Chemistry–A European Journal
Research Article
doi.org/10.1002/chem.202200457
Chemistry Europe
European Chemical Societies Publishing
www.chemeurj.org

Nickel and Copper Catalyzed *ipso*-Phosphonodifluoromethylation of Arylboronic Acids with $BrCF_2P(O)(OEt)_2$ for the Synthesis of Phosphonodifluoromethylarenes

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Abstract: A convenient method for the direct ipso-phosphonodifluoromethylation of arylboronic acids via nickel-copper co-catalysis is disclosed. This work, which utilizes inexpensive first row transition metals, represents a facile alternative to the traditional palladium catalyzed approach. The method utilizes inexpensive commodity chemicals and substrates while tolerating a variety of biologically relevant functional groups. Structurally diverse phosphonodifluoromethylarenes are furnished in good yields under short reaction times. Control experiments to probe possible reaction pathways are also included.

Organofluorine chemistry is especially relevant in medicinal chemistry due to the unique properties of fluorinated molecules.[1–3] The last decade has seen a large uptick in the number of difluoromethylation and difluoromethylenation strategies, owing to the unique behavior of the CF_2 moiety.[4–7] Research has revealed a bioisosteric relationship between the $-CF_2$-group and commonly encountered groups such as thiols, ethers and carbonyl compounds, leading to an increase in CF_2-containing drugs and drug candidates.[8–11] Among these groups, difluoromethylphosphonates are very attractive moieties due to their use as isopolar analogues to the corresponding phosphate esters[12] and their modified stability to hydrolytic enzymes.[13] Consequently, CF_2-phosphonates are sought-after functionalities for novel drug design (Figure 1).[12–14] Tenofovir disoproxil (**A**) is used for the treatment of hepatitis B and prevention of HIV.[15,16]

The antiviral cidofovir (**B**) is used for the treatment of cytomegalovirus retinitis and poxvirus infections.[17] Alkyl phosphonates are also found in serine protease inhibitors such as **C**. The phosphotyrosyl mimetic PTP1B **D** is a phosphatase inhibitor and showcases the significance of the CF_2 moiety by increasing the acidity of the phosphonate and enhances its ability to form hydrogen bonds.[18]

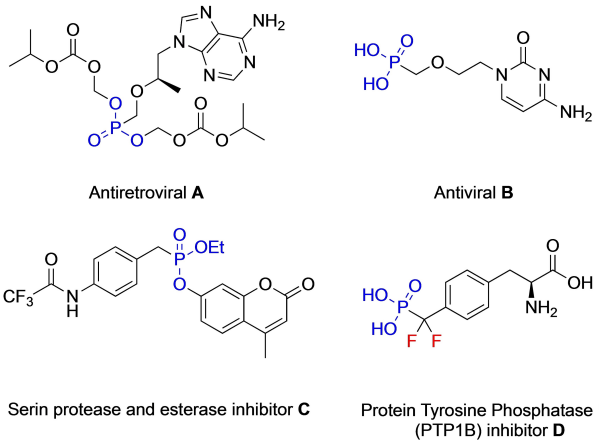

Figure 1. Phosphonate and difluoromethylphosphonate-containing bioactive drugs.

The synthesis of a multitude of difluoromethyl phosphonates and their use in phosphonodifluoromethylation reactions has been previously documented.[19] In 1993 Smyth and Burke reported the reaction of in situ prepared sodium di-tert-butoxyphosphanide with aryl aldehydes and an excess of DAST which afforded the first example of aryldifluoromethylphosphonates (Scheme 1a).[20] Diethyl (difluoromethyl)trimethylsilylphosphonate has also been employed as a reagent for the preparation of phosphonodifluoromethylarenes. Diverse aryl electrophiles have been used in these procedures, affording the desired compounds with the aid of stoichiometric copper salts. (Scheme 1b).[21] Other strategies have employed bromo(difluoromethyl)phosphonate with stoichiometric zinc powder and copper salts to afford the desired compounds through the generation of more reactive organometallic intermediates (Scheme 1c).[22] Bromo(difluoromethyl)phosphonate has also served as the reagent of choice for

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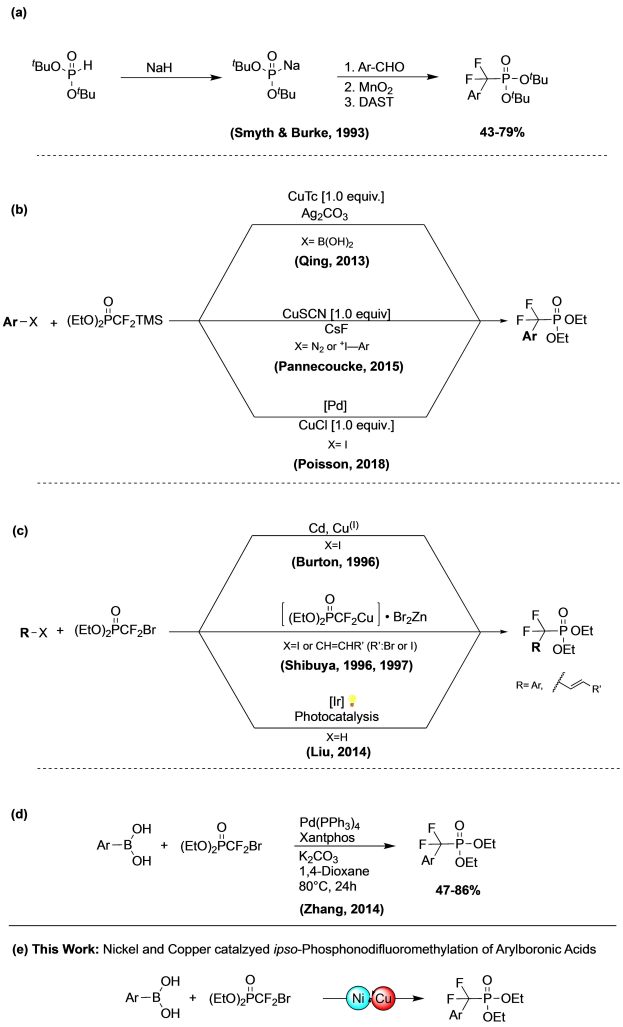
Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202200457



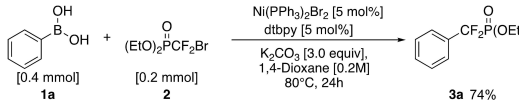
Scheme 1. Strategies for the synthesis of phosphonodifluoromethylarenes.

photochemical methods. However, these approaches offer no regioselectivity in their direct C(sp^2)-H difluoromethylation and utilize excess substrate in order to inflate reaction efficiency (Scheme 1c).[22] Lastly, in 2014, Zhang and coworkers reported the palladium-catalyzed Suzuki-Miyaura cross-coupling of $BrCF_2P(O)(OEt)_2$ with arylboronic acids (Scheme 1d).[23] The high cost of traditionally employed metals like palladium can prohibit their use in certain applications, making methods employing cheaper and more earth-abundant first row transition metals like nickel and copper desirable. Furthermore, the use of more cost-effective ligands in these transformations would enable greater applicability. For these reasons, we herein report an improved and efficient method for the *ipso*-phosphonodifluoromethylation of arylboronic acids with $BrCF_2P(O)(OEt)_2$ via a synergistic Ni–Cu catalytic system (Scheme 1e). The proposed methodology serves as a cost-effective and improved alternative to the traditional Pd catalyzed coupling reaction.

Phenylboronic acid (**1a**) was selected as the model substrate. Initial optimization trials focused on finding the most suitable nickel catalyst. See the Supporting Information for a full table of optimization trials. Drawing inspiration from previous work by Zhang[23] and Wang,[24] these initial catalyst screening experiments were conducted with K_2CO_3 (base) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy) (ligand) in dioxane at 80 °C for 24 h. We chose $Ni(PPh_3)_2Br_2$ as the catalyst for the initial trial. With substrate **1a** as the limiting reagent we investigated the optimal concentration for the system. The reaction was performed at 0.2 M and the desired product **3a** was obtained in 74% yield (Table 1, entry 1 standard conditions). Next, by changing the equivalents of base to 1.0 the desired product was obtained in 25% yield (Table 1, entry 2). By increasing the equivalents of K_2CO_3 under otherwise similar conditions, the yield of **3a** was improved to 51% (Table 1, entry 3). To investigate the need for a well-defined Ni(II)-phosphine complex, we pre-stirred $NiBr_2$ with 10 mol% dtbpy at room temperature prior to the addition of $BrCF_2P(O)(OEt)_2$ **2**. Upon reacting for 24 h, no product was observed (Table 1, entry 4). Incorporation of 10 mol% of PPh_3 (Table 1, entry 5) resulted in only trace amounts of **3a**. Thus, we concluded that a pre-generated nickel-phosphine complex is necessary to enable the formation of the desired product. Setting **2** as the limiting reagent (Table 1, entry 6) matched our previous maximum yield of 25% (Table 1, entry 1). Next, various nickel-phosphine complexes with different bidentate phosphine ligands were investigated under similar conditions, and the desired product was obtained in lower yields in all cases (Table 1, entries 7–10). Of the bases studied, the best results were obtained with 3 equivalents of K_2CO_3.

Previous studies have established the beneficial role played by copper co-catalysts in enhancing cross-coupling reactions.[23,25,26] Our results showed that by adding 5 mol% of CuBr and increasing the equivalents of K_2CO_3 (Table 2, entry 1), the yield of **3a** remained unchanged when compared to our

Table 1. Screening of nickel catalysts.

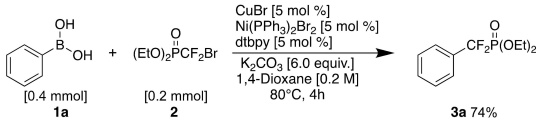


[0.4 mmol] **1a** [0.2 mmol] **2** **3a** 74%

Entry	Deviation from standard conditions[a]	Yield [%][e]
1	None	74
2	**1a** as limiting reagent, K_2CO_3 [1.0 equiv][b]	25
3	Same as 2 but with K_2CO_3 [3.0 equiv]	51
4	Same as 3 but with $NiBr_2$ [5 mol%], dtbpy [10 mol%][c]	0
5	Same as 4 but with PPh_3 [10 mol%][c]	6
6	Same as 3 but with dtbpy [5 mol%] and **2a** as limiting reagent [d]	25
7	As optimized but with $Ni(PPh_3)_2Cl_2$	66
8	As optimized but with Ni(dppp)Cl_2	17
9	As optimized but with Ni(dppe)Cl_2	62
10	As optimized but with Ni(dppe)Br_2	57

[a] Optimized conditions: 0.4 mmol $PhB(OH)_2$, 0.2 mmol $BrCF_2P(O)(OEt)_2$, 0.6 mmol K_2CO_3, 5 mol% $Ni(PPh_3)_2Br_2$, 5 mol% dtbpy, 1 mL 1,4-dioxane [0.2 M], 80 °C, 24 h. [b] 0.2 mmol $PhB(OH)_2$, 0.4 mmol $BrCF_2P(O)(OEt)_2$, 0.1 M (2 mL of 1,4-dioxane). [c] Pre-mixing Ni salt and ligands for 30 minutes at rt. [d] 0.4 mmol $PhB(OH)_2$, 0.2 mmol $BrCF_2P(O)(OEt)_2$, 0.6 mmol K_2CO_3, 5 mol% $Ni(PPh_3)_2Br_2$, 5 mol% dtbpy, 2 mL 1,4-dioxane [0.1 M], 80 °C, 24 h. [e] ^{19}F NMR yield determined with fluorobenzene as an internal standard.

Table 2. Optimization of Cu-salts and base equivalents.



Entry	Deviation from optimized conditions[a]	Yield [%][b]
1	None	74
2	As optimized but, K_2CO_3 [3.0 equiv]	66
3	As optimized but, K_2CO_3 [4.5 equiv]	61
4	As optimized but with $CuBr_2$	68
5	As optimized but with CuI	61
6	As optimized but with $Cu(OTf)_2$	62
7	Same as 2 but without Ni catalyst	0
8	Same as optimized but without Ni catalyst	0

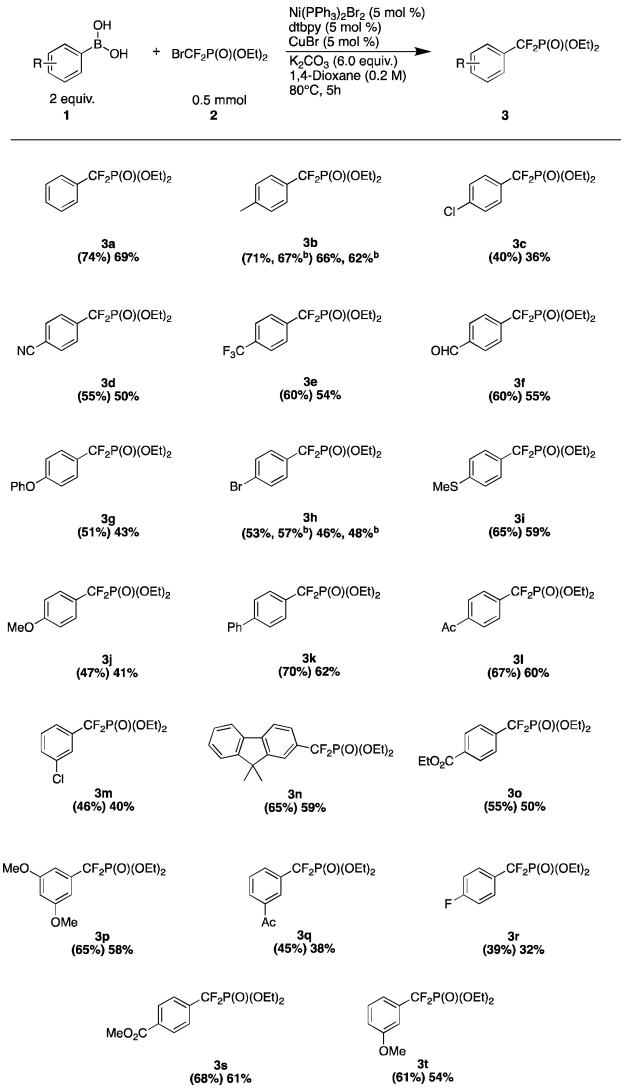
[a] Optimized conditions: 0.4 mmol $PhB(OH)_2$, 0.2 mmol $BrCF_2P(O)(OEt)_2$, 1.2 mmol K_2CO3, 5 mol% $Ni(PPh_3)_2Br_2$, 5 mol% dtbpy, 5 mol% CuBr, 1 mL 1,4-dioxane [0.2 M], 80 °C, 4 h. [b] ^{19}F NMR yield determined with fluorobenzene as an internal standard.

previously optimized conditions (Table 1, entry 1). Modifying the equivalents of base did not show improvement on the reaction yield (Table 2, entries 2–3). Interestingly, monitoring the reaction by ^{19}F NMR showed that the addition of Cu salts significantly shortened the reaction time from 24 h to 4 h (see Supporting Information). When exploring the scope, some substrates were run for 5 h to ensure full consumption of **2**. The use of other copper salts (Table 2, entries 4–6) did not improve the yield. Our results also show (Table 2, entry 7–8) that a copper catalyst alone is not sufficient to enable the reaction in the absence of the nickel catalyst under our conditions.

With our optimized conditions in hand, the scope of this reaction was investigated using various substituted boronic acids (Scheme 2). Alkyl and aryl substituted boronic acids **1b** and **1k** yielded 71% and 70% of **3b** and **3k**, respectively.

Considering the propensity of aryl halides to react with transition metals like copper and nickel, we tested substrates **1c**, **1h** and **1r** under our optimized conditions, which smoothly furnished **3c**, **3h** and **3r**. It should be emphasized that electrophilic substituents withstand our conditions. Nucleophilic phosphonodifluoromethylation has been previously performed on ketones, aldehydes, and esters.[19] These groups are tolerated under the reaction conditions, as exemplified by the facile generation of products **3f**, **3l**, **3o**, **3q**, and **3s** with no observable addition of phosphonodifluoromethide to the carbonyl carbon. Similarly, nitriles have also been used as electrophiles in nucleophilic fluoroalkylation reactions.[27] Example **3d** was synthesized without any addition at the electrophilic nitrile carbon.

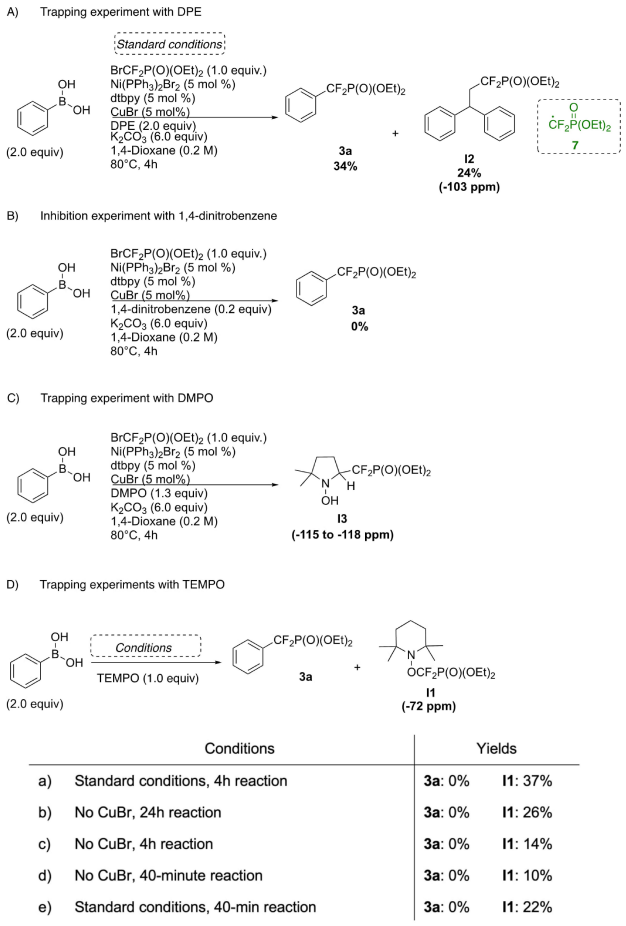
Several other commonly encountered functional groups including thiomethyl (**3i**), alkoxy/aryloxy (**3g**, **3j**), and trifluoromethyl (**3e**) were also found compatible with the presented conditions. Our investigations revealed that *ortho* substituents suppressed the reaction regardless of the electronics, likely due to steric reasons, as seen with 2-nitro- and 2-methoxyphenylboronic acids. Alkylboronic acids and heterocycles were not tolerated.[28] To investigate the involvement of a phosphonodifluoromethyl radical **7**, several radical-trapping



Scheme 2. [a] Substrate scope of the nickel and copper co-catalyzed *ipso*-phosphonodifluoromethylation of arylboronic acids. Isolated yields. [a] Yields in parentheses were determined by ^{19}F NMR using fluorobenzene as internal standard. [b] Performed at 1 mmol scale.

and inhibition experiments were conducted (Scheme 3). The first control experiment (Scheme 3A) using DPE resulted in the formation of the phosphonodifluoromethylated adduct **I2**, observed by ^{19}F NMR and a significant decrease in product **3a** formation.

Next, the addition of 1,4-dinitrobenzene as an ET scavenger[23] completely suppressed the formation of the desired product **3a** (Scheme 3B).Additionally, the formation of adduct **I3** upon the addition of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) to the reaction mixture was confirmed by ^{19}F NMR (see Supporting Information) (Scheme 3C). The results from these experiments support the hypothesis that a difluoromethylphosphonate radical may be involved in the reaction pathway. Similarly, we wanted to determine the presence of **7** in both the copper/nickel dual catalytic system and the nickel catalyzed reaction. For this purpose, we conducted trials **a** and **b** shown



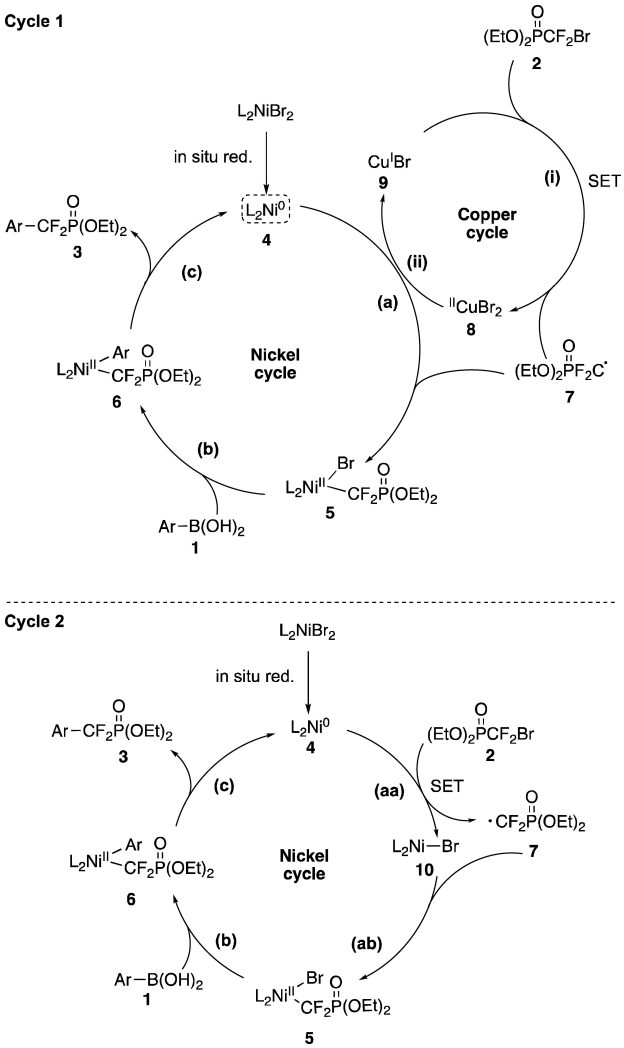
	Conditions	Yields	
a)	Standard conditions, 4h reaction	**3a**: 0%	**I1**: 37%
b)	No CuBr, 24h reaction	**3a**: 0%	**I1**: 26%
c)	No CuBr, 4h reaction	**3a**: 0%	**I1**: 14%
d)	No CuBr, 40-minute reaction	**3a**: 0%	**I1**: 10%
e)	Standard conditions, 40-min reaction	**3a**: 0%	**I1**: 22%

Scheme 3. Radical trapping and quenching experiments with DPE, 1,4-dinitrobenzene, DMPO, and TEMPO.

in Scheme 3C wherein 1 equiv. TEMPO was present from the onset of the reaction, which yielded 37% and 26% of the TEMPO-$CF_2P(O)(OEt)_2$ adduct **I1** respectively, and completely inhibited the formation of **3a**. In the course of our optimization, we observed that the addition of an equimolar loading (1:1) of copper(I) bromide:$Ni(PPh_3)Br_2$ significantly decreased the reaction time while providing similar yields to the nickel catalyzed system. Therefore, we conducted trial **c** with only Nickel (no CuBr) in the same amount of time as the optimized conditions. This experiment produced less than half the yield of the TEMPO adduct **I1** (14%), thus showcasing the effect of copper in the radical generation.

Lastly, to determine the rate of formation of **7**, we conducted trials with (trial **e**) and without (trial **d**) copper and analyzed determined the amount of TEMPO adduct after 40 minutes. The results show that trial **e** produced 2.2 times (22%) the amount of **I1** compared to trial **e** (10%), showcasing the faster rate of radical formation with copper in the reaction.

Although the exact role of copper and the synergistic effect with nickel remain unknown, a preliminary mechanistic pathway is proposed. As demonstrated by previous literature,[29–32] a single-electron-transfer radical process is a plausible step for both, the catalytic cycle with only nickel, and the Ni/Cu system. In the proposed cycle with copper (Scheme 4 cycle 1), the first step (**i**) involves a SET process by copper to generate the difluoromethylphosphonate radical **7**. The reduction of the newly formed copper species **8** simultaneously promotes the oxidation of the active nickel(0) catalyst **4** (step **ii**). This step potentially results in the formation of a Ni(I) species that subsequently reacts with the fluoroalkyl radical **7** to form intermediate **5**. Upon the addition of the arylboronic acid **1**, a new organonickel species **6** is formed (step **b**). Reductive elimination from **6** yields the desired phosphonodifluoromethylarene **3**, regenerating Ni^0 catalyst **4** (step **c**). The proposed cycle without copper (Scheme 4 cycle 2) is based on Zhang's prior work with palladium where a Pd^0-promoted SET is proposed. Analogously we propose a SET between Ni(0) and bromodifluoromethylphosphonate to generate radical **7** (step **aa**). This radical then reacts with species **10** to generate Ni(II) intermediate **5**. From that point, the cycle follows the same steps (**b** and **c**) as the previous cycle. Further studies are ongoing to determine the exact roles of the catalysts.



Scheme 4. Proposed catalytic cycles.

In conclusion, we have developed a new and efficient method for the synthesis of phosphonodifluoromethylarenes via a nickel and copper co-catalyzed cross-coupling reaction between arylboronic acids and diethyl (bromodifluoromethyl)phosphonate. The protocol utilizes inexpensive and commercially available substrates and catalysts, as well as low-cost ligands, allowing the incorporation of the synthetically valuable difluoromethylphosphonate group in good yields, with higher functional group tolerance and shorter reaction times compared to previous reports.

Acknowledgements

The Loker Hydrocarbon Research Institute is acknowledged for funding.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: boronic acid · catalysis · copper · cross-coupling · fluorine · nickel · phosphonodifluoromethyl

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Manuscript received: February 11, 2022
Accepted manuscript online: May 23, 2022
Version of record online: June 8, 2022