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Solvent control of product diversity in palladium-catalyzed addition of arylboronic acid to aryl aldehydes

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ABSTRACT

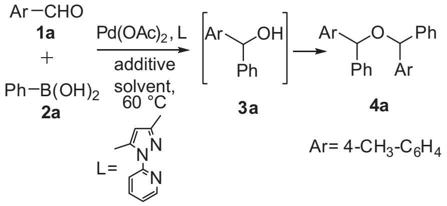
In Pd-catalyzed arylboronic acid addition to aryl aldehydes, the expected carbinol or asymmetrical ether can be obtained as the major product by altering aqueous solvent composition. Exploiting this methodology with 2-formylbiphenyls as reaction partner, a fluorene scaffold can be readily constructed in two steps.

Diarylcarbinol derivatives are important intermediates for the synthesis of natural products, pharmacologically active compounds as well as new materials.[1] Transition metal catalyzed addition of organometallic reagents to aldehydes is a mild and efficient method widely used for the synthesis of substituted carbinols. Among organometallic compounds, organoboron reagents[2] have achieved prominence because of their air and moisture stability, low toxicity, and ease of handling. Transition metal catalyzed 1,2-addition of organoboron reagents to aldehydes has drawn much attention since Miyaura and co-workers reported Rh-catalyzed addition of arylboronic acid to aldehydes.[3] Subsequently, various catalytic systems were developed and they are primarily based on Rh[4] and Pd.[5]

As a part of our ongoing research with palladium-ligand chemistry in catalysis, we investigated Pd-catalyzed 1,2-addition reaction of boronic acids and aldehydes as a model reaction. In our laboratory, pyrazole based ligands were successfully used in palladium-catalyzed coupling reactions.[6] In the present work, we describe the use of 3,5-dimethyl-1-(2′-pyridyl)pyrazole (L)[7] as a ligand in Pd-catalyzed addition of arylboronic acids to aryl aldehydes. We demonstrate that the reaction medium plays a decisive role in determining the product formation from the same combination of reactants.

Initially, we selected phenylboronic acid and 4-methylbenzaldehyde as reaction partners and $Pd(OAc)_2$ as the metal catalyst precursor in the presence of different bases and solvents (Scheme 1). No reaction occurred until triflic acid (TfOH) was used as an additive instead of a base and water as the solvent. The starting aldehyde was consumed in 8 h at 60 °C to generate ether **4a** as the only product in high yield (see entry-13, Table S1 of Supplementary data). It is possible that the symmetrical ether **4a** was formed in situ by the acid catalyzed self-condensation of the initially formed 1,2 addition product that is, phenyl(*p*-tolyl)methanol (**3a**). The formation of this undesired product **4a** led us to explore alternative conditions to prepare the desired carbinol **3a** from this reaction.

Interestingly, we found that compound **3a** was produced in 10% yield along with compound **4a** (61%) (see entry-17, Table S1) in dioxane/water (1:1). Formation of compound **3a** prompted us to play with the ratio of dioxane and water in the addition reaction with TfOH as an additive. Gratifyingly, we observed that dioxane/water (5:1) was the best solvent system at 80 °C to furnish carbinol **3a** exclusively in 81% yield.



Scheme 1. Addition of phenylboronic acid to 4-methylbenzaldehyde.

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These results clearly indicate that solvent composition controls the product diversity. Therefore, we adopted the solvent composition of dioxane/water (5:1) and TfOH as an additive in all cases to prepare the desired carbinols from the addition reaction of boronic acids to aldehydes. A range of the substituted benzaldehydes afforded 1,2-addition product in good to excellent yields by this condition (Table 1). Steric factor appears to influence the yield to some extent. For example, 1-naphthyl or 2-naphthyl-aldehyde required more time to produce carbinols in good yields (entries 8 and 9; Table 1). Also, addition of 1-naphthylboronic acid and mesitylboronic acid to 4-nitrobenzaldehyde resulted in lower yield compared to phenylboronic acid (compare entries-3 and 4 with entry-2, Table 1). No perceptible product formation was observed if the ligand L is omitted from the reaction mixture.

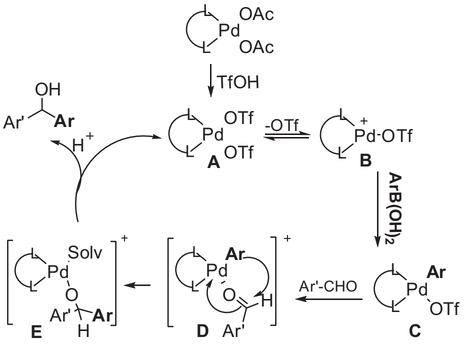
A tentative reaction mechanism is illustrated in Scheme 2. It has been suggested earlier[8] that transmetalation of an electrophilic Pd(II) intermediate such as **B** can lead to intermediate **C**. Coordination of the aldehyde to the electrophilic metal center followed by migration of the aryl group to the activated aldehyde then leads to intermediate **E** from which the carbinol is released and the catalyst is regenerated.

In the absence of dioxane in the solvent these carbinols were easily converted to symmetric ethers in situ. A few substituted benzaldehydes were tested under this reaction condition and all of them furnished corresponding symmetrical ethers in excellent yields (Table 2).

Formation of symmetrical ethers from this reaction is indicative of the intermediacy of a benzylic carbocation (Scheme 3).

Above hypothesis is supported by an independent experiment (Scheme 4). Compound **3a** was synthesized by the Grignard method, and heated with TfOH (2 equiv) in water at 60 °C in the absence of metal and ligand. The product obtained was characterized from NMR spectroscopy and found to be identical with compound **4a** as shown in Table 2.

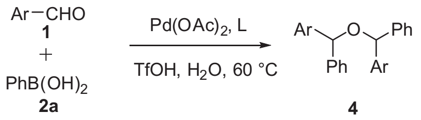
Although not explicitly stated, a similar benzylic carbocation is probably the putative intermediate in the formation of triarylmethanes as reported by Lin and Lu.[5f] Nitromethane was used as a solvent and the catalyst was a Pd(II) cation. Water was clearly detrimental to the reaction. In our case, on the other hand, water is the best solvent when benzylic carbocation is formed leading to the formation of the ether as the only product. We, therefore, added 1,3,5-trimethoxybenzene to the reaction mixture from the beginning and the reaction was conducted in water alone (Scheme 5). Instead of the symmetrical ether an unsymmetrical triarylmethane was the only isolable product (60%) in this reaction further confirming the intermediacy of a carbocation.



Scheme 2. Tentative mechanism for the formation of carbinol.

Table 2

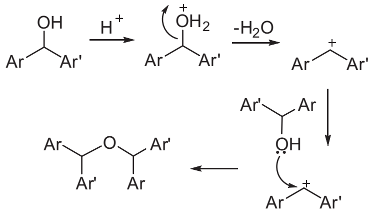
Formation of symmetrical ether[a]



Entry	Ar	Time (h)	Product	Yield[b] (%)
1	4-Me-Ph	8	**4a**	90
2	4-^{i}Pr-Ph	6	**4b**	80
3	4-F-Ph	8	**4c**	85
4	3-OMe-Ph	8	**4d**	82

[a] Reaction condition: ArB(OH)$_2$ (1.2 mmol), RCHO (1.0 mmol), TfOH (2 mmol), H_2O (2 mL), Pd(OAc)$_2$ and L (4 mol %).

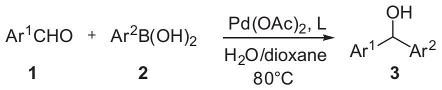
[b] Isolated yield.



Scheme 3.

Table 1

Addition of arylboronic acid to arylaldehydes[a]



Entry	Ar^1	Ar^2	Time (h)	Product	Yield[b] (%)
1	4-CH$_3$-C$_6$H$_4$	Ph	7	**3a**	81
2	4-NO$_2$-C$_6$H$_4$	Ph	2	**3b**	98
3	4-NO$_2$-C$_6$H$_4$	1-Naph	2	**3c**	88
4	4-NO$_2$-C$_6$H$_4$	Mesityl	9	**3d**	61
5	3-NO$_2$-4-Cl-C$_6$H$_3$	Ph	2	**3e**	92
6	4-F-C$_6$H$_4$	Ph	4	**3f**	80
7	4-CF$_3$-C$_6$H$_4$	Ph	4	**3g**	94
8	1-Naph	Ph	8	**3h**	76
9	2-Naph	Ph	8	**3i**	79
10	3,4-Di-Cl-C$_6$H$_3$	Ph	5	**3j**	84
11	4-^{i}Pr-C$_6$H$_4$	Ph	7	**3k**	78
12[c]	4-NO$_2$-C$_6$H$_4$	Ph	2	**3b**	—

[a] Reaction condition: aldehyde (1 mmol), boronic acid (1.2 mmol), Pd(OAc)$_2$ (4 mol %), L (4 mol %), TfOH (2 mmol), dioxane/H_2O (2 mL/0.4 mL).

[b] Isolated yield.

[c] No L was used.

We sought to utilize the benzylic carbocation in the synthesis of the fluorene nucleus, an important structural motif in polycyclic aromatic hydrocarbons that are useful advanced materials with remarkable photonic and electronic properties, such as light-emitting diodes (OLEDs), solar cells, thin film transistors, etc.[9] Some fluorene derivatives are useful precursors for the synthesis of ligand in organometallic chemistry[10] and some of them exhibit bioactivities[11] as well.

The reported methods for the synthesis of substituted fluorenes include Friedel–Crafts ring closure of biarylalcohols promoted by Lewis or Bronsted acid,[9h,i,12] Pd-catalyzed coupling reaction,[13] annulation reaction,[14] and some other methods.[15] Metal catalyzed synthesis of fluorene suffers from harsh reaction condition and/or use of phosphine ligands. In case of Friedel–Crafts ring closure, biaryl alcohols had to be first synthesized and isolated from 2-formylbiphenyl derivatives by air and moisture sensitive Grignard reagents.[12a,b]

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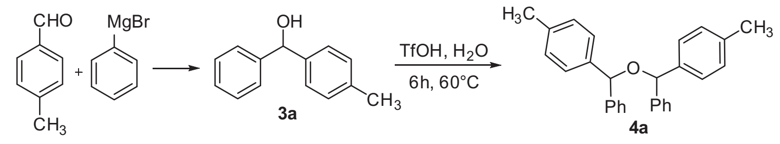
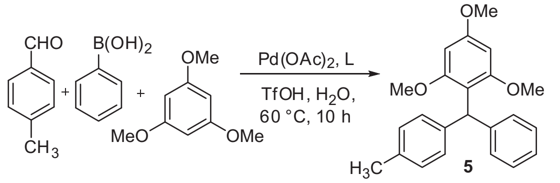


Scheme 4.



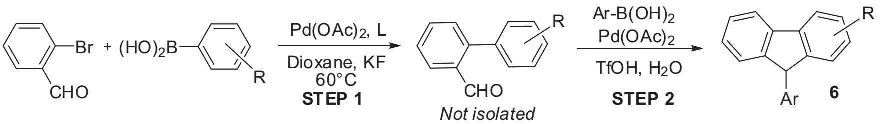
Scheme 5.

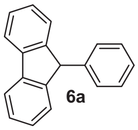
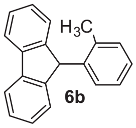
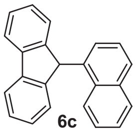
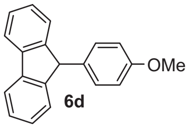
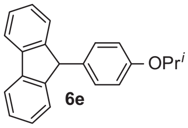
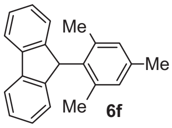
We presumed that, in our case, after the addition of boronic acid to 2-formylbiphenyl, intramolecular aromatic electrophilic substitution reaction (Friedel–Crafts type) by the incipient benzylic carbocation followed by aromatization would yield 9*H*-arylfluorene. The 2-formylbiphenyl derivatives, in turn can be synthesized in one pot from 2-bromobenzaldehydes by the Suzuki–Miyaura coupling reaction using the same palladium catalyst.

Initially, 2-bromobenzaldehyde and phenylboronic acid were added together in the presence of $Pd(OAc)_2$ (2 mol %) and L (2 mol %) and the reaction mixture was stirred in dioxane at 60 °C. Within 1.5 h, the starting material was consumed and new spot of 2-formylbiphenyl was developed (by TLC). The reaction mixture was filtered off, concentrated, and dried. Phenylboronic acid, $Pd(OAc)_2$ (4 mol %), L (2 mol %), TfOH (2 equiv), and water were added to the crude reaction mixture and heated at 80 °C for 10 h. The desired 9-arylfluorene (**6a**) was isolated in 26% yield along with biarylalcohol (**7**) and its corresponding ether derivative (**8**).

Optimization of the reaction condition to improve the yield of 9-phenylfluorene from 2-formylbiphenyl required a few additional experiments (Table S2 of Supplementary data). Reactions were

Table 3
Formation of 9-arylfluorene[a]



Entry	Step 1		Step 2			Final product	Overall yield[b] (%)
	R	Time (h)	Ar	Time (h)	Temp (°C)		
1	H	1.5	Ph	2	60	 **6a**	90
2	H	1.5	2-Me-Ph	2	60	 H3C **6b**	86
3	H	1.5	1-Naph	8	60	 **6c**	70
4	H	1.5	1-Naph	3	80		81
5	H	1.5	4-OMe-Ph	4	60	 OMe **6d**	86
6	H	1.5	4-OPr^i-Ph	4	60	 OPr^i **6e**	84
7	H	1.5	Mesityl	8	60	 Me Me Me **6f**	73
8	H	1.5	Mesityl	3	80		80

(*continued on next page*)

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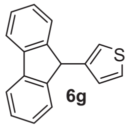
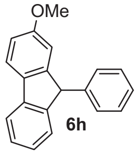
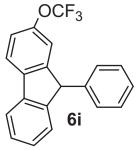
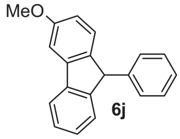
Table 3 (*continued*)

Entry	Step 1		Step 2			Final product	Overall yield[b] (%)
	R	Time (h)	Ar	Time (h)	Temp (°C)		
9	H	1.5	3-Thiophene	8	60	 **6g**	67
10	H	1.5	3-Thiophene	3	80		79
11	4-OMe	1.5	Ph	2	60	 **6h**	88
12	4-OCF_3	3	Ph	12	60	 **6i**	67
13	4-OCF_3	3	Ph	5	80		79
14	3-OMe	2	Ph	2	60	 **6j**	86

[a] Reaction condition-Step 1: 2-bromobenzaldehyde (1 mmol), boronic acid (1.2 mmol), $Pd(OAc)_2$ and L (2 mol %), KF (3 mmol), dioxane (1.5 mL); step 2: boronic acid (1.2 mmol), $Pd(OAc)_2$ (2 mol %), H_2O (0.4 mL), TfOH (2 mmol).

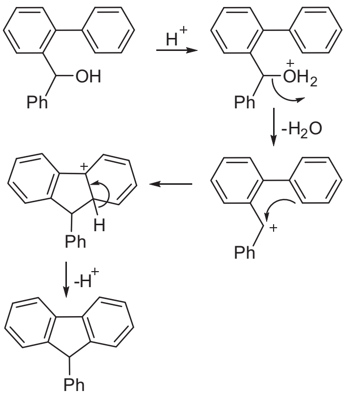
[b] Isolated yield.

performed at different dioxane/water ratios.[16] It was observed that the presence of water is mandatory for this reaction to occur; dioxane/H_2O ratio 5:1 provided the best yield of product. Coincidentally it was the same dioxane/water ratio that afforded 1,2 addition product from substituted aryl benzaldehydes (see Table 2). It was also found that two equivalents of TfOH was necessary for the production of fluorene in high yield.

Several 9-arylfluorene derivatives were successfully synthesized in good to excellent overall yields under optimized condition starting from 2-bromobenzaldehydes and functionalized boronic acids (Table 3). Differently substituted boronic acids can be employed both in the first and the second step as per the requirement, allowing for a great diversity.

A range of functional groups was also tolerated under the reaction condition. Steric factors appear to influence the rate and yield of this reaction to some extent. Hindered boronic acids such as mesitylboronic acid or 1-naphthylboronic acid required more time to attain completion. Elevation of temperature in the second step for the hindered boronic acid addition resulted in higher yield at a relatively rapid rate (entries 4 and 8; Table 3). Heterocyclic rings such as thiophene can also be appended at 9-position of fluorene by taking 3-thiopheneboronic acid in the second step (entries 9 and 10; Table 3). Lack of reactivity on account of electron deficiency in the nucleophilic aromatic ring (entries 12 and 13; Table 3) can be compensated by increase in the reaction temperature from 60 °C to 80 °C.

Formation of fluorene is a culmination of carbocation chemistry as described earlier and depicted in Scheme 6.



Scheme 6.

In summary, we demonstrated that by suitably altering the aqueous solvent composition, it is possible to obtain a carbinol or an ether as the major product of palladium-catalyzed addition of $ArB(OH)_2$ to Ar′-CHO. With 2-formylbiphenyls as reaction partner, fluorenes can be readily synthesized. The 2-formylbiphenyl substrate synthesized from the Suzuki–Miyaura reaction sequence can be used for the cyclization step without purification. The synthetic protocol described herein has three practical advantages: first, they can be performed without any precaution to exclude moisture or air; second, carbinol synthesis via hazardous Grignard addition can be avoided for the synthesis of substituted fluorenes; and third, two Pd-catalyzed reactions can be carried out sequentially without the need to purify the products in between.

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Supplementary data

Supplementary data (experimental procedure, optimization of reaction conditions and characterisation data of all products listed in the tables) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.07.073.

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16. Dioxane was chosen as a partner solvent because the Suzuki-Miyaura coupling reaction was done in dioxane and the product of the coupling step was directly used in the next operation.

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