

Ni-Catalyzed Borylation of Aryl Fluorides via C–F Cleavage

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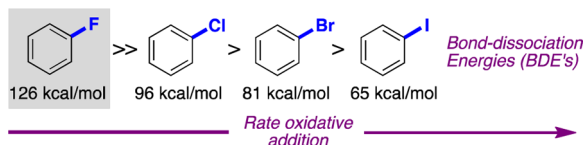
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S Supporting Information

ABSTRACT: A Ni-catalyzed borylation via C–F activation is described. This protocol is distinguished by a wide scope, including unactivated fluoroarenes, without compromising its efficiency and scalability, thus representing a significant step-forward toward the implementation of C–F activation protocols.

Metal-catalyzed cross-coupling reactions of organic halides have become indispensable tools in modern synthetic chemistry.¹ The reactivity trend of organic halides is inversely proportional to their bond-dissociation energy, with C–F bonds arguably possessing the shortest bond length in the organic halide series (Scheme 1).² Indeed, C–F bonds are the strongest

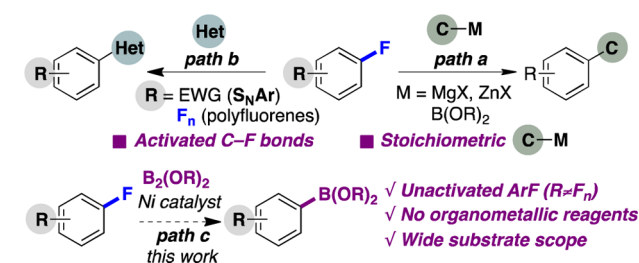
Scheme 1. Bond-Strength of C–Halide Bonds



C–heteroatom bonds in nature, conferring a remarkable metabolic activity that makes them particularly attractive in pharmaceuticals as bioisosteres of C–H bonds.³ Not surprisingly, these features have inspired chemists to design catalytic C–F cleavage protocols,⁴ aiming at providing new tools for lead generation in drug discovery.

In contrast with the wealth of literature data using C–X bonds (X = I, Br, Cl), catalytic C–F bond-activation is still relatively rare, an observation that is in line with the exceptional strength of the C–F bond.⁴ Prompted by the seminal work of Kumada,⁵ the vast majority of these processes are still based on C–C bond-formation using stoichiometric and highly reactive organometallic reagents possessing polarized carbon–metal bonds (Scheme 2, path a).⁶ Alternatively, catalytic dehydrofluorination events have recently gained considerable momentum.⁷ Interestingly, a close look into the literature data revealed that C–heteroatom bond-formation has hardly been considered, remaining essentially confined to nucleophilic aromatic substitution techniques with particularly activated fluoroarenes⁸ or heavily fluorinated aromatic substrates⁹ (Scheme 2, path b). These features contribute to the perception that direct C–F activation of unactivated fluoroarenes might constitute a daunting, yet highly rewarding, scenario in C–heteroatom bond-formation.¹⁰ If successful, this technique will offer unconventional new tactics in retrosynthetic analysis while

Scheme 2. Catalytic C–F Bond-Cleavage Scenarios

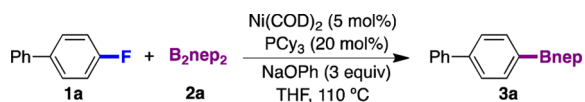


exploiting new opportunities in the C–F cleavage arena.¹¹ Prompted by the versatility and pivotal role of organoboron reagents as reaction intermediates,¹² as well as our ongoing interest in inert bond-activation,¹³ we report herein an unconventional Ni-catalyzed C–F bond-cleavage/C–B bond-formation of monofluoroarenes (Scheme 2, path c).^{14,15} This protocol represents a powerful alternative to other borylation techniques based on more reactive carbon–halide bonds,¹⁶ suggesting that iterative scenarios might come into play when dealing with the functionalization of polyhalogenated frameworks. This method is characterized by its wide substrate scope and by obviating the need for stoichiometric organometallic reagents, representing a significant step-forward for the implementation of C–F bond-cleavage in cross-coupling reactions.¹⁷ Preliminary mechanistic studies suggest a scenario consisting of a C–F bond-oxidative addition to Ni(0) complexes.

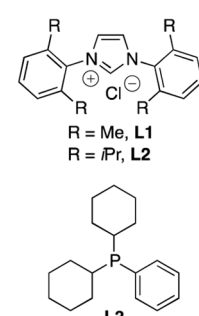
We started our investigations with **1a** as our model substrate (Table 1). After judicious optimization of all reaction parameters,¹⁸ we identified that a protocol consisting of **2a**, Ni(COD)₂, PCy₃, and NaOPh in THF was particularly suited for our purposes, affording **3a** in a 81% isolated yield (entry 1).¹⁹ As expected, the nature of the ligand played a critical role on the reaction outcome; while otherwise related phosphine ligands did not provide even traces of **3a** in the crude mixtures (entry 4), markedly inferior results were observed when employing *N*-heterocyclic carbenes (entries 2 and 3). Intriguingly, the C–B bond-formation was found to be strongly dependent on the metal–ligand ratio, with the commonly employed 1:2 (Ni:L) ratio providing clearly inferior results.²⁰ Interestingly, a significant erosion in yield was observed when operating under Ni(II) regimes (entries 5 and 6) or by using [Ni(PCy₃)₂]₂N₂ (entry 7). While tentative, these results suggest that COD might be acting as a noninnocent ancillary ligand to stabilize the active propagating Ni(0) species.²¹ We found negligible amounts of **3a**

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Table 1. Optimization of the Reaction Conditions^a


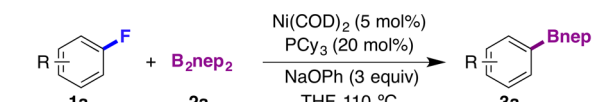
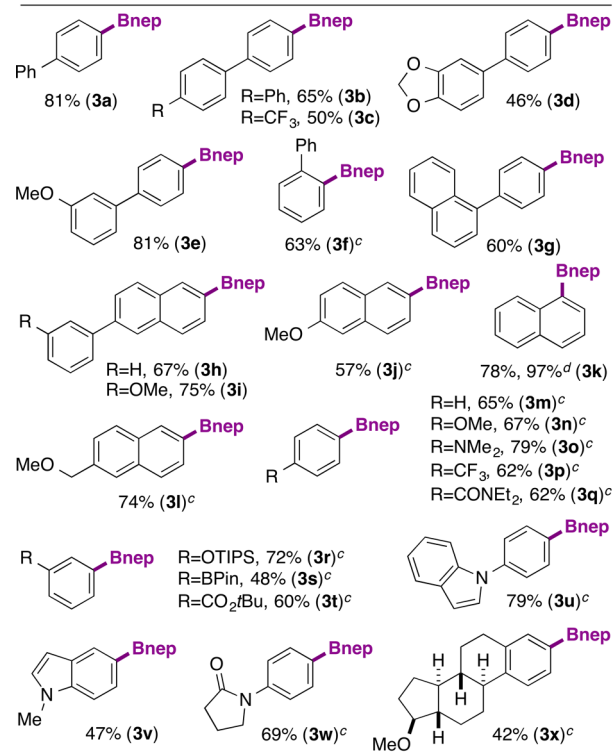
Entry	Change from standard conditions	3a(%) ^b
1	none	81 ^c (59) ^d
2	L1 instead of PCy ₃	46
3	L2 instead of PCy ₃	35
4	L3 (PPh ₃) instead of PCy ₃	0 (0)
5	NiCl ₂ -glyme instead of Ni(COD) ₂	30
6	NiBr ₂ (PCy ₃) ₂ instead of Ni(COD) ₂	49 ^d
7	Using [Ni(PCy ₃) ₂](N ₂)	26 ^d
8	DMF (PhMe) instead of THF	7
9	CsF instead of NaOPh	9
10	NaOtBu instead of NaOPh	9
11	HCO ₂ Na instead of NaOPh	0
12	without Ni(COD) ₂ /PCy ₃	0
13	without PCy ₃	3
14	without NaOPh	13
15	with B ₂ pin ₂ (2b) instead of 2a	0



^aReaction conditions: **1a** (0.50 mmol), **2a** (1.50 mmol), Ni(COD)₂ (5 mol %), PCy₃ (20 mol %), NaOPh (1.50 mmol), THF (2 mL; 0.25 M) at 110 °C for 12 h. ^bGC yields using decane as internal standard. ^cIsolated yield, average of at least two independent runs. ^dUsing PCy₃ (10 mol %). B₂pin₂ = bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). B₂nep₂ = 5,5-dimethyl-1,3,2-dioxaborolane.

in the crude mixtures when employing additives known to efficiently activate diboron reagents such as CsF or NaOtBu (entries 9–11),²² showing that NaOPh uniquely assisted the borylation event.²³ At present, we do not have an explanation for such distinctive reactivity profile. Although a Suzuki–Miyaura coupling scenario of **1a** with in situ formed **3a** might come into play,^{6c} we found that this was not the case.²⁴ As anticipated, careful control experiments revealed that all reaction parameters were critical for success (entries 12–14), suggesting that a nucleophilic aromatic substitution pathway might not come into play.⁸ Notably, no borylation was detected with B₂pin₂ (**2b**; entry 15), an observation that illustrates that a subtle balance of steric effects on the boron reagent is required for the C–B bond-forming reaction.

Prompted by these results, we next focused our attention on the generality of our Ni-catalyzed borylation protocol (Table 2). From the results summarized in Table 2, it is evident that our C–F bond-cleavage/C–B bond-formation turned out to be rather general. Notably, the reaction could be easily scaled-up on a gram scale without further optimization, delivering **3k** in essentially quantitative yield (97%). It is worth noting that an otherwise identical reactivity was found for regular monofluoroarenes regardless of the electronic nature of the aryl fluoride utilized (**3m–3q**), thus providing additional compelling evidence that a nucleophilic aromatic substitution scenario is highly unlikely.⁸ Remarkably, the reactivity of regular monofluoroarenes was comparable to π -extended systems, an observation that is in sharp contrast with other Ni-catalyzed inert bond-activation protocols.^{25,26} As shown for **3f**, the presence of an ortho-substituent did not significantly hamper the reactivity. The chemoselectivity of the borylation event was nicely illustrated by the fact that amines (**3o**), silyl ethers (**3r**), acetals (**3d**), esters (**3t**), or amides (**3q** and **3w**), among others, were perfectly accommodated.²⁷ Similarly, we found that nitrogen-containing heterocycles posed no problems (**3u** and **3v**). Although Ni complexes are suited for borylation events via C(sp²)–, C(sp³)–OMe,^{13a,28} or C(sp²)–NCOR cleavage,²⁹ we found that the

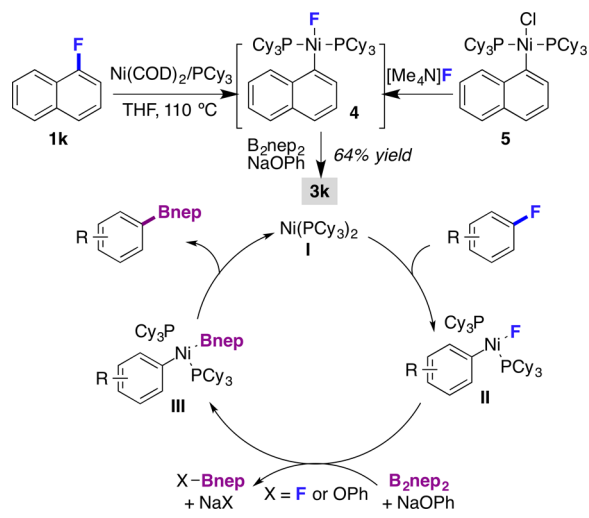
Table 2. Scope of the Borylation Event^{a,b}



^aReaction conditions: same as those for Table 1 (entry 1). ^bIsolated yields, average of at least two independent runs. ^cUsing Ni(COD)₂ (10 mol %). ^dReaction performed with **1k** (1.0 g, 6.90 mmol scale).

presence of aryl(benzyl) methyl ethers or amides did not compete with productive C–F cleavage/C–B bond-formation (**3e**, **3i**, **3j**, **3l**, **3n**, and **3w**). Interestingly, pinacolborane residues were well tolerated, allowing for preparing bifunctional borylated arenes in a straightforward fashion (**3s**).³⁰ In light of these results, we anticipated that our borylation event could be applied for late-stage diversification of advanced fluorinated intermediates such as **1x**. As shown, this was indeed the case, and **3x** could be prepared under otherwise identical reaction conditions in moderate yield. Taken together, the results compiled in Table 2 clearly demonstrate the prospective impact of our C–B bond-formation, even with unactivated substrates, thus significantly increasing the overall synthetic utility of fluoroarenes as new platforms for molecular diversity.

Taking into consideration the high activation energy of C–F bonds,² it comes as no surprise that oxidative addition complexes via C(sp²)–F activation have essentially been isolated and characterized with particularly activated polyfluoroarenes or substrates containing proximal directing groups.⁴ In sharp contrast, a direct oxidative addition of an unactivated monofluoroarene to Ni(0) via C(sp²)–F cleavage has not yet been observed. To such end, we decided to *in situ* monitor the course of the reaction of **1k** with Ni(COD)₂/PCy₃ in THF by NMR spectroscopy (Scheme 3). Notably, we cleanly observed a rather characteristic chemical shift at 17.8 ppm (d, J_{P-F} = 45 Hz) and –368 ppm (t, J_{P-F} = 45 Hz) by ³¹P- and ¹⁹F-NMR spectroscopy, respectively. This result is consistent with **4** possessing the Ni atom in a square-planar environment

Scheme 3. Mechanistic Rationale



surrounded by two phosphorus atoms in trans coordination geometry. We corroborated its structure by an authentic sample of **4** that was prepared from **5** by anion metathesis.³¹ Importantly, upon exposure of **4** to B_2nep_2 and NaOPh in THF we found that **3k** was obtained in 64% yield, an otherwise similar result to that shown in Table 2 under catalytic conditions. While we cannot certainly rule out other conceivable reaction pathways,³² at present we support a scenario consisting of an initial oxidative addition into the $C(sp^2)-F$ bond (**II**) followed by boryl transfer assisted by NaOPh (**III**) and a final $C-B$ bond-reductive elimination, thus delivering the targeted borylated arene while regenerating the active propagating $Ni(PCy_3)_2$ species (**I**).

In summary, we have described the first Ni-catalyzed borylation of monofluoroarenes. This work constitutes a rare example of C -heteroatom bond-formation via catalytic $C-F$ cleavage of unactivated fluoroarenes. The protocol is distinguished by its wide scope without compromising its practicability, efficiency, and scalability. Further investigations aimed at promoting related C -heteroatom bond-formations are currently ongoing in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08103.

Experimental procedures and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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sincerely thank Dr. Fedor Miloserdov for providing an authentic sample of **4** and Prof. Vladimir V. Grushin for insightful mechanistic discussions.

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(18) See [Supporting Information](#) for details

(19) Unreacted starting material and marginal reduction of C–F bond account for the mass balance.

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