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C–H Functionalization

Pd(II)-Catalyzed C–H Activation of Styrylindoles: Short, Efficient, and Regioselective Synthesis of Functionalized Carbazoles

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Abstract: A novel Pd^{II}-catalyzed approach for the direct synthesis of highly functionalized carbazoles from unprotected styrylindoles has been developed. The reaction features a variety of olefin substrates, which are readily switchable by subtle tuning of the reaction conditions. Investigations of the mechanism suggest that the C–H activation proceeds via enamine formation.

In the past two decades, transition-metal-catalyzed C–C bond formations[1] by C–H activation have gained considerable attention, and have become one of the most attractive alternatives for the conversion of unfunctionalized substrates into a variety of heterocycles, natural products, pharmaceuticals, and functional materials. Regioselective C–H functionalization of heterocyclic substrates by electrophilic palladation has been noted in recent years.[2] After the discovery of the Fujiwara–Moritani reaction,[3] several groups[4] have explored the regioselective migratory insertion for electron-rich olefins by using heteroatom-based directing groups.

The carbazole framework is present in numerous natural products, which are of immense biological importance.[5,6] Many of these exhibit significant photophysical and physiological activities.[7] Ellipticine, antiostatin A_4, hyellazole, clausenaline, murrayanine, and carbazomycine B are notable examples of carbazole alkaloids (Figure 1). Because of their significant importance, a number of methods are available in the literature for the synthesis of carbazoles.[8–10] However to the best of our knowledge, C–H activation of (*E*)-3-styryl-1*H*-indoles with alkenes has not been reported and remains challenging. Recently, Itami[11a] and Yu[11b] have explored the Diels–Alder[12] reaction for the synthesis of carbazole from *N*-methylindole using the tri- and bimetallic systems of Pd-Cu-Ag and Pd-Cu, respectively. Arguably, alkenylation of substituted benzenes, containing a directing group (DG), with alkenes is one of the most frequently applied methods to generate olefins through Pd-catalyzed directed C–H activation (Scheme 1i).[13] An elegant regioselective functionalization of indoles using a Pd catalyst has already been reported by Gaunt and Carretero (Scheme 1ii).[14]

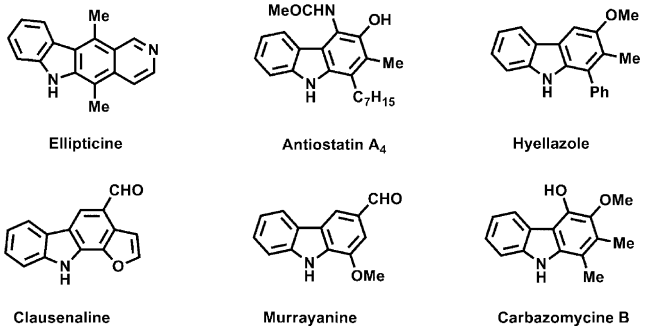
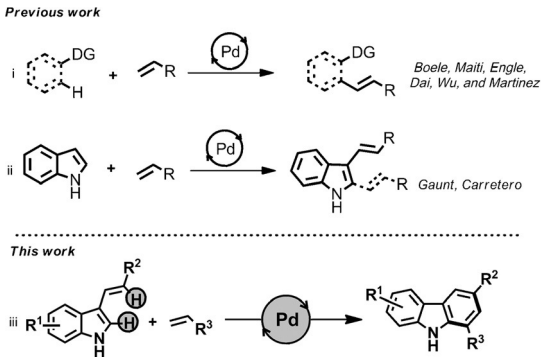


Figure 1. Selected examples of carbazole alkaloids.



Scheme 1. Heteroatom-directed C–H activation.

In continuation of our ongoing research work on transition-metal-catalyzed synthesis of heterocycles,[15] we envisioned that functionalized carbazoles could be obtained directly from styrylindoles, through successive regioselective C–H activation by electrophilic palladation using a variety of olefins (Scheme 1iii).

To identify the optimal conditions for the reaction, a variety of reported Pd catalysts, along with various combinations of organic solvents, were examined in the reaction of (*E*)-methyl 3-(1*H*-indol-3-yl)acrylate (**1a**) with styrene (**2a**) (Table 1). Using Gaunt conditions[14a] of $Pd(OAc)_2$ (10 mol%) with oxidant (1.8 equiv) in DMF/DMSO (9:1) at 70 °C for 18 h, the desired product **3a** was obtained in 10% yield (Table 1, entry 1). Increasing the temperature from 70 to 100 °C provided **3a** only in 20% yield (Table 1, entry 2). When $Pd(OAc)_2$ (10 mol%) was

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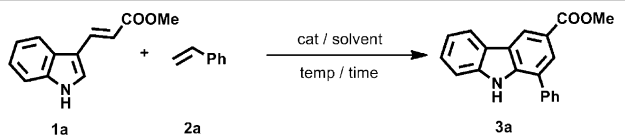
Table 1. Optimization of the reaction conditions.[a]



Entry	Catalyst	Solvent	Time [h]	Yield [%][b] **3a**
1[c,d]	$Pd(OAc)_2$	DMF/DMSO (9:1)	18	10
2[c]	$Pd(OAc)_2$	DMF/DMSO (9:1)	18	20
3[c]	$Pd(OAc)_2$	DMF/DMSO (7:1)	18	25
4[c]	$Pd(OAc)_2$	DMF/DMSO (5:1)	18	30
5[c]	$Pd(OAc)_2$	DMF/DMSO (5:1)	36	50
6[c]	$[PdCl_2(PPh_3)_2]$	DMF/DMSO (5:1)	36	60
7[c]	$[PdCl_2(PPh_3)_2]$	DMF/DMSO (5:1)	40	68
8	**$[PdCl_2(PPh_3)_2]$**	**DMF/DMSO (5:1)**	**40**	**70**
9[e]	$[PdCl_2(PPh_3)_2]$	DMF/DMSO (5:1)	40	70
10	$[PdCl_2(PPh_3)_2]$	DMF	40	25
11	$[PdCl_2(PPh_3)_2]$	NMP	40	00
12	$[PdCl_2(PPh_3)_2]$	DMA	40	30
13	$[PdCl_2(PPh_3)_2]$	DMSO	40	trace

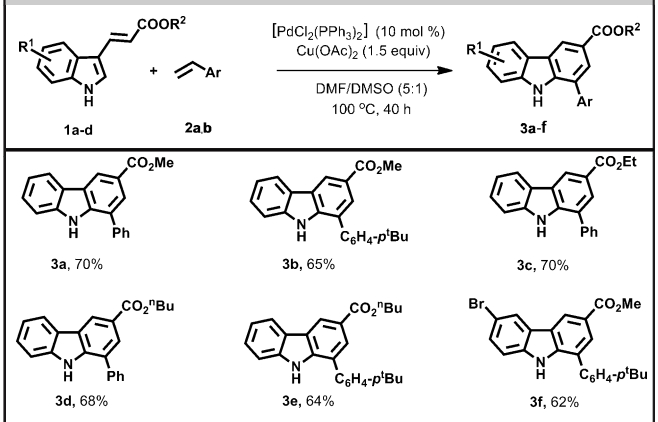
[a] Reactions were performed using 3-acrolyl indole (**1a**; 0.5 mmol), **2a** (1.0 mmol), catalyst (10 mol%), and $Cu(OAc)_2$ (1.5 equiv) in solvent (2.0 mL) at 100 °C. [b] Isolated yield. [c] $Cu(OAc)_2$ (1.8 equiv). [d] At 70 °C. [e] 15 mol% of catalyst used.

used in DMF/DMSO (7:1), **3a** was obtained in 25% yield (entry 3). It is interesting to note that the use of DMF/DMSO in a 5:1 ratio provided **3a** in an improved yield (entry 4). On running the reaction for 36 h, the desired product **3a** was obtained in 50% yield (entry 5). The use of $[PdCl_2(PPh_3)_2]$ provided **3a** in an improved yield (entry 6). Increase in the reaction time from 36 to 40 h further improved the yield of **3a** (entry 7). A slight decrease in the oxidant loading from 1.8 to 1.5 equiv, led to the formation of **3a** in 70% yield (entry 8). No significant change in the yield of the product **3a** was observed on using 15 mol% of the Pd catalyst (entry 9). The role of DMSO as an oxidant has also been identified.[16] Inferior results were obtained when DMF, NMP, DMA, and DMSO were used on their own as a solvent (entries 10–13).

With the optimized conditions in hand, the generality and scope of the reaction was examined (Table 2). A variety of indoloacrylates (**1a**–**d**), bearing electron-neutral and -deficient substituents, reacted with styrenes (**2a** and **2b**) to provide functionalized carbazoles (**3a**–**f**) in 62–70% yield with excellent functional-group tolerance. The reaction of (*E*)-methyl 3-(1*H*-indol-3-yl) acrylate (**1a**) with styrene (**2a**) and *tert*-butyl styrene (**2b**) provided the desired products **3a** and **3b** in 70 and 65% yields, respectively. When the ethyl group was used as R^2, the reaction was well implemented to form the intriguing cyclized product **3c** in 70% yield. The reaction of butylindoloacrylate (**1c**) with electron-rich alkenes, **2a** and **2b**, provided the products **3d** and **3**–**e** in good yields (68 and 64%, respectively); however, the reaction of the electron-deficient substrate 5-bromoindole (**1d**) with **2b** provided the desired product **3f** only in moderate yield (Table 2).

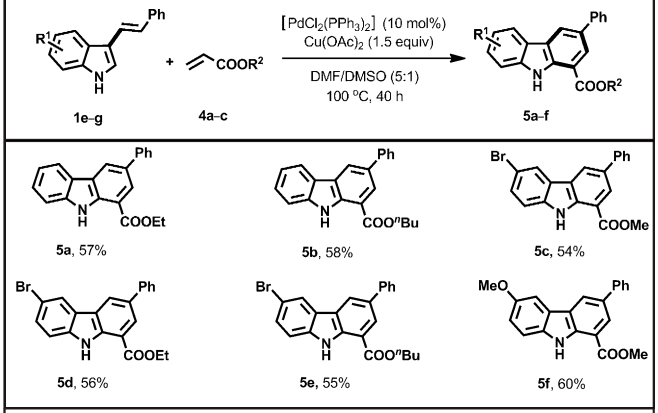
Encouraged by the above results, the reactions for the C–H activation of styrene-substituted indoles with acrylate was next performed (Table 3). The reaction of electron-rich styryl-1*H*-

Table 2. C–H Activation of styrylindoles with styrenes.[a]



[a] Reactions were performed using **1** (0.5 mmol), styrene (**2**; 1.0 mmol), $[PdCl_2(PPh_3)_2]$ (10 mol%), and $Cu(OAc)_2$ (1.5 equiv) in DMF/DMSO (5:1; 2.0 mL) at 100 °C for 40 h; isolated yields are given.

Table 3. C–H activation of styrene-substituted indoles with acrylates.[a]



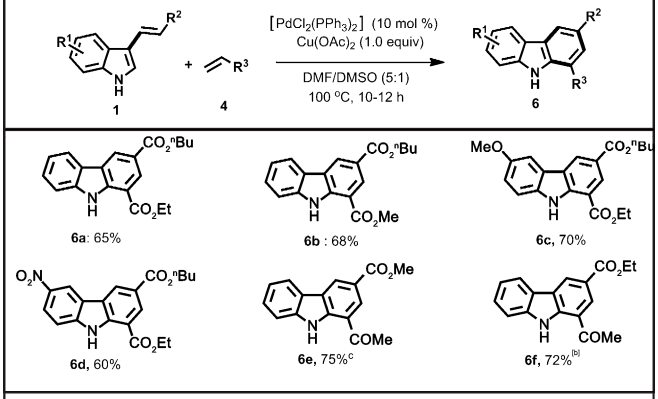
[a] Reactions were performed using **1** (0.5 mmol), acrylates (**4**; 1.0 mmol), $[PdCl_2(PPh_3)_2]$ (10 mol%), and $Cu(OAc)_2$ (1.5 equiv) in DMF/DMSO (5:1; 2.0 mL) at 100 °C for 40 h; isolated yields are given.

indole (**1e**) with electron-deficient acrylates (**4a** and **4b**) provided the desired products **5a**and**5b** in 57 and 58% yields, respectively. When bromo and methoxy groups were used as R^1, the reaction was well implemented to form the intriguing cyclized products **5c**–**f** in moderate to good yields (Table 3).

We further extended the scope of the reaction by using styrylindoles (**1**) with a variety of alkenes (**4**) under optimized conditions for 10–12 h (Table 4). The reactions of butylstyrylindoles (**1c** and **1h**) with ethylacrylate (**4a**) and methylacrylate (**4c**) provided the carbazoles **6a**–**c** in good yields with excellent regioselectivities. It is interesting to note that substrate **1i**, bearing a strong electron-withdrawing $-NO_2$ group, provided the desired product **6d** in 60% yield. The reaction of styrylindoles **1a**- and -**1b** with methyl vinyl ketone (**4d**) fruitfully provided the corresponding carbazoles **6e**-and **6f** in 75 and 72% yields, respectively

In order to support the proposed mechanistic pathway, various preliminary experiments were performed (Scheme 2). For

Table 4. C–H Activation of acrylate-substituted indoles with electron-deficient alkenes.[a]



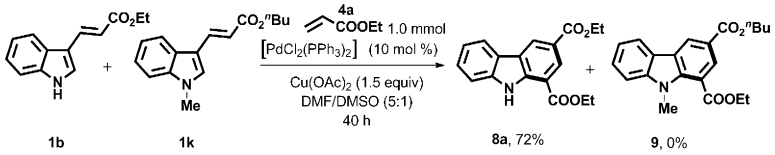
[a] Reactions were performed using **1** (0.5 mmol), acrylates (**4**; 1.0 mmol), $[PdCl_2(PPh_3)_2]$ (10 mol%), and $Cu(OAc)_2$ (1.0 equiv) in DMF/DMSO (5:1; 2.0 mL) at 100 °C for 12 h; isolated yields are given. [b] Time = 10 h.

reaction conditions (Scheme 3). Astonishingly, the carbazole **8a** was obtained in 72% yield; however, the carbazole **9** (with *N*-methyl) was not observed. The formation of **8a** invokes the different N-deprotonating/protonating abilities of **1b** and **1k**. These results suggest that the presence of free NH-group of the indole is crucial for the reaction.

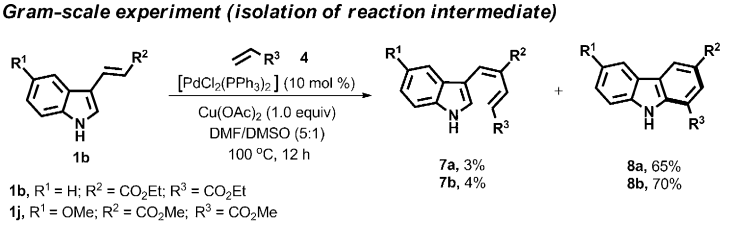
To further provide the support for our mechanism, we performed additional experiments using deuterated reagents (Scheme 4). The isotopic labeling study of **1b** with deuterated styrene (**10**) provided the isotopic carbazole **11** in 40% yield. This control experiment suggests that the C–H activation is occurring regioselectively first onto the alkene.

Based on the evidences from the control experiments, two plausible pathways are proposed in Scheme 5.[17] The mechanism is initiated by the flow of electrons in **1**. Based on an enamine-like motif **i**, this flow of electrons would be consistent with an attack of the carbon adjacent to R^2 and palladium. The loss of an NH proton would lead to the formation of a palladi-

the validation of a possible reaction intermediate, we performed gram-scale experiments using styrylindoles **1b** and **1j** with alkenes **4a** and **4c**. Thus, carbazoles **8a** and **8b** were obtained in 65 and 70% yields, respectively, along with the intermediates



Scheme 3. Study of protected and deprotected styrylindoles.

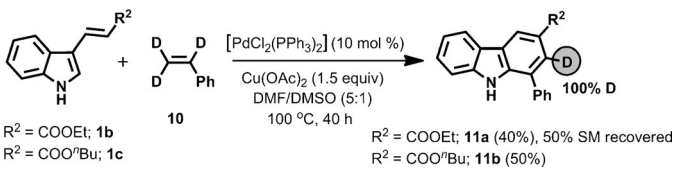


Scheme 2. Control experiments.

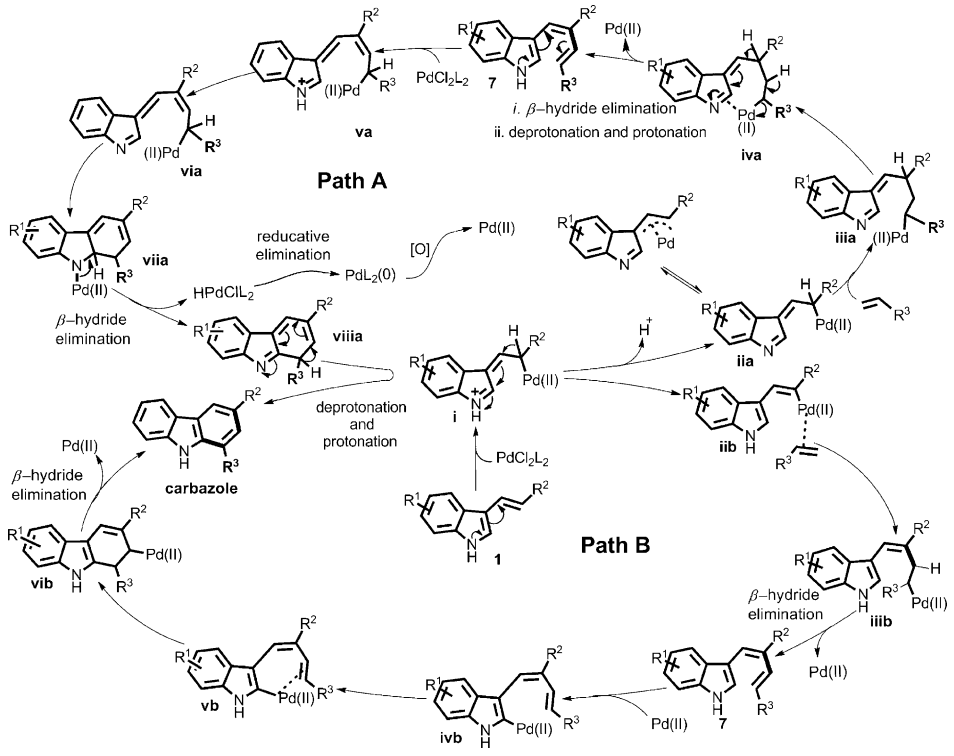
7a and **7b** in 3 and 4% yields, respectively (Scheme 2i). The treatment of intermediate **7b** with $[PdCl_2(PPh_3)_2]$ (5 mol%) and $Cu(OAc)_2$ (1.0 equiv), provided the carbazole **8b** in 80% yield (Scheme 2ii). However, under thermal conditions and in the absence of a Pd catalyst, the carbazole was not observed. These observations clearly support the formation of carbazoles through successive C–H activation steps.

We next carried out the reaction of **1b** (free NH indole) and **1k** (*N*-methyl indole) with ethyl acrylate using the optimized

um-allyl system **iia** (Path A). The regioselective olefin insertion at the α-position of R^2 will generate the species **iiia**. The newly formed Pd–C bond would next attack the imine (C=N) to establish the tricyclic core skeleton **iva**. The intermediate **7** would be formed through the β-hydride elimination followed by N-protonation and C–H deprotonation on the C–H bond next to R^2. The intermediate **7** would undergo the same C–Pd bond-forming process as mentioned above with a proton loss of the N–H bond and nucleophilic attack of the terminal carbon carrying R^3 to palladium to form skeleton **via**, which will then undergo intramolecular carbopalladation of the C=N bond (**viia**) leading to the formation of carbazoles through β-hydride elimination (**viiia**) followed by a C–H deprotonation/N-protonation sequence. The palladium(II)–hydrido complex reduces into Pd^0, which is then oxidized by $Cu(OAc)_2$ to Pd^{II} (Path A). Alternatively, the regioselective palladation can also take place on styrylindole (**1**) at the α-position of R^2 (Path B). The intermediate **7** is produced following



Scheme 4. Isotopic labeling studies.



Scheme 5. Plausible mechanism.

the oxidative Heck cycle through regioselective palladation (**i**), olefin insertion (**iib**), and *syn* β-hydride elimination of Pd from **iiib**. Further the catalytic cycle is completed by C2-palladation (**ivb**), followed by the oxidative intramolecular cyclization (**vb**) and β-hydride elimination (**vib**), which leads to the carbazole formation (Path B). To support the mechanism, the key intermediate **7** was isolated and confirmed by NMR and HRMS spectra. In Path A, the steps rely on N–H deprotonation, which cannot be accomplished with N-CH_3 system. This was indeed found experimentally as shown in Scheme 3, which favors the proposed mechanism via enamine formation.

In conclusion, a novel Pd^{II}-catalyzed approach for the direct synthesis of highly functionalized carbazoles from unprotected styrylindoles has been developed. The three pairs of substrate scopes, namely acrylate-substituted styrylindoles with styrene, styrene indoles with acrylates, and acrylate-substituted styrylindoles with arylate/ketone were established for the synthesis of the functionalized carbazoles. The results of the control experiments, deuterium labeling and isolation of the key intermediate suggests that the mechanism of C–H activation proceeds via enamine formation (Path A over Path B).

Experimental Section

General procedure for the synthesis of substituted carbazoles

In an oven-dried round bottomed flask, a solution of vinylindole derivatives (0.5 mmol) in DMF/DMSO (5:1; 2 mL), $[PdCl_2(PPh_3)_2]$ (10 mol%), $Cu(OAc)_2$ (1.5 equiv), and styrene derivatives/acrylates (1.0 mmol) were added under an inert atmosphere. The resulting reaction mixture was heated at 100 °C for 10–40 h and progress of the reaction was monitored by TLC. After complete consumption of vinylindole, the reaction was brought to room temperature. Note: an additional amount of acrylate was added, if required, for complete conversion. The reaction mixture was diluted with ethyl acetate (10 mL) and water (15 mL), and then filtered through a plug of celite. The layers were separated, and the organic layer was washed with aqueous saturated brine solution and dried over Na_2SO_4. The organic layer was concentrated under reduced pressure and the resulting crude material was purified by column chromatography on silica gel (hexane/ethylacetate = 90:10). The structure and purity of known starting materials were confirmed by comparison of their physical and spectral data (^{1}H NMR, ^{13}C NMR, and HRMS).

Acknowledgements

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Keywords: carbazoles · C–H activation · palladium · regioselectivity · styrylindoles

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