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# Pd-catalyzed direct arylation of electron-deficient polyfluoroarenes with aryliodine(III) diacetates

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## ABSTRACT

A Pd-catalyzed direct arylation of electron-deficient polyfluoroarenes with readily available aryliodine(III) diacetates was developed with moderate to good yields. The process exhibited good functional tolerance with respect to methyl, methoxy, bromo, chloro, trifluoromethyl, cyano, and aldehyde groups. Mechanistic studies revealed this coupling involved in situ generation of aryl iodide from heating-promoted decomposition of aryliodine(III) diacetate, followed by coupling with polyfluoroarenes substrates to afford the desired products.

For environmental and economical attractiveness, transition-metal-catalyzed direct arylation of aromatic C–H bonds has been a powerful tool for straightforward synthesis of valuable biaryl products from a large pool of arenes over the last decades, which usually performs a practical alternative route to the traditional cross-coupling reactions and becomes the focus of many research activities.[1] Of these reactions, electron-deficient polyfluoroarenes are extensively employed in a wide range of areas to prepare corresponding polyfluorobiaryl structural motif, ranging from the elaboration of pharmaceutical chemistry to materials science.[2,3] In this regard, some initial works include the Pd-catalyzed selective C–H bond arylation of electron-deficient polyfluoroarenes with aryl halides to synthesis of fluorobiaryl or heterocycle-containing biaryl molecules,[4] and further effort made by Daugulis led to the development of Cu-catalyzed direct arylation of polyfluoroarenes via C–H bond activation with aryl halides.[5] Su and others established oxidative C–H arylation of polyfluoroarenes with arylboronic acids,[6] organosilicon reagents,[7] and arenediazonium tetrafluoroborates,[8] respectively. However, some of the coupling partners in these reported transformations often suffer from limitations for disadvantage with regard to the use of unstable or hard to prepare organometallic reagents. In addition, elegant works in oxidative cross-coupling of polyfluoroarenes via C–H bond activation with alkenes,[9] alkynes,[10] (hetero)arenes,[11] aromatic carboxylic acids,[12] amines,[13] and sulfoximines[14] has been reported. Among these reported reactions, polyfluorobiaryls can be successfully obtained from new methodologies via oxidative cross-coupling of electron deficient polyfluoroarenes with C–H activation of (hetero)arenes[11] or decarboxylation of aromatic carboxylic acids.[12] In contrast to arylation reactions of polyfluoroaromatic C–H bond with (hetero)arenes or aromatic carboxylic acids as aryl source that have recently been attracted great attentions, nevertheless, to the best of our knowledge, no example of the direct C–H bond functionalization of electron-deficient polyfluoroarenes with aryliodine(III) diacetates as aryl source has been revealed.

Phenyliodine(III) diacetate is one of the most useful hypervalent iodine reagents, Kitamura reported an easy and cheap procedure to synthesize (diacetoxyiodo)arenes by the reaction of arenes with iodine under mild conditions (Ar-H + $I_2$).[15] Therefore, basing on its readily availability and rich chemistry,[16–18] phenyliodine(III) diacetate is widely used in considerable organic synthesis, it is not only served as a surrogate for oxidant in oxidative transformations,[17] but applied for radical reactions to generate oxygen-centered radicals and carbon-centered radicals with potential utility.[18] Furthermore, although apparent progress has been made on transition-metal-mediated coupling reactions between diaryliodonium salts as the arylation reagent and arene,[19] phenol ester,[20] alkene[21] and various nucleophiles,[22] the employment of aryliodine(III) diacetate as the arylation or acetoxylation reagents in the oxidative transformations also received considerable attentions,[23] for example, efforts made by Mao[23a] and Magedov[23b] have led to the development of palladium-catalyzed arylation of alkenes with aryliodine(III) diacetate; Suna[23c] and others[23d–f] disclosed Pd-catalyzed acetoxylation of (hetero)arenes or olefins with the employment of aryliodine(III) diacetate. Recently, the group of

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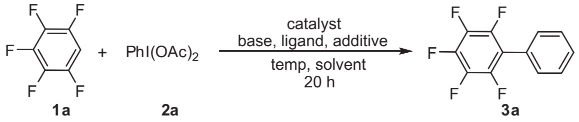
Cheng[24a] and Fairlamb[24b] reported direct arylation of benzoxazole C–H bonds with aryliodine(III) diacetate. With particular interest in the transformation reaction of electron-deficient arene C–H bond, we describe that such an attempt to use $ArI(OAc)_2$ reagents in an oxidative electron-deficient polyfluoroarene C–H bond transformation resulted in the direct arylation reaction of electron-deficient polyfluoroarene with Pd/Ag bimetallic system, and this observation represents a beneficial complement to the well documented versions of direct arylation reaction of electron-deficient polyfluoroarenes.

We initiated our investigation by taking reaction of pentafluorobenzene **1a** with iodobenzene diacetate **2a** as the model reaction for the optimization studies. Table 1 presents some selected results from these optimization studies that showed the effects of the solvent, base, and other factors on the reaction outcome. At first, using a stoichiometric $K_3PO_4$ as base in the model reaction in DMF solvent, it was found that the catalyst greatly affects reaction efficiency, the reaction of **1a** with **2a** conducted in the presence of 10 mol % $Pd(OAc)_2$ as catalyst under nitrogen atmosphere furnished desired product 2,3,4,5,6-pentafluorobiphenyl **3a** in 54% isolated yield in DMF at 130 °C (entry 3, Table 1), however, either inferior yield (23%) displayed when 20 mol % CuI instead of 10 mol % $Pd(OAc)_2$ or no product was obtained when Pd catalyst was absent (entries 1–2), the results indicated that Pd catalyst has an essential role in the catalytic reaction. Subsequently, a brief survey of the solvents under otherwise identical conditions, including polar and less polar solvents, revealed that better yields could be obtained in polar solvents than that in less polar solvent such as toluene (entries 4–9). Considering DMSO could play an important role and function as a ligand to activate the Pd catalyst and prevent the formation of palladium black,[11c,24b,25] thus, different bases were screened in the model reaction in 5% DMSO/DMF (v/v) mixed solvents (entries 10–14). Among them, $K_3PO_4$, KOAc, $KO^tBu$, $K_2CO_3$, $LiO^tBu$, and $Ag_2CO_3$ appeared to be the best choice and had a significant influence on the reaction, delivering **3a** in synthetically useful levels (76% yield) (entry 14). The effect of different loading of $Ag_2CO_3$ was the next variable evaluated, decreasing the amount of $Ag_2CO_3$ to 1.5 equiv gave comparable yield (75%), however, further reducing $Ag_2CO_3$ loading to 1 equiv led to a slightly lower yield (70%) (entries 15 and 16). Varying the ratio of DMSO to DMF in the mixed solvents system led to change in the yield, as a result, replacing 5% DMSO–DMF with 2.5% DMSO–DMF depressed the yield (entry 17). The influence of reaction temperature on the catalytic process was also investigated, studies showed that lowering reaction temperature to 110 °C did not affect the efficiency (74%), whereas unsatisfied yield (64%) was obtained when reaction conducted at 90 °C (entries 18–19). Reaction time also had significant effect on this reaction, and a shorter reaction time did not contribute to increasing the yield (entry 20).

After identifying the factors influencing the reaction outcome, the scope of this protocol with respect to polyfluoroarene was explored by employing the conditions of entry 18 in Table 1. As shown in Table 2, beside the pentafluorobenzene, a broad array of polyfluoroarenes, tetrafluoro-, trifluoro-, and even some polychloroarenes were chemoselectively arylated with (diacetoxyiodo)benzene **2a** under the standard conditions to furnish corresponding products in moderate to good yields. Electron-rich substituents such as methyl and methoxy, electron-deficient substituents such as bromo, trifluoromethyl, cyano, and aldehyde groups all could be quite well tolerated, and it was observed that the reaction was facilitated when a substituent at the *para*-position of tetrafluorobenzene derivative has electron-donating effect or p–pi conjugation effect (**3a–d**), on the contrary, the reaction was undermined when an electron-withdrawing group at the *para*-position of tetrafluorobenzene derivative (**3e–g**). 1,2,3,5-tetrafluorobenzene and 1,2,4,5-tetrafluorobenzene, each of which possesses two potential reaction sites, generated mixtures of mono- and di-substituted arylation products (**3i** and **3i′**, **3j** and **3j′**) in 62% and 57% overall yield, respectively. Interestingly, arylation of pentachlorobenzene was also achieved (**3h**), the low yield suggested that a C–H bond flanked with chlorine atoms was less

**Table 1**
Selected results of screening the optimal conditions[a]

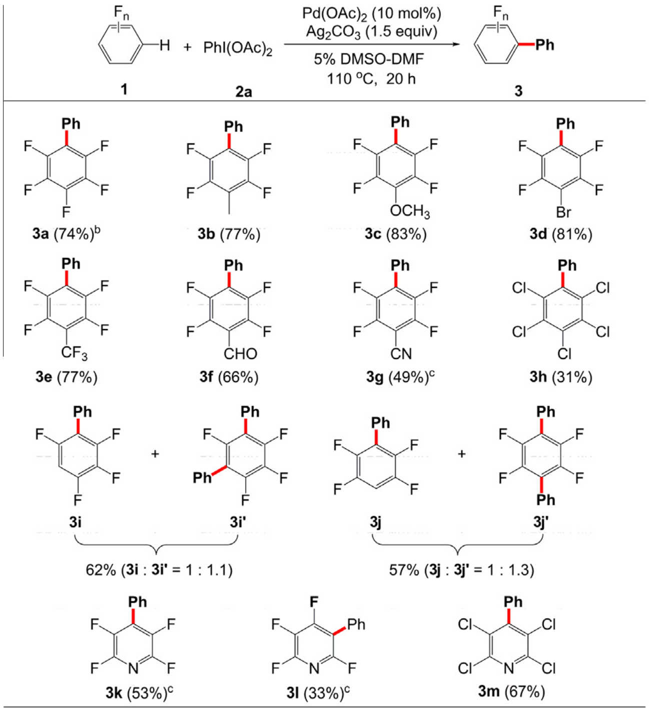


| Entry | Catalyst (mol %) | Base (equiv) | Temp. (°C) | Solvent | Isolated yield (%) |
|---|---|---|---|---|---|
| 1 | – | $K_3PO_4$ (**2**) | 130 | DMF | 0 |
| 2 | CuI (**20**) | $K_3PO_4$ (**2**) | 130 | DMF | 23 |
| 3 | $Pd(OAc)_2$ (**10**) | $K_3PO_4$ (**2**) | 130 | DMF | 54 |
| 4 | $Pd(OAc)_2$ (**10**) | $K_3PO_4$ (**2**) | 130 | DMSO | 37 |
| 5 | $Pd(OAc)_2$ (**10**) | $K_3PO_4$ (**2**) | 130 | NMP | 36 |
| 6 | $Pd(OAc)_2$ (**10**) | $K_3PO_4$ (**2**) | 130 | $CH_3CN$ | 24 |
| 7 | $Pd(OAc)_2$ (**10**) | $K_3PO_4$ (**2**) | 130 | THF | 20 |
| 8 | $Pd(OAc)_2$ (**10**) | $K_3PO_4$ (**2**) | 130 | Toluene | <5 |
| 9 | $Pd(OAc)_2$ (**10**) | $K_3PO_4$ (**2**) | 130 | 5% DMSO–DMF | 39 |
| 10 | $Pd(OAc)_2$ (**10**) | KOAc (**2**) | 130 | 5% DMSO–DMF | 43 |
| 11 | $Pd(OAc)_2$ (**10**) | $KO^tBu$ (**2**) | 130 | 5% DMSO–DMF | 40 |
| 12 | $Pd(OAc)_2$ (**10**) | $K_2CO_3$ (**2**) | 130 | 5% DMSO–DMF | <5 |
| 13 | $Pd(OAc)_2$ (**10**) | $LiO^tBu$ (**2**) | 130 | 5% DMSO–DMF | 35 |
| 14 | $Pd(OAc)_2$ (**10**) | $Ag_2CO_3$ (**2**) | 130 | 5% DMSO–DMF | 76 |
| 15 | $Pd(OAc)_2$ (**10**) | $Ag_2CO_3$ (**1.5**) | 130 | 5% DMSO–DMF | 75 |
| 16 | $Pd(OAc)_2$ (**10**) | $Ag_2CO_3$ (**1**) | 130 | 5% DMSO–DMF | 70 |
| 17 | $Pd(OAc)_2$ (**10**) | $Ag_2CO_3$ (**1.5**) | 130 | 2.5% DMSO–DMF | 69 |
| **18** | **$Pd(OAc)_2$ (10)** | **$Ag_2CO_3$ (1.5)** | **110** | **5% DMSO–DMF** | **74** |
| 19 | $Pd(OAc)_2$ (**10**) | $Ag_2CO_3$ (**1.5**) | 90 | 5% DMSO–DMF | 64 |
| 20[b] | $Pd(OAc)_2$ (**10**) | $Ag_2CO_3$ (**1.5**) | 110 | 5% DMSO–DMF | 66 |

[a] Conditions: **1a** (0.2 mmol), **2a** (1.2 equiv), solvent (2 mL), 20 h.

[b] Reaction run for 10 h.

**Table 2**
Pd-catalyzed direct arylation of polyfluoroarenes with iodobenzene diacetate[a]



[a] Reaction conditions: polyfluoroarene **1** (0.2 mmol), **2a** (1.2 equiv), $Pd(OAc)_2$ (10 mol %), $Ag_2CO_3$ (1.5 equiv), 5% DMSO–DMF (2 mL), 110 °C, 20 h.

[b] 1 mmol scale.

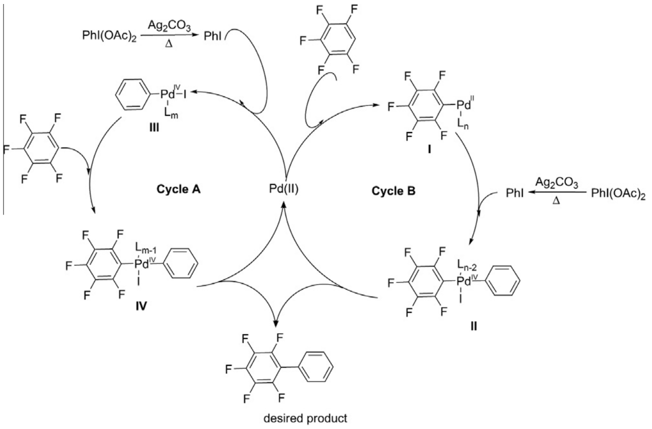
[c] Reaction conducted at 130 °C.

reactive probably due to its decreased acidity. Heteroaromatic compounds proved to be suitable substrates, regardless of the presence of fluoro or chloro substituent on the pyridine ring (**3k**, **3l**, and **3m**), albeit in moderate yields for tetrafluoropyridine (**3k** and **3l**) under a slightly elevated temperature. Notably, 1-bromo-2,3,5,6-tetrafluorobenzene, pentachlorobenzene, and tetrachloropyridine formed the hoped-for products (**3d**, **3h**, and **3m**) with the halogen moieties (–Br, Cl) remaining intact, which could be used for installing other functional groups via the transformations of the C–Hal bonds, providing the potential application of this methodology. This reaction can be scaled up, for example, as illustrated by the reaction on 1 mmol scale that offered an equal yield (74%) comparable to that on 0.2 mmol scale (**3a**, Scheme 1).

Using Kitamura's method (Ar-H + $I_2$),[15] (diacetoxyiodo)benzene derivatives **4a**–**c** were prepared from corresponding arene under mild conditions. Subsequently, the direct arylation coupling of (diacetoxyiodo)benzene derivatives with pentafluorobenzene **1a** was also investigated under standard conditions. The results are summarized in Table 3, (diacetoxyiodo)benzene derivatives bearing methyl, bromo, and chloro groups served as arylating reagents for the direct arylation of pentafluorobenzene and proceeded with quantitative conversion. The phenyl core of $ArI(OAc)_2$ bearing electron-donating group gave moderate yield (**4a**), whereas bearing electron-withdrawing groups furnished good yields, for example, satisfied yields were gave when p-halogen (Br, Cl) substitution on the phenyl ring of (diacetoxyiodo)benzene (**4b–c**).

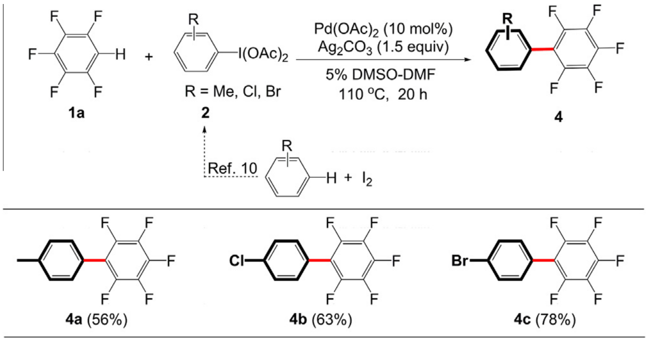
Some observations were performed to gain some insights into the reaction mechanism. Firstly, GC–MS and NMR spectroscopic analysis revealed that iodobenzene was produced when heating compound **2a** with 1 equiv of $Ag_2CO_3$ in 5% DMSO–DMF under nitrogen at 110 °C for 2 h, this result is consistent with the literature reported by Fairlamb and co-workers very recently.[24b] Moreover, the reaction of pentafluorobenzene **1a** with this freshly generated iodobenzene under the standard reaction conditions was analyzed by $^1H$ NMR and got indication of stoichiometric conversion into desired product **3a**. Although the reaction between polyfluoroarenes and iodobenzene was reported by Fagnou and others,[4a,4b,4d] however, the reaction of polyfluoroarenes with (diacetoxyiodo)arenes provides an indirect method to produce polyfluorobiaryls via the coupling of electron-deficient polyfluoroarenes with arenes.

Consequently, two different Pd(II)/Pd(IV) mechanisms were assumed for this arylation of pentafluorobenzene with iodobenzene diacetate.[6,24a] As illustrated in Scheme 1, Cycle A involves the initial formation of aryl-Pd(IV) species **III** via the oxidative addition of the in situ generated iodobenzene to original Pd(II), followed by the palladation of pentafluorobenzene via concerted metalation–deprotonation[4a] and subsequent reductive elimination. Cycle B begins with the formation of pentafluorophenyl-Pd(II) species **I** via the activation of the C–H bond of pentafluorobenzene, followed by the oxidative addition of the in situ generated iodobenzene to pentafluorophenyl-Pd(II) species and then reductive elimination. In this regard, multiple roles were assigned to $Ag_2CO_3$ as the base and promoter in transformation. Considering the oxidative addition of the in-situ generated iodobenzene to original Pd(II) is easier than that to pentafluorophenyl-Pd(II) species **I**, thus, the reaction is possible to favor Cycle A as the catalytic cycle in this transformation.



**Scheme 1.** Two assumed mechanisms of the transformation.

**Table 3**
Pd-catalyzed direct arylation of pentafluorobenzene with (diacetoxyiodo)benzene derivatives[a]



[a] Reaction conditions: Pentafluoroarene **1a** (0.2 mmol), **2** (1.2 equiv), $Pd(OAc)_2$ (10 mol %), $Ag_2CO_3$ (1.5 equiv), 5% DMSO-DMF (2 mL), 110 °C, 20 h.

In summary, we have established a new Pd-catalyzed method for direct arylation of various electron-deficient polyfluoroarenes featuring the use of inexpensive and readily available aryliodine(III) diacetates as the aryl source. Preliminary mechanistic studies disclosed that this reaction involved in situ generation of aryl iodide from the heating of aryliodine diacetate in the presence of a base, followed by coupling of polyfluoroarene to give the target product. The characteristics of good functional group tolerance and yields provide the described procedure with a broad utility in organic synthesis. Efforts are currently underway to improve the efficiency of this reaction further and investigate the mechanism more detailedly.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.11.033.

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