DOI: 10.1002/adsc.201701039
Advanced Synthesis & Catalysis

Synthesis of Carbazoles from 2-Iodobiphenyls by Palladium-Catalyzed C–H Activation and Amination with Diaziridinone

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Received: August 7, 2017; Revised: October 31, 2017; Published online: December 29, 2017

Supporting information for this article is available on the WWW under https://doi.org/10.1002/adsc.201701039

Abstract: A facile and efficient approach has been developed for the synthesis of carbazoles from 2-iodobiphenyls and diaziridinone under palladium catalysis. A wide range of carbazoles were synthesized in good to excellent yields, and indole derivatives were obtained by using styrenes as the substrate. The palladacycles obtained from 2-iodobiphenyls acted as the key intermediate, and the reaction should proceed *via* a tandem Pd-catalyzed C–H activation/dual C–N bond formation sequence.

Keywords: Palladacycles; C–H activation; amination; synthetic methods; carbazoles

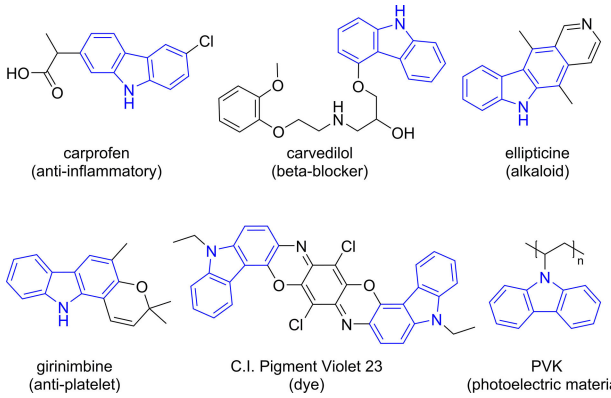


Figure 1. Natural products, bioactive compounds, dyes, and photoelectric materials containing carbazoles.

Carbazoles are a class of important aromatic nitrogen heterocycles. They are common structural motifs prevalent in bioactive natural products and therapeutic agents.[1] Moreover, carbazoles have also found extensive applications in materials science due to their unique thermal, electrical, and optical properties (Figure 1).[2] It is not surprising that continuous efforts have been devoted to exploring new methods for the synthesis of carbazoles. Currently, a variety of methods have been developed to create carbazole molecular scaffolds.[3] These methods generally follow two modes: 1) the construction of a side benzene ring from indole derivatives; 2) the construction of a middle pyrrole ring from benzene derivatives.[3b] Among the current methods, transition metal-catalyzed reactions play significant roles and provide novel and powerful synthetic means for carbazoles.[4]

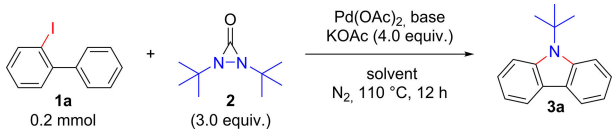
The past few decades have witnessed noticeable progress in C–H functionalization.[5] Direct C–H functionalization reactions have great advantages compared to traditional ones relying on the transformation and conversion of active functional groups, and they are emerging as novel and efficient strategies in organic synthesis. The synthetic methods of carbazoles *via* C–H activation have also been reported. Carbazole skeletons could be constructed through C–H amination,[6] C–H arylation,[7] and coupling of two C–H bonds.[8]

Recently, we found that dibenzopalladacyclopentadienes obtained *via* C–H activation of 2-iodobiphenyls exhibited novel reactivities.[9] These palladacycles consist of two carbon-Pd bonds, which can be functionalized and therefore offer opportunities to develop novel organic reactions. On the other hand, due to their unique and versatile reactivities, diaziridinones are important synthetic intermediates and have been utilized to develop a variety of novel organic reactions.[10] Recently, the Shi group reported that palladacycles consisting of C(sp^2)- and C(sp^3)-Pd bonds could react with diaziridinone to form indolines.[11] In these reactions, the two carbon-Pd bonds were functionalized and transformed into two C–N bonds. Inspired by these excellent reactions, we envisioned that dibenzopalladacyclopentadienes might

react with diaziridinone to generate carbazoles. Herein, we report a facile protocol for the synthesis of carbazoles starting from 2-iodobiphenyls and diaziridinone *via* Pd-catalyzed C–H activation and dual C–N bond formation. The protocol was also applicable to the synthesis of indole derivatives by using styrenes as the substrates.

We commenced our studies by investigating the reaction of 2-iodobiphenyl **1a** and diaziridinone **2**. As shown in Table 1, desired carbazole product **3a** was formed in 44% yield in the presence of 10 mol% $Pd(OAc)_2$, 2.0 equivalents of K_2CO_3, and 4.0 equivalents of KOAc (entry 1). Whereas replacing K_2CO_3 with Li_2CO_3 or Na_2CO_3 resulted in lower yields (entries 2 and 3), the yield was improved to 53% by using Cs_2CO_3 (entry 4). Solvent screening showed that the reactions almost failed to generate the desired product in other screened solvents except DMA, which gave the same yield as DMF (entries 5–8).

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



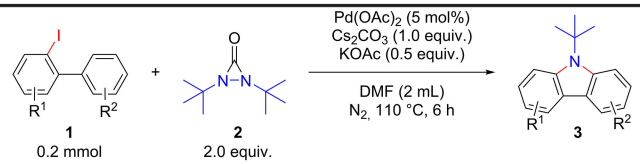
Entry	base (equiv.)	solvent (mL)	Pd (mol%)	yield (%)
1	K_2CO_3 (2.0)	DMF (1)	10	44
2	Li_2CO_3 (2.0)	DMF (1)	10	16
3	Na_2CO_3 (2.0)	DMF (1)	10	25
4	Cs_2CO_3 (2.0)	DMF (1)	10	53
5	Cs_2CO_3 (2.0)	DMA (1)	10	53
6	Cs_2CO_3 (2.0)	dioxane (1)	10	n.r.
7	Cs_2CO_3 (2.0)	MeCN (1)	10	trace
8	Cs_2CO_3 (2.0)	toluene (1)	10	n.r.
9	Cs_2CO_3 (2.0)	DMF (2)	10	90
10	Cs_2CO_3 (2.0)	DMF (2)	5	90
11[b]	Cs_2CO_3 (2.0)	DMF (2)	5	90
12[c]	Cs_2CO_3 (2.0)	DMF (2)	5	78
13[b]	Cs_2CO_3 (1.0)	DMF (2)	5	91
14[b]	Cs_2CO_3 (0.5)	DMF (2)	5	36
15[b]	/	DMF (2)	5	6
16[b,d]	Cs_2CO_3 (1.0)	DMF (2)	5	95
17[b,e]	Cs_2CO_3 (1.0)	DMF (2)	5	80
18[b,d]	Cs_2CO_3 (1.0)	DMF (2)	2	63
19[b,d,f]	Cs_2CO_3 (1.0)	DMF (2)	5	62
20[b,d,g]	Cs_2CO_3 (1.0)	DMF (2)	5	95 (91)[h]

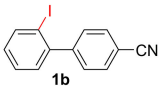
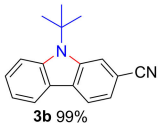
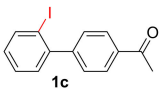
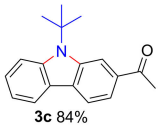
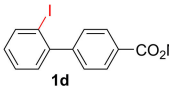
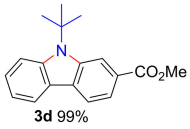
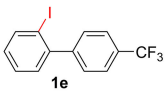
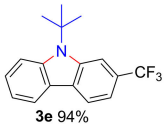
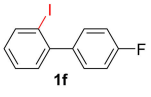
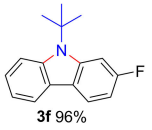
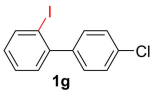
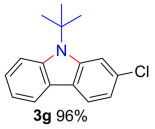
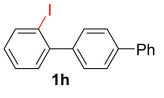
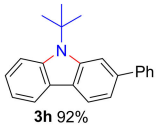
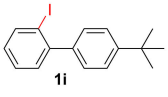
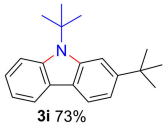
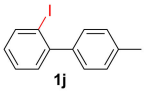
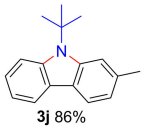
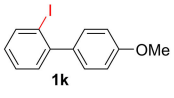
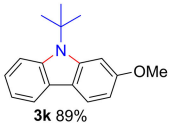
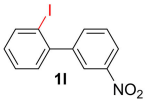
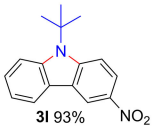
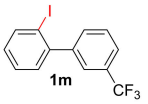
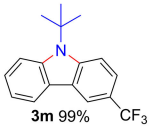
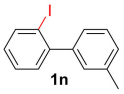
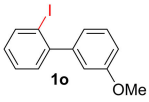
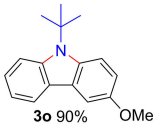
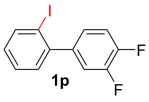
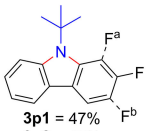
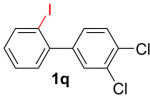
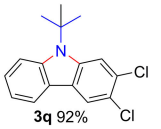
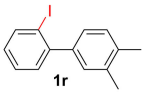
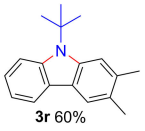
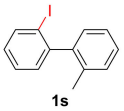
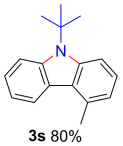
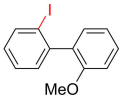
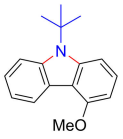
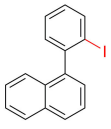
[a] The yields were determined by ^1H NMR analysis of crude reaction mixture using CH_2Br_2 as the internal standard.
[b] 2.0 equiv. of **2**.
[c] 1.0 equiv. of **2**.
[d] 0.5 equiv. of KOAc.
[e] No KOAc.
[f] 100 °C.
[g] 6 h.
[h] Isolated yield.

Surprisingly, the yield increased to 90% when the reaction mixture was diluted with 2 mL DMF (entry 9). The reason remains to be investigated. After achieving the excellent yield, we turned to further optimize the reaction conditions by trying to lower the amount of the reagents in the reaction. First, we reduced the catalyst loading to 5 mol%, and the yield remained constant (entry 10). Two equivalents of **2** were sufficient and necessary to afford the high yield (entries 11 and 12). The amount of Cs_2CO_3 could also be reduced to 1.0 equivalent without affecting the yield (entry 13). However, the use of 1.0 equivalent of Cs_2CO_3 was necessary since the yield decreased dramatically in the presence of 0.5 equivalent of Cs_2CO_3 and only a trace amount of the desired product was formed when Cs_2CO_3 was removed (entries 14 and 15). Reducing KOAc to 0.5 equivalent led to a slightly higher yield (entry 16). However, the yield decreased when KOAc was removed (entry 17). Although the roles of Cs_2CO_3 and KOAc in the reaction remain to be investigated, some studies suggested that bases should play an important role in the generation of the active Pd(0) species and KOAc could promote C–H activation.[12] A yield of 63% was still obtained when the loading of $Pd(OAc)_2$ was reduced to 2 mol% (entry 18), and the reaction was low-yielding at a lower temperature (entry 19). Finally, the optimal yield was still obtained when the reaction time was shortened to 6 hours (entry 20).

With the optimal conditions in hand, we then explored the scope of the protocol for the synthesis of carbazoles towards various substituted 2-iodobiphenyls. First, we examined the compatibility of functional groups by investigating the reactions of 4′-substituted 2-iodobiphenyls. As shown in Table 2, a range of electron-withdrawing groups, including cyano, carbonyl, ester, and trifluoromethyl, were compatible, and the corresponding carbazoles were formed in good to excellent yields (entries 1–4). Both fluoro and chloro groups were well-tolerated, and 2-iodo-4′-phenylbiphenyl was also suitable (entries 5–7). All the reactions were high-yielding. Electron-donating groups, such as *tert*-butyl, methyl, and methoxy, were also compatible, furnishing carbazoles in good yields (entries 8–10). Next, we investigated the reactivities of 2-iodobiphenyls possessing substituents at other positions. A range of 2-iodobiphenyls containing various functionalities at 3′-positions including electron-withdrawing and electron-donating groups underwent the dual amination reaction in excellent yields (entries 11–14). 3′, 4′-Disubstitued 2-iodobiphenyls were also suitable (entries 15–17). For the majority of the substrates containing 3′-substituents, the reactions occurred at the less hindered positions selectively. However, due to the small size of fluorine, two regioisomers were formed for **1p** (entry 15). 2′-Substituted substrates, including those containing methyl

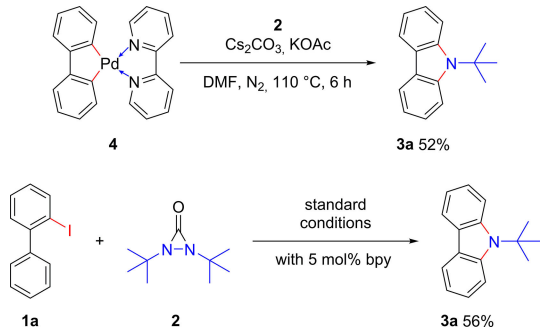
Table 2. Substrate scope.



entry	substrate	product
1	 **1b**	 **3b** 99%
2	 **1c**	 **3c** 84%
3	 **1d**	 **3d** 99%
4	 **1e**	 **3e** 94%
5	 **1f**	 **3f** 96%
6	 **1g**	 **3g** 96%
7	 **1h**	 **3h** 92%
8	 **1i**	 **3i** 73%
9	 **1j**	 **3j** 86%
10	 **1k**	 **3k** 89%
11	 **1l**	 **3l** 93%
12	 **1m**	 **3m** 99%
13	 **1n**	 **3n** 92%
14	 **1o**	 **3o** 90%
15	 **1p**	 **3p1** = 47% **3p2** = 45%
16	 **1q**	 **3q** 92%
17	 **1r**	 **3r** 60%
18	 **1s**	 **3s** 80%
19	 **1t**	 **3t** 78%
20	 **1u**	**3u** 86%
21	**1v**	**3v** 84%
22	**1w**	**3w** 93%
23	**1x**	**3x** 83%
24	**1y**	**3n** 82%
25	**1z**	**3z** 78%
26	**1aa**	**3aa** 88%
27	**1ab**	**3ab** 90%
28	**1ac**	**3ac** 87%
29	**1ad**	**3a** 80%
30	**1ae**	**3ae** 80%

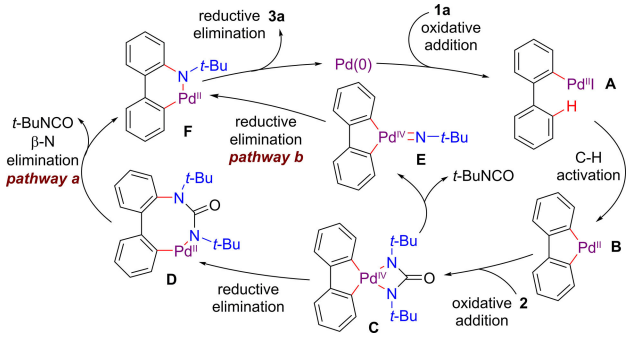
or methoxy group and 1-(2-iodophenyl)naphthalene, were also suitable, but the yields were comparatively lower (entries 18–20). The lower yields should be due to the steric hindrance caused by 2′-substituents, which could suppress the formation of the five-membered palladacycle. The reactivities of substrates containing functional groups on the iodo-attached benzene rings were then explored. A range of functionalities at the positions *para* to the iodo groups, including ester, chloro, fluoro, and methyl groups, were well-tolerated (entries 21–24). Even sterically hindered 3-methyl-2-iodobiphenyl **1z** could react with diaziridinone, furnishing product **3z** in 78% yield (entry 25).[13] The substrates bearing substituents on both of the benzene rings and 4-iodophenanthrene could also be transformed into corresponding carbazoles in high yields (entries 26–27). Interestingly, the rigid planar substrate **1ac** was also compatible (entry 28). It should be mentioned that 2-bromobiphenyl was also reactive, albeit in a lower yield (entry 29). Notably, the vinyl C–H bond could also be activated under the standard conditions, and substrate **1ae** underwent the C–H amination reaction to form indole derivative **3ae** (entry 30).[14]

To get evidence to prove that the reaction proceeded *via* a palladacycle as the intermediate, we prepared complex dibenzopalladacyclopentadiene **4** (Scheme 1).[15] When palladacycle **4** was subjected to the standard conditions, desired carbazole **3a** was formed. However, the yield was much lower than that in the catalytic reaction of 2-iodobiphenyl. The lower yield could be caused by the negative impact of the bipyridine ligand on the reaction. To prove this assumption, the reaction of **1a** and **2** was carried out in the presence of 5 mol% 2, 2′-bipyridine, and it was found that the yield decreased dramatically to 56%. These experimental results support that the palladacycle acted as the key intermediate in the carbazole-forming reaction.



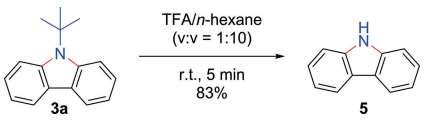
Scheme 1. Mechanistic studies.

On the basis of the above experimental results and the previous reports,[11] a tentative mechanism was proposed as shown in Scheme 2. The catalytic cycle starts with the oxidative addition of 2-iodobiphenyls to Pd(0) to form Pd(II) species **A**, which undergo intramolecular C–H activation to furnish pallada(II) cycle **B**. Next, **B** inserts into the N–N bond of diaziridinone *via* oxidative addition to give pallada (IV)cycle **C**. Eight-membered pallada(II)cycle **D** was then formed after the reductive elimination of intermediate **C**. Finally, the β-N elimination and subsequent reductive elimination lead to the product and the regeneration of Pd(0) catalyst (pathway a). It should be mentioned that a Pd(IV)-nitrene pathway cannot be ruled out (pathway b).



Scheme 2. Proposed mechanism.

Finally, the *tert*-butyl groups of the products could be removed readily with trifluoroacetic acid (TFA), providing unprotected carbazoles (Scheme 3).



Scheme 3. Removal of the *tert*-butyl group of product **3a**.

In conclusion, we have developed a facile and efficient approach for the synthesis of carbazoles starting from 2-iodobiphenyls and diaziridinone. A wide range of carbazoles can be synthesized in good to excellent yields. Indole derivatives could also be obtained in the case of styrene as the substrate. Mechanistic studies provided evidence to support the intermediacy of a dibenzopalladacyclopentadiene in the reaction, and the reaction proceeds *via* a tandem Pd-catalyzed C–H activation/dual C–N bond formation sequence.

Experimental Section

A 35 mL Schlenk tube equipped with a stir bar was charged with palladium acetate (2.3 mg, 0.01 mmol, 5 mol%), cesium

carbonate (65 mg, 0.2 mmol, 1.0 equiv.), potassium acetate (9.8 mg, 0.1 mmol, 0.5 equiv.), 2-iodobiphenyls (0.2 mmol, 1.0 equiv.), di-*tert*-butyldiaziridinone (68 mg, 0.4 mmol, 2.0 equiv.), and DMF (2 mL). The tube was sealed with a Teflon® high pressure valve, evacuated and backfilled with N_2 (5 times). After the reaction mixture was stirred in a preheated oil bath (110 °C) for 6 h, it was allowed to cool down to room temperature. The reaction mixture was diluted with ethyl acetate (20 mL) and treated with brine (twice). The organic layer was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified on preparative thin layer chromatography (PTLC) to give substituted *N*-*tert*-butylcarbazoles.

Acknowledgements

The work was supported by the National Natural Science Foundation of China (*No. 21672162*) *and Shanghai Science and Technology Commission* (*14DZ2261100*).

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