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Pd-Catalyzed Intramolecular Oxidative C–H Amination: Synthesis of Carbazoles

So Won Youn,* Joon Hyung Bihn, and Byung Seok Kim

Department of Chemistry and Research Institute for Natural Sciences, Hanyang University, Seoul 133-791, Korea

sowony73@hanyang.ac.kr

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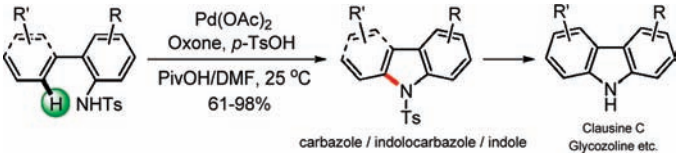
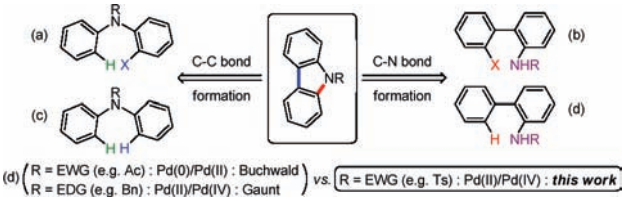
ABSTRACT



A Pd-catalyzed oxidative C–H amination of *N*-Ts-2-arylanilines under ambient temperature using Oxone as an inexpensive, safe, and easy-to-handle oxidant has been developed. This process represents a green and practical method for the facile construction of carbazoles with a broad substrate scope and wide functional group tolerance.

Carbazoles have attracted considerable attention in biological and material sciences as a ubiquitous structural motif with wide-ranging physiological and photophysical properties.[1,2] Thus, a number of synthetic strategies have been reported for the construction of these privileged molecular entities. Among the repertoire of synthetic methods, transition-metal-catalyzed C–C or C–N bond forming reactions are the most powerful and attractive considering that the starting material could be easily prepared with synthetic convergency and practicality (Scheme 1).

Scheme 1. Carbazole Synthesis via C–C or C–N Bond Formation



C–H bond functionalization has emerged as an efficient, atom-economical, and eco-friendly process with widespread applications and industrial potential.[3,4] Indeed, powerful variants of pathways (a)[5] and (b)[6] in Scheme 1 have been demonstrated where C–H bond

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(3) Selected reviews on C–H activation: (a) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (b) Dyker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1698. (c) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633. (d) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731. (e) Dick, A. R.; Sanford, M. S. *Tetrahedron* **2006**, *62*, 2439. (f) Godula, K.; Sames, D. *Science* **2006**, *312*, 67. (g) Beccalli, E. M.; Broggini, G.; Martinelli, M.; Sottocornola, S. *Chem. Rev.* **2007**, *107*, 5318. (h) Zhang, M *Adv. Synth. Catal.* **2009**, *351*, 2243. (i) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094. (j) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147.

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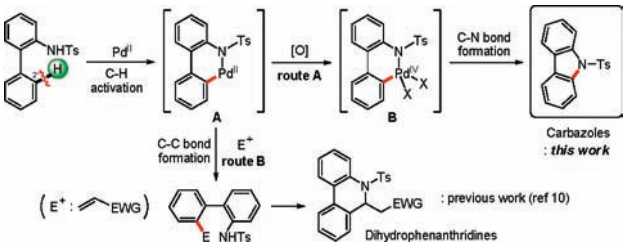
activation was followed by subsequent C−C (Scheme 1c)[7] or C−N (Scheme 1d)[8] bond formation to afford carbazoles.[9]

Recently, we reported a Pd-catalyzed domino reaction of *N*-Ts-2-arylanilines with activated olefins that involved a directed C−H activation, C−C bond formation, and intramolecular conjugate addition reaction to generate dihydrophenanthridines in good to excellent yields (Scheme 2, route B).[10] In this process, reactions proceeded smoothly at room temperature via C−H activation followed by oxidative C−C bond formation at the C2′-position. Inspired by this finding, we reasoned that a carefully chosen oxidant would promote the oxidation of palladacycle **A** followed by reductive elimination of the so-obtained Pd^{IV} species (**B**) with concomitant C−N bond formation,[11] leading to a carbazole product (Scheme 2, route A). Although an analogous reaction using 2-arylanilines bearing a *N*-electron-withdrawing group (e.g., R = Ac, Scheme 1d) has been demonstrated by Buchwald and co-workers, the elevated temperature with the prolonged reaction time reported therein may present limitations to the substrate scope and practicality.[8a,b] Furthermore, a Pd^0/Pd^{II} process[12] has been put forward to account for the electronic influence of the substrates examined.[8a,b] In contrast, Gaunt and co-workers had demonstrated a related process that operates at ambient temperature through a Pd^{II}/Pd^{IV} catalytic cycle with 2-arylanilines bearing an electron-donating group (e.g., R = Bn, Scheme 1d),[8d] though the costly use of $PhI(OAc)_2$ as the oxidant may appear less attractive together with stoichiometric formation of a toxic byproduct, i.e., PhI. While significant progress has been made in transition-metal-catalyzed C−H amination by several leading research groups,[13−15] practical synthetic methods for the construction of the carbazole system via catalytic C−H amination using environmentally benign and inexpensive oxidants under mild conditions are yet to be realized. In view of the prevalence of the carbazole motif in bioactive alkaloids and electronic materials, such a synthetic method is particularly valuable. Here, we report a Pd-catalyzed intramolecular oxidative C−H amination of *N*-Ts-2-arylanilines that involves a directed C−H activation followed by a subsequent C−N bond formation via a Pd^{II}/Pd^{IV} process (R = Ts in Scheme 1d and route A in Scheme 2), leading to carbazoles as valuable chemical entities. In particular, the reaction conditions described herein significantly improved the efficiency and practicality of carbazole formation through the use of Oxone as an environmentally benign, nontoxic, easy-to-handle, and inexpensive oxidant, under mild conditions, to promote the formation of Pd^{IV} species followed by C−N bond

Scheme 2. Pd-Catalyzed Synthesis of N-Heterocycles from 2-Arylanilines through C−H Activation at the C2′-Position



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(8) Examples of coupling reactions between C−H and N−H bonds: (a) Tsang, W. C. P.; Zheng, N.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 14560. (b) Tsang, W. C. P.; Munday, R. H.; Brasche, G.; Zheng, N.; Buchwald, S. L. *J. Org. Chem.* **2008**, *73*, 7603. (c) Li, B.-J.; Tian, S.-L.; Fang, F.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2008**, *47*, 1115. (d) Jordan-Hore, J. A.; Johansson, C. C. C.; Gulias, M.; Beck, E. M.; Gaunt, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 16184 and ref 7e. During the preparation of this manuscript, Chang and co-workers reported an example of Cu-catalyzed or metal-free synthesis of carbazoles from 2-benzenesulfonamidobiphenyls; see: (e) Cho, S. H.; Yoon, J.; Chang, S. *J. Am. Chem. Soc.* **2011**, *133*, 5996. The reaction reported herein is believed to operate through a radical mechanism where the Cu species serves as a Lewis acid to activate the hypervalent iodine(III) reagent. In contrast, our reaction proceeded smoothly in the presence of TEMPO, and the use of Oxone in the absence of a Pd catalyst did not promote any reaction even at a high temperature (80 °C).

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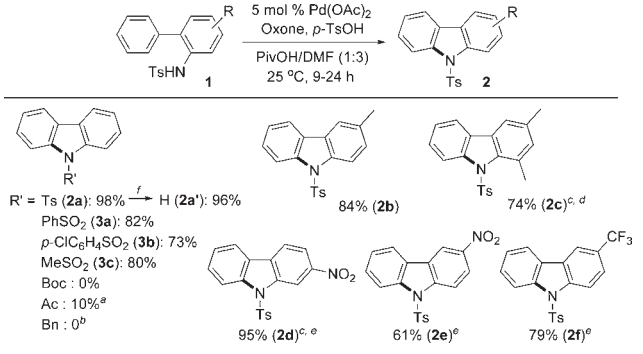
(15) Selected examples of Pd-catalyzed intramolecular amination of aromatic C−H bonds: (a) Inamoto, K.; Saito, T.; Hiroya, K.; Doi, T. *J. Org. Chem.* **2010**, *75*, 3900. (b) Mei, T.-S.; Wang, X.; Yu, J.-Q. *J. Am. Chem. Soc.* **2009**, *131*, 10806. (c) Wasa, M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2008**, *130*, 14058. (d) Inamoto, K.; Saito, T.; Hiroya, K.; Doi, T. *Synlett* **2008**, 3157. (e) Inamoto, K.; Saito, T.; Katsuno, M.; Sakamoto, T.; Hiroya, K. *Org. Lett.* **2007**, *9*, 2931.

construction via reductive elimination.[16] This protocol, using sulfonamide derivatives as an electron-withdrawing alternative, should prove complementary to Gaunt's earlier report.[8d] Last but not least, as we shall see, high functional group tolerance in this newly developed process is also highly noteworthy.

In light of our recent success in Pd-catalyzed domino reactions of *N*-Ts-2-arylanilines with activated olefins,[10] we began our studies on the proposed oxidative C−H amination reaction using *N*-Ts-2-phenylaniline (**1a**) as the test substrate. Our studies revealed the inexpensive, safe, and easy-to-handle Oxone as the oxidant of choice for this transformation, and the pivalic acid (PivOH)[17]/DMF cosolvent system proved the most ideal.[18] Moreover, the use of *p*-TsOH as an additive along with PivOH/DMF further improved the reaction yield. Lastly, among all the Pd complexes examined, $Pd(OAc)_2$ was found to be the most effective Pd catalyst for this reaction, and no reaction occurred in the absence of $Pd(OAc)_2$ even at a high temperature (80 °C). This result is notable in view of the recent report by Chang et al., where a hypervalent iodine(III)-mediated oxidative radical process at elevated temperature promoted the formation of carbazoles from sulfonamides under metal-free conditions.[8e] Inclusion of TEMPO as an additive had no deleterious effect on the efficiency of the carbazole formation, providing evidence in support of a nonradical mechanistic pathway. Continuation of our reaction optimization ultimately secured a reagent blend consisting of $Pd(OAc)_2$ (5 mol %), Oxone (1 equiv), and *p*-TsOH (0.5 equiv) in PivOH/DMF (1:3), which operates at rt to afford *N*-Ts-carbazole **2a** with an impressive 98% yield (Scheme 3).

Scheme 3. Substituent Effect of the Aniline Moiety of 2-Phenylanilines



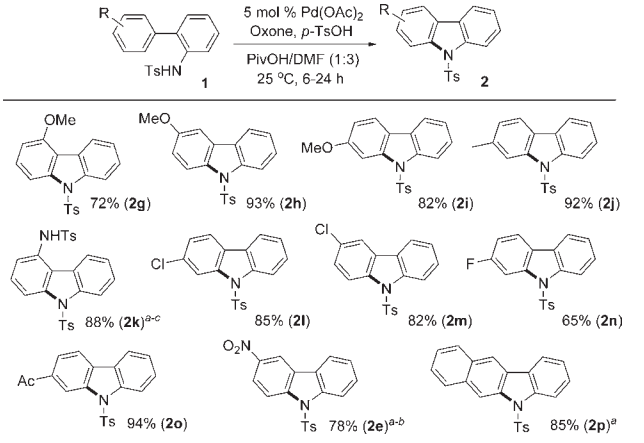
[a]Determined by ^{1}H NMR. [b]Decomposed. [c]10 mol % $Pd(OAc)_2$. [d]80 °C. [e]40 °C. [f]With nBu_4NF in THF at reflux for 4 h.

Before proceeding, a cursory survey of the effect of N-protecting groups including sulfonyl (e.g., Ts, $PhSO_2$, Ms), acyl (e.g., Ac, Bz), carboalkoxy (e.g., Boc), and alkyl (e.g., Me, Bn) reconfirmed the effectiveness of sulfonyl, especially *p*-toluenesulfonyl (Ts), as the preferred group for this reaction (Scheme 3).[18] In sharp contrast to the earlier reports,[8] alkyl-protected amines led to a complex reaction mixture and no reaction was observed with anilides under our optimized conditions. These findings also appear to be consistent with the fact that no reaction took place using oxidants generally employed in the Pd^0/Pd^{II} catalytic pathway ($Cu(OAc)_2$, benzoquinone, and AgOAc), suggesting a mechanistic difference with the related C−H amination of *N*-Ac-2-arylanilines reported by the Buchwald group.[8a−c] The reaction in hand that operates in the presence of strong oxidants (e.g., Oxone, $PhI(OAc)_2$, $K_2S_2O_8$) at ambient temperature is in closer analogy with that developed by the Gaunt group with the nitrogen guarded by an electron-donating group[8d] through the Pd^{II}/Pd^{IV} pathway.[16]

With the optimized reaction conditions in hand, we set out to explore the substrate scope of this process by first examining the substituent effect of the tosylamide bearing an aromatic ring (Scheme 3, **2b**−**2f**). Similar to our previous work,[10] a subtle change in the acidity of the NH moiety through the introduction of substituents including Me, NO_2, and CF_3 at the C4- or C5-position had a significant influence on the chemical reactivity, an observation that is in line with the protecting group effect described earlier. As such, a delicately balanced acidity of the NH group through the nitrogen protecting group and the aryl substituent of the protected aniline is required to achieve high efficiency for this reaction. A sterically hindered substrate with a substituent at the C6-position required more forcing conditions, giving product **2c** in 74% yield.

The substituent effect of the 2-aryl moiety of substrate **1** was also explored (Scheme 4). In this context, both electron-donating and -withdrawing substituents were well tolerated, with the exception of a substrate bearing a strongly electron-withdrawing group (e.g., NO_2) at the C3′-position, which required more forcing reaction

Scheme 4. Substituent Effect of the 2-Aryl Moiety of *N*-Ts-2-Arylanilines



[a]10 mol % $Pd(OAc)_2$. [b]80 °C. [c]Without *p*-TsOH.

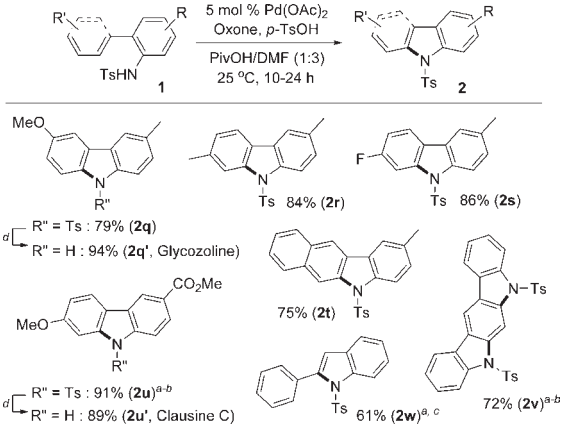
(16) For selected examples using Oxone as an oxidant for C−C or C−O bond formations, see: Hull, K. L.; Lanni, E. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 14047 and ref 11f.

(17) For the effect of PivOH, see ref 7d and references therein.

(18) For details, see Supporting Information.

conditions to afford product **2e** with comparable yield. Furthermore, while the reaction with the 2′-OMe substituted substrate proceeded uneventfully at rt (**2g**, 72% yield), the reaction of the 2′-NHTs substituted substrate required a higher catalyst loading (10 mol % $Pd(OAc)_2$) at an elevated temperature (80 °C) and the exclusion of *p*-TsOH from our standard conditions, to afford **2k** in 88% yield. On the other hand, C3′-substituted substrates showed remarkable regioselectivity, leading to products originating from activation of the less hindered C−H bond (**2h**, **2m**, **2p**, and **2e**, Scheme 4). This method also proved useful in the preparation of carbazoles with substitution on both aromatics rings, leading to products **2q**−**u** in good yields (Scheme 5). The functional group compatibility of the developed reaction conditions is particularly noteworthy, including but not limited to methoxy, halogen, ketone, ester, amino, and nitro groups. Halogenated substrates afforded products with the halogen substituents remaining intact, where the formation of dehalogenated products was not observed (**3b**, Scheme 3; **2l**−**n**, Scheme 4; **2s**, Scheme 5).

Scheme 5. Pd-Catalyzed C−H Amination for the Synthesis of Various Substituted Carbazoles



[a]10 mol % $Pd(OAc)_2$. [b]40 °C. [c]Without *p*-TsOH at 80 °C. [d]With nBu_4NF in THF at reflux for 2.5 h.

As a further demonstration of the developed method in the construction of N-heterocycles, *N*,*N*′-bistosyl-2,2″-diamino-[1,1′;3′,1″]terphenyl provided fused pentacyclic indolo[2,3-*b*]carbazole **2v** in good yield (Scheme 5).[19a] It is also noteworthy that the vinylic C−H bond of *N*-Ts-2-styrylaniline could engage in C−H amination to afford 2-substituted indole **2w** (Scheme 5). The synthesis of two naturally occurring carbazoles, glycozoline[19b] (**2q**′, Scheme 5), and clausine C[19c] (**2u**′, Scheme 5), as well as 9*H*-carbazole (**2a**′, Scheme 3), was achieved through deprotection of the Ts group.

To gain insight into this reaction, we first performed competition experiments with a series of 3′-substituted *N*-Ts-2-phenylanilines.[18] This study revealed an electronic dependence on variation of the substituent from electron-donating to electron-withdrawing, an observation that is consistent with the initial electrophilic cyclopalladation. Further evidence in support of the electrophilic nature of this process was made available through kinetic isotope studies, where competition experiments demonstrated modest but notable secondary intermolecular (k_H/k_D = 1.41) and intramolecular (k_H/k_D = 2.03) kinetic isotope effects.[18,20]

In summary, we have developed an effective Pd-catalyzed oxidative C−H amination of *N*-Ts-2-arylanilines under ambient temperature using Oxone as an inexpensive, safe, and easy-to-handle oxidant. This method offers a straightforward access to a wide range of carbazoles, an important structural motif in natural and designed compounds with interesting biological and physical properties. Equally noteworthy is the functional group tolerance of the developed reaction, a feature that should permit further transformation of the carbazole product and provide an entry to structurally diverse heterocycles. In view of the growing understanding of transition-metal-mediated C−H activation/functionalization processes, the reaction described herein showcased a reactivity profile that is notably different to those previously reported.[8] Further investigations to expand the scope of this reaction are currently underway in our laboratory.

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Supporting Information Available. Full experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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