Palladium-Catalyzed Addition of Arylboronic Acids to *N*-Tosylarylimines

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Abstract: Pd-catalyzed addition of arylboronic acids to *N*-tosylarylimines was described by employing easily prepared, air-stable aminophosphine ligands, cheap inorganic base, and common organic solvents, providing diarylmethylamine derivatives through one-pot synthesis in moderate to good yields. The efficiency of this reaction was demonstrated by the compatibility with nitro, trifluoromethyl, fluoro, chloro, and methoxy groups. Moreover, rigorous exclusion of air/moisture is not required in these transformations.

Key words: *N*-tosylarylimines, arylboronic acids, palladium-catalyzed, aminophosphine ligands, diarylmethylamine derivatives

In the past few years, great strides have been made in the development of the methods of insertion unsaturated carbon–heteroatom multiple bonds (C=O,[1] C=N,[2] C≡N[3]) into carbon–metal bonds. The addition of arylmetallic reagents to imines catalyzed by transition metal has drawn considerable attentions.[4] The addition products are important precursors for the synthesis of many pharmacologically active compounds. For instance, the 1,1-diarylalkyl structural segment is found in antimuscarinics,[5] antidepressants,[6] and endothelin antagonists.[7] Common strategies involve the catalytic asymmetric additions of organozinc reagents to *N*-sulfonylimines, *N*-phosphinoylimines, *N*-formylimines, and *N*-arylimines.[8] However, these protocols suffer from several limitations, such as the narrow substrate scopes, the use of unusual ligands, the inherent air- and water-sensitivity, and the tedious separation of the toxicity-containing byproducts. The development of practical synthetic methods for the preparation of the multifunctional diarylmethylamines and their derivatives is highly desirable. The use of organoboronic reagents has been winning high prestige in the metal-catalyzed C–C bond formation as a result of their relative stability toward air and moisture, good functional group tolerance, commercial availability, and low toxicity as well as ease of synthesis.[9] Recently, many efforts have been made in the rhodium-catalyzed addition of organoboronic reagents to imines.[10] Very recently, Lin reported C_2-symmetrical tetrahydropentalenes as new chiral diene ligands for highly enantioselective Rh-catalyzed arylation of *N*-tosylarylimines with arylboronic acids.[10a] Since Pd atom is more electronegative than Rh atom, the polarity of C–Pd bond is poorer than C–Rh bond, so C–Pd bond is harder to insert into C=N bond. Thus, such transformations catalyzed by palladium were scarcely reported. Lately, Lu reported cation palladium(II)-catalyzed addition of arylboronic acids to *N*-*tert*-butanesulfinyl imino esters for the synthesis of arylglycine derivatives.[11] Hu and coworkers have reported palladacycles were highly active catalysts for the addition reactions of arylboronic acids to aldehydes, α,β-unsaturated ketones, ketoesters, and aldimines.[12] Among the conditions described above, examples of palladium-catalyzed tuned by tertiary phosphine are scarce or have not been reported. The electron density and the hindrance of the P atom on the aminophosphine ligand may be tuned facilely, which may have dramatic effect on the reactivity. Furthermore, the chiral groups may be introduced into the phosphine ligands for asymmetric addition of arylboronic acids to C=N. Thus, it is of great importance to develop the tertiary phosphine-mediated transformation. Herein, we describe an efficient palladium-catalyzed addition of arylboronic acids to *N*-tosylarylimines in the presence of *i*-Pr_2NPPh_2, providing diarylmethylamine derivatives in moderate to good yields.

The electron-withdrawing tosyl group on the nitrogen atom may enhance the activity of C=N in such transformations. Thus we initially chose the addition of phenylboronic acid to *N*-tosylphenylimine as the model reaction by employing $PdCl_2$ as the palladium source, Na_2CO_3 as the base, and anhydrous dioxane as the solvent; 4 Å molecular sieve (MS) were added to inhibit the decomposition of *N*-tosylarylimines in the catalytic system. Since ligands always play important roles in transition-metal-catalyzed chemistry, we first turned our attentions to the screening of ligands (Table 1). In our catalytic system, bidentate phosphine ligands such as dppp, dppe, dppb, (*S*)-binap, and dppf were much less effective, monodentate phosphine ligands **L6**–**L14** had no catalytic activity with the exception of P(1-naphthyl)$_3$, which could promote the arylation of aldehydes to furnish carbinol derivatives in good to excellent yields,[13] affording the desired product in only 26% yield. In our previous work, the aminophosphine ligands were highly efficient ligands in Suzuki–Miyaura cross-coupling reaction, as well as in copper and amine-free Sonogashira reaction.[14] Accordingly, a series of aminophosphine ligands were tested in the model reaction. To our delight, the ligand **L15** provided the desired

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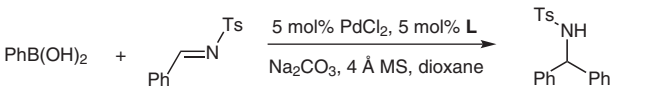
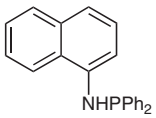
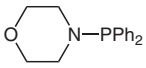
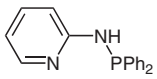
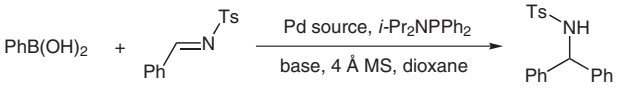
Table 1 Ligand Screening[a]



Ligand		Yield (%)
L1	dppe	<5
L2	dppp	<5
L3	dppb	<5
L4	(*S*)-binap	<5
L5	dppf	<5
L6	Ph_3P	<5
L7	$P(2\text{-furyl})_3$	<5
L8	$P(2\text{-tolyl})_3$	<5
L9	$P(2\text{-thienyl})_3$	<5
L10	$P(4\text{-tolyl})_3$	<5
L11	$P(1\text{-naphthyl})_3$	27
L12	$P(4\text{-FC}_6H_4)_3$	<5
L13	$P(4\text{-MeOC}_6H_4)_3$	<5
L14	$P(4\text{-ClC}_6H_4)_3$	<5
L15	$i\text{-Pr}_2NPPh_2$	65
L16	$i\text{-Pr}_2NP(2\text{-tolyl})_2$	<5
L17		<5
L18		<5
L19		<5

[a] All the reactions were run with *N*-tosylphenylimine (130 mg, 0.5 mmol), phenylboronic acid (122 mg, 1.0 mmol), Na_2CO_3 (159 mg, 1.5 mmol), $PdCl_2$ (4.4 mg, 5 mol%), 4 Å MS (100 mg), and *i*-Pr_2NPPh_2 (7.2 mg, 5 mol%) in dioxane (3 mL) at 80 °C for 24 h under N_2 atmosphere and anhydrous solvent with isolated yields.

Table 2 Effects of Pd Sources, Bases, Solvents, and Ligands on the Pd-Catalyzed Addition of Phenylboronic Acid to *N*-Tosylphenylimine[a]



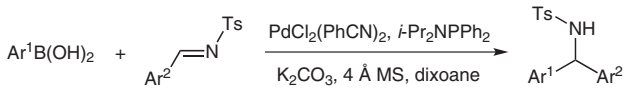
Entry	Pd source	Base	Solvent	L/Pd ratio	Yield (%)
1	$PdCl_2$	Li_2CO_3	dioxane	1	23
2	$PdCl_2$	Na_2CO_3	dioxane	1	60
3	$PdCl_2$	Rb_2CO_3	dioxane	1	68
4	$PdCl_2$	Cs_2CO_3	dioxane	1	<5
5	$PdCl_2$	DABCO	dioxane	1	<5
6	$PdCl_2$	NaOH	dioxane	1	<5
7	$PdCl_2$	Et_3N	dioxane	1	<5
8	$PdCl_2$	K_2CO_3	dioxane	1	<5
9	$PdCl_2$	K_2CO_3	DMF	1	<5
10	$PdCl_2$	K_2CO_3	DMAC	1	<5
11	$PdCl_2$	K_2CO_3	DME	1	10
12	$PdCl_2$	K_2CO_3	THF	1	61
13	$PdCl_2$	K_2CO_3	toluene	1	49
14	$PdCl_2$	K_2CO_3	MeCN	1	35
15	$Pd(OAc)_2$	K_2CO_3	dioxane	1	23
16	$Pd(PPh_3)_2$	K_2CO_3	dioxane	1	38
17	$Pd_2(dba)_3$	K_2CO_3	dioxane	1	46
18	$PdCl_2(PPh_3)_2$	K_2CO_3	dioxane	1	41
19	$PdCl_2(MeCN)_2$	K_2CO_3	dioxane	1	65
20	$PdCl_2(PhCN)_2$	K_2CO_3	dioxane	1	83
21	$PdCl_2(PhCN)_2$	K_2CO_3	dioxane	1	83
22	$PdCl_2(PhCN)_2$	K_2CO_3	dioxane	0.5	71

[a] All reactions were run with *N*-tosylphenylimine (130 mg, 0.5 mmol), phenylboronic acid (122 mg,1.0 mmol), base (1.5 mmol), Pd source (5 mol%), 4 Å MS (100 mg), and *i*- Pr_2NPPh_2 (5 mol%) in anhydrous solvent (3 mL) at 80 °C for 24 h under N_2 atmosphere with isolated yield.

product in 65% yield, while others were totally ineffective.

Next, further investigations into optimization of other reaction conditions (Table 2), such as bases, solvents, and palladium sources as well as the ratios of Pd/**L15** were conducted. Among the bases we employed, K_2CO_3 was superior to some other bases such as Li_2CO_3, Na_2CO_3, Rb_2CO_3, Cs_2CO_3, NaOH, and $K_3PO_4 \cdot 3H_2O$, and the product was isolated in 68%. The choice of solvents was also crucial to the success of the catalytic system. Dioxane was tested to be the best among the common solvents such as DMAC, DMF, DME, toluene, THF, and MeCN, $PdCl_2(PhCN)_2$ exhibited the highest catalytic activity among $PdCl_2$, $Pd(OAc)_2$, $Pd_2(dba)_3$, $PdCl_2(PPh_3)_2$, $PdCl_2(PhCN)_2$, $PdCl_2(MeCN)_2$, and $Pd(PPh_3)_4$. Increasing the amount of **L15** in the system had little influence on the yield, but reducing the amount of **L15** caused the yield to decrease sharply from 83% to 71%, respectively.

Table 3 Pd-Catalyzed Addition of Arylboronic Acids to Electron-Deficient *N*-Tosylarylimines and Electron-Neutral Analogues[a]

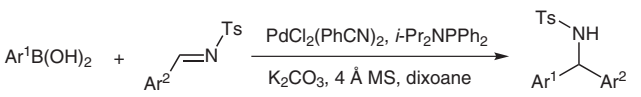


Entry	Ar^1	Ar^2	Product	Yield (%)
1	Ph **1a**	Ph **2a**	**3aa**	83 (77)
2	**1a**	4-FC_6H_4 **2b**	**3ab**	85 (80)
3	**1a**	4-$F_3CC_6H_4$ **2c**	**3ac**	77 (70)
4	**1a**	4-ClC_6H_4 **2d**	**3ad**	69 (54)
5	**1a**	4-BrC_6H_4 **2e**	**3ae**	75 (70)[b]
6	**1a**	4-$O_2NC_6H_4$ **2f**	**3af**	60 (55)[c]
7	4-$MeOC_6H_4$ **1b**	**2a**	**3ba**	76
8	3-$MeOC_6H_4$ **1c**	**2a**	**3ca**	60
9	4-MeC_6H_4 **1d**	**2a**	**3da**	73
10	4-$F_3CC_6H_4$ **1e**	**2a**	**3ea**	66
11	3-$F_3CC_6H_4$ **1f**	**2a**	**3fa**	65
12	4-ClC_6H_4 **1g**	**2a**	**3ga**	70
13	4-FC_6H_4 **1h**	**2a**	**3ha**	73
14	3-thienyl **1i**	**2a**	**3ia**	31

[a] All reactions were run with *N*-tosylarylimine (0.5 mmol), arylboronic acid (1.0 mmol), K_2CO_3 (207 mg 1.5 mmol), $PdCl_2(PhCN)_2$ (9.6 mg, 5 mol%), *i*-Pr_2NPPh_2 (7.2 mg 5 mol%), and 4 Å MS (100 mg) in anhydrous dioxane (3 mL) at 80 °C for 24 h with the isolated yield under N_2 atmosphere or air atmosphere (in the parentheses).
[b] *N*-[Biphenyl-4-yl(phenyl)methyl]-4-methylbenzenesulfonamide was obtained using 3 equiv of phenylboronic acid.
[c] (4-Nitrophenyl)(phenyl)methanol was obtained in 21% (20%) yield.

With the optimized conditions in hand, the reactions of different arylboronic acids with various *N*-tosylarylimines were examined to explore the scopes of the reaction (Table 3 and Table 4). First, we examined the *N*-tosylphenylimine and *N*-tosylarylimines with electron-withdrawing substituents in our catalytic system. To our delight, the reaction proceeded smoothly in the presence of a variety of functional groups including nitro, trifluoromethyl, fluoro, chloro, and bromo groups. It was noteworthy that the chloro group of both the substrates could keep untouched for further functionization (Table 3, entries 4, 12; Table 4, entries 6, 12), while the *N*-tosylarylimines with bromo group provided the further Suzuki coupling product **3ae** in 75% yield (Table 3, entry 5). Arylboronic acids with electron-withdrawing substituents, which are less nucleophilic, hence transmetalate more slowly than electron-neutral analogues, are prone to homocoupling and protodeboronation side reactions.[15] However, **1e**, **1f**, and **1g** were good substrates in our reaction system, and **3ea**, **3fa**, **3ga** were isolated in 66%, 65% and 70% yields, respectively (Table 3, entries 10–12). Thien-3-yl boronic acid **1i** still worked smoothly in this procedure, although the yield of **3ia** was decreased to 31%, which may be ascribed to the fact that heteroatoms in the heteroarylboronic acid could coordinate to transition metal (Table 3, entry 14).[16]

Table 4 Pd-Catalyzed Addition of Arylboronic Acids to Electron-Rich *N*-Tosylarylimines and Crowded Analogues[17]



Entry	Ar^1	Ar^2-	Product	Yield (%)
1	**1a**	2-furyl **2g**	**3ag**	70 (57)
2	**1a**	4-EtC_6H_4 **2h**	**3ah**	71 (63)
3	**1a**	4-MeC_6H_4 **2i**	**3ai**	75 (70)
4	**1a**	4-$MeOC_6H_4$ **2j**	**3aj**	65 (64)
5	**1a**	3,4-$(OCH_2O)C_6H_3$ **2k**	**3ak**	50 (45)
6	**1a**	2-ClC_6H_4 **2l**	**3al**	70 (55)
7	**1a**	1-naphthyl **2m**	**3am**	80 (75)
8	**1a**	2,5-$(Me)_2C_6H_3$ **2n**	**3an**	62 (56)
9	1-naphthyl **1j**	**2a**	**3ja**	43
10	2-MeC_6H_4 **1k**	**2a**	**3ka**	63
11	4-FC_6H_4 **1h**	**2i**	**3hi**	70
12	4-ClC_6H_4 **1g**	**2i**	**3gi**	80

[a] All reactions were run with *N*-tosylarylimine (0.5 mmol), arylboronic acid (1.0 mmol), K_2CO_3 (207 mg, 1.5 mmol), $PdCl_2(PhCN)_2$ (9.6 mg, 5 mol%), *i*-Pr_2NPPh_2 (7.2 mg, 5 mol%), and 4 Å MS (100 mg) in anhydrous dioxane (3 mL) at 80 °C for 24 h under N_2 atmosphere or air atmosphere (in parentheses).

Next, we chose to test the generality of the addition of arylboronic acids to *N*-tosylarylimines possessing electron-donating groups or crowded substrates, which may decrease reactivity in the transformation. However, all reactions proceeded smoothly in our procedure and no obvious electron effect was observed. The hindrance in the ortho acids either on the arylboronic acids or *N*-tosylarylimines had little effect in the reaction, for example, **3al**, **3am**, **3an**, **3ja**, **3ka** were produced in 75%, 80%, 62%, 43%, and 63% yields, respectively. Moreover, rigorous exclusion of the air was not required in our procedure and the reaction could be conducted under air atmosphere.

In conclusion, the addition reaction of arylboronic acids to *N*-tosylarylimines catalyzed by the combination of simple palladium precursor and easily handled *i*-Pr_2NPPh_2 has proved to be an efficient and versatile alternative for the synthesis of multifunctional diarylmethylamines. The use of easily prepared ligand, as well as no requirement to exclude air all together is the most attracting characters in this reaction. Mechanistic investigations and the application to asymmetric synthesis are the focus of ongoing efforts in our laboratory.

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(17) **General Procedures**

A Schlenk reaction tube was charged with $PdCl_2(PhCN)_2$ (9.6 mg, 0.05 mmol), *i*-Pr_2NPPh_2 (7.2 mg, 0.05 mmol), arylboronic acids (1.0 mmol), *N*-tosylarylimines (0.5 mmol), K_2CO_3 (207 mg, 1.5 mmol), 4 Å MS (100 mg), and anhydrous dioxane (3 mL). The reaction tube was purged with N_2 under salted ice (ca. –10 °C). The mixture was stirred for 0.5 h at r.t. Then, the mixture was heated at 80 °C for the given time. After completion of the reaction, as indicated by TLC, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on a silica gel to give the product.