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## Palladium-Catalyzed Cascade Metallo-Ene/Suzuki Coupling Reaction of Allenamides

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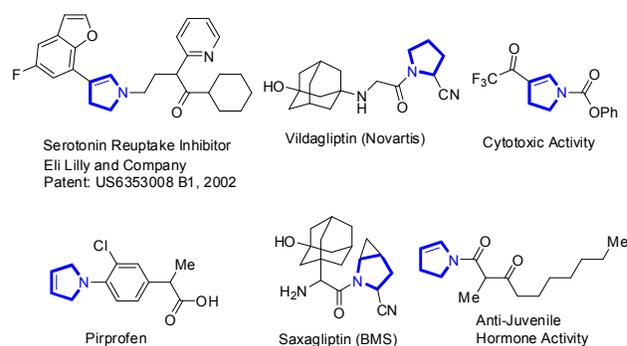
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A new type of cascade metallo-ene/Suzuki coupling reaction of allenamides catalyzed by palladium has been described. A variety of polyfunctionalized 2,3-dihydropyrrole derivatives which are important structural motifs for bioactive molecules, were furnished with excellent yields. Two new  $Csp^3-Csp^2$  bonds were constructed in one pot efficiently. The reductive elimination from  $\pi$ -allyl palladium complex presented excellent regioselectivity to terminal C1 position. The unique terminal alkene was one of the most easily functional group, providing these molecules potential transformation to much more complicated molecules.

The synthesis of polyfunctionalized pyrroles remains an attractive objective due to the versatile existing in biological, pharmaceutical and organic chemistry.<sup>1</sup> A lot of drugs and bioactivated compounds have been reported, such as serotonin reuptake inhibitor from Eli Lilly,<sup>2</sup> Vildagliptin from Novartis,<sup>3</sup> Saxagliptin from BMS,<sup>4</sup> Pirprofen and so on (Figure 1).<sup>5</sup> Therefore, it is quite important to develop efficient methodologies for the construction of pyrrole scaffold.

In the past few decades, numerous elegant methodologies have been developed to construct the pyrrole motif. In particularly, transition metal-catalyzed cyclization reactions represent a powerful and atom economic strategy,<sup>6</sup> such as Ni,<sup>7</sup> Pd,<sup>8</sup> Pt,<sup>9</sup> Rh<sup>10</sup> and Ru<sup>11</sup>. During our research on the cyclization reactions, the allenamines as a unique building block cause our attention, which is potential to construct nitrogen-containing heterocyclic derivatives easily. Very recently, our group realized a pd-catalyzed cyclization-Heck



**Figure 1. Representative bioactive molecules bearing 2,3-dihydropyrrole scaffolds.**

reaction of allenamides to construct 1,2,3,4-tetrahydropyridine derivatives.<sup>12</sup> Considering our interest on ene reactions, we attempt to introduce the allenamines to ene reaction, developing novel methodologies in the construction of functionalized pyrroles.

The ene reaction is mechanistically related to the much more famous Diels-Alder reaction, both of which proceeds through cyclic transition states involving six electrons. However, the higher activation energy for an ene reaction limits the application of ene reaction in organic synthesis.<sup>13</sup> In the past few decades, a series of mild ene reactions have been developed by chemists, during which metallo-ene reaction shows highly efficiency and promising application.<sup>14</sup> Recently, some catalytic, enantioselective metallo-ene processes are realized, arousing more interests to metallo-ene reaction.<sup>15</sup> It is well known intramolecular metallo-ene reaction, working *via* the interception of allylmetal intermediates with adjoining  $\pi$ -unsaturation, is an important subdivision of ene reaction,<sup>16</sup> which has made significant contributions to build densely functionalized cyclic molecules.<sup>14h, 17</sup>

Although the metallo-ene reaction could be seen as mechanistically analogous to traditional ene reaction, significant differences between these two processes are still apparent (Scheme 1). According to the traditional ene reaction, [1,5]-hydride shift is underwent accompanying the formation of new  $Csp^3-Csp^3$  bond. In the metallo-ene reaction of diene, the generated transient allylmetal intermediate could produce a new intermediate I, which could be further functionalized *via* coupling reactions (Scheme 1a).

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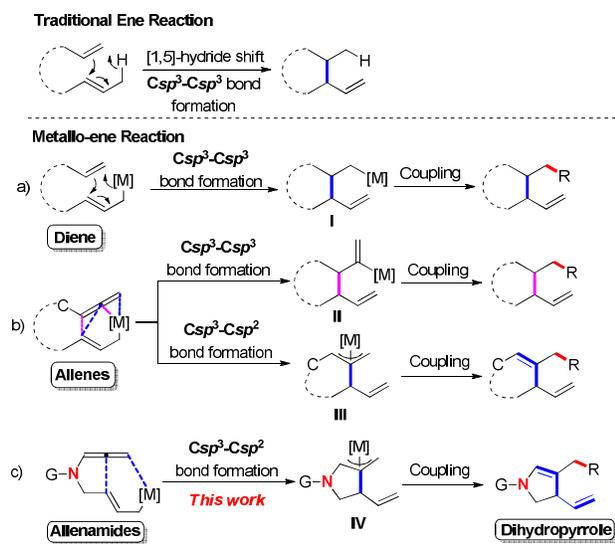
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**Scheme 1. The Traditional ene Reaction and Metallo-ene Reaction.**

In the allene system, the insertion of  $\pi$ -allylic metal-complex to the internal or external double bond of allene could generate intermediates II or III, which could be transformed into more functionalized molecules (Scheme 1b). Bäckvall group made a great contribution to the carbocyclization of allene recently,<sup>18</sup> including that a stereoselective Pd-catalyzed carbocyclization of allenic allylic carboxylates.<sup>18x</sup> In 2008, Tsukamoto group reported a Pd-catalyzed arylation cyclization of allenyl enones.<sup>19</sup> However, there is few report on the allenamides metallo-ene reaction.

Allenamides, functionally derived from allenamines, involving the amido group inducing delocalization of the lone-pair electrons on nitrogen and consequently exhibiting improved stability, have become a versatile and powerful building block in synthetic chemistry.<sup>20</sup> Pursuing our interests in developing new methodologies for the synthesis of nitrogen-containing heterocyclic derivatives, we hypothesize that the allenamines would be competent at performing an intramolecular metallo-ene reaction, furnishing a  $\pi$ -allylic intermediate IV, which could be further functionalized *via* coupling reaction (Scheme 1c).

In this work, we realized a palladium-catalyzed metallo-ene/Suzuki coupling reaction of allenamides to construct polyfunctionalized 2,3-dihydropyrrole derivatives, accompanying two new  $Csp^3-Csp^2$  bonds formation. We initially investigated the cascade reaction with allenamines **1a** with (4-methoxyphenyl)boronic acid **2a** in the presence of 10 mol% Pd(PPh<sub>3</sub>)<sub>4</sub> and 2.0 equiv. of K<sub>2</sub>CO<sub>3</sub> at 50 °C in toluene under N<sub>2</sub>. To our delight, the desired 2,3-dihydropyrrole derivatives **3aa** was isolated in 45% yield (Entry 1). Then different solvents were screened, such as dioxane, DMF, DCM and MeCN, among which dioxane could increase the yield slightly to 54% (Entries 2-5). Subsequently, both inorganic and organic bases were investigated (Entries 2-5). Gratifyingly, the yield was increased dramatically to 75% when K<sub>3</sub>PO<sub>4</sub> was applied (Entry 8). When Pd(OAc)<sub>2</sub> combined with PPh<sub>3</sub> was used as catalyst, product **3aa** was obtained in 50% yield. However, the employment of bidentate ligands, such as dppm, dppp, dppb, and Binap, could not promote this transformation, accompanying the formation of 4,4'-dimethoxy-1,1'-biphenyl and decomposition of **1a** (Entries 10,12-15). To our surprise, when dppe was used, the metallo-ene/reduction reaction was happened,

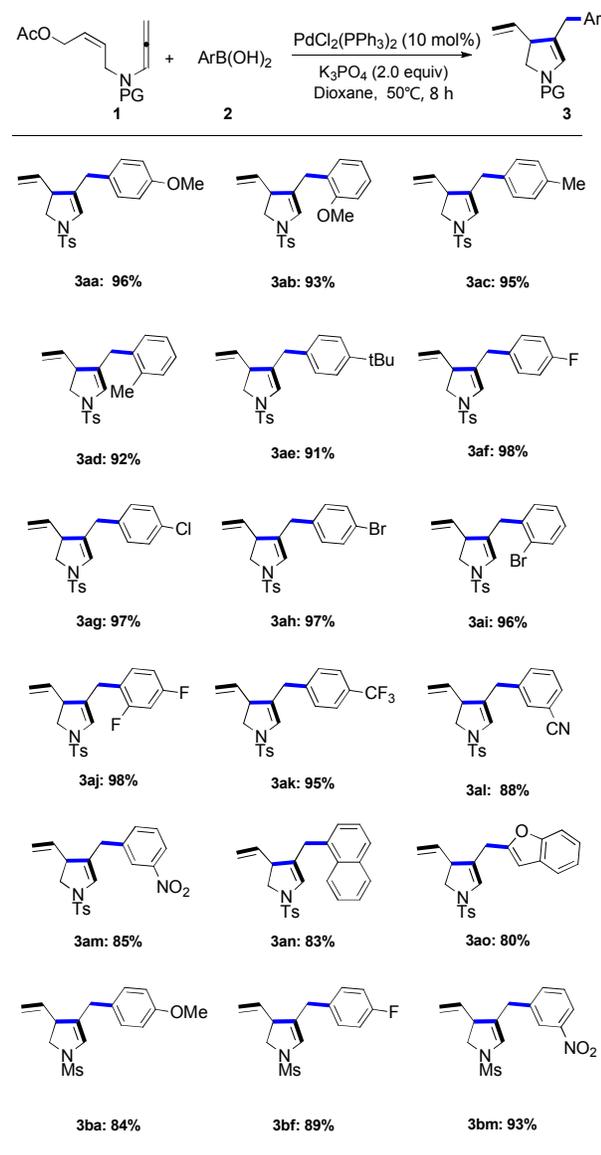
providing **3ab** in 70% yield without the detection of **3aa** (Entry 11). The results from bidentate ligands indicated the unsuccessful of transmetalation with boronic acid **2a**, which might due to the big steric-hindrance of bidentate ligands. We are excited to achieve an excellent yield of 95% when PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> was applied (Entry 16). Two rhodium catalysts were examined, while no positive results were detected (Entries 17 and 18). Basing on these results, the optimized conditions were determined to include PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> combined with K<sub>3</sub>PO<sub>4</sub> in dioxane at 50 °C under N<sub>2</sub> atmosphere (Entry 16).

With the optimized conditions in hand, we then aimed to explore the substrate scope of this cascade metallo-ene/Suzuki coupling reaction. A variety of boronic acid were examined under the optimal conditions. The substrates with electron-donating group methoxyl or methyl at ortho/para-position afforded the corresponding products in excellent yields (**3aa-3ad**). The (4-tert-butyl)phenyl)boronic acid could also form 2,3-dihydropyrrole derivatives **3ae** in 91% yield. Remarkably, the halides substitutions at boronic acid showed not only excellent compatibility but also excellent conversion (**3af-3aj**). Notably, bromo could survive very well under these conditions without bromo corrosion (**3ah** and **3ai**). The electron-withdrawing substituents, such as CF<sub>3</sub>, CN and NO<sub>2</sub>, could efficiently produce the desired molecules (**3ak-3am**). Furthermore, condensed rings such as naphthalen-1-ylboronic acid and benzofuran-2-ylboronic acid could also deliver the coupling

**Table 1. Palladium-Catalyzed Metallo-Ene/Suzuki Coupling Reaction of Allenamides<sup>a</sup>**

Entry	Base	[Cat]	ligand	Solvent	Yield of <b>3aa</b> (%) <sup>b</sup>
1	K <sub>2</sub> CO <sub>3</sub>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	\	toluene	45
2	K <sub>2</sub> CO <sub>3</sub>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	\	dioxane	54
3	K <sub>2</sub> CO <sub>3</sub>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	\	DMF	50
4	K <sub>2</sub> CO <sub>3</sub>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	\	DCM	33
5	K <sub>2</sub> CO <sub>3</sub>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	\	MeCN	53
6	Na <sub>2</sub> CO <sub>3</sub>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	\	dioxane	45
7	KOAc	Pd(PPh <sub>3</sub> ) <sub>4</sub>	\	dioxane	36
8	K <sub>3</sub> PO <sub>4</sub>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	\	dioxane	75
9	Et <sub>3</sub> N	Pd(PPh <sub>3</sub> ) <sub>4</sub>	\	dioxane	32
10	Cy <sub>2</sub> NMe	Pd(PPh <sub>3</sub> ) <sub>4</sub>	\	dioxane	45
9	K <sub>3</sub> PO <sub>4</sub>	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	dioxane	50
10	K <sub>3</sub> PO <sub>4</sub>	Pd(OAc) <sub>2</sub>	dppm	dioxane	ND
11	K <sub>3</sub> PO <sub>4</sub>	Pd(OAc) <sub>2</sub>	dppe	dioxane	70 <sup>c</sup>
12	K <sub>3</sub> PO <sub>4</sub>	Pd(OAc) <sub>2</sub>	dppp	dioxane	ND
13	K <sub>3</sub> PO <sub>4</sub>	Pd(OAc) <sub>2</sub>	dppb	dioxane	ND
14	K <sub>3</sub> PO <sub>4</sub>	Pd(OAc) <sub>2</sub>	dppf	dioxane	ND
15	K <sub>3</sub> PO <sub>4</sub>	Pd(OAc) <sub>2</sub>	Binap	dioxane	ND
<b>16</b>	<b>K<sub>3</sub>PO<sub>4</sub></b>	<b>PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub></b>	\	<b>dioxane</b>	<b>96</b>
17	K <sub>3</sub> PO <sub>4</sub>	[Rh(OH)cod] <sub>2</sub>	PPh <sub>3</sub>	dioxane	ND
18	K <sub>3</sub> PO <sub>4</sub>	[RhClcod] <sub>2</sub>	PPh <sub>3</sub>	dioxane	ND

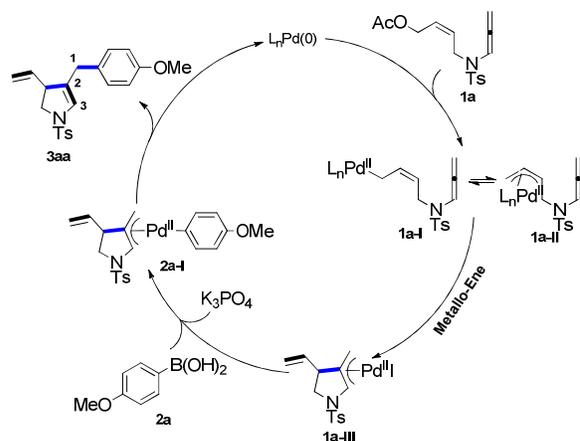
<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2a** (0.22 mmol), [Pd] (0.02 mmol), base (0.4 mmol), solvent (2.0 mL). Isolated yields. <sup>c</sup>**3ab** was obtained.

**Table 2. Scope of Cascade Metallo-Ene/Suzuki Coupling Reaction<sup>a,b</sup>**

<sup>a</sup>Reaction Conditions: **1a** (0.2 mmol), **2** (0.22 mmol), PdCl<sub>2</sub>(dppf) (0.02 mmol), K<sub>3</sub>PO<sub>4</sub> (0.4 mmol), dioxane (2.0 mL), 50°C, 8h. <sup>b</sup>Isolated yields.

products in good yields (**3an-3ao**). In addition, the corresponding products from methyl sulfonyl substrates were obtained in satisfied yields as well (**3ba**, **3bf**, and **3bm**). Although *p*-nitrobenzenesulfonyl protected allenamides could deliver the corresponding products, the easy decomposition made the products be stored for only few hours (See SI).

Combined with the proposed mechanism by Bäckvall group,<sup>18</sup> a possible pathway for this palladium-catalyzed cascade metallo-ene/Suzuki coupling reaction of allenamides was shown in Scheme 2. In the beginning, oxidative addition of an allyl acetate **1a** to Pd(0) gives intermediate **1a-I** ( $\eta^1$  form), which also existed as  $\pi$ -allyl palladium intermediate **1a-II** ( $\eta^3$  form). The following insertion to the allene generates the first  $Csp^3-Csp^3$  bond formation and metallo-ene reaction delivered another  $\pi$ -allyl palladium intermediate **1a**

**Scheme 2. Proposed Mechanism for the Cascade Metallo-Ene/Suzuki Coupling Reaction.**

-III. Subsequently, transmetalation with boronic acid **2a** produced palladium complex **2a-I**, which then formed the second  $Csp^3-Csp^3$  bond and gave final product **3aa**. It was worth mentioning that highly reductive elimination selectivity with terminal C1 but not internal C3 was observed.

In conclusion, we have developed a highly efficient palladium-catalyzed cascade metallo-ene/Suzuki coupling reaction of allenamides, delivering polyfunctionalized 2,3-dihydropyrrole derivatives in excellent yields. In this transformation, two new  $Csp^3-Csp^2$  bonds were constructed in one pot. The reductive elimination from  $\pi$ -allyl palladium complex **2a-I** presented excellent regioselectivity, providing the terminal C1 position coupling product without detection of internal C3 coupling product. The unique terminal alkene as one of the most easily functional group endowed these molecules versatile transformation to much more complicated molecules. Further applications are in progress in our laboratory.

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