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Aryl/heteroaryl pentafluorobenzenesulfonates (ArOPFBs): new electrophilic coupling partners for room temperature Suzuki-Miyaura cross-coupling reactions

Jayan T Joseph [a,b], Ayyiliath M Sajith [b], Revanna C Ningegowda [b], Archana Nagaraj [b], K. S. Rangappa [a], Sheena Shashikanth [a,*]

[a] *Department of Studies in Chemistry, Manasagangothri, University of Mysore, Mysore 570006, India*
[b] *Syngene International Ltd., Biocon Park, Bommasandra IV Phase, Jigani Link Road, Bangalore 560099, India*
[*] Corresponding author. E-mail address: shashis1956@gmail.com

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ABSTRACT

The first cross-coupling reaction between aryl/heteroaryl pentafluorobenzenesulfonates and aryl/heteroaryl boronic acids under mild conditions is described. The successful synthesis of highly ortho substituted biaryls and high chemoselectivity of these bench stable intermediates over tosylates, triflates, mesylates and chlorides increases its scope as a valuable cross-coupling partner. The generality of this protocol was further extended to other boron containing nucleophiles (boronates, trifluoroborates) and alkyl boronic acids.

1. Introduction

The Suzuki-Miyaura cross-coupling methodology is, debatably, one of the most malleable method, employed in the area of organic synthesis for carbon-carbon bond forming reactions.[1] The presence of biaryls and heterobiaryls in advanced materials,[2] molecules of biological importance[3] and natural products,[1] highlights the significance of developing efficient protocols for their synthesis. Over the decades, the use of aryl/heteroaryl bromides and iodides as electrophilic cross-coupling partners has been well documented in literature.[1] Activated aryl/heteroaryl chlorides, as cross-coupling partners are also well studied by various researchers across the globe.[4]

Efforts to utilize pseudo halides (triflates, tosylates, mesylates, nonaflates, phosphates, diaryl sulfates, fluorosulfates)[5,6] has expanded the substrate scope for these transformations, thereby, making it widely applicable in the field of diversity oriented synthesis (DOS). Despite these advances in pseudo halides as cross-coupling partners, the necessity to use highly demanding catalytic systems[5-7] opens the room for developing new coupling partners, which can effect these transformations under mild conditions. Considering the utility of carbon-carbon bonds, we shifted our focus on developing a new electrophilic cross-coupling partner for the Suzuki-Miyaura reaction.

2. Results/discussion

At the outset of our studies, we were interested in developing an efficient protocol which allows the use of aryl/heteroaryl pentafluorobenzenesulfonates in carbon-carbon bond forming reaction under mild conditions. By doing so, the phenolic group can be used as a means to introduce the desired functionality in the aromatic/heteroaromatic ring and then be converted into a carbon-carbon bond via a pentafluorobenzenesulfonate intermediate.[8] To the best of our knowledge, this is the first report on Suzuki-Miyaura cross-coupling process employing aryl/heteroaryl pentafluorobenzenesulfonates.

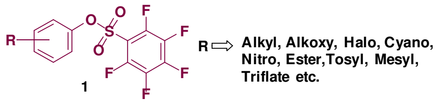
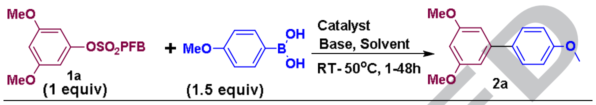


Figure 1: Pentafluorobenzenesulfonate intermediates.

For this study, a wide range of activated and deactivated aryl/heteroaryl pentafluorobenzene sulfonates (ArOPFBs) were synthesized from the corresponding phenols (Figure 1). These intermediates were obtained as crystalline solids and can be stored under normal lab conditions for long period of time.

Literature studies indicate that, electrophiles containing an electron donating group are often difficult coupling partners in Suzuki-Miyaura reaction.[9] Accordingly, we used a deactivated 3,5-dimethoxyphenyl pentafluoro benzenesulfonate and 4-methoxyphenyl boronic acid as the model substrate for optimization of reaction conditions (Table 1). Also, a procedure employed by Buchwald et al for the carbon-carbon bond forming process of tosylates was used on our model substrate.[6c] To our delight, excellent conversion was observed in our model reaction (Table 1, entry 1). The temperature of this reaction was kept at 50 degrees, speculating the increased reactivity of our electrophilic coupling partner compared to tosylate. Further optimization revealed that the conversion can be effected even at room temperature (28°C, Table 1, entry 2). Encouraged by these exciting results, we next shifted our focus on optimizing the reaction parameters with respect to Pd source, base and solvent. Evaluation of Pd sources using mild catalysts like $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_4$, $PdCl_2$, $Pd(OAc)_2$, $Pd(CH_3CN)_2Cl_2$ as shown in Table 1. However, the use of $Pd(PPh_3)_2Cl_2$ provided the best results (Table 1, entry 6, 9-11). Among the bases screened, use of $K_3PO_4.H_2O$ and KOAc were found to give superior results (Table 1). Reaction optimization with respect to solvents showed that reaction could be best performed in alcoholic solvents and toluene. Surprisingly, no product formation was observed when the reaction was performed in THF and dioxane and only starting material was recovered (Table 1, entry 16 and 18).

Table 1. Optimization of the reaction conditions.[a]

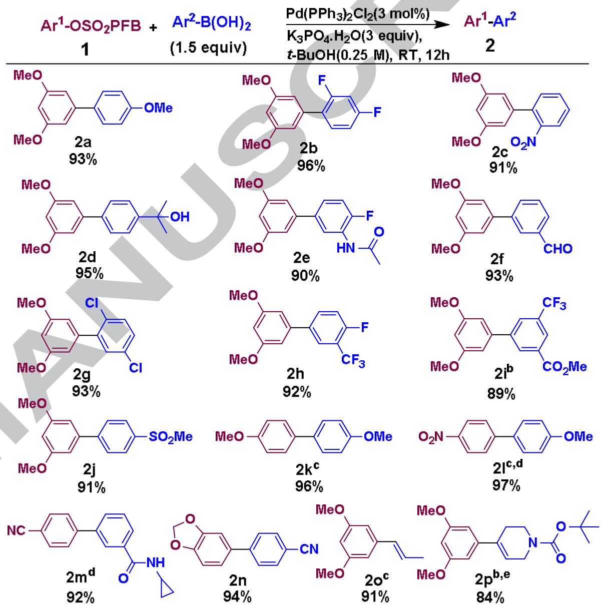


Entry	Catalyst (mol %)	Base	Solvent	Temp./Time	2a (%)[b]
1	$Pd(OAc)_2$ (2), XPhos (5)	$K_3PO_4.H_2O$	t-BuOH	50°C/1h	96
2	$Pd(OAc)_2$ (2), XPhos (5)	$K_3PO_4.H_2O$	t-BuOH	RT/6h	95
3	$Pd(OAc)_2$ (2)	$K_3PO_4.H_2O$	t-BuOH	RT/12h	72
4	$PdCl_2$ (2)	$K_3PO_4.H_2O$	t-BuOH	RT/12h	32
5	$Pd(PPh_3)_4$ (5)	$K_3PO_4.H_2O$	t-BuOH	RT/12h	68
6	$Pd(PPh_3)_2Cl_2$ (5)	$K_3PO_4.H_2O$	t-BuOH	RT/12h	95
7	$Pd(PPh_3)_2Cl_2$ (5)	$K_3PO_4.H_2O$	t-BuOH	50°C/2h	94
8	$Pd(CH_3CN)_2Cl_2$ (5)	$K_3PO_4.H_2O$	t-BuOH	RT/12h	62
9	$Pd(PPh_3)_2Cl_2$ (3)	$K_3PO_4.H_2O$	t-BuOH	RT/12h	93
10	$Pd(PPh_3)_2Cl_2$ (1)	$K_3PO_4.H_2O$	t-BuOH	RT/24h	85
11	$Pd(PPh_3)_2Cl_2$ (0.5)	$K_3PO_4.H_2O$	t-BuOH	RT/48h	78
12	$Pd(PPh_3)_2Cl_2$ (5)	K_2CO_3	t-BuOH	RT/12h	67
13	$Pd(PPh_3)_2Cl_2$ (5)	Na_2CO_3	t-BuOH	RT/12h	61
14	$Pd(PPh_3)_2Cl_2$ (5)	Cs_2CO_3	t-BuOH	RT/12h	68
15	$Pd(PPh_3)_2Cl_2$ (5)	KOAc	t-BuOH	RT/12h	81
16	$Pd(PPh_3)_2Cl_2$ (5)	$K_3PO_4.H_2O$	Dioxane	50°C/3h	02
17	$Pd(PPh_3)_2Cl_2$ (5)	$K_3PO_4.H_2O$	ACN	50°C/3h	43
18	$Pd(PPh_3)_2Cl_2$ (5)	$K_3PO_4.H_2O$	THF	50°C/3h	00
19	$Pd(PPh_3)_2Cl_2$ (5)	$K_3PO_4.H_2O$	IPA	RT/12h	78
20	$Pd(PPh_3)_2Cl_2$ (5)	$K_3PO_4.H_2O$	EtOH	RT/12h	82
21	$Pd(PPh_3)_2Cl_2$ (5)	$K_3PO_4.H_2O$	MeOH	RT/12h	63
22	$Pd(PPh_3)_2Cl_2$ (5)	$K_3PO_4.H_2O$	Toluene	50°C/3h	73
23	$Pd(PPh_3)_2Cl_2$ (5)	$K_3PO_4.H_2O$	DMF	50°C/3h	57

[a] Reaction conditions: **1a**(0.5 mmol), boronic acid (0.75 mmol), catalyst, base, solvent (2 mL), [b] Isolated yield.

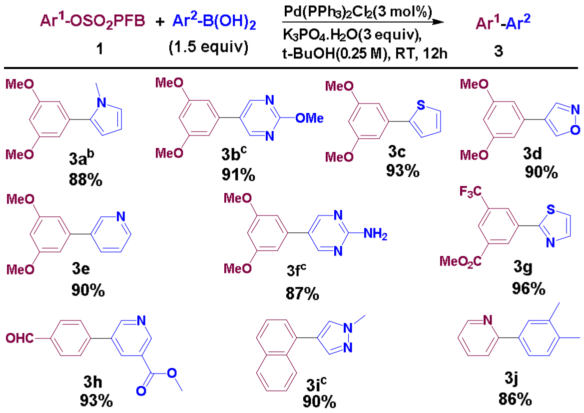
The standardized condition (Table 1, entry 9) was next applied to a wide range of aryl/heteroaryl pentafluoro benzenesulfonates and boron nucleophiles bearing either electron donating or withdrawing groups (Table 2). To our delight, all substrates studied produced excellent results. Notably, 4-nitro and 4-cyano pentafluorobenzene sulfonate (activated systems) reacted much faster without any deleterious side reactions (**2l** and **2m**). We also found that deactivated systems such as 4-methoxyphenyl and 3,4-methylynedioxyphenyl pentafluorobenzenesulfonates could be efficiently utilized as electrophilic substrates (**2k** and **2n**). A good deal of generality was also observed for boron nucleophiles with diverse functionalities (halide, methoxy, ester, amide, aldehyde, nitrile etc.); even boronic acids which are prone to protodeboronation gave high yields of products (**2b**, **2c** and **2h**). We have also demonstrated that vinyl boron nucleophiles can be an efficient alkenylating agent for ArOPFBs (**2o** and **2p).**

Table 2: Suzuki-Miyaura cross-coupling of ArOPFBs.[a]



[a] Yields represent isolated yields (average of two runs): **1**(0.5 mmol), boronic acid (0.75 mmol), $Pd(PPh_3)_2Cl_2$(3 mol %), $K_3PO_4.H_2O$ (3 equiv), *t*-BuOH (2 mL), RT, 12h. [b] Pinacolate ester was used. [c] BF_3K salt was used. [d] Reaction time-0.5h. [e] At 50°C, 6h.

Table 3: Suzuki-Miyaura cross-coupling of ArOPFBs with Heteroaryl Boronate/acids.[a]

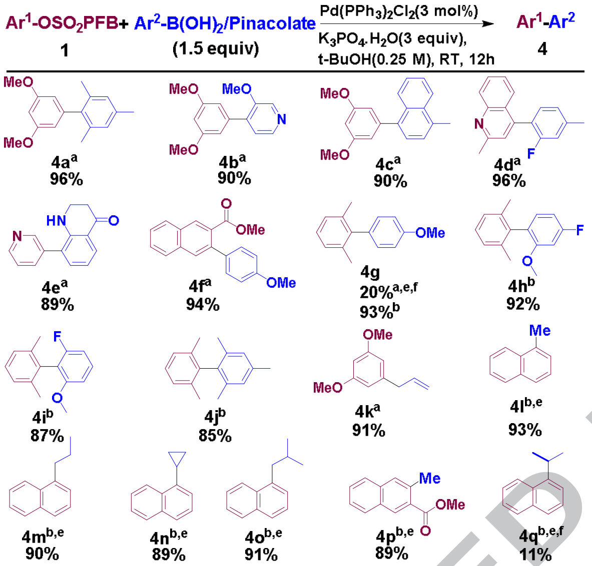


[a] Yields represent isolated yields (average of two runs): **1**(0.5 mmol), Boronic acid (0.75 mmol), $Pd(PPh_3)_2Cl_2$(3 mol%), $K_3PO_4.H_2O$ (3 equiv), t-BuOH (2 mL), RT, 12h. [b] Pinacolate ester was used. [c] at 50°C for 6h.

The importance of heterocyclic analogues in the field of medicinal chemistry and many other areas prompted us to further expand the scope of this protocol on heteroaromatic systems. This methodology was found to give excellent results with pyrrole, pyrazole, isoxazole and thiazole boronic acids which are considered to be challenging substrates in Suzuki-Miyaura cross-coupling (Table 3).[10] The compatibility of heterocyclic substrates as electrophilic coupling partners was also examined. (**3j**, **4d** and **4e**).

Efficient synthesis of sterically crowded biaryls by metal mediated cross-coupling process has gained significant importance in recent years. Literature reports reveals that highly substituted ortho biaryls can be synthesized using sterically demanding catalytic systems from their respective halides.[11]

Table 4: Hindered Suzuki–Miyaura couplings with ArOPFBs.[a]



[a]Yields represent isolated yields (average of two runs): **1**(0.5 mmol), Boronic acid (0.75 mmol), $Pd(PPh_3)_2Cl_2$(3 mol%), $K_3PO_4.H_2O$ (3 equiv), t-BuOH (2 mL), RT, 12h. [b]Reaction conditions: 1(0.5 mmol), Boronic acid (0.75 mmol), Pd(OAc)2(2 mol%), Xphos(5 mol%), $K_3PO_4.H_2O$ (3 equiv), *t*-BuOH (2 mL), RT, 12h. [c]Pinacolate ester was used. [d]Trimethyl borxine was used. [e]Reaction at 50°C for 12h. [f]GC conversion.

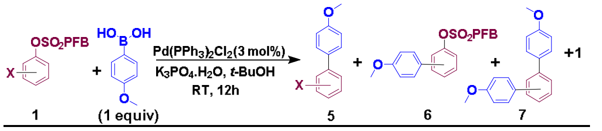
In our trials, successful synthesis of these highly ortho substituted biaryls have been achieved using conventional catalyst systems {$Pd(PPh_3)_2Cl_2$ and $Pd(OAc)_2$/X-Phos} at room temperature (Table 4). To the best of our knowledge, this is the first report on the use of pseudo halide in the synthesis of highly ortho substituted biaryls. We observed that the sterics on the nucleophilc counterpart did not affect the reaction yield and the reaction could be successfully driven to completion by using $Pd(PPh_3)_2Cl_2$ as catalyst. For example, mesytylene, 3-methoxypyridine-4-yl, 4-methyl-1-naphthyl, 2-fluoro 4-methylphenyl boronic acids reacted well under this condition (**4a-f**). Remarkably, even mono ortho substituted ArOPFBs were successfully coupled with $Pd(PPh_3)_2Cl_2$ and excellent yields were obtained (**4d** and **4f**). However, efforts to cross couple 2,6-dimethylphenyl pentafluorobenzenesulfonate with 4-methoxyphenyl boronic acid using $PdCl_2(PPh_3)_2$ was not successful even at elevated temperature (**4g**). Gratifyingly, with Buchwald's X-Phos ligand and $Pd(OAc)_2$, excellent conversion to product was observed and nearly a quantitative yield could be achieved at room temperature. The successful synthesis of tri and tetra ortho substituted biaryls (**4h-j**) under this enhanced conditions highlights the potential scope of this electrophilic substrate.

From these results and also from literature survey, [6c] we speculate that the transmetalation process was facile with $Pd(PPh_3)_2Cl_2$ for sterically congested boronic acids. But, ortho di substitution on the aryl pentafluorobenzene sulfonate was enough to prevent complete conversions to cross-coupled product using $Pd(PPh_3)_2Cl_2$.The yields were improved dramatically when $Pd(OAc)_2$ and X-Phos was used for these substrates (**4g-j**). We believe that the catalyst's high efficacy in the formation of tri- and tetra-ortho substituted biaryls is due to the formation of highly active mono-ligated palladium species - $L_1Pd(0)$, thereby increasing the rates oxidative addition, transmetalation, and reductive elimination steps in the catalytic cycle.[12]

The scope of this highly efficient synthetic protocol was further extended to alkyl boronic acids.[13] To our delight, $Pd(OAc)_2$/X-Phos was also found to be instrumental in driving these reactions to success. Excellent yields with alkyl boron nucleophiles (allyl, propyl and isobutyl) were obtained (**4k, 4m** and **4o**). Trimethylboroxine has been found to be a useful partner for the methylation of sterically congested naphthalene substrates (**4l** and **4p**). Among the secondary alkyl boronic acids, cyclopropyl boronic acid gave best results as reported with other electrophiles (**4n** and **4q**).[8b]

Chemoselective monofunctionalization through Suzuki-Miyaura cross-coupling strategy can be a powerful tool in the area of organic synthesis.[4b,14] For previously described palladium catalysts, the general order of reactivity is the following: I >Br ≥ OTf >> Cl.[4b] We have established with our studies, that using $Pd(PPh_3)_2Cl_2$ catalyst, it is possible to cross-couple a difunctionalized arene chemoselectively.

Table 5: Chemoselective Suzuki Cross-Coupling of ArOPFBs.[a]



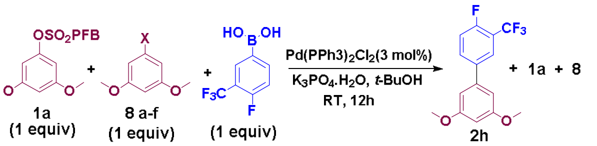
Entry	X	5(%)[b]	6(%)[b]	7(%)[b]	Recovery of 1(%)[b]
1	4-Iodo (1s)	12	39	24	18
2	4-Bromo (1l)	27	23	31	12
3	4-Chloro (1m)	82 (74)[c]	2	2	9
4	3-OTs (1n)	91 (86)[c]	0	0	4
5	3-OMs (1p)	89 (81)[c]	0	0	7
6	3-OTf (1o)	68 (57)[c]	6	9	11

[a]Reaction conditions: **1**(0.5 mmol), Boronic acid (0.5 mmol), $Pd(PPh_3)_2Cl_2$(3 mol%), $K_3PO_4.H_2O$ (3 equiv), *t*-BuOH (2 mL), RT, 12h. [b]Conversion by GCMS-FID. [c]Isolated yield.

For this study, a wide range of difunctionalized arenes as shown in Table 5**,** were synthesized and subjected to Suzuki-Miyaura coupling process using 1 equiv. of boronic acid at room temperature. Not surprisingly, comparable reactivity was observed for iodo, bromo and OPFBs leading to mixture of products (Table 5, entry 1 and 2). In case of ArOPFBs with chloro, tosylate, mesylate and triflate functionalities, the reactions proceeded with high degree of chemoselectivity and good yields of mono cross-coupled products were obtained (Table 5, entry 3-6).

Another set of crossover experiments, outlined in Table 6 was conducted to establish the reactivity trends of arylpentafluoro benzenesulfonate intermediate (**1a**) relative to the most common electrophiles employed in Suzuki coupling. For this study, an equimolar mixture of **1a** and **8** with 3 mol% $Pd(PPh_3)_2Cl_2$ in *t*-BuOH was treated with 1 equiv. of boronic acid. Upon completion, the reactions were monitored by GCMS FID. The experimental results revealed that ArOPFBs have comparable reactivity to iodides and bromides, but more reactive than chloro, tosylate, mesylate and triflate intermediates (Table 6).

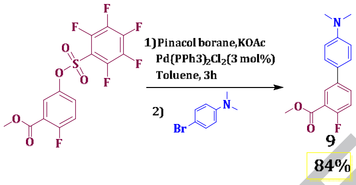
Table 6: Crossover Experiments of ArOPFBs with other Electrophiles.[a]



Entry	X	2h (%)[b]	Recovery of 1(%)[b]	Recovery of 8(%)[b]
1	Iodo (8a)	88	63	11
2	Bromo (8b)	89	42	47
3	Chloro (8c)	87	6	91
4	OTs (8d)	91	5	94
5	OMs (8e)	87	8	90
6	OTf (8f)	86	16	78

[a]Reaction conditions: **1**(0.5 mmol), **8**(0.5 mmol), Boronic acid (0.5 mmol), $Pd(PPh_3)_2Cl_2$(3 mol%), $K_3PO_4.H_2O$ (3 equiv), *t*-BuOH (2 mL), RT, 12h. [b]Isolated yield.

We have also demonstrated the synthesis of aryl boronate from pentafluorobenzene sulfonate and its subsequent conversion to biaryls by a one pot process as shown in **Scheme 1**.



Scheme 1: One pot synthesis of biaryls.

3. Conclusion

In conclusion, we have disclosed a new class of palladium-catalyzed cross-coupling partners involving aryl/heteroaryl pentafluorobenzenesulfonate. The ease of preparation of these bench stable intermediates, use of $Pd(PPh_3)_2Cl_2$ as mild catalyst, rapid reaction conditions, wide substrate scope, high chemoselectivity and facile synthesis of highly ortho substituted biaryls make this method especially attractive. Further investigations into the utility of these electrophiles in other metal-mediated processes are currently underway and will be reported in due course.

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Supplementary data

Supplementary data (Copies of the ^1H and ^{13}C NMR spectra of the products) associated with this article can be found, in the online version.

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Graphical Abstract

Aryl/heteroaryl pentafluorobenzene sulfonates (ArOPFBs): new electrophilic coupling partners for room temperature Suzuki-Miyaura cross-coupling reactions

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Jayan T Joseph [a,b], Ayyiliath M Sajith [b], Revanna C Ningegowda [b], Archana Nagaraj [b], K. S. Rangappa [a], Sheena Shashikanth [a,]*

[a] *Department of Studies in Chemistry, Manasagangothri, University of Mysore, Mysore 570006, India*

[b] *Syngene International Ltd., Biocon Park, Bommasandra IV Phase, Jigani Link Road, Bangalore 560099, India*