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Pd-catalyzed addition of boronic acids to vinylogous imines: a convenient approach to 3-*sec*-alkyl substituted indoles

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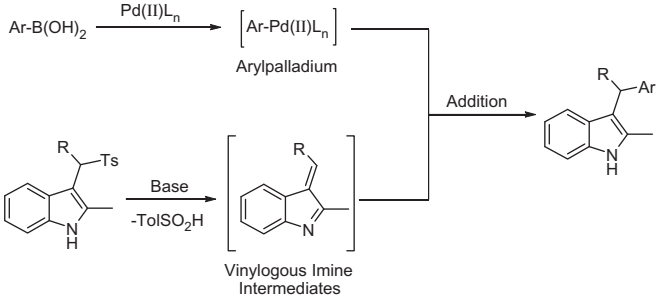
ABSTRACT

A convenient approach to 3-*sec*-alkyl substituted indoles was developed via palladium-catalyzed addition of arylboronic acids to vinylogous imines generated in situ from sulfonylindoles under mild conditions.

The conjugate addition of carbon nucleophiles to activated olefins is one of the most important reactions for carbon–carbon bond formation.[1] Transition metal-catalyzed addition reactions of arylboronic acids to carbon–carbon double bonds-containing compounds and derivatives have emerged as useful transformations for organic synthesis in part due to the nature of nontoxic and air/moisture stability of arylboronic acids.[2] Recently, Rh(I)-catalyzed addition reactions of arylboronic acids to various electrophiles have been remarkably developed and widely used.[3] Compared with numerous reports of Rh(I)-catalyzed addition reactions to unsaturated bonds, Pd(II)-catalyzed nucleophilic addition reactions of arylboronic acids are relatively rare. This is mostly due to that arylrhodium species are more nucleophilic and capable of addition to electrophiles, while arylpalladium species are relatively more electrophilic and the addition reactions will be troubled by the formation of the Heck-type coupling products.[4] But, as an important complement to Rh(I)-catalyzed addition reactions, these years, Pd(II)-catalyzed nucleophilic addition reactions of arylboronic acids have also attracted much attention and many successful examples have been reported.[5]

Vinylogous imine intermediate based on indole skeleton has been proved to be a good electrophilic species and useful intermediate in indole transformations.[6] It can be generated using both acidic[7] and basic[8] reaction conditions and upon nucleophilic addition affords the corresponding substituted indoles. In 2006, Petrini and co-workers described an innovative approach to this structural motif using 3-(1-arylsulfonylalkyl) indole precursors.[9] This kind of sulfonylindole is able to eliminate arenesulfinic acid under the basic condition, leading to reactive vinylogous imine intermediate. Several addition reactions involving this intermediate have been reported, and the desired substituted indoles were obtained conveniently.[10]

Given the fact that *sec*-alkyl-3-substituted indoles are common structural motifs in a number of biologically active natural products and pharmaceutical compounds,[11] the significance of developing a new synthetic method for this kind of indole derivatives is obvious.[12,13] Very recently, we have developed a catalyzed system to access *sec*-alkyl-3-substituted indoles by Rh(I)-catalyzed addition reaction of arylboronic acids to vinylogous imines generated in situ from sulfonylindoles.[10j] Focus on the synthesis of



Scheme 1. Nucleophilic addition to vinylogous imines generated in situ from sulfonylindoles.

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indoles and indole derivatives, we herein disclosed a Pd(II)-catalyzed addition reaction of vinylogous imines with organoboronic acids, and by this strategy a potential entry to biologically active indole derivatives would be supplied (Scheme 1).

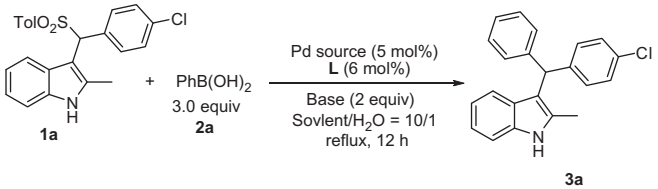
Our investigation started with the reaction of sulfonylindole **1a** with phenylboronic acid **2a** (3.0 equiv) using $PdCl_2$ (5.0 mol %) as the catalyst, 2,2′-bipyridine (6 mol %) as the ligand in THF/H_2O (10:1) under basic condition (K_2CO_3 2.0 equiv). To our disappointment, although the mixture was stirred for 12 h and only little amounts of the desired product **3a** were isolated (Table 1, entry 1), some undetermined byproducts were also detected. After screening the solvent, the best result could be obtained in Toluene/H_2O (10:1), moderate yields of **3a** were obtained (53%) (Table 1, entries 2–4). A number of bases were evaluated, KOH, Cs_2CO_3, and NaOH were little effective, K_3PO_4 gave moderate yields and K_2CO_3 was found to be the most suitable base for this reaction (Table 1 entries 5–8). Next, the effect of different ligands was examined. Bidentate nitrogen ligand such as 1,10-phenanthroline afforded the product in poor yield (Table 1, entry 9). Monophosphine ligand is more suitable in this reaction: PPh_3 gave moderate yield of **3a**, and when the bulky and electron-rich P(1-nap)$_3$ was used, the product **3a** was obtained in 82% yield (Table 1, entries 10 and 11). However, other bidentate phosphines such as dppf, dppe, and dppb exhibited lower performance (Table 1, entries 12–14). Subsequently, the effect of palladium sources was studied and we found that $Pd(OAc)_2$ showed better catalytic activity than $PdCl_2$, the yield of product **3a** was increased to 88% (Table 1, entries 15–17). Finally, without addition of water the yield of **3a** decreased sharply to 56% (Table 1, entry 18). Thus, phenylboronic acid **2a** (3.0 equiv), $Pd(OAc)_2$ (5 mol %), P(1-nap)$_3$ (6 mol %), K_2CO_3 (2.0 equiv), and Toluenen/H_2O (10:1) were chosen as the optimized conditions.

With the optimized conditions in hand, we turned our attention to investigate the scope of this transformation. The results are summarized in Table 2. As expected, various sulfonylindoles underwent the reaction smoothly, giving the corresponding products with moderate to excellent yields. When the substituents R^2 are aromatic ones, this palladium-catalyzed reaction exhibited a superior activity than the rhodium-catalyzed reaction (2 mol % $Rh[(COD)Cl]_2$, KOH as base, dioxane/water = 10/1, reflux, 12 h) which we have reported recently[10j] (Table 2, entries 1–4). For example, phenyl or *para*-position of the phenyl ring with Me or MeO reacted with phenyl boronic acid and all gave good yields of products. It is worth noting that sulfonylindoles with aliphatic substituents also exhibited good reactivity in this reaction, aliphatic substituents such as isopropyl, pentyl, cyclohexyl, and *tert*-butyl all afforded good yields of conjugate addition products (Table 2, entries 5–8). At last the influence of different arylboronic acids was also examined. The steric hindrance on the phenyl ring of arylboronic acid inhibited the transformation (Table 2, entries 10 and 11), and electron-donating substituents at the phenyl ring of boronic acids were beneficial for this transformation (Table 2, entries 12 and 13), whereas the electron-withdrawing group decreased the efficiency (Table 2, entry 14).

Previously 1,4-addition reactions using arylpalladium species were mostly based on α,β-unsaturated carbonyl compounds, and the mechanism has been well studied: insertion of an unsaturated ketone into the Ar–Pd bond gives a C- or O-bound enolate, which yields 1,4-adduct via hydrolysis with water.[2c] Based on this mechanism and excellent reports,[5] a possible mechanism for the Pd(II)-catalyzed addition reaction of arylboronic acids to the vinylogous imines is proposed as shown in Scheme 2. First, transmetalation generates the arylpalladium species **A** from arylboronic acid and palladium catalyst, followed by insertion of the olefin into the carbon–palladium bond giving intermediates **B**. Rearomatization of indole leading the formation of intermediates **C**. Protonolysis of **C** gives the corresponding conjugate addition products **3** with the regeneration of the divalent palladium species making the catalytic cycle possible.

In summary, palladium-catalyzed addition of arylboronic acids to vinylogous imines generated in situ from sulfonylindoles was successfully developed. This method is an important complement

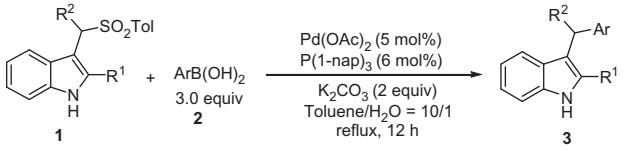
Table 1
Optimizing the conditions for the reaction of arylsulfonyl indole **1a** with phenyl boronic acid **2a**



Entry[a]	Pd source	Ligand	Base	Solvent	Yield[b] (%)
1	$PdCl_2$	2,2′-Dipridyl	K_2CO_3	THF	12
2	$PdCl_2$	2,2′-Dipridyl	K_2CO_3	Toluene	53
3	$PdCl_2$	2,2′-Dipridyl	K_2CO_3	Dioxane	27
4	$PdCl_2$	2,2′-Dipridyl	K_2CO_3	CH_2Cl_2	<5
5	$PdCl_2$	2,2′-Dipridyl	KOH	Toluene	21
6	$PdCl_2$	2,2′-Dipridyl	K_3PO_4	Toluene	45
7	$PdCl_2$	2,2′-Dipridyl	Cs_2CO_3	Toluene	14
8	$PdCl_2$	2,2′-Dipridyl	NaOH	Toluene	18
9	$PdCl_2$	1,10-Phenanthroline	K_2CO_3	Toluene	18
10	$PdCl_2$	PPh_3	K_2CO_3	Toluene	45
11	$PdCl_2$	P(1-nap)$_3$	K_2CO_3	Toluene	82
12	$PdCl_2$	dppf	K_2CO_3	Toluene	<5
13	$PdCl_2$	dppe	K_2CO_3	Toluene	<5
14	$PdCl_2$	dppb	K_2CO_3	Toluene	18
15	$Pd(OAc)_2$	P(1-nap)$_3$	K_2CO_3	Toluene	88
16	$Pd(OCOCF_3)_2$	P(1-nap)$_3$	K_2CO_3	Toluene	74
17	$Pd(CH_3CN)_2Cl_2$	P(1-nap)$_3$	K_2CO_3	Toluene	77
18[c]	$Pd(OAc)_2$	P(1-nap)$_3$	K_2CO_3	Toluene	56

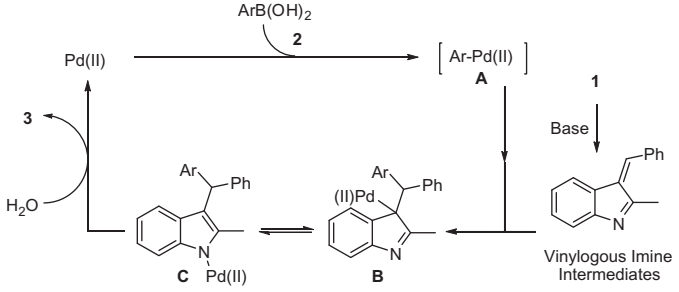
[a] Reaction conditions: Pd source (5 mol %), **L** (6 mol %), **1a** (0.2 mmol), **2a** (0.6 mmol), solvent (3 mL), H_2O (0.3 mL), reflux, 12 h.
[b] Isolated yields based on **1a**.
[c] No water was added.

Table 2
Substrate scope for Pd-catalyzed reaction of sulfonyl indoles **1** with arylboronic acids **2**[14]



Entry [a]	R^1	R^2	Ar	Yield[b] (%)
1	Me	4-ClC_6H_4	Ph	88 (**3a**)
2	Me	Ph	Ph	86 (**3b**)
3	Me	4-MeC_6H_4	Ph	82 (**3c**)
4	Me	4-$MeOC_6H_4$	Ph	81 (**3d**)
5	Me	*i*-Pr	Ph	90 (**3e**)
6	Me	*n*-Pentyl	Ph	74 (**3f**)
7	Me	Cy	Ph	87 (**3g**)
8	Me	*t*-Bu	Ph	76 (**3h**)
9	H	*n*-Pentyl	Ph	64 (**3i**)
10	Me	*n*-Pentyl	2-$MeOC_6H_4$	32 (**3j**)
11	Me	*n*-Pentyl	3-$MeOC_6H_4$	67 (**3k**)
12	Me	*n*-Pentyl	4-$MeOC_6H_4$	80 (**3l**)
13	Me	*n*-Pentyl	4-MeC_6H_4	82 (**3m**)
14	Me	*n*-Pentyl	4-$CF_3C_6H_4$	50 (**3n**)

[a] Reaction conditions: $Pd(OAc)_2$ (5 mol %), P(1-nap)$_3$ (6 mol %), **1** (0.2 mmol), **2** (0.6 mmol), Toluene (3 mL), H_2O (0.3 mL), reflux, 12 h.
[b] Isolated yields based on **1**.



Scheme 2. Proposed mechanism for the Pd(II) catalyzed conjugate addition reaction.

to Rh(I)-catalyzed addition reactions which we have reported recently and provides a potential and facile access to 3-*sec*-alkyl substituted indole derivatives. Further study will be directed toward the development of asymmetric version of this reaction.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.05.056.

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14. *General procedure for Pd-catalyzed reactions of boronic acids to sulfonylindoles*: A 10 mL Schlenk tube was charged with $Pd(OAc)_2$ (2.25 mg, 5 mol %), P(1-nap)$_3$ (4.95 mg, 6 mol %), sulfonylindoles **1** (0.2 mmol), boronic acids **2** (0.6 mmol), K_2CO_3 (54.40 mg, 0.4 mmol) and then evacuated under vacuum and placed under a nitrogen atmosphere. Toluene (3 mL) and water (0.30 mL) were added subsequently. The mixture was stirred at 100 °C for 12 h. Then water (10 mL) was added and the mixture was extracted with CH_2Cl_2 (15 mL) for three times. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure, the residue was subjected to flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 10:1) to yield the corresponding products **3**.