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Pd-Catalyzed Tandem C–H Azidation and N–N Bond Formation of Arylpyridines: A Direct Approach to Pyrido[1,2-*b*]indazoles

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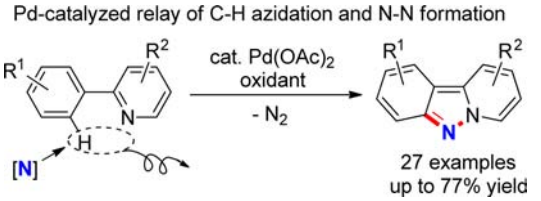
ABSTRACT



A novel Pd-catalyzed nitrogenation of arylpyridines via C–H azidation has been developed. Direct C–N and N–N formations are achieved for this N-atom incorporation transformation using azides as the N-atom source. This method provides an alternatively concise approach for the construction of bioactively important pyrido[1,2-*b*]indazoles.

Recently, transition-metal-catalyzed organic reactions involving C–H bond cleavage have been significantly developed as atom- and step-economical tools in organic synthesis.[1] During the past several decades, transition-metal-catalyzed dehydrogenation cyclization to construct dibenzofurans, carbazoles, phenanthridin-6(5*H*)-ones, fluorens, and fluorenones have been well developed[2−4] (Scheme 1a). Foreseeably, the incorporation of an atom into the above systems through the degydrogenative strategy would substantially broaden the field of cyclization and offer more functionalized cyclic compounds. However, there is a rare example of incorporating one (hetero-) atom into biaryl to construct heterocycles. Very recently, Lei and co-workers achieved a significant Pd-catalyzed dehydrogenative carbonylation of diaryl ethers to form xanthones (Scheme 1b).[5]

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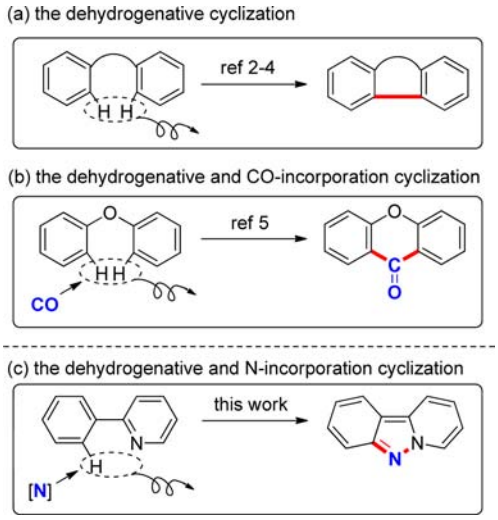
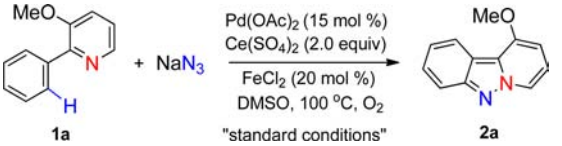
Scheme 1. Dehydrogenative and Atom-Incorporation Strategies



Due to the diverse pharmacological activities, indazoles are widely used in the pharmaceutical industry in many drugs and drug candidates.[6] Pyrido[1,2-*b*]indazoles are a class of bioactive molecules containing this pharmacophore, and some analogues are known to exhibit anticancer activities.[7] Therefore, the efficient synthesis of pyrido[1,2-*b*]indazoles has attracted much attention for a long time due to the promise of drug candidates which contain this skeleton. The traditional strategies toward the synthesis of pyrido[1,2-*b*]indazole derivatives suffer from multistep procedures, the lack of atom economy,[8] or a limited substrate scope.[9] We envisioned that pyrido-[1,2-*b*]indazoles could be constructed by incorporating one N-atom into heteroarenes. Herein, we report the first Pd-catalyzed nitrogenation reaction of 2-arylpyridines for the synthesis of pyrido[1,2-*b*]indazoles (Scheme 1c).

The significance of the present finding is threefold: (1) To the best our knowledge, this is the first example of implanting one N-atom from an external nitrogen source into 2-arylpyridines via C−H activation. (2) Although some elegant examples of catalytic C−N formation via C−H activation with azides as the nitrogen source have been reported,[10−12] the direct C−H azidation[13] and subsequent transformation of arenes still offer a distinct challenge. Recently, by using a pyridyl directing group, Yu et al. achieved the elegant Cu-mediated C−H functionalizations of 2-phenylpyridines with various nucleophilic anion sources.[14] However, the direct C−H azidation of 2-phenylpyridine did not occur under the reported conditions. Herein, the present study demonstrates the first example of Pd-catalyzed direct C−H azidation of arylpyridines and subsequent relay of intramolecular N−N bond formation. (3) This transformation provides as well an alternatively concise approach to bioactive pyrido[1,2-*b*]-indazoles from readily available arylpyridines.

Table 1. Effects of the Reaction Parameters in the Palladium-Catalyzed Nitrogenation Reaction[a]



entry	change from the "standard conditions"	yield of **2a** (%)[b]
1	none	77
2	no $Pd(OAc)_2$	0
3	no $Ce(SO_4)_2$ [with 1.0 equiv of $Pd(OAc)_2$]	0
4	no $FeCI_2$	56
5	Ar instead of O_2	61
6	Selectfluor instead of $Ce(SO_4)_2$	10
	dioxane instead of DMSO	
7	CAN instead of $Ce(SO_4)_2$	15
8	DDQ instead of $Ce(SO_4)_2$	0
9	$TMSN_3$ instead of NaN_3	0
10	DMF instead of DMSO	0

[a] Reaction conditions: **1a** (0.3 mmol), NaN_3 (2.0 equiv), $Pd(OAc)_2$ (15 mol %), $Ce(SO_4)_2$ (2.0 equiv), $FeCl_2$ (20 mol %), DMSO (4 mL), stirred at 100 °C under O_2 (1 atm) for 79 h. CAN = Ceric ammonium nitrate, DDQ = 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone, $TMSN_3$ = Trimethylsilyl azide. [b] Isolated yields.

We commenced our hypothesis with 3-methoxy-2-phenylpyridine **1a** and sodium azide (NaN_3) as a model reaction (Table 1). After extensive screening of different parameters, the optimum reaction conditions were determined to be $Pd(OAc)_2$ (15 mol %), $Ce(SO_4)_2$ (2.0 equiv), $FeCl_2$ (20 mol %), and DMSO (4 mL), under O_2 (1 atm) at 100 °C, which provided the desired nitrogenation product **2a** in 77% yield (entry 1). The structure of **2a** was further

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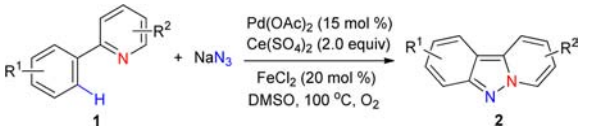
corroborated by X-ray diffraction (see Figure S1, Supporting Information (SI)). Both $Pd(OAc)_2$ and $Ce(SO_4)_2$ were required for this transformation (entries 2 and 3). The efficiency of this transformation can be promoted by the addition of $FeCl_2$ or under a molecular oxygen atmosphere (entries 4 and 5). The yield decreased when Selectfluor was employed as the oxidant (entry 6). The other commonly used single electron oxidants such as CAN and DDQ were less effective or ineffective for the reaction (entries 7 and 8). Notably, no products were detected with $TMSN_3$ as the nitrogen source (entry 9). The reaction in DMF did not work (entry 10).

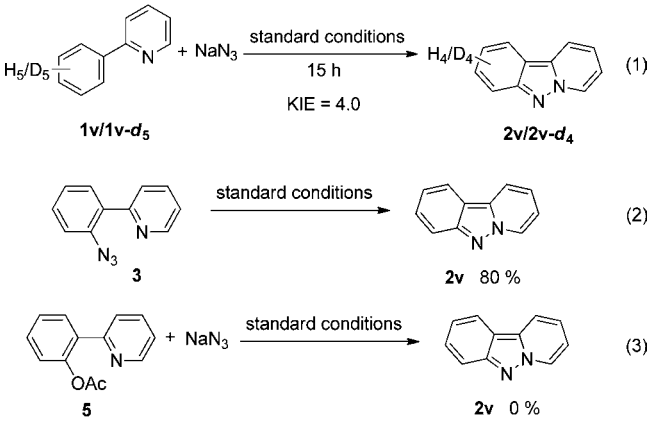
Table 2. Palladium-Catalyzed Nitrogenation Reaction[a]



entry	product	yield [%][b]	entry	product	yield (%)[b]
1	**2a**: R = H	77	16	**2p**: R = H	72
2	**2b**: R = Me	71	17	**2q**: R = 4-Me	60
3	**2c**: R = *i*Pr	71	18	**2r**: R = 5-Me	62
4	**2d**: R = *t*Bu	75			
5	**2e**: R = F	52			
6	**2f**: R = Cl	48			
7	**2g**: R = CF_3	41			
8	**2h**: R = COOMe	60			
9	**2i**	70	19	**2s**: R = *i*Pr	62
			20	**2t**: R = *n*Bu	65
			21	**2u**: R = Ph	55
10	**2j**: R = 4-Me	44	22	**2v**: R = H	45
11	**2k**: R = 5-Me	35	23	**2w**: R = Me	51
12	**2l**: R = 3,5-diMe	48	24	**2x**: R = *t*Bu	50
			25	**2y**: R = F	32
			26	**2z**: R = Cl	42
13	**2m**: R = H	70			
14	**2n**: R = 4-Me	61			
15	**2o**: R = 5-Me	61	27	**2aa**	43

[a] Reaction conditions: **1** (0.3 mmol), NaN_3 (2.0 equiv), $Pd(OAc)_2$ (15 mol %), $Ce(SO_4)_2$ (2.0 equiv), $FeCl_2$ (20 mol %), DMSO (4 mL), stirred at 100 °C under O_2 (1 atm) for 79−82 h. [b] Isolated yields.

With these optimized conditions in hand, the scope of the present protocol was investigated (Table 2). 3-Methoxy-2-arylpyridines could be smoothly transformed into the desired products (entries 1−8, Table 2). A significant variation on the benzene ring of 3-methoxy-2-arylpyridines was tolerated, including electron-donating groups (e.g., Me, *i*Pr, *t*Bu) and electron-withdrawing groups (e.g., F, Cl, COOMe). Substrates bearing a stronger electron-withdrawing group (e.g., CF_3) also could be successfully converted to the desired product in 41% yield. It is noteworthy that the use of 3-methyl-2-phenylpyridine proved to be effective, resulting in the formation of the corresponding pyrido[1,2-*b*]indazole derivative in 70% yield (entry 9, Table 2). However, 4-methyl, 5-methyl, or 3,5-dimethyl-substituted-2-phenylpyridines produced the corresponding products with relatively diminished efficiencies (entries 10−12, Table 2). Notably, nitrogenation of the sterically hindered ortho-alkoxy, or phenoxy-substituted substrates proceeded well giving the corresponding products in 55−72% yields (entries 13−21, Table 2). Meanwhile, substrates with either electron-donating groups (e.g., Me, *t*Bu) or electron-withdrawing groups (e.g., F, Cl) at the para position of the phenyl ring were tolerated in this transformation, leading to the corresponding products in moderate yields (entries 23−26, Table 2). Furthermore, when 1-phenylisoquinoline was employed, the desired indazolo[3,2-*a*]isoquinoline product **2aa** was obtained in 43% yield (Table 2, entry 27).



To further obtain insights into this unique procedure, preliminary mechanistic experiments were investigated. A significant kinetic isotope effect (KIE, k_H/k_D = 4.0)

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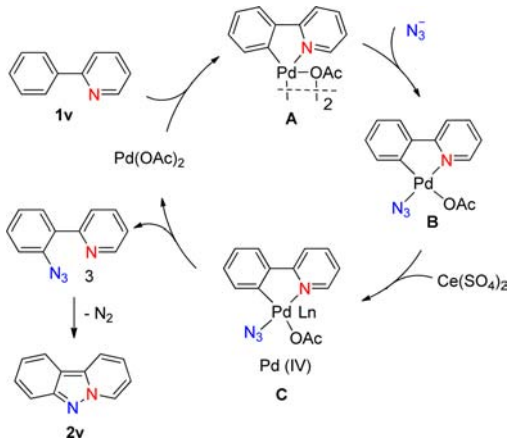
Scheme 2. Proposed Mechanism



was observed (eq 1; also see SI), suggesting that the C−H bond cleavage is likely involved in the rate-limiting step.[15] We envisioned that the direct C−H azidation products may serve as the key intermediates in this transformation. To verify this possibility, compound **3** was synthesized and subjected to the standard conditions (eq 2). As expected, the desired pyrido[1,2-*b*]indazole **2v** was obtained in 80% yield. Moreover, 2-(2-azidophenyl)-3-methoxy-pyridine (**4**) was detected during the nitrogenation process of 3-methoxy-2-phenylpyridine (**1a**) with NaN_3 (see SI). To further explore the reaction mechanism, the reaction progress of **1a** was monitored by ^1H NMR spectroscopy (see SI). The relatively apparent signal of methoxyl hydrogen in the azidation product **4** appeared 4 h after the reaction started. This signal became strong during the early stage and disappeared at the end of the reaction. Meanwhile, the consumption of **1a** and production of **2a** were also observed in the spectrum as the reaction proceeded (see SI). These results indicate that the azidation product **4** is indeed the key intermediate of this transformation.

On the basis of the above results, a possible mechanism is proposed in Scheme 2. A Pd-catalyzed nitrogenation reaction is initiated by the chelation-directed cyclopalladation to form cyclopalladium(II) dimeric intermediate **A**. Subsequently, Pd(II) **A** is involved in ligand exchange with the azide group to generate species **B**, which is then oxidized into a possible Pd(IV) intermediate **C** by $Ce(SO_4)_2$.[16] The reductive elimination of Pd(IV) intermediate **C** then occurs to afford the *ortho*-azido product **3** with the regeneration of the Pd(II) catalyst. The reaction of **5** did not work under the standard conditions (eq 3), which excludes the possibility of the reductive elimination of Pd(IV) intermediate **C** to form **5**[17] as the intermediate. Finally, the thermal decomposition of the azide product **3** delivers pyrido[1,2-*b*]-indazole **2v** under reaction conditions with heating.[8d,18]

In conclusion, we have developed a novel Pd-catalyzed nitrogenation of arylpyridines via C−H activation using azides as the N-atom source. This study realized the Pd-catalyzed relay of direct C−H azidation of arylpyridines and subsequent intramolecular N−N bond formation. The bioactively important pyrido[1,2-*b*]indazoles can be easily constructed from readily available 2-arylpyridines by this concise approach. Further mechanistic studies and applications of this transformation are underway in our laboratory.

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Supporting Information Available. Experimental details, NMR spectra analysis of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) In our experiments, the transformation of azide product **3** to pyrido[1,2-*b*]indazole **2v** under the standard conditions in the presence and absence of a catalyst gave the same yields (80%), which also indicated that the catalyst was not involved in the last step.

The authors declare no competing financial interest.