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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201800729

Link to VoR: http://dx.doi.org/10.1002/adsc.201800729

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Ni-Catalyzed Decarboxylative Cross-Coupling of Potassium Polyfluorobenzoates with Unactivated Phenol and Phenylmethanol Derivatives

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Received: ((will be filled in by the editorial staff))

This paper is dedicated to Professor Xiyan Lu on the occasion of his 90th birthday.

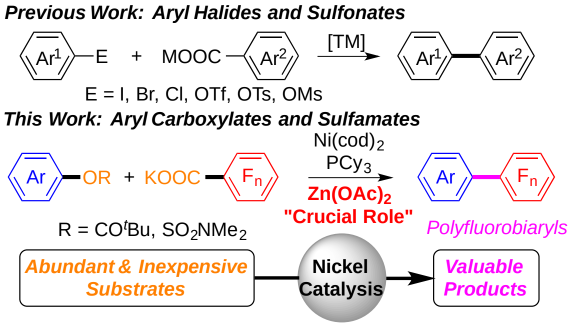
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract. A Ni-catalyzed decarboxylative cross-coupling of potassium polyfluorobenzoates with unactivated phenol and phenylmethanol derivatives is described. This novel transformation provides a practical and efficient protocol towards the synthesis of important polyfluorobiaryls and polyfluorinated diarylmethanes, and greatly enlarges the range of electrophiles utilized in decarboxylative coupling. Remarkably, preliminary mechanistic studies indicated the essential role of $Zn(OAc)_2$ might lie in the enhancement of decarboxylation step.

Keywords: decarboxylative cross-coupling; C–O bond functionalization; nickel-catalyzed; phenol derivatives; polyfluorobiaryls

The biaryl scaffold constitutes the core structure of a wide variety of naturally occurring and manmade compounds, such as pharmaceuticals, agrochemicals, ligands, organic materials etc.[1] In recent years, transition-metal-catalyzed decarboxylative cross-coupling has emerged as a significant alternative to traditional cross-coupling reactions towards biaryls synthesis (Scheme 1).[2] This method utilizes inexpensive, highly stable and readily available carboxylic acids instead of expensive and sensitive organometallic reagents, and generates CO_2 instead of metal halide byproducts. In the past decade, great progress has been made in the decarboxylative cross-coupling enabling the use of various aryl halides including iodides, bromides and chlorides as electrophiles.

Phenol derivatives are abundant, inexpensive, highly stable and readily available chemicals. Activated aryl sulfonates including triflates, tosylates and mesylates have been employed as versatile alternatives to aryl halides in various transformations including decarboxylative cross-coupling.[3] During the past decade, the C–O bond functionalization of simpler and less activated phenol derivatives[4] especially aryl carboxylates and sulfamates to construct carbon-carbon[5] and carbon-heteroatom[6] bonds has attracted considerable attentions. However, to the best of our knowledge, the decarboxylative cross-coupling involving aryl carboxylates and sulfamates as electrophiles has never been realized (Scheme 1).

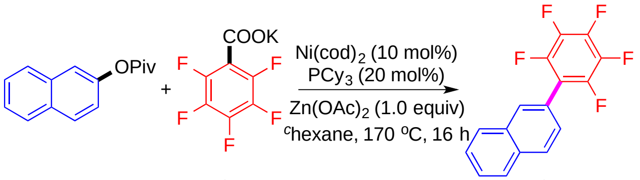


Scheme 1. Biaryl synthesis via classical decarboxylative cross-coupling.

Herein, we communicate the decarboxylative cross-coupling of potassium polyfluorobenzoates with unactivated phenol and phenylmethanol derivatives to afford polyfluorobiaryls and polyfluorinated diarylmethanes via nickel catalysis under simple reaction conditions. Remarkably, polyfluorobiaryls find important application in the fields of medicinal chemistry[7] and material science[8]. This novel protocol provides a significant implement to the former synthetic routes of polyfluorobiaryls such as Suzuki-Miyaura cross-coupling of pentafluorophenylboronic acid[9] and C–H arylation of polyfluoroarene[10].

We began by investigating the decarboxylative cross-coupling of 2-naphthyl pivalate **1a** with potassium perfluorobenzoate **2a** in the presence of nickel catalyst. After extensive screening, the best result was obtained when the reaction was conducted under the conditions consisting of Ni(cod)$_2$ (10 mol%; cod = 1,5-cyclooctadiene), tricyclohexylphosphine (PCy$_3$, 20 mol%), and Zn(OAc)$_2$ (1.0 equiv) in ^{c}hexane at 170 °C for 16 h affording the product **3a** in 81% GC yield and 76% isolated yield (Table 1). It is noteworthy that C–F bonds survived under the conditions.[11]

Table 1. Ni-catalyzed decarboxylative cross-coupling of **2a** with **1a**: effects of reaction parameters.



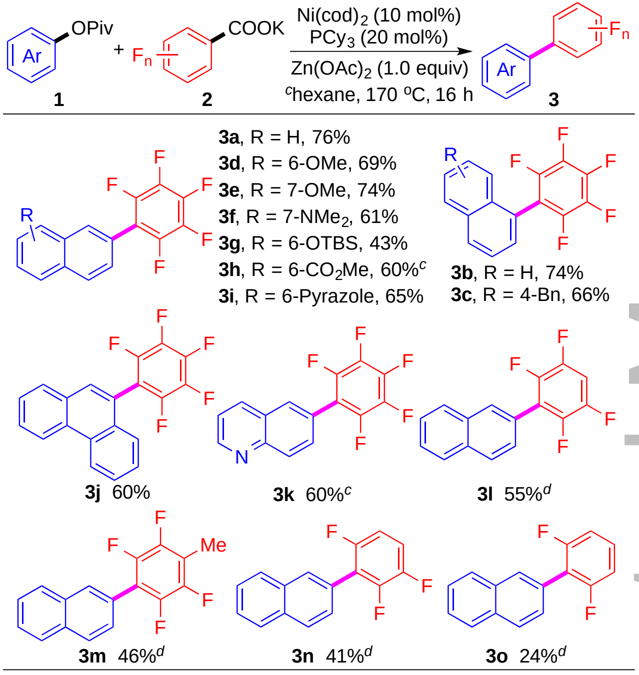
1a **2a** **3a**

Entry	Variation from “standard conditions”^{a}	Yield[%]^b
1	none	81(76)^c
2	No Ni(cod)$_2$	0
3	PMe$_3$ instead of PCy$_3$	trace
4^d	dppf instead of PCy$_3$	19
5^e	IPr•HCl instead of PCy$_3$	trace
6	No Zn(OAc)$_2$	6
7	Cu(OAc)$_2$ instead of Zn(OAc)$_2$	0
8	AgOAc instead of Zn(OAc)$_2$	trace
9	ZnCl$_2$ instead of Zn(OAc)$_2$	trace
10	Ag$_2$CO$_3$ instead of Zn(OAc)$_2$	6
11	Cu$_2$O instead of Zn(OAc)$_2$	trace
12	toluene instead of ^{c}hexane	63
13	diglyme instead of ^{c}hexane	0
14	DMF instead of ^{c}hexane	0
15	150 °C instead of 170 °C	52
16^f	150 °C instead of 170 °C	69^c

a) Standard reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Ni(cod)$_2$ (0.02 mmol), PCy$_3$ (0.04 mmol), Zn(OAc)$_2$ (0.2 mmol), ^{c}hexane (3.0 mL), 170 °C, 16 h. b) The yield was determined by GC, and calibrated using ^{n}dodecane as internal standard. c) Isolated yield in parenthesis. d) dppf (0.02 mmol). e) NaO^{t}Bu (0.04 mmol). f) Ni(cod)$_2$ (0.04 mmol), PCy$_3$ (0.08 mmol).

The effect of alteration to the “standard conditions” is listed in Table 1. When no catalyst presented, essentially no reaction occurred. Trimethylphosphine (PMe$_3$) as ligand afforded only trace amount of desired product. The use of bidentate phosphine ligand (dppf) and N-heterocyclic carbene ligand (IPr•HCl) showed much less or little efficiency. The use of Zn(OAc)$_2$ as additive was crucial to the success of this reaction as only 6% GC yield was obtained in the absence of Zn(OAc)$_2$. The use of other additives such as Cu(OAc)$_2$, AgOAc and ZnCl$_2$ afforded trace or no product. Ag$_2$CO$_3$ and Cu$_2$O, the commonly used additives for decarblyxlative cross-coupling were ineffective for this transformation. Replacing ^{c}hexane by toluene afforded lower yield of desired product. No product was obtained employing diglyme and DMF as solvent. Lowering the reaction temperature to 150 °C led to 52% GC yield while increasing the catalyst loading at 150 °C afforded 69% isolated yield.

Table 2. Ni-catalyzed decarboxylative cross-coupling of potassium polyfluorobenzoates with aryl pivalates.^{a,b}

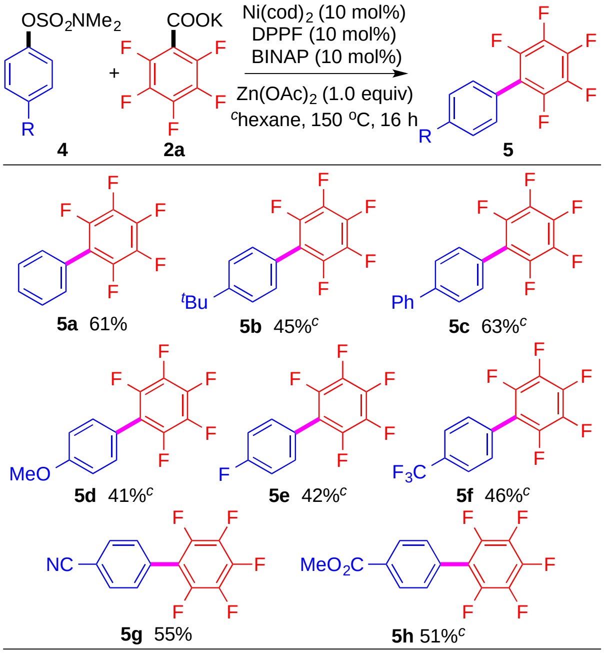


a) Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), Ni(cod)$_2$ (0.02 mmol), PCy$_3$ (0.04 mmol), Zn(OAc)$_2$ (0.2 mmol), ^{c}hexane (3.0 mL), 170 °C, 16 h. b) Isolated yield. c) 190 °C. d) toluene/DMA (2.0 mL/0.2 mL), 190 °C.

Furthermore, the reactivity of various C–O bond electrophiles with **2a** was tested under the standard conditions (see Table S1 in the Supporting Information). 2-Naphthyl acetate and benzoate both showed lower reactivity than 2-naphthyl pivalate. No product was obtained in the reaction of 2-naphthyl carbonate while the decarboxylative coupling of 2-naphthyl carbamate and sulfonmate resulted in lower yields than 2-naphthyl pivalate. Both naphthalen-2-ol and 2-methoxynaphthalene were inactive under the present reaction conditions.

With the optimized reaction conditions in hand, a variety of aryl pivalates **1** was subjected to this decarboxylative cross-coupling reaction (Table 2). 1-Naphthyl pivalate **1b** showed similar reactivity as 2-naphthyl pivalate. Generally, naphthyl pivalates bearing with electron-donating and electron-withdrawing groups worked well under the standard conditions affording the desired polyfluorobiaryls in moderate to good yields. Naphthyl pivalates bearing benzyl, methoxy, dimethylamino and pyrazole groups could be well tolerated under standard reaction conditions. In a similar manner, 9-phenanthrenyl pivalate **1j** was also suitable substrate. Ester and silyl ether group could also be tolerated under modified conditions with higher temperature. To our delight, heteroaryl pivalate **1k** reacted well to form the corresponding product in 60% yield under modified conditions with higher temperature. The decarboxylative cross-coupling of other potassium polyfluorobenzoates with **1a** was also examined. Employing the modified reaction conditions with mixed solvent (toluene/DMA) and higher temperature, the decarboxylative cross-coupling of potassium tetrafluorobenzoate, 4-methyl tetrafluorobenzoate and trifluorobenzoate with **1a** furnished the polyfluorobiaryls in satisfied yields. As to the reaction of potassium difluorobenzoate, low yield of the desired product was obtained.

Table 3. Ni-catalyzed decarboxylative cross-coupling of potassium pentafluorobenzoates with aryl sulfamates.[a,b]

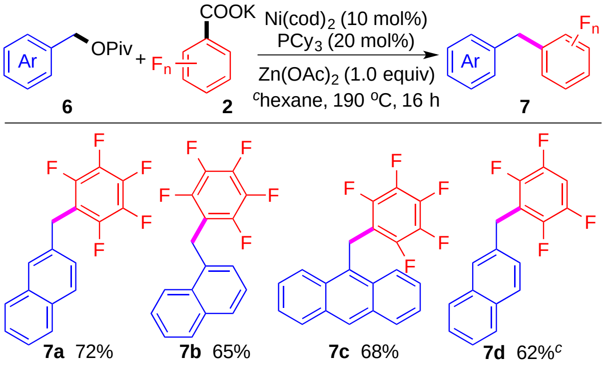


[a] Reaction conditions: **4** (0.2 mmol), **2a** (0.4 mmol), Ni(cod)$_2$ (0.02 mmol), DPPF (0.02 mmol), BINAP (0.02 mmol), Zn(OAc)$_2$ (0.2 mmol), ^{c}hexane (3.0 mL), 150 °C, 16 h. [b] Isolated yield. [c] Ni(cod)$_2$ (0.04 mmol), DPPF (0.04 mmol), BINAP (0.04 mmol).

Phenyl pivalates showed much less reactivity affording trace amount of desired products under present reaction conditions. Similar phenomenon was observed in other reports on transformation of inert C–O bonds.[12] Switching the substrates from phenyl pivalates to phenyl sulfamates, no product was obtained under standard conditions. Employing both DPPF (1,1'-Bis(diphenylphosphino)ferrocene) and BINAP (2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl) as ligand allowed this decarboxylative cross-coupling process to occur smoothly while trace or low yield was obtained utilizing DPPF or BINAP alone as ligand (Table 3). Various phenyl sulfamates bearing both electron-donating and –withdrawing functional groups afforded the desired polyfluorobiphenyls in moderate yields.

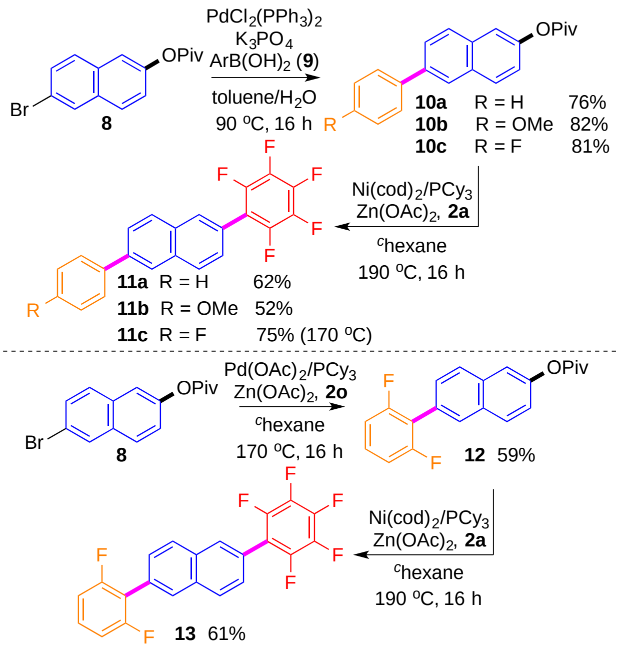
Encouraged by our success on aryl C–O electrophiles, we further investigated the decarboxylative cross-coupling of potassium polyfluorobenzoates with benzylic pivalates (Table 4).[13] By employing modified reaction conditions of aryl pivalates with higher temperature, 2-naphthylmethyl pivalate **6a** and 1-naphthylmethyl pivalate **6b** reacted well with potassium pentafluorobenzoates to furnish the desired polyfluorinated diarylmethanes in good yields. Similarly, 9-anthracenylmethyl pivalate **6c** was also suitable substrate. The decarboxylative cross-coupling of potassium tetrafluorobenzoates with **6a** afforded the desired product in 62% yield employing mixed solvent consisting toluene and DMA.

Table 4. Ni-catalyzed decarboxylative cross-coupling of potassium polyfluorobenzoates with benzylic pivalates.[a, b]



[a] Reaction conditions: **4** (0.2 mmol), **2** (0.4 mmol), Ni(cod)$_2$ (0.02 mmol), PCy$_3$ (0.04 mmol), Zn(OAc)$_2$ (0.2 mmol), ^{c}hexane (3.0 mL), 190 °C, 16 h. [b] Isolated yield. [c] **2b** (0.6 mmol), toluene/DMA (2.0 mL/0.2 mL)

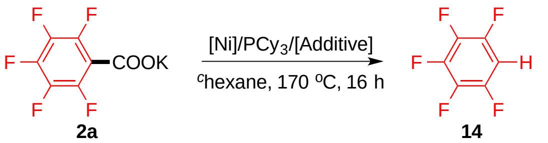
The synthetic versatility of this nickel-catalyzed decarboxylative cross-coupling involving inert C–O bond is demonstrated. As shown in Scheme 2, a range of polyflurotriaryls could be synthesized from 6-bromonaphthyl pivalate **8** via Suzuki coupling and subsequent decarboxylative cross-coupling. In addition, two different polyfluorophenyl groups are installed to **8** via sequential decarboxylative cross-coupling reactions.



Scheme 2. Synthetic application

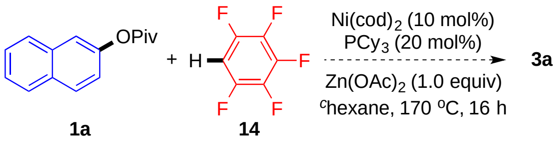
Furthermore, the decarboxylation of **2a** was investigated to gain brief insights to the mechanism of this decarboxylative cross-coupling (Table 5).[3j], [3k], [14] Pentafluorobenzene **14** was obtained in 9% yield in ^{c}hexane at 170 °C within 16 h while the adding of nickel catalysts like $Ni(cod)_2$ and $NiCl_2$ or additives like $ZnCl_2$, Ag_2CO_3 and Cu_2O gave similar results. Remarkably, the adding of $Zn(OAc)_2$ as additive dramatically enhanced the decarboxylation of **2a** affording **14** in 59% yield while similar yields were obtained employing the combination of nickel catalysts and $Zn(OAc)_2$. The results obtained above indicated the crucial $Zn(OAc)_2$ probably improves the reaction efficiency by enhancing the decarboxylation step. In addition, no **3a** was obtained in the reaction of **1a** with **14** under standard conditions, which ruled out the possibility of this pathway (Scheme 3).

Table 5. The Decarboxylation Reaction of **2a**: Effects of Reaction Parameters[a].



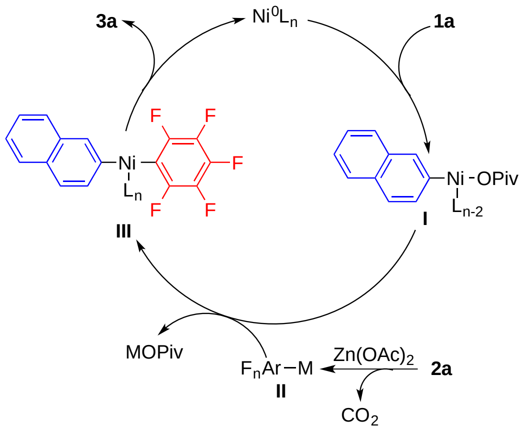
entry	[Ni]/PCy3	[Additive]	yield (%)[b]
1	-	-	9
2	$Ni(cod)_2/PCy_3$	-	7
3	$NiCl_2/PCy_3$	-	15
4	-	$Zn(OAc)_2$	59
5	-	$ZnCl_2$	9
6	-	Ag_2CO_3	10
7	-	Cu_2O	7
8	$Ni(cod)_2/PCy_3$	$Zn(OAc)_2$	61
9	$NiCl_2/PCy_3$	$Zn(OAc)_2$	65

[a] Reaction conditions: **2a** (0.4 mmol), [Ni] (0.02 mmol), PCy_3 (0.04 mmol), [Additive] (0.2 mmol), ^{c}hexane (3.0 mL), 170 °C, 16 h. [b] The yield was determined by GC, and calibrated using ^{n}dodecane as internal standard.



Scheme 3. Reaction of **1a** with **14** under standard conditions.

On the basis of the above results and previous reports,[3j], [14a], [15] we proposed a mechanism for this decarboxylative cross-coupling (Scheme 4). The oxidative addition of 2-naphthyl pivalate **1a** to the Ni^0-PCy_3 species generated the intermediate **I**. The subsequent transmetallation step with intermediate **II** that was obtained via the decarboxylation of potassium pentafluorobenzoates **2a** with the aid of $Zn(OAc)_2$ afforded intermediate **III**. The following reductive elimination of **III** furnished the product **3a** and regenerated the active Ni^0 species.



Scheme 4. Proposed mechanism.

In summary, the first nickel-catalyzed decarboxylative cross-coupling of potassium polyfluorobenzoates with unactivated phenol and phenylmethanol derivatives is disclosed. A variety of functional groups were tolerated, and various polyfluorobiaryl and polyfluorinated diarylmethanes were obtained in moderate to good yields. Remarkably, preliminary mechanistic studies indicated the effect of the crucial $Zn(OAc)_2$ might lie in the enhancement of decarboxylation step. Additional exploration of the substrate scope and mechanistic studies are currently underway and will be reported in the due course.

Experimental Section

A 25-mL pressure tube equipped with a magnetic stirring bar was dried with a heat-gun under reduced pressure and filled with nitrogen after cooling to room temperature. After adding aryl pivalate (0.2 mmol), and potassium polyfluorobenzoate (0.4 mmol), the tube was introduced inside a nitrogen-atmosphere glovebox. In the glovebox, Ni(cod)$_2$ (0.02 mmol, 5.6 mg), PCy$_3$ (0.4 mmol, 11.2 mg) and Zn(OAc)$_2$ (0.2 mmol, 36.7 mg) were added to the tube, which was sealed with O-ring tap and then taken out of the glovebox. Then, cyclohexane (3.0 mL) was added to the vessel under nitrogen atmosphere. The vessel was then heated at 170 ^{o}C for 16 h in a heating module with stirring. After that, the reaction mixture was cooled to room temperature, filtered, concentrated and directly purified by preparative thin-layer chromatography (petroleum ether/ethyl acetate as the eluent) to afford the product.

Acknowledgements

This work was supported by the grants from the National Natural Science Foundation of China (21602096) and Nanchang University (06301425).

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Nickel-Catalyzed Decarboxylative Cross-Coupling of Potassium Polyfluorobenzoates with Unactivated Phenol and Phenylmethanol Derivatives

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