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Pd-Catalyzed Tandem Coupling Reaction of 2-*gem*-Dibromovinylanilines and *N*-Tosylhydrazones to Construct 2-(1-phenylvinyl)-indoles

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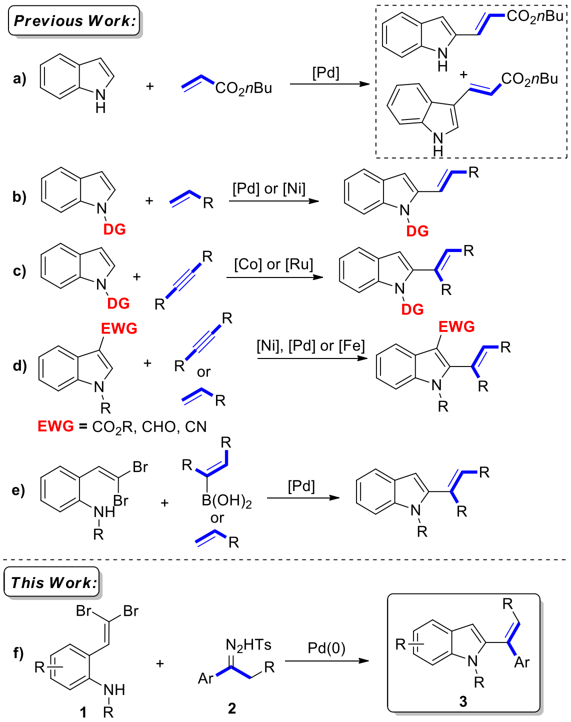
Abstract. A novel palladium(0)-catalyzed intermolecular coupling reaction of 2-*gem*-dibromovinylanilines and *N*-tosylhydrazones was reported to construct 2-(1-phenylvinyl)-indoles efficiently. The indole bearing 1, 1-disubstituted alkenes were obtained in one step with short reaction time, in high yields and broad substrate scope. The formed indole derivates could be easily transformed into much more valuable molecules.

Keywords: Palladium; 2-*gem*-dibromovinylanilines; Hydrazones; Alkenylindoles; Alkenylation

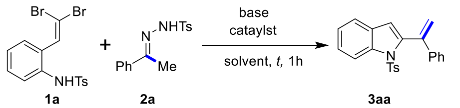
The indole scaffold is an integral feature of several biologically active compounds, natural products and pharmaceuticals.[1] In the past few decades, tremendous advances have been made in the development of functionalized indoles.[2] 2-Alkenylindoles are important building blocks in organic synthesis, which exist in many important naturally alkaloids.[3] However, direct alkenylation of indoles at the C2-position is a challenging subject due to the reaction selectivity at C2/C3-position.[4] To date, alkenylation of indoles at the C2-position is less reported.[5] In 2005, Gaunt's group developed a palladium(II)-catalyzed alkenylation of indoles to afford C2- or C3-alkenylated products by adjusting the solvent and additives.[5a] However, the yields of C2 alkenylation were quite low and substrates were limited to a few examples (Scheme 1a). Ricci and co-workers achieved regioselective C2 alkenylation of indoles, directed by a *N*-2-pyridylmethyl group with the assistance of Pd catalyst (Scheme 1b).[5b] Simultaneously, Arrayás's group reported a palladium(II)-catalyzed alkenylation of indoles at the C2-position by using excess of alkenes with *N*-pyridylsulfonyl as a directing group (Scheme 1b).[5c] Recently, Punji and co-workers described a Ni-catalyzed regioselective C2 alkenylation of indoles through utilizing alkenyl bromides, directed by a *N*-2-pyrimidinyl group under relatively mild conditions (Scheme 1b).[5f] Schipper and other groups successively achieved Co or Ru catalyzed intermolecular C2-alkenylation of indoles by using alkynes instead of alkenes, in which *N*,*N*-dimethylcarbonyl or pyrimidyl group was employed as a directing group (Scheme 1c).[6]



Scheme 1. Different Approaches to Alkenylindoles.

Moreover, some examples without *N*-directing groups were developed. In 2006, Nakao, Hiyama and co-workers described a C2-addition to internal alkynes under mild nickel catalysis.[4a] In recent years, Yoshikai's group[4b] demonstrated an iron-catalyzed directly C2-alkenylation of indoles bearing formyl group at the C3 position with alkynes. Miura' *et al.*[4c] investigated the oxidative coupling of indole-3-carboxylic acids with alkenes to afford the corresponding 2-alkenylindoles *via* directly C-H alkenylation and decarboxylation catalyzed by palladium (Scheme 1d). Basically, these methodologies require the electron-withdrawing groups at C3-position, such as CN, CO_2R and CHO. Besides the direct alkenylation of indoles at C2-position, Lautens and co-workers demonstrated a one-pot palladium-catalyzed tandem reaction to give a broad scope of substituted 2-vinylic indoles from *gem*-dibromovinylanilines and alkenyl boronic acids[7a] or alkenes[7b] (Scheme 1e). However, most of the processes provided 1, 2-disubstituted alkenes, except that the reaction reported by Lautens and co-workers produced 1,1-disubstituted alkenes *via* Suzuki coupling. In 1980s, Akgün's groups developed a process towards 1,1-disubstituted alkenes at the C2-position of indole *via* the aldol reaction of 2-lithioindoles, followed by an elimination reaction of the resulting indole-carbinols to form the 2-vinylindoles.[8] However, this reaction required multiple steps to complete, which limited the application.

Table 1. Optimization of reaction conditions.[a]



Entry	[Pd] (mol %)	Solvent	Base (equiv.)	Ligand	t [°C]	Yield[b] (**3aa**)
1	$PdCl_2$ (10)	dioxane	*t*BuOLi (3.0)	PPh_3	110	62%
2	$Pd(OAc)_2$ (10)	dioxane	*t*BuOLi (3.0)	PPh_3	110	72%
3	$Pd(dba)_2$ (10)	dioxane	*t*BuOLi (3.0)	PPh_3	110	77%
4	$Pd(dba)_2$ (10)	dioxane	*t*BuOLi (3.0)	PCy_3	110	20%
5	$Pd(PPh_3)_4$ (10)	dioxane	*t*BuOLi (3.0)	-	110	75%
6	***$PdCl_2(PPh_3)_2$ (10)***	***dioxane***	***tBuOLi (3.0)***	***-***	***110***	***88%***
7	$PdCl_2(PPh_3)_2$ (10)	dioxane	DMAP (3.0)	-	110	NR
8	$PdCl_2(PPh_3)_2$ (10)	dioxane	*t*BuOK (3.0)	-	110	75%
9	$PdCl_2(PPh_3)_2$ (10)	dioxane	TEA (3.0)	-	110	NR
10	$PdCl_2(PPh_3)_2$ (10)	dioxane	$CsCO_3$ (3.0)	-	110	79%
11	$PdCl_2(PPh_3)_2$ (10)	dioxane	CsF (3.0)	-	110	60%
12	$PdCl_2(PPh_3)_2$ (10)	PhMe	*t*BuOLi (3.0)	-	110	52%
13	$PdCl_2(PPh_3)_2$ (10)	DMF	*t*BuOLi (3.0)	-	110	80%
14	$PdCl_2(PPh_3)_2$ (10)	DME	*t*BuOLi (3.0)	-	110	76%
15	$PdCl_2(PPh_3)_2$ (10)	THF	*t*BuOLi (3.0)	-	110	52%
16	$PdCl_2(PPh_3)_2$ (10)	dioxane	*t*BuOLi (3.0)	-	100	70%
17	$PdCl_2(PPh_3)_2$ (10)	dioxane	*t*BuOLi (3.0)	-	90	68%
18	$PdCl_2(PPh_3)_2$ (10)	dioxane	*t*BuOLi (3.0)	-	120	81%
19	$NiCl_2(PPh_3)_2$ (10)	dioxane	*t*BuOLi (3.0)	-	110	ND
20	$RhCl(PPh_3)_3$ (10)	dioxane	*t*BuOLi (3.0)	-	110	38%

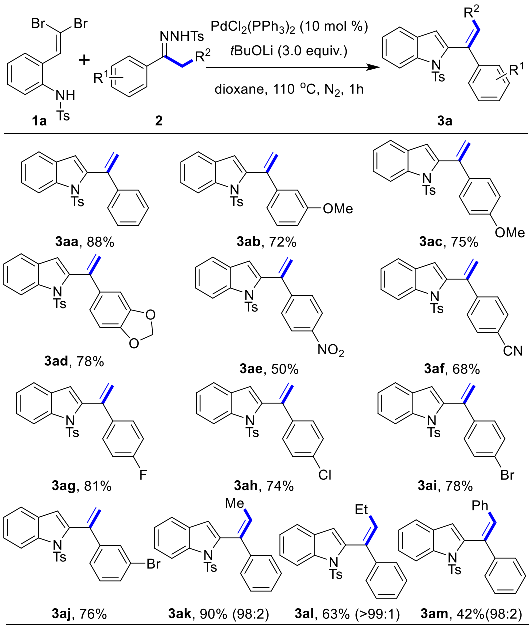
[a]Reaction conditions: **1a** (1.0 equiv., 0.3 mmol), **2a** (2.0 equiv., 0.6 mmol), [Pd] (10 mol %), base (3.0 equiv., 0.9 mmol), solvent (4 mL), N_2, 1 h, 110 °C. [b]Isolated Yields.

Diazo compounds have been frequently exploited as carbene or metal carbene precursors. In 2001, Van Vranken's group[9] developed the first palladium-catalyzed cross-coupling involving a carbene-insertion reaction, who used trimethylsilyldiazomethane as the carbene precursor and benzyl halides as electrophiles. In 2007, Barluenga and co-workers demonstrated the first cross-coupling reaction between *N*-tosylhydrazones and aryl halides, during which aryl migratory insertion mechanism was also suggested.[10] From then on, the *N*-tosylhydrazones as carbene precursor were extensively investigated.[11]

On the basis of pioneering study and our work[2j] in developing new methodologies to functionalized indoles, we disclose a palladium(0)-catalyzed alkenylation of indoles at the C2-position from 2-*gem*-dibromovinylanilines and hydrazones, during which indole ring bearing 1,1-disubstituted alkenes were obtained in one step (Scheme 1f).

Initially, our study commenced from the reaction of 2-*gem*-dibromovinylanilines **1a** with *N*-tosylhydrazones **2a** catalyzed by $PdCl_2/PPh_3$ using 3.0 equivalent *t*BuOLi as base in dioxane under N_2 atmosphere (Entry 1, Table 1). As expected, the desired indole derivatives **3aa** was obtained in 62% yield (Entry 1). The yield could be increased to 72% when $Pd(OAc)_2$ was used, and it was elevated to 77% by using $Pd(dba)_2$ (Entries 2 and 3). However, the yield was decreased to 20% by using PCy_3 as ligand (Entry 4). To our delighted, the yield was increased to 88% by employing $PdCl_2(PPh_3)_2$ as catalyst (Entry 6). Subsequently, the bases such as DMAP, *t*BuOK, TEA, $CsCO_3$, and CsF were screeninged, while no better results were obtained than *t*BuOLi (Entries 7-11). Furthermore, we examined several solvents, such

Table 2. Scope of *N*-Tosylhydrazones in the Construction of tandem reaction.[a]



[a]Reaction conditions: **1a** (0.3 mmol), **2** (0.6 mmol), $PdCl_2(PPh_3)_2$ (10 mol %), *t*BuOLi (0.9 mmol), dioxane (4 mL), N_2, 1 h, 110 °C. [b]Isolated Yields.

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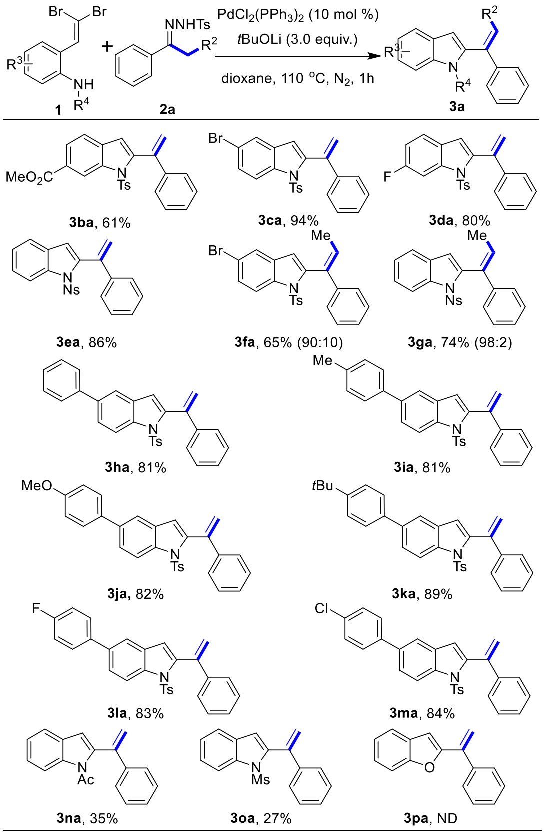
as PhMe, DMF, DME and THF. Unfortunately, no positive results were obtained (Entries 12-15). When the temperature was lowered down to 100 °C and 90 °C, the yield was decreased to 70% and 68% sharply (Entry 16-17). High temperature reduced the yield slightly (Entry 18). In addition, we examined different metal catalysts, but these catalysts were unsuitable for this transformation (Entry 19-20). Finally, $PdCl_2(PPh_3)_2$ (10 mol %) and *t*BuOLi (3.0 equiv.) in anhydrous dioxane at 110 °C under N_2 atmosphere were chosen to the standard conditions (Entry 6).

With the optimized conditions in hand, the substrate scope of *N*-tosylhydrazones was investigated with 2-*gem*-dibromovinylanilines, and the results were illustrated in Table 2. The substitutions on phenyl group of *N*-tosylhydrazones exhibited quite good tolerance. Both electron-donating groups (*m*-OMe, *p*-OMe and $-OCH_2O-$) and electron-withdrawing groups (NO_2 and CN) could give the corresponding products in moderate to good yields (**3ab-3af**). Not only fluro and chloro substituted *N*-tosylhydrazones performed smoothly, but also the substrates bearing *m*- and *p*-Br substitutions could survive well under the standard conditions, which could be readily transformed to more valuable molecules *via* cross-coupling reactions (**3ag-3aj**). Furthermore, the tri-substituted alkenes were synthesized from the corresponding *N*-tosylhydrazones, which exhibited high *Z*-selectivity determined by **NOE** (**3ak-3am**). In addition, we investigated the scope of heteroaromatic hydrazones, such as pyridyl and furyl hydrazones. Unfortunately, the reaction of 2-*gem*-dibromovinylanilines with pyridyl hydrazones could not be converted to the desired product. For the reaction of furyl hydrazones, we isolated one spot from the mixture, however, the ^1H NMR showed it was a mixture which could not be purified although we tried a lot of methods (see the Supporting Information **IX**).

Table 3. Scope of gem-dibromovinylaniline derivatives.[a]

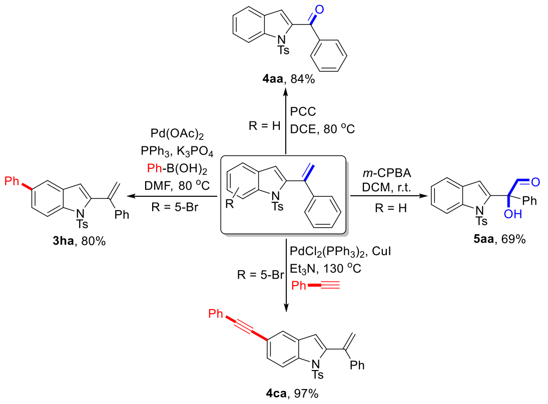


[a]Reaction conditions: **1** (0.3 mmol), **2a** (0.6 mmol), $PdCl_2(PPh_3)_2$ (10 mol %), *t*BuOLi (0.9 mmol), dioxane (4 mL), N_2, 1 h, 110 °C. [b]Isolated Yields.

Subsequently, the substitutions on 2-*gem*-dibromovinylaniline were then investigated in Table 3. Substrates bearing strong electron-withdrawing groups as $-CO_2Me$, provided the corresponding products in 61% yield (**3ba**). The Br and F substitutions could survive well, giving **3ca** and **3da** in 94% and 80% yields respectively. Ns-protected 2-*gem*-dibromovinylaniline was also suitable for this transformation, providing the desired product in 86% yield (**3ea**). The tri-substituted alkenes were obtained in good yields with excellent *Z*-selectivity (**3fa** and **3ga**). Furthermore, substrates with different aryl groups, such as Ph, 4-Me-Ph, 4-OMe-Ph, 4-*t*Bu-Ph, 4-F-Ph and 4-Cl-Ph, provided the desired products in good yields (**3ha-3ma**). We examined different nitrogen-protected 2-*gem*-dibromovinylanilines, such as N-Ac and N-Ms. Although the substrates **1n** and **1o** could give the corresponding products, the yields were relatively low (**3na**: 35%; **3oa**: 27%). In addition, we tested the reaction of 2-*gem*-dibromovinylphenols with **2a**, but no desired product was detected (**3pa**).

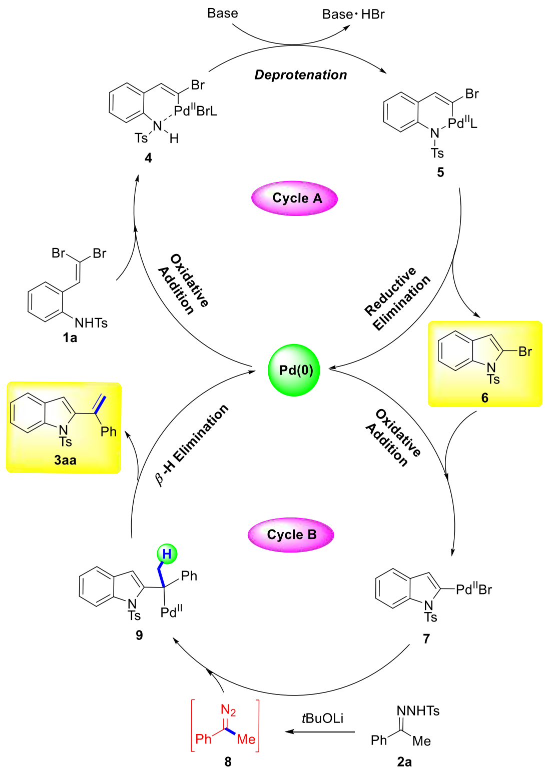
To show the synthetic versatility of this methodology, several derivatizations of the products were performed, and the results were shown in Scheme 2. The oxidative cleavage of double bond using PCC in DCE provided the corresponding ketone in 84% yield.[12] On the other hand, the oxidation with *m*-chloroperbenzoic acid could afford hydroxyaldehyde in 69% yield.[13] Furthermore, the products bearing bromo group could be functionalized *via* coupling reactions, such as Suzuki-Miyaura Coupling[14] and Sonogashira reaction[15], providing the coupled derivatives in considerable yields (80% and 97%).

Scheme 2. Derivatization of the 2-(1-phenylvinyl)-indole derivatives.



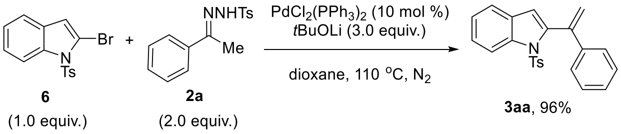
Based on the pioneering work and the results of our study, a plausible mechanism including two catalytic cycles for this tandem coupling reaction is proposed in Scheme 3.[7][11][16] In cycle A, oxidative addition of palladium(0) to *gem*-dibromovinylaniline **1a** provides the stabilized palladacycle **4**. The deprotonation of aniline affords palladium complex **5**, which then produces compound **6** *via* reductive elimination. Compound **6** could be observed by TLC and GC-MS, and it disappears in the end of the reaction. If the transformation was interrupted before finished, compound **6** could be isolated and then be converted to **3aa** under the standard conditions in high yield. In cycle B, the oxidative addition of compound **6** to palladium(0) generates palladium(II) complex **7**, which subsequently forms alkylpalladium species **9** with carbene intermediate generated from diazo compound **8**. Finally, the *β*-H elimination of complex **9** delivers the desired product 2-(1-phenylvinyl)-indole **3aa**.

Scheme 3. Possible mechanism for the tandem reaction.



To prove mechanism for the tandem reaction, we carried out the control experiments using 2-Br indole and *N*-tosylhydrazones under the standard conditions (Scheme 4), and the desired product was obtained in 96% yield, indicating this mechanism for the tandem reaction is convincing.

Scheme 4. Control experiment.



In summary, we have demonstrated a novel palladium-catalyzed construction of 2-(1-phenylvinyl)-indoles utilizing 2-*gem*-dibromovinylanilines and hydrazones. The indoles bearing 1, 1-disubstituted alkene are furnished in one pot. This tandem reaction could be finished in 1 hour, and produce the corresponding products in high yields with a broad substrate scope. Notably, this methodology shows excellent *Z*-selectivity for tri-substituted alkenes. Meanwhile, the products are easily to be transformed into much more valuable indole derivates. Further investigation to the application of this strategy is underway.

Experimental Section

The 2-*gem*-dibromovinylanilines **1a** (135 mg, 0.3 mmol, 1.0 equiv.) and *N*-tosylhydrazones **2a** (174 mg, 0.6 mmol, 2.0 equiv.), *t*BuOLi (75 mg, 0.9 mmol, 3.0 equiv.) and $PdCl_2(PPh_3)_2$ (22 mg, 0.03 mmol, 10 mol %) were added bottle. Adding 4 ml of anhydrous dioxane into mixture with stirred, and reaction was heated with 110℃ for 1 h. Lastly, the extractive was extracted with EA and washed with water to get crude product. The crude product was purified by column chromatography (PE:EA, 30:1) to give the **3aa** (98.6 mg, 0.264 mmol, 88 %) as white solid.

Acknowledgements

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UPDATE

Pd-Catalyzed Tandem Coupling Reaction of 2-*gem*-Dibromovinylanilines and *N*-Tosylhydrazones to Construct 2-(1-phenylvinyl)-indoles

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