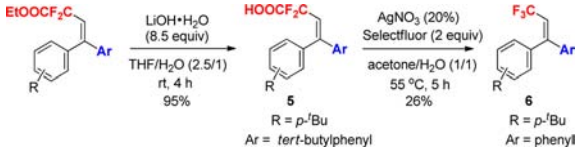


[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), ethyl difluoroiodoacetate (0.3 mmol), $Pd(PPh_3)_4$ (5 mol %), 1,4-dioxane (1.0 mL), 8 h, 80 °C, under argon. [b]Isolated yields.

proceeded with good yield (71%). Unfortunately, alkylboronic acid and styreneboronic acid failed to give the desired products (**4k** and **4l**).

Aryldifluoroalkylated products from these reactions are versatile synthetic intermediates. To prove the potential of this palladium-catalyzed process in organic synthesis, the produced products were selected as an intermediate to synthesize other fluoroalkylated organic molecules (Scheme 5). For instance, the

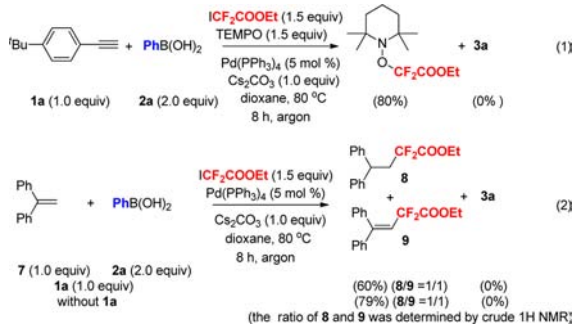
Scheme 5. Synthetic Transformations



compound 4,4-bis(4-(*tert*-butyl)phenyl)-2,2-difluorobut-3-enoic acid **5** was readily obtained by alkaline hydrolysis of the product **4m** in THF/H_2O with LiOH as a base.[8d] The compound **5** could be converted to the CF_3-containing product **6** in the presence of Selectfluor, although the yield was only 26%.[21] The trifluoromethyl-substituted compounds often displayed certain unique properties, including lipophilicity, better receptor binding selectivity, and metabolic stability.[22] Derivatizations of such aryldifluoroalkylated products highlighted the synthetic utility of this palladium catalytic system.

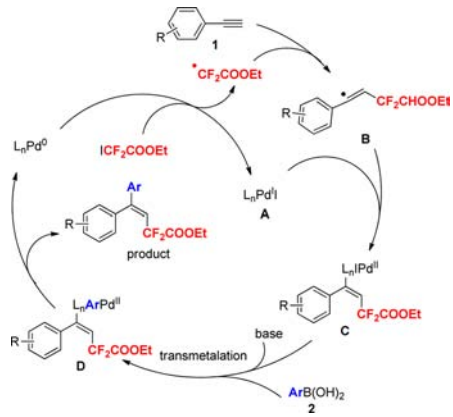
In order to rationalize the reaction pathway, two control experiments were performed. When 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added under standard conditions, no product **3a** was obtained and 80% of TEMPO−CF_2COOEt adduct was detected (Scheme 6, eq 1). When a stoichiometric amount of 1,1-diphenylethylene was used to trap the radical, no desired product was formed. By contrast, the same yields of **8** and **9** were obtained, and the yield could be increased to 79% in the absence of alkyne (Scheme 6, eq 2). These results indicate that a difluoroalkyl radical addition pathway might be involved in this

Scheme 6. Probe of the Reaction Mechanism by Trapping the Radical Intermediates



process. On the basis of the above experiments and relevant results reported,[23] a plausible mechanism was proposed in Scheme 7. Ethyl difluoroiodoacetate was first reduced by

Scheme 7. Proposed Mechanism



[Pd^0Ln] to give the difluoroalkyl radical and Pd(I) species **A**. The difluoroalkyl radical attacked the C−C triple bond of alkyne **1** to generate the radical intermediate **B**. The radical intermediate **B** reacted with Pd(I) species **A** leading to the Pd(II) species **C**. Transmetalation occurs between the Pd(II) species **C** and arylboronic acids to generate palladium(II) aryl complex **D** in the presence of the base. Subsequent reductive elimination of palladium(II) aryl complex **D** produced the aryldifluoroalkylated product and regenerated [Pd^0Ln] simultaneously.

In conclusion, we have successfully developed a palladium-catalyzed aryldifluoroalkylation of alkynes with ethyl difluoroiodoacetate and arylboronic acids in one pot. A variety of alkynes and arylboronic acids can be applied in this reaction, which makes it a general method for the synthesis of such fluoro-containing products. Preliminary mechanistic investigations indicated that a possible radical pathway was involved in this transformation. Further investigations on reaction mechanism and synthetic application of this transformation are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02512.

Detailed experimental procedures and spectral data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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