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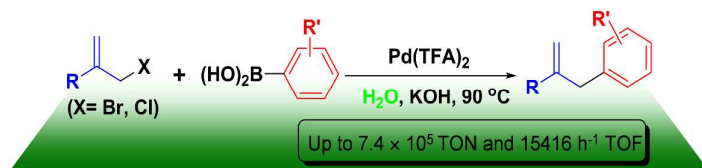
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Pd-Catalyzed Ligand-free Suzuki Reaction of β -Substituted Allylic Halides with Arylboronic Acids in Water

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The combination of $\text{Pd}(\text{TFA})_2$ and KOH could efficiently catalyze the reaction of β -substituted allylic halides with arylboronic acids in water.



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COMMUNICATION

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The catalyst system consisting of $\text{Pd}(\text{TFA})_2$ and KOH allows for a wide range of β -substituted allylic halides to react efficiently with various arylboronic acids in neat water under ligand-free conditions, affording the allylated arenes in high yields with broad functional group tolerance and up to 7.4×10^5 TON and 15416 h^{-1} TOF.

As one of the most powerful protocols for the construction of C-C bonds in organic synthesis, Pd-catalyzed Suzuki reaction has been extensively studied with a great success during the last several decades.¹ Recently there has been much research interest in developing catalyst systems capable of allowing this cross coupling reaction to be performed in water. The attractiveness of water lies in that it is cheap, clean, non-toxic, non-flammable, non-explosive and non-carcinogenic, and its high heat capacity can help prevent exothermic reactions from overheating on a large scale. Obviously, carrying out organic reactions in water would lead to substantial environmental, economical and safety gains.² As a result, a number of catalytic Suzuki reactions have proved to be feasible in water,³ and strategies developed to overcome the major concern about water solubility of catalysts and substrates include the use of water-soluble ligands,⁴ phase-transfer catalysis,⁵ organic co-solvents⁶, microwave or ultrasound.⁷ Of particular note is that recent developments have enabled the aqueous Suzuki reactions to proceed smoothly in neat water under ligand-free conditions without calling for any phase-transfer catalyst, co-solvent or degassing.⁸

Allylated arenes are valuable reagents for the construction of useful molecules,⁹ and they are also important structural motifs present in many biologically active natural products.¹⁰ Therefore, a significant amount of effort has been focused on the efficient preparation of these compounds, and many methods are now available in the literature.¹¹ Among these known methods, the Pd-catalyzed Suzuki reaction of allylic halides,^{12,13} esters¹⁴ and alcohols¹⁵ with organoboronic compounds has received increasing attention due to its simplicity, tolerance of various functional groups and the easy availability of reagents, and it is notable that this kind of transformation could benefit considerably from the use of aqueous solvents as the reaction media.^{13e,h,k-n,14j,m,15c} More recently, Scrivanti and Ueda disclosed that allylic bromides could efficiently react with aryl- and vinylboronic acids under transition-metal-free conditions to give the corresponding products in high yields.¹⁶ Nevertheless, despite the exciting progress, those reported examples mainly

dealt with the cross-coupling reactions of γ -substituted allylic substrates, and less attention has been paid to the reactions involving β -substituted allylic derivatives, with only several reports available in the literature.^{13k-n} As part of our continuing effort on the development of catalysis in water,¹⁷ herein, we report a highly efficient palladium-catalyzed ligand-free Suzuki reaction of β -substituted allylic bromides and chlorides with aryl- and vinylboronic acids in neat water without requiring any organic solvent, surfactant or inert gas protection, in which excellent group compatibility and up to 7.4×10^5 TON and 15416 h^{-1} TOF were observed.

Preliminary screening for optimal reaction conditions was performed with (3-bromoprop-1-en-2-yl)benzene (**1a**) and 4-methoxyphenylboronic acid (**2a**) as the model substrates. Following the previous reports by Scrivanti and Ueda,¹⁶ we first tried the coupling reaction of **1a** and **2a** without employing any transition-metal catalyst. However, no reaction occurred using either Scrivanti's or Ueda's protocol (Table 1, entries 1-2). Obviously, in this case the use of transition-metal catalyst is required. Considering a number of attractive advantages of using water as a solvent for organic reactions,^{2,3} we therefore chose water as the reaction medium for subsequent study. In the presence of catalytic amount of $\text{Pd}(\text{OAc})_2$ (0.01 mol%), we carried out the coupling reaction with NEt_3 as the base in pure water, and a 18% yield of the expected product **3aa** was achieved (Table 1, entry 3). However, employing $\text{Pd}_2(\text{dba})_3$, PdCl_2 or Pd/C led to lower yields (Table 1, entries 4-6). $\text{Pd}(\text{PPh}_3)_4$ afforded a 40% yield (Table 1, entry 7), and the best yield of 68% was obtained in the case of $\text{Pd}(\text{TFA})_2$ (Table 1, entry 8). In order to improve the reaction efficiency, we then explored the performance of other bases. Clearly, the reaction was sensitive to the choice of base (Table 1, entries 9-19). It is notable that HNiPr_2 , reported to be highly effective in Pd-catalyzed Suzuki reaction of aryl halides with aryl boronic acids in neat water,^{8a} gave a good yield of 85% (Table 1, entry 10), and KOH resulted in the best reactivity with a nearly quantitative yield (Table 1, entry 19). As expected, a control experiment indicated that no reaction took place in the absence of palladium catalyst (Table entry 20). Recent studies disclosed that TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and HQ (hydroquinone) could greatly facilitate the Pd-catalyzed cross coupling reactions,¹⁸ but only reduced reactivity was observed in our case (Table 1, entries 21-22). Lower temperature disfavored the reaction as the yield of **3aa** dropped to 75% at 70°C (Table 1, entry 23). The protocols

developed respectively by Liu,^{8a} Bora^{8b} and Hirao,^{8c} reported to be highly effective for the Suzuki reaction of aryl halides in neat water, were also examined (Table 1, entries 24-26). Only Liu's protocol proved equally effective (Table 1, entry 26), but the high catalyst loading made it less attractive. Remarkably, the catalyst loading could be decreased to 0.001 mol% without compromising catalytic activity (Table 1, entry 24). It is worth noting that at an even lower loading of 0.0001 mol% (S/C = 1000000) of the catalyst, a good yield of 74% was still obtained albeit over a longer reaction time of 48 h (Table 1, entry 25), corresponding to 7.4 × 10⁵ TON and 15416 h⁻¹TOF. It should be pointed out that the homocoupling reaction of **2a** and isomerization of the product were not detected in all cases. Under the same reaction conditions, the reaction of **2a** with 2-phenylprop-2-en-1-ol or 2-phenylallyl acetate was attempted, but we did not observe any product. Noteworthy is that all the reactions were performed smoothly in air without an inert atmosphere.

Table 1 Screening conditions for Pd-catalyzed Suzuki reaction of **1a** and **2a**^a


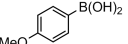



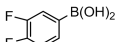
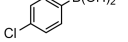


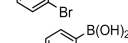

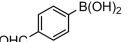
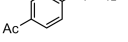


Entry	Solvent	[Pd]	Base	Time (h)	Yield(%) ^b
1	toluene	none	K ₂ CO ₃	3	nd
2 ^c	CH ₂ Cl ₂ /H ₂ O	none	Cs ₂ CO ₃	18	nd
3	H ₂ O	Pd(OAc) ₂	NEt ₃	3	18
4	H ₂ O	Pd ₂ (dba) ₃	NEt ₃	3	8
5	H ₂ O	PdCl ₂	NEt ₃	3	16
6	H ₂ O	Pd/C	NEt ₃	3	11
7	H ₂ O	Pd(PPh ₃) ₄	NEt ₃	3	40
8	H ₂ O	Pd(TFA) ₂	NEt ₃	3	68
9	H ₂ O	Pd(TFA) ₂	HNEt ₂	3	16
10	H ₂ O	Pd(TFA) ₂	HNiPr ₂	3	85
11	H ₂ O	Pd(TFA) ₂	Cy ₂ NMe	3	9
12 ^c	H ₂ O	Pd(TFA) ₂	NaOAc	3	28
13	H ₂ O	Pd(TFA) ₂	NaOH	3	55
14	H ₂ O	Pd(TFA) ₂	K ₂ CO ₃	3	37
15	H ₂ O	Pd(TFA) ₂	KF	3	51
16	H ₂ O	Pd(TFA) ₂	Cs ₂ CO ₃	3	26
17	H ₂ O	Pd(TFA) ₂	Na ₂ CO ₃	3	34
18	H ₂ O	Pd(TFA) ₂	K ₃ PO ₄	3	58
19	H ₂ O	Pd(TFA) ₂	KOH	3	95
20	H ₂ O	none	KOH	3	nd
21 ^d	H ₂ O	Pd(TFA) ₂	KOH	3	73
22 ^e	H ₂ O	Pd(TFA) ₂	KOH	3	60
23 ^f	H ₂ O	Pd(TFA) ₂	KOH	3	75
24 ^g	H ₂ O	Pd/C	K ₂ CO ₃	3	nd
25 ^h	H ₂ O	PdCl ₂	K ₂ CO ₃	3	nd
26 ⁱ	H ₂ O	Pd(OAc) ₂	HNiPr ₂	3	92
27 ^j	H ₂ O	Pd(TFA) ₂	KOH	12	86
28 ^k	H ₂ O	Pd(TFA) ₂	KOH	48	74

^aReaction conditions: **1a** (1.0 mmol), **2a** (1.2 mmol), catalyst (0.01 mol%), base (1.2 mmol), solvent (3.0 mL), 90 °C. nd: not detected. ^b Isolated yield. ^c1.5 eq. of Cs₂CO₃ were added. ^d0.1 eq. of TEMPO was added. ^e0.1 eq. of HQ was added. ^fReaction temperature 60 °C. ^g**1a** (1.0 mmol), **2a** (1.0 mmol), Pd/C (0.3 mol%), base (3.0 mmol), H₂O (10.0 mL), 25 °C. ^h**1a** (0.50 mmol), **2a** (0.55 mmol), PdCl₂ (2 mol%), base (1.5 mmol), Na₂SO₄ (8 mol%), H₂O (4.0 mL), 25 °C. ⁱ**1a** (0.50 mmol), **2a** (0.75 mmol), Pd(OAc)₂ (0.25 mol%), base (1.0 mmol), H₂O (1.0 mL), 100 °C. ^jS/C = 100000. ^kS/C = 1000000.

Having established the optimized reaction conditions, we then investigated the reaction of **1a** with other organoboronic acids. As

can be seen from Table 2, a range of arylboronic acids reacted smoothly with **1a** in neat water in the presence of 0.01 mol% Pd(TFA)₂ to produce the expected 2,3-diarypropenes in good to excellent yields in 3 h (Table 2, entries 1-20). It was found that the reaction was highly tolerant of various functional groups with different electronic and steric properties. Notably, the sensitive halogen substituent (Br and Cl) in the aromatic ring of arylboronic acids could well survive under the current conditions, affording the corresponding products in high yields (Table 2, entries 8-11). Interestingly, the presence of a hydroxyl group on the aryl ring of arylboronic acid did not affect the reaction, and the expected product **3am** could be obtained in 90% yield (Table 2, entry 12). Steric hindrance seems to have little influence on the reaction efficiency as evidenced by the fact that arylboronic acids bearing substituents at the 2-position showed good reactivity (Table 2, entries 4, 5, 9, 11, 19). The reactions involving heteroarylboronic and alkenylboronic acids were also highly efficient, delivering the corresponding products in 83-93% yields (Table 2, entries 21-25). To showcase the practicability of this process, we tried the cross coupling of 5 g of **1a** with **2a** (30.61 mmol) in the presence of 0.01 mol% Pd(TFA)₂ in water. The reaction afforded the desired product **3aa** in 91% isolated yield in 8 h.

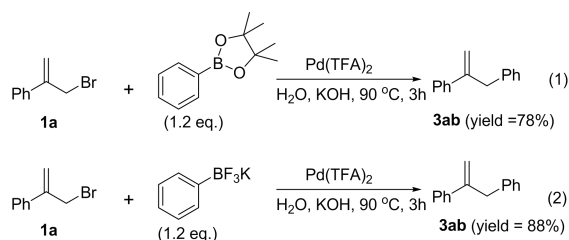
Table 2. Pd-catalyzed Suzuki reaction of **1a** with organoboronic acids in water^a

Entry	Organoboron	Yield (%) ^b (product)
1		2b 90 (3ab)
2		2c 92(3ac)
3		2d 87(3ad)
4		2e 84(3ae)
5		2f 81(3af)
6		2g 90(3ag)
7		2h 88(3ah)
8		2i 91(3ai)
9		2j 90(3aj)
10		2k 89(3ak)
11		2l 90(3al)
12		2m 90(3am)
13		2n 87(3an)
14		2o 81(3ao)
15		2p 88(3ap)

16		2q	87(3aq)
17		2r	84(3ar)
18		2s	88(3as)
19		2t	83(3at)
20		2u	79(3au)
21		2v	83(3av)
22		2w	85(3aw)
23		2x	88(3ax)
24		2y	92(3ay)
25		2z	93(3az)

^aConditions: **1a** (1.0 mmol), **2** (1.2 mmol), Pd(TFA)₂ (0.01 mol%), KOH (1.2 mmol), H₂O (3.0 mL), 90 °C, 3h. ^bIsolated yield.

The reaction of **1a** with other organoboronic derivatives under the optimized reaction conditions was subsequently investigated. The arylboronic ester, 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane, underwent smooth allylation in water, affording the expected product **3ab** in 78% yield (Scheme 1, (1)). A better yield of 88% was achieved with potassium phenyl trifluoroborate as the coupling partner (Scheme 1, (2)).



Scheme 1 Allylation of other organoboronic derivatives.

We then turned our attention to the coupling reactions of other β -arylated allylic halides with organoboronic acids, and the results are summarized in Table 3. Under the same conditions as described above, it was found that various allylic bromides with different substituents on the aryl ring could undergo successful coupling reaction with a range of organoboronic acids, and the presence of functional groups in both coupling partners did not affect the transformation (Table 3, entries 1-25). For example, the allylic bromide **1g** bearing a sensitive bromine substituent on the aryl ring could be efficiently transformed into the target products with high yields, leaving the sp² C-Br bond intact (Table 3, entries 17-18). The effectiveness of the current catalyst system was further demonstrated in the arylation of allylic chloride. When (3-chloroprop-1-en-2-yl)benzene (**1k**) was employed, the coupling reaction proceeded effectively, affording the target compound **3aa** and **3aq** in 91% and 89% yield, respectively (Table 3, entries 26-27). The β -alkylated allylic halide **1l** also cross-coupled with aryl and vinyl boronic acids to give the expected products in good yields (Table 3, entries 28-31).

Table 3. Pd-catalyzed Suzuki reaction of β -arylated allylic halides with organoboronic acids in water^a

$\text{Ar}-\text{CH}=\text{CH}-\text{CH}_2-\text{Br} \quad \text{1} + \quad \text{RB(OH)}_2 \quad \text{2} \xrightarrow[\text{H}_2\text{O, KOH, 90 } ^\circ\text{C}]{\text{Pd(TFA)}_2} \text{Ar}-\text{CH}=\text{CH}-\text{R} \quad \text{3}$					
Entry	Allylic halide	Organoboron	Yield(%) ^b (product)		
1			2a	82(3ba)	
2			2b	79(3bb)	
3			2k	80(3bk)	
4			2o	78(3bo)	
5			2s	84(3bs)	
6			2u	88(3bu)	
7			2c	75(3cc)	
8			2q	78(3cq)	
9			2b	76(3db)	
10			2c	79(3dc)	
11			2q	77(3dq)	
12			2r	82(3er)	
13			2x	89(3ex)	
14			2y	81(3ey)	
15			2z	88(3ez)	
16			2x	85(3fx)	
17			2k	80(3gk)	
18			2x	90(3gx)	
19			2b	83(3hb)	
20			2a	85(3ia)	
21			2b	95(3ib)	
22			2u	80(3iu)	
23			2a	88(3ja)	
24			2b	85(3jb)	
25			2u	83(3ju)	

26		1k		2a	91(3aa)
27		1k		2q	89(3aq)
28		1l		2b	83 (3lb)
29		1l		2c	80 (3lc)
30		1l		2q	75 (3lq)
31		1l		2x	79 (3lx)

^aConditions: allylic halide **1** (1.0 mmol), organoboronic acid **2** (1.2 mmol), Pd(TFA)₂ (0.01 mol%), KOH (1.2 mmol), water (3.0 mL), 90 °C, 3 h. ^b Isolated yield.

be compatible with a wide range of functional groups in both coupling partners, and could be performed in air under a catalyst loading as low as 0.00001 mol% with TON up to up to 7.4×10^5 and TOF up to 15416 h⁻¹. Unlike most of the older ligand-free water based methods, our method did not require the addition of surfactants, phase-transfer agents or co-solvents or using microwave or ultrasound. The present catalysis offers an efficient, green and practical new method for accessing allylated arenes.

Experimental section

General procedure for allylation of arylboronic acid in water

A mixture of allylic halide **1** (1.0 mmol), arylboronic acid **2** (1.2 mmol), KOH (84.17 mg, 1.5 mmol), palladium trifluoroacetate (0.033 mg, 0.0001 mmol) in water (3.0 mL) in a round-bottom flask was stirred and heated at 90 °C for 3 h. Then the flask was removed from the oil bath and cooled to room temperature. Water (5.0 mL) was added, and the mixture was extracted with CH₂Cl₂ (3 × 5.0 mL). The combined organic extracts were dried over anhydrous Na₂SO₄, concentrated in vacuo. The residue was then purified via flash chromatography on silica gel using a mixture of ethyl acetate and hexane to give the pure product.

Acknowledgements

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Notes and references

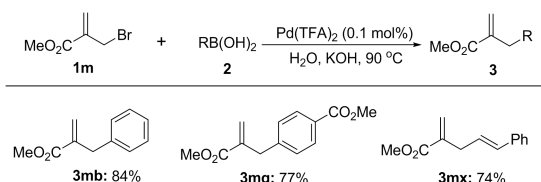
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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

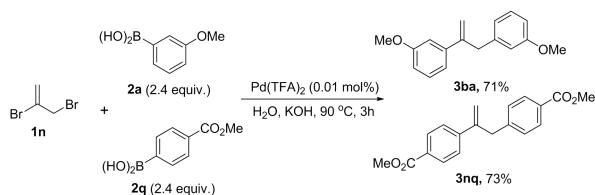
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To expand the scope of our catalyst system further, the coupling reactions of other types of β-substituted allylic halide with organoboronic acids were studied. However no reaction was observed in the coupling reaction of **1m** with organoboronic acids under the same reaction conditions. This problem could be resolved simply by increasing the S/C ratio to 1000, which allowed the smooth allylation of **2b**, **2q** and **2x** to give good results (Scheme-2).



Scheme 2 The reactions of substrate **1m** with organoboronic acids.

We also explored the reaction of the di-bromo-substituted substrate **1n** with arylboronic acids (Scheme-3). It was found that the double allylated products **3ba** and **3aq** were isolated in good yields, and the vinyl bromide could not be tolerated. Similar observation has been reported by Ikegami and co-workers in the aqueous Suzuki reaction catalyzed by assembled Pd complex.¹³¹



Scheme 3 Allylation of the di-bromo-substituted substrate **1n**.

Conclusions

In summary, we have demonstrated that in the presence of catalytic amount of Pd(TFA)₂ the allylation of various organoboronic acids with different β-substituted allylic halides could proceed efficiently in neat water without using any ligand and organic solvent. Key to the success of the reaction is the choice of base and catalyst precursor. The reaction was found to

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