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COMMUNICATION

Pd-catalyzed Divergent Trifluoroethylation and Arylation of Arylboronic Acids by Aryl(2,2,2-trifluoroethyl)iodonium Triflates

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**The highly electrophilic aryl(2,2,2-trifluoroethyl)iodonium triflates are first used as trifluoroethyl and aryl transfer reagents in Pd-catalyzed functionalization of arylboronic acids. The electron-rich arylboronic acids reacting with aryl(2,2,2-trifluoroethyl)iodonium triflates (2a-b) in CH_3CN in the presence of $Pd_2(dba)_3$ and K_3PO_4 at room temperature provided trifluoroethyl arenes in up to 82% yield, whereas the reactions of both electron-rich and -poor arylboronic acids with 2a-b in DMF in the presence of Pd[P(t-Bu)$_3$]$_2$ and Cs_2CO_3 at 40 ^{o}C afforded the arylation products in up to 99% yield. This tunable protocol allows for a mild access to trifluoroethyl arenes or biaryls in good to high yields without addition of extra ligands.**

Fluorine-containing organic compounds have found wide applications in the areas of chemistry, biology, and materials science over the past several decades.[1] Because only few naturally-occurring organofluorides were discovered in nature, the fluorinated organic compounds including the recent prevalent CF_3CH_2-subsituted ones have to be manually synthesized.[2,3,4] The first direct 2,2,2-trifluoroethylation was reported by McLoughlin and Thrower in 1969.[5] Since then, especially in the last several years, the direct 2,2,2-trifluoroethylation of organic scaffolds, such as arylboronic acids or esters, aryl iodides, arene, alkynes, and alkenes, by CF_3CH_2X (X = Br, I), CF_3CHCl_2, $CF_3CH_2SO_2Y$ (Y = Na, Cl), CF_3CH_2OTs, or $CF_3CH_2NH_2$, has been explosively investigated.[6,7,8] These commercially available trifluoroethylation reagents, however, suffer from disadvantages,[3] which lead to that the incorporation of CF_3CH_2 functionality by transition-metal mediated/catalyzed direct 2,2,2-trifluoroethylation is less effective than that indirectly by trifluoromethylation under the similar reaction conditions.[4] To solve these problems, the exploitation of effective catalytic systems and versatile trifluoroethylation reagents would be increasingly important.[3]

Aryl(perfluoroalkyl)iodoniums, first synthesized by Yagupolskii and then developed by Umemoto and Togni, are well-known electrophilic perfluoroalkylation reagents.[2e,2h,9] Among these salts,

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aryl(2,2,2-trifluoroethyl)iodoniums have been demonstrated as the efficient trifluoroethylation reagents for heteroatom and soft carbon nucleophiles, such as amines, peptides, alcohols, phenols, thiols, sulfides, thioglycosides, phosphines, carbanions, silyl enol ethers and etc, which construct the crucial N-CH_2CF_3, O-CH_2CF_3, S-CH_2CF_3, P-CH_2CF_3, and C-CH_2CF_3 bonds in a large number of bioactive molecules.[10] Aryl(2,2,2-trifluoroethyl)iodoniums have shown much more powerful "CH_2CF_3" transfer ability than CF_3CH_2X (X = I, OTf, OTs) in S_N2-type conversions.[10] Inspired by our previous works on trifluoromethyl sulfonium salts,[2h] we imagine that the highly electrophilic aryl(2,2,2-trifluoroethyl)iodoniums may be good participants in transition-metal mediated/catalyzed cross-coupling reactions. To our knowledge, there is only one report of transition-metal mediated/catalyzed direct 2,2,2-trifluoroethylation using aryl(2,2,2-trifluoroethyl)iodonium as the "CH_2CF_3" source.[11]

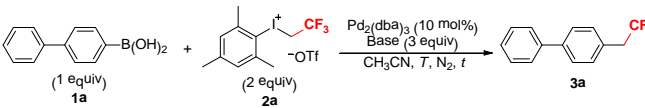Previous direct and "indirect" trifluoroethylations
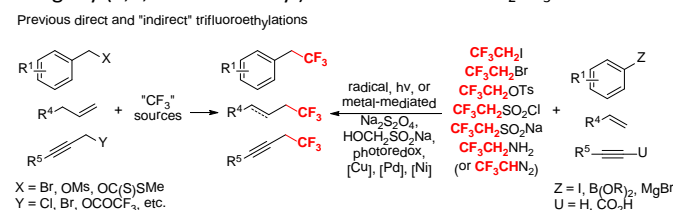
To gain more insights into this area, we initially tested the reaction of 1,1'-biphenyl-4-ylboronic acid (**1a**) with mesityl(2,2,2-trifluoroethyl)iodonium triflate (**2a**) in the presence of diverse Pd-catalysts at room temperature (see SI). It was found that the reaction with Pd(dba)$_2$ or Pd$_2$(dba)$_3$ worked better than those with PdCl$_2$, Pd(PCy)$_3$, Pd(OAc)$_2$, and Pd[P(t-Bu)$_3$]$_2$ in CH_2Cl_2 using NaHCO$_3$, which gave **3a** in 9% or 6% yield, respectively. CH_3CN seems to be the appropriate solvent among CH_2Cl_2, 1,4-dioxane, toluene, DMF, DMSO, and THF (see SI). The reaction of **1a** with **2a** in CH_3CN in the presence of Pd$_2$(dba)$_3$ (10 mol%) and NaHCO$_3$ (1 equiv) at room temperature under a N_2 atmosphere for 24 h provided **3a** in 15% yield. Moreover, the choice of bases has a big impact on the reaction (see SI). Treatment of **1a** with **2a** in CH_3CN in the presence of 2 equiv of NaHCO$_3$ or CsF supplied **3a** in 26% or 29% yield, respectively, while the reaction run with K$_3$PO$_4$ (2 equiv) afforded **3a** in 52% yield. Taking Cs$_2$CO$_3$ instead of K$_3$PO$_4$ led to 2% of **3a** and 19% of 2,4,6-Trimethyl-1,1':4',1''-terphenyl (**4a**) (see SI). Further increasing the equivalent of K$_3$PO$_4$ (to 3 equiv) and prolonging the reaction time (to 48 h) gently improved the yield of **3a** (58%, entry 5, Table 1).

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Table 1 Trifluoroethylation of **1a** by **2a** at room temperature in the presence of Pd$_2$(dba)$_3$.[a]
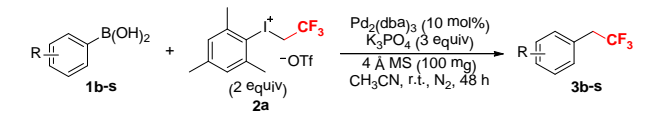
entry	base	T (°C) / t (h)	yield (**3a**, %)[b]
1[c]	NaHCO$_3$	r.t. / 24	26
2[c]	K$_3$PO$_4$	r.t. / 24	52
3[c]	Cs$_2$CO$_3$	r.t. / 24	2
4[c]	*t*-BuOK	r.t. / 24	12
5	K$_3$PO$_4$	r.t. / 48	58
6[d]	K$_3$PO$_4$	r.t. / 24	42
7[e]	K$_3$PO$_4$	r.t. / 24	67
8[e]	**K$_3$PO$_4$**	**r.t. / 48**	**80 (73)**
9[e,f]	K$_3$PO$_4$	r.t. / 48	76
10[e,g]	K$_3$PO$_4$	r.t. / 48	70
11[e]	none	r.t. / 48	39
12	none	r.t. / 48	0
13[c,h]	**Cs$_2$CO$_3$**	**40 / 48**	**96 (84)**[i]
14[c,h,j]	Cs$_2$CO$_3$	40 / 48	91[i]

[a] Reaction conditions: **1a** (0.1 mmol) / **2a** (0.2 mmol) / base (0.3 mmol) / Pd$_2$(dba)$_3$ (10 mol%) / solvent (2 mL) / N$_2$. [b] Yields were determined by HPLC using 4-(2,2,2-trifluoroethyl)-1,1'-biphenyl (**3a**) as the external standard (see SI). Isolated yield is depicted in the parentheses. [c] Base (0.2 mmol). [d] H$_2$O (32.4 mg, 1.8 mmol) was added. [e] 4 Å molecular sieves (4 Å MS, 100 mg) was used. [f] 7.5 mol% Pd$_2$(dba)$_3$. [g] 5 mol% Pd$_2$(dba)$_3$. [h] DMF was used as the solvent and Pd[P(*t*-Bu)$_3$]$_2$ (10 mol%) as the catalyst. Yield of 2,4,6-trimethyl-1,1':4',1''-terphenyl (**4a**). [j] 5 mol% Pd[P(*t*-Bu)$_3$]$_2$.

The reaction is sensitive to the additives. When 18 equiv of water was added into a mixture of **1a** (0.1 mmol), **2a** (0.2 mmol), K$_3$PO$_4$ (0.3 mmol), Pd$_2$(dba)$_3$ (10 mol%), and CH$_3$CN (2 mL) at room temperature under a N$_2$ atmosphere for 24 h, **3a** was obtained in 42% yield (entry 6, Table 1). This is contradictory to the Pd-catalyzed trifluoroethylation using CF$_3$CH$_2$I, where the water benefited the reaction.[8a,8b] Notably, if 4 Å molecular sieves, anhydrous Na$_2$SO$_4$ or CaSO$_4$, or allochroic silicagel was employed in the reaction, higher yields of **3a** was achieved (59-67% yield, see SI). The reaction of **1a** (0.1 mmol) with **2a** (0.2 mmol) and K$_3$PO$_4$ (0.3 mmol) in the presence of 10 mol% Pd$_2$(dba)$_3$ and 4 Å molecular sieves (100 mg) in CH$_3$CN at room temperature under a N$_2$ atmosphere for 48 h afforded **3a** in 80% yield (entry 8, Table 1). Further prolonging the reaction time to 3 days didn't continuously improve the reaction (see SI). Elevating the reaction temperature from r.t. to 30 °C facilitated the transformation, which gave **3a** in 72% yield after 24 h (72% vs 67%), while the reaction run at 50 °C for 24 h afforded a lower yield of **3a** (59% vs 67%) (see SI). Furthermore, the addition of bulky phosphine ligands into the reaction mixtures of **1a** (0.1 mmol), **2a** (0.2 mmol), K$_3$PO$_4$ (0.3 mmol), Pd$_2$(dba)$_3$ (10 mol%), 4 Å molecular sieves (100 mg), and CH$_3$CN (2 mL) moderately inhibited the trifluoroethylation, providing **3a** in 35-63% yield (see SI). Decreasing the catalyst loading of Pd$_2$(dba)$_3$ from 10 mol% to 7.5 mol% or 5 mol% only slightly lowered the yields of **3a** (entries 9 and 10, Table 1). The reaction of **1a** with **2a** in the absence of base gave **3a** in 39% yield (entry 11, Table 1). If the reaction was run with neither base nor

additive, no **3a** was obtained (entry 12, Table 1), indicating that the base is essential to the reaction. Interestingly, if the reaction of **1a** and **2a** was conducted in DMF in the presence of Cs$_2$CO$_3$ (2 equiv) and Pd[P(*t*-Bu)$_3$]$_2$ (10 mol%) at 40 °C for 48 h, the mesitylation product (**4a**) was obtained in 96% yield (84% isolated yield) (entry 13, Table 1). The reaction run at room temperature could also afford **4a** in good yields (see SI). The uses of Cs$_2$CO$_3$, Pd[P(*t*-Bu)$_3$]$_2$[12] and DMF facilitated the arylation and prohibited the trifluoroethylation.

Moreover, the addition of 2 equiv of TEMPO into the reaction mixture of **1a**, **2a**, K$_3$PO$_4$, Pd$_2$(dba)$_3$, 4 Å molecular sieves, and CH$_3$CN severely inhibited the trifluoroethylation, which might be attributed to the direct decomposition of **2a** by TEMPO (see SI). In contrast, when styrene was used as a radical trapping agent instead of TEMPO in the reaction, **3a** was formed in 84% yield (vs 80%). Furthermore, if TEMPO or styrene was employed in the arylation of **1a** by **2a** in the presence of Cs$_2$CO$_3$ and Pd[P(*t*-Bu)$_3$]$_2$ in DMF, no significant changes in the yield of **4a** were observed. These data suggest a non-radical process for the transformations. Since CF$_3$CH$_2$I was detected by ^{19}F NMR spectroscopy in the reaction mixture of **1a**, **2a**, Cs$_2$CO$_3$, Pd[P(*t*-Bu)$_3$]$_2$, and DMF (see SI), the cleavage of the C$_{Ar}$-I bond of **2a** should be involved in the conversion. However, arylation of **1a** by mesityl iodide cannot be excluded, which was generated from the decomposition of **2a** during the reaction (see SI). This is because **1a** reacting with mesityl iodide at 40 °C under the standard arylation conditions could also give **4a** in high yield (see SI). Nevertheless, the same reaction at room temperature provided **4a** in a much lower yield than that with **2a** in either the presence or absence of the additives, implying that arylation of **1a** by **2a** is not identical to that by mesityl iodide (see SI). Importantly, the control experiments also support that **2a** is a powerful arylation reagent, which is ranged between mesityl iodide and dimesityliodonium triflate (see SI).

Table 2 The Pd-catalyzed trifluoroethylation of arylboronic acids by **2a** or **2b** at room temperature.[a]
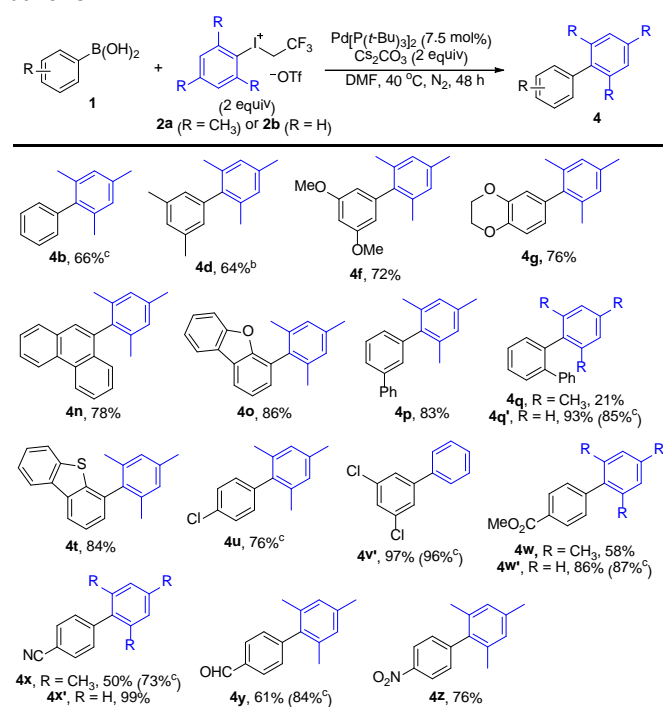

[a] Reaction conditions: **1a** (0.4 mmol) / **2a** (0.8 mmol) / K$_3$PO$_4$ (1.2 mmol) / Pd$_2$(dba)$_3$ (0.04 mmol) / 4 Å MS (400 mg) / CH$_3$CN (8 mL) / r.t. / N$_2$ / 2 d. Isolated yields. [b] Yield was determined by ^{19}F NMR

spectroscopy using PhCF$_3$ as an internal standard. [c] **2b** (2 equiv) was used instead of **2a**.

With the optimized reaction conditions in hand, the scopes of the reactions were examined (**Table 2**). To our delight, arylboronic acids such as phenyl-, *p*-tolyl-, (3,5-dimethylphenyl)-, (4-methoxyphenyl)-, (2,3-dihydrobenzo[1,4]dioxin-6-yl)-, (4-(*tert*-butyl)phenyl)-, (4-phenoxyphenyl)-, (4-(benzyloxy)phenyl)-, and (4-(benzyloxy)-3-chlorophenyl)boronic acids (**1b-e**, **1g-k**) reacting with **2a** in CH$_3$CN in the presence of 10 mol% of Pd$_2$(dba)$_3$ at room temperature under N$_2$ for 48 h gave the corresponding 2,2,2-trifluoroethylation products (**3b-e**, **3g-k**) in 47-82% yields. Treatment of naphthalen-2-ylboronic acid (**1l**), (6-methoxynaphthalen-2-yl)boronic acid (**1m**), phenanthren-9-ylboronic acid (**1n**), or dibenzofuran-4-ylboronic acid (**1o**) with **2a** under the standard reaction conditions afforded **3l**, **3m**, **3n**, or **3o** in 68%, 57%, 50%, or 44% yield, respectively. The position of substituents on the phenyl rings has great influence on the reaction. For instance, the reaction of [1,1'-biphenyl]-3-ylboronic acid (**1p**) with **2a** provided **3p** in 59% yield, whereas [1,1'-biphenyl]-2-ylboronic acid (**1q**) reacting with **2a** furnished trace of **3q**, which was determined by ^{19}F NMR.

When the reaction of **1b**, **1d**, **1f**, **1g**, **1n**, **1o**, or **1p** and **2a** was performed in DMF in the presence of 5-10 mol% Pd[P(*t*-Bu)$_3$]$_2$ and 2 equiv of Cs$_2$CO$_3$ at 40 ^{o}C, the respective arylation product **4b**, **4d**, **4f**, **4g**, **4n**, **4o**, or **4p** rather than **3b**, **3d**, **3f**, **3g**, **3n**, **3o**, or **3p** was obtained (64-86% yields, **Table 3**). In contrast to trifluoroethylation, the Pd-catalyzed arylation of the sterically hindered **1q** with **2a** gave **4q** in 21% yield. Furthermore, dibenzothiophen-4-ylboronic acid (**1t**) and the electron-deficient arylboronic acids such as (4-(methoxycarbonyl)phenyl)-, (4-cyanophenyl)-, (4-formylphenyl)-, and (4-nitrophenyl)boronic acids (**1w-z**), which failed to trifluoroethylate by **2a** in CH$_3$CN in the presence of Pd$_2$(dba)$_3$, were all favorably mesitylated under the standard reaction conditions (50-84% yields). The reactions with 10 mol% Pd[P(*t*-Bu)$_3$]$_2$ gave higher yields of the arylation products (e.g. **4x** and **4y**).

Table 3 The Pd-catalyzed arylation of arylboronic acids by **2a** or **2b** at 40 ^{o}C.[a]

4b, 66%[c]   **4d**, 64%[b]   **4f**, 72%   **4g,** 76%

4n, 78%   **4o**, 86%   **4p**, 83%   **4q**, R = CH$_3$, 21%
4q', R = H, 93% (85%[c])

4t, 84%   **4u**, 76%[c]   **4v'**, 97% (96%[c])   **4w**, R = CH$_3$, 58%
4w', R = H, 86% (87%[c])

4x, R = CH$_3$, 50% (73%[c])
4x', R = H, 99%   **4y**, 61% (84%[c])   **4z**, 76%

In addition to **2a**, phenyl(2,2,2-trifluoroethyl)iodonium triflate (**2b**) is an available reagent in these reactions. Treatment of **1a** with **2b** in the presence of K$_3$PO$_4$, 10 mol% Pd$_2$(dba)$_3$, and 4 Å molecular sieves in CH$_3$CN at room temperature under N$_2$ for 48 h provided **3a** in 69% yield, while the reaction of **1a** and **2b** in DMF in the presence of 10 mol% Pd[P(*t*-Bu)$_3$]$_2$ and Cs$_2$CO$_3$ (2 equiv) at 40 ^{o}C under N$_2$ for 48 h afforded 1,1':4',1''-terphenyl (**4a'**) in 93% yield (see SI). The steric hindrance and electronic nature of ary(2,2,2-trifluoroethyl)iodoniums may affect the reactions.[13] The relatively electron-poor and less sterically hindered phenyl group of **2b** seems easier to transfer. The reaction of **1x** with **2a** (steric and electron-rich) under the standard conditions provided **4x** in 50% yield, whereas the reaction of **1x** with **2b** (less steric and electron-rich) furnished **4x'** in 99% yield. Even the steric **1q** reacted with **2b** under the standard reaction conditions producing **4q'** in 93% yield (vs **4q** in 21% yield). Increasing the catalyst loading of Pd[P(*t*-Bu)$_3$]$_2$ from 7.5 mol% to 10 mol%, no remarkable improvement of the arylation with **2b** was observed (e.g. **4q'**, **4v'**, and **4w'**); this is different from that using **2a** as the reagent (e.g. **4x** and **4y**). On the other hand, the commonly used trifluoroethylation reagents like **2c-e** were investigated in the reaction. Treatment of **1a** with **2c**, **2d**, or **2e** under the standard reaction conditions, no desired product (**3a**) was obtained, indicating that aryl(2,2,2-trifluoroethyl)iodoniums are much more effective than trifluoroethyl iodide and sulfonates in Pd-catalyzed direct trifluoroethylation of arylboronic acids without using extra ligands.
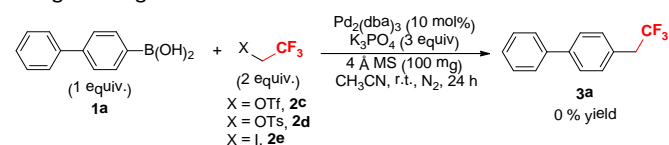
Scheme 1 The failure of Pd-catalyzed trifluoroethylation with **2c-e**

In conclusion, we have found that aryl(2,2,2-trifluoroethyl)iodonium triflates can be used as "CH$_2$CF$_3$" and aryl transfer reagents in the Pd-catalyzed transformation of arylboronic acids. The nature of Pd-catalysts, bases, and solvents dramatically influenced the reaction. When the reaction of the electron-rich arylboronic acids with **2a** or **2b** was performed in CH$_3$CN in the presence of Pd$_2$(dba)$_3$ and K$_3$PO$_4$ at room temperature, the trifluoroethylation products were obtained in good yields. While reaction of either the electron-rich or -poor arylboronic acids with **2a** or **2b** was run in DMF in the presence of Pd[P(*t*-Bu)$_3$]$_2$ and Cs$_2$CO$_3$ at 40 ^{o}C, the arylation products were prepared in good to high yields. Iodonium **2b** appears to be a better arylation reagent than **2a** in the reaction. This tunable protocol provides a mild access to trifluoroethyl arenes and biaryls without additional ligands, which represents the first use of aryl(2,2,2-trifluoroethyl)iodoniums as both trifluoroethylation and arylation reagents in the presence of Pd-catalysts. The application of this strategy to new systems and the mechanistic study of the transformations are currently underway in our lab.

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