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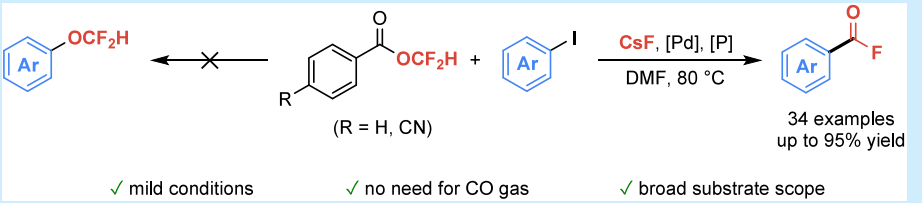
Pd-Catalyzed Fluorocarbonylation of Iodoarenes with Difluoromethyl Benzoates

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ABSTRACT: Palladium-catalyzed fluorocarbonylation of iodoarenes using difluoromethyl benzoate (DFBz) or difluoromethyl *p*-cyano-benzoate (DFBz-CN) as a fluorocarbonylation reagent has been developed, affording structurally diverse acyl fluorides as products. Both DFBz and DFBz-CN reagents are conveniently prepared through insertion of difluorocarbene into the O−H bonds of carboxylic acids. The activation of these two difluoromethyl benzoates with CsF generates formyl fluoride (HCOF), which readily decomposes into CO and HF. Therefore, both DFBz and DFBz-CN can be successfully used as safe surrogates of CO. This study provides not only a new synthetic method for fluorocarbonylation but also intriguing insights into the different reactivity between the previously known trifluoromethyl benzoate (TFBz, an effective CF_3O^- synthon) and the currently studied difluoromethyl benzoate (DFBz, not a satisfactory HCF_2O^- synthon).

Fluorinated molecules hold substantial importance in contemporary chemical synthesis owing to the unique capability of fluorine atoms to modulate critical physicochemical properties, including metabolic stability, lipophilicity, and bioequivalence.[1] Beyond their biological relevance, these compounds serve as versatile synthons in demanding synthetic transformations.[2] Among them, acyl fluorides exemplify highly reactive fluorinated species, where both the resonance (electron-donating) and inductive (electron-withdrawing) effects of fluorine represent a delicate equilibrium between electrophilic reactivity and structural stability.[3] This trade-off allows acyl fluorides to function as selective synthetic intermediates, efficiently conjugating nucleophiles like alcohols, thiols, and amines to construct structurally diverse biolinkers.[4] Additionally, their utility extends to serving as multifunctional reagents, functioning simultaneously as fluorine donors and carbonyl transfer agents in multicomponent reactions (Scheme 1A).[5]

Current synthetic strategies for the preparation of acyl fluorides mainly fall into two categories: (1) dehydroxyfluorination of carboxylic acids, which typically relies on harsh reaction conditions and hazardous fluorinating agents such as cyanuric fluoride,[6] HF·pyridine,[7] DAST,[8] and Deoxo-Fluor,[9] and (2) transition-metal-catalyzed fluorocarbonylation of halocarbons, which is limited by its dependence on highly toxic carbon monoxide (CO) as the carbonyl source, thereby restricting practical applications.[5] These inherent limitations underscore the need for safer and more sustainable synthetic methods for acyl fluoride synthesis.

The past decade has witnessed renewed interest in fluorocarbonylation, which is driven by advances in safer CO surrogates.[10] Early approaches by Undo (using *N*-formylsaccharin)[4] and Shibata (using 2-difluoromethoxypyridine[11]) as a formyl fluoride precursor demonstrated the Pd-catalyzed fluorocarbonylation under palladium catalysis. While formyl fluoride (HCOF) is postulated as the active species, its intrinsic instability and low operational concentrations pose significant challenges. Notably, Shibata's protocol requires NaH for reagent synthesis, which may complicate large-scale applications. These limitations underscore the critical need for simplified reagents to enhance synthetic practicality.

Previously, we developed trifluoromethyl benzoate (TFBz) as a bench-stable trifluoromethoxylation reagent, enabling controlled release of the trifluoromethoxide anion (CF_3O^-) for nucleophilic trifluoromethoxylation of arynes and alkyl halides (Scheme 1B).[12] Owing to the rapid decomposition of the difluoromethoxide anion (HCF_2O^-) into F^- and HCOF,[13] however, extending this strategy to the analogous difluoromethyl benzoate (DFBz) for the nucleophilic difluoromethoxylation failed. Even under CsF-induced conditions at −50

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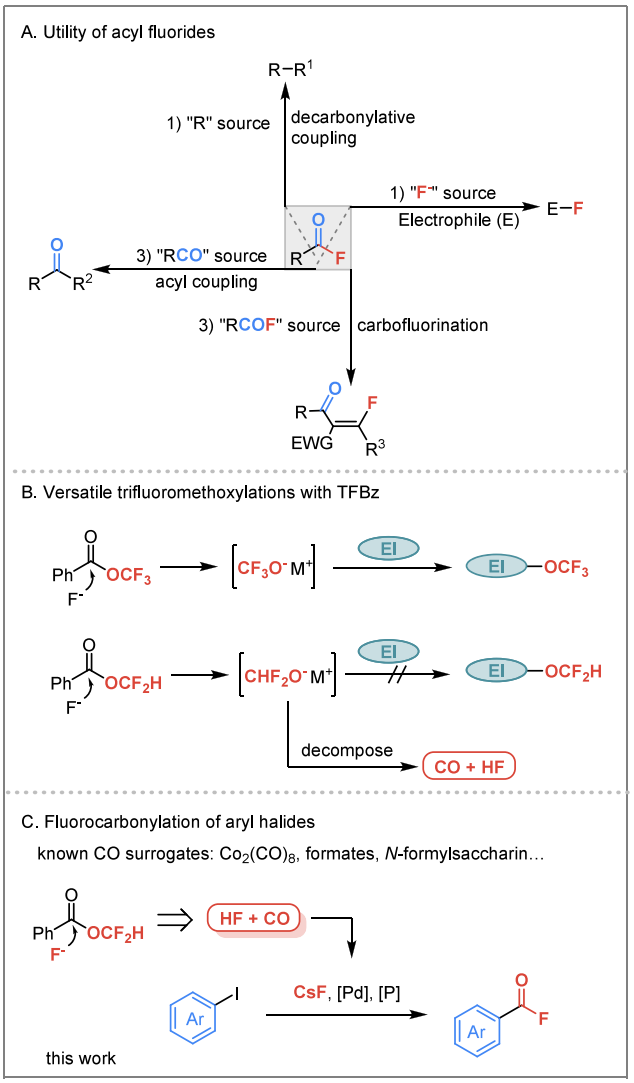


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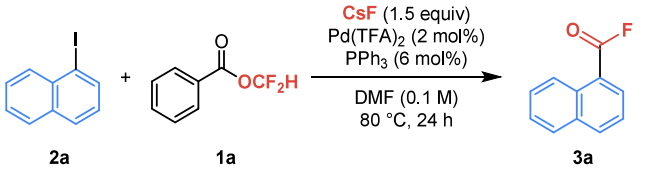
Scheme 1. Utility and Synthesis of Acyl Fluorides



°C, DFBz still underwent slow decomposition, smoothly liberating the CO gas. However, the absence of NMR signals for both HCF_2O^- and HCOF during the decomposition led us to conclude that HCOF itself also underwent rapid decomposition into CO under these conditions (see Mechanistic Studies in the Supporting Information for details). This discovery revealed the potential use of DFBz as a masking CO precursor. Intrigued by this discovery, we established a mild Pd-catalyzed fluorocarbonylation of iodoarenes using DFBz as a surrogate of CO.

To synthesize DFBz, we utilized a streamlined one-step synthesis via the insertion of difluorocarbene into the O−H bond of benzoic acid.[14] Employing the cost-effective and commercially available fluorosulfonyldifluoroacetic acid ($FSO_2CF_2CO_2H$, Chen's reagent) as the difluorocarbene precursor, we successfully synthesized DFBz (**1a**). Subsequently, we commenced a study of the fluorocarbonylation of iodoarenes employing DFBz, and the reaction conditions were optimized using 1-iodonaphthalene (**2a**) as the model substrate (Table 1). Initially, inspired by previously reported examples,[15] we examined the reaction with commercially available $Pd(TFA)_2$ (2 mol %) as the catalyst, PPh_3 (6 mol %) as the ligand, CsF as the fluoride additive, and DMF as the

Table 1. Optimization of the Reaction Conditions



entry	deviations from the standard conditions[a]	yield (%)[b]
1	none	51
2	$Pd(OAc)_2$ instead of $Pd(TFA)_2$	28
3	$Pd(PPh_3)_4$ instead of $Pd(TFA)_2$, without PPh_3	28
4	DMSO instead of DMF	29
5	Johnphos instead of PPh_3	65
6	3 mol % Xantphos instead of PPh_3	99
7	3 mol % Xantphos, KF instead of CsF	57
8	0.1 equiv of CsF	7
9	1 mol % $Pd(TFA)_2$, 1.5 mol % Xantphos	72

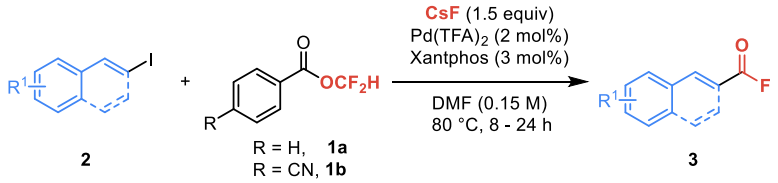
[a]Standard conditions: **2a** (0.2 mmol, 1.0 equiv), **1a** (0.4 mmol, 2.0 equiv), and CsF (0.3 mmol, 1.5 equiv) in DMF (2 mL) at 80 °C under N_2 for 24 h. [b]Yields were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

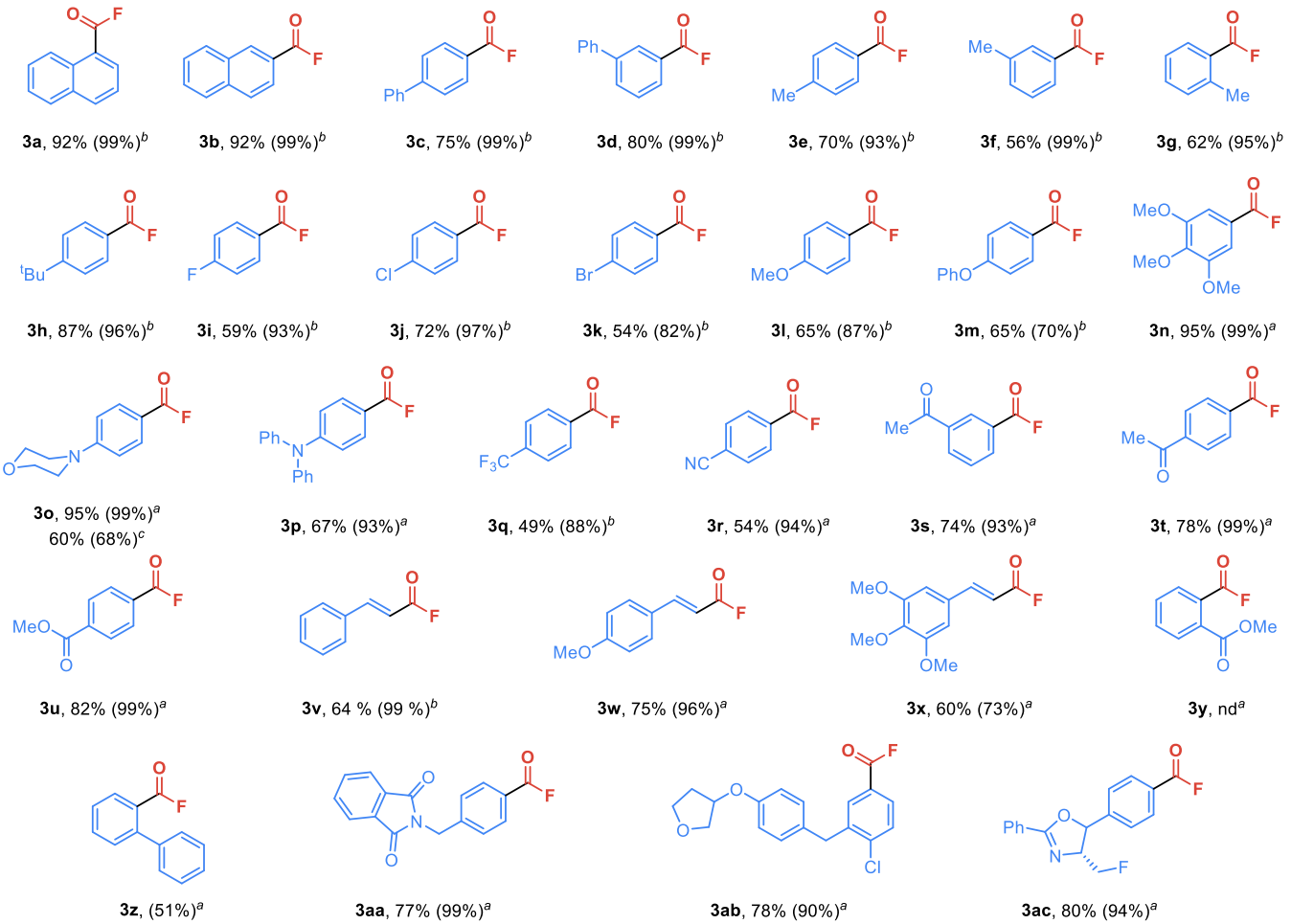
solvent, and the desired product **3a** was formed in 51% yield (entry 1). Replacing the $Pd(TFA)_2$ catalyst with $Pd(OAc)_2$ or $Pd(PPh_3)_4$ significantly decreased the product yield to 28% (entry 2 or 3, respectively). Solvent screening revealed the critical role of DMF, as the use of DMSO or MeCN as a solvent substantially reduced the reaction efficiency, and nonpolar solvents (such as toluene or CH_2Cl_2) completely suppressed product formation (entry 4; see the Supporting Information for details). Ligand optimization revealed that the use of Johnphos increased the yield to 65% while the use of Xantphos remarkably enhanced the yield to 99% (entries 5 and 6). The examination of fluoride sources demonstrated the superiority of CsF (99% yield), and the use of KF (57% yield) or a substoichiometric amount (0.1 equiv) resulted in a decreased yield (entry 7 or 8, respectively). Reducing the catalyst loading (from 2 to 1 mol %) maintained a respectable yield (72%, entry 9).

Having established the optimal reaction conditions (Table 1, entry 6), we investigated the substrate generality using diverse aryl and alkenyl iodides (Scheme 2). To enhance product isolation efficiency, difluoromethyl benzoate (**1a**) and 4-cyanobenzoate (**1b**) derivatives were strategically employed as fluorocarbonylation reagents, with **1a** being utilized for more polar substrates and **1b** being utilized for less polar counterparts. Notably, 2-naphthyl iodide exhibited reactivity comparable to that of its 1-naphthyl isomer (**3a** and **3b**), affording equivalent product yields. Substrates **2c** (4-phenyliodobenzene) and **2d** (3-phenyliodobenzene) demonstrated exceptional conversion with nearly quantitative NMR yields (99%), ultimately affording isolated yields of 75% and 80%, respectively. The reaction exhibited remarkable tolerance to steric effects, as evidenced by comparable outcomes from *o*-, *m*-, and *p*-methyl-substituted phenyl iodides (**3e**−**3g**, respectively). Due to the lower volatility, 4-*tert*-butylphenyl iodide (**2h**) achieved an enhanced isolated yield of 87% despite showing similar NMR conversion to methyl-substituted analogues. The protocol displayed excellent functional group compatibility, successfully accommodating halogen substituents (F, Cl, and Br) without obvious cleavage (**3i**−**3k**, respectively), thereby preserving opportunities for postsyn-

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Scheme 2. Substrate Scope of Fluorocarbonylation of Iodoarenes





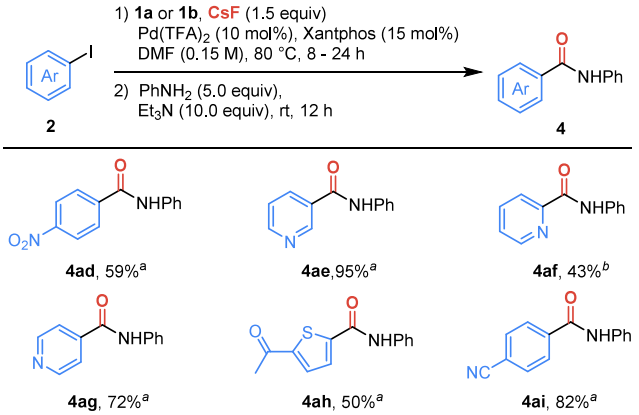
[a]Yields refer to isolated products on a 0.3 mmol scale. Yields in parentheses were determined by ^{19}F NMR spectroscopy with $PhCF_3$ as an internal standard. Reaction conditions: **2** (0.3 mmol), **1a** (0.6 mmol, 2.0 equiv), CsF (0.45 mmol, 1.5 equiv), $Pd(TFA)_2$ (2 mol %), and Xantphos (3 mol %) in DMF (2 mL) at 80 °C under a N_2 atmosphere. [b]Reaction conditions: **1b** (0.36 mmol, 1.2 equiv) instead of **1a**. [c]Reaction conditions: **2o** (2.0 mmol), **1a** (4.0 mmol, 2.0 equiv), CsF (3.0 mmol, 1.5 equiv), $Pd(TFA)_2$ (2 mol %), and Xantphos (3 mol %) in DMF (15 mL) at 80 °C under a N_2 atmosphere.

thetic modifications. Both electron-donating (methoxy, phenoxy, and amino) and electron-withdrawing groups (trifluoromethyl, cyano, acetyl, and ester) were well-tolerated, with minimal impact on reaction efficiency (**3l**−**3u**). A moderate NMR yield was also achieved for sterically hindered substrate **2z**; however, complete reaction inhibition occurred with 2-methyl carboxylate substrate **2y**. Vinyl iodides proved to be competent substrates, delivering moderate yields (**3v**−**3x**). The methodology was extended successfully to heterocyclic systems, achieving good to excellent yields with morpholinyl (**3o**) and phthalimidyl (**3aa**) moieties. Additionally, facile fluorocarbonylation of empagliflozin and chloramphenicol derivatives (**2ab** and **2ac**, respectively) demonstrates the broad applicability of this approach. Gratifyingly, the reaction can also be scaled up; when the reaction was carried out on a 2 mmol scale, **3o** was isolated in a moderate yield.

Given the mild and efficient nature of this fluorocarbonylation methodology, we subsequently performed a one-pot fluorocarbonylation−amination sequence to showcase the operational versatility of this approach. The diminished yields observed with 2 mol % catalyst loading likely stem from sulfur and nitrogen coordination effects and their inherent toxicity within the substrate heterocycles, necessitating a slight increase in catalyst quantity (10 mol %) to improve synthetic efficiency. Employing aniline as the amination partner, this protocol successfully converted diverse heterocyclic iodides, 4-nitroiodobenzene, and 4-cyanoiodobenzene through the fluorocarbonylation−amination cascade, delivering target compounds in moderate to excellent yields (Scheme 3).

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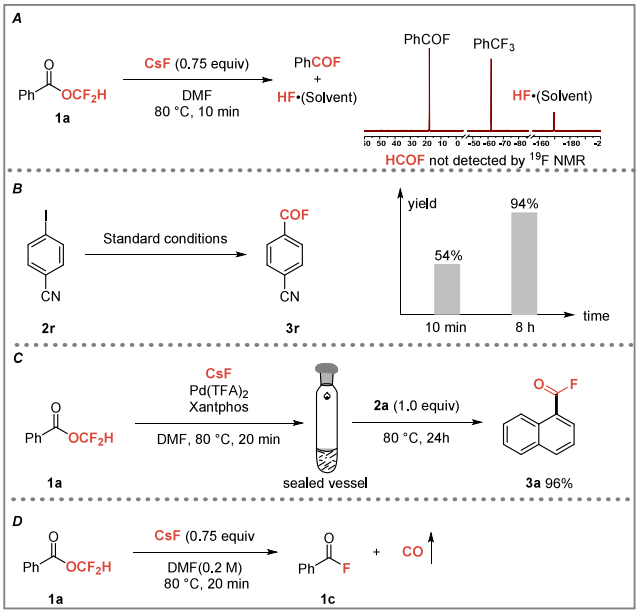
Scheme 3. One-Pot Fluorocarbonylation−Amination Protocol



[a]Yields refer to isolated products on a 0.3 mmol scale. Reaction conditions: **2** (0.3 mmol, 1.0 equiv), **1a** (0.6 mmol, 2.0 equiv), CsF (0.45 mmol, 1.5 equiv), $Pd(TFA)_2$ (10 mol %), and Xantphos (15 mol %) in DMF (2 mL) at 80 °C under N_2 and then addition of $PhNH_2$ (1.5 mmol 5.0 equiv) and Et_3N (3.0 mmol 10.0 equiv). [b]Reaction conditions: **1b** (0.36 mmol, 1.2 equiv) instead of **1a**.

The previous work has postulated the involvement of HCOF as the reactive intermediate in fluorocarbonylation reactions;[11] however, due to the reported instability of HCOF,[16] we investigated the mechanism and proposed a different perception to their hypothesis through systematic experimental validation. Crucially, the characteristic ^{19}F NMR signal of HCOF whose chemical shift occurs at 45.45 ppm[17] remained undetectable under our reaction conditions (Scheme 4A),

Scheme 4. Mechanistic Studies



aligning with its documented thermal instability and rapid decomposition into HF/CO at ambient temperatures, a process exhibiting autocatalytic acceleration in the presence of HF.[16] The thermodynamic incongruity of HCOF serving as the reactive species becomes particularly evident, given the increased temperatures typically required for fluorocarbonylation. Control experiments with substrate **1a** and CsF exclusively yielded benzoyl fluoride and a species considered as a HF−solvent−fluoride complex via NMR analysis, with no spectral evidence of the existence of HCOF (Scheme 4A). Kinetic profiling revealed progressive product accumulation from 54% (10 min) to 94% (8 h), inconsistent with transient intermediate-mediated pathways (Scheme 4B). Sequential thermal activation of **1a**/CsF at 80 °C for 20 min prior to the introduction of iodoarene achieved a 96% yield of **3a** after 12 h, effectively decoupling the direct involvement of HCOF from productive catalysis (Scheme 4C). Direct thermal treatment of **1a**/CsF at 80 °C induced vigorous gas evolution without detectable HCOF signals, while subsequent gas-phase analysis by trapping with an aqueous $PdCl_2$ solution confirmed that CO is the predominant decomposition product via qualitative detection of palladium black (Scheme 4D; see Mechanistic Studies in the Supporting Information for details). These cumulative findings conclusively exclude HCOF as an essential intermediate, prompting a re-evaluation of the operative catalytic cycle in such transformations.

Building upon established mechanistic frameworks for palladium-catalyzed fluorocarbonylation, we present an alternative catalytic cycle that diverges from the previously postulated pathway[11] (Figure 1). Central to our proposal is

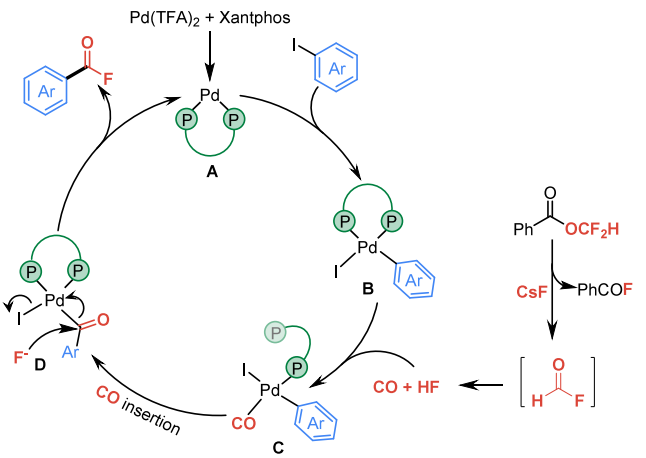


Figure 1. Proposed mechanism.

the pivotal involvement of CO and fluoride ions as key reactive species, superseding the conventionally assumed yet thermodynamically unstable HCOF intermediate. The catalytic cycle is initiated via oxidative addition of the iodoarene substrate to $Pd(0)L_2$ complex **A** generated in situ, forming metallacyclic intermediate **B**. Concurrently, CsF-mediated activation of difluoromethyl benzoate liberates HCF_2O^-, which undergoes rapid decomposition to CO and HF.[15] This liberated CO coordinates with intermediate **B** to yield carbonyl-palladium species **C**, followed by migratory insertion to generate acyl-palladium intermediate **D**. The catalytic manifold culminates in reductive elimination accompanied by fluoride−iodide exchange,[14] ultimately delivering the target fluorocarbonylated product while regenerating the active Pd(0) catalyst.

In conclusion, palladium-catalyzed fluorocarbonylation of aryl iodides was accomplished by using difluoromethyl esters as key reagents. These esters, readily synthesized via insertion of difluorocarbene into carboxylic acid O−H bonds, exhibit superior electrophilicity relative to common alkyl esters. This enhanced reactivity facilitates nucleophilic attack by fluoride

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ions, thereby generating formyl fluoride intermediates. Acting as synthetic surrogates for the combined "CO + HF" system, such formyl fluoride species remain underexplored in fluorocarbonylation strategies for acyl fluoride production. This work not only underscores the role of fluorine substitution in modulating ester reactivity but also broadens the scope of difluorocarbene chemistry in synthetic applications.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.5c04039.

Experimental procedures, detailed reaction optimization, characterization data, and NMR spectra for all products (PDF)

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Notes

The authors declare no competing financial interest.

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