

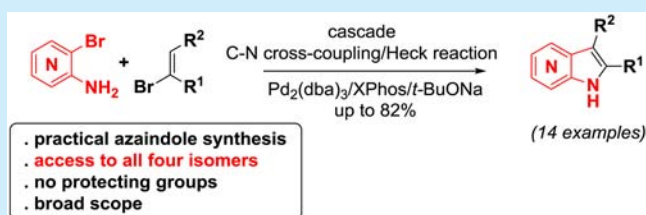
Synthesis of Substituted 4-, 5-, 6-, and 7-Azaindoles from Aminopyridines via a Cascade C–N Cross-Coupling/Heck Reaction

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S Supporting Information

ABSTRACT: A practical palladium-catalyzed cascade C–N cross-coupling/Heck reaction of alkenyl bromides with amino-*o*-bromopyridines is described for a straightforward synthesis of substituted 4-, 5-, 6-, and 7-azaindoles using a Pd₂(dba)₃/XPhos/*t*-BuONa system. This procedure consists of the first cascade C–N cross-coupling/Heck approach toward all four azaindole isomers from available aminopyridines. The scope of the reaction was investigated and several alkenyl bromides were used, allowing access to different substituted azaindoles. This protocol was further explored for *N*-substituted amino-*o*-bromopyridines.



Azaindoles are bioisosteres of the indole nucleus, a privileged structure, which have enticed the interest of the scientific community for their physicochemical^{1,2} and pharmacological properties^{3,4} with potential applications in the field of medicinal chemistry. Recently, several bioactive azaindole have been described, including the synthetic analogues of the natural variolins, possessing CDK (cyclin-dependent kinase) inhibitory activity^{5,6} among others.^{7–11} Due to their important value, methods for the synthesis of azaindoles and derivatives have attracted considerable interest from the scientific community.^{12,13}

Common synthetic strategies to prepare azaindoles rely on the use of aminopyridines, followed by building up the pyrrole ring. The strategy parallels the indole synthesis starting from anilines. However, the electron-deficient nature of the pyridine ring alters the electronic properties of the conjugated system in such a way that many classic indole synthetic methods are not as efficient or simply do not work.¹⁴ Several synthetic routes to prepare azaindole from aminopyridines have been developed, involving classic Pd-catalyzed reactions,¹⁴ such as Sonogashira (Scheme 1A, eq 1),¹⁵ Heck (Scheme 1A, eq 5),^{16,17} and Suzuki (Scheme 1A, eq 6)¹⁸ couplings; Pd-catalyzed reactions, also applied for the indole synthesis, such as the Larock indole synthesis (Scheme 1A, eq 2);¹⁹ and the reported methods by Lautens (Scheme 1A, eq 3)²⁰ and Cacchi (Scheme 1A, eq 4).²¹ Nevertheless, these methods were shown to have some drawbacks such as being not fully regioselective, having a limited substrate scope, or requiring the preparation of a specific molecular template. Additionally, most methods are restricted to the preparation of only one or two azaindole isomers.^{12,22}

Aminopyridines are challenging starting materials in metal-catalyzed reactions²³ due to the chelating properties of the pyridine ring and especially due to their electronics; each aminopyridine has a distinct reactivity. Thus, despite the

availability of aminopyridines, they have been scarcely explored on cascade reactions toward azaindole synthesis.

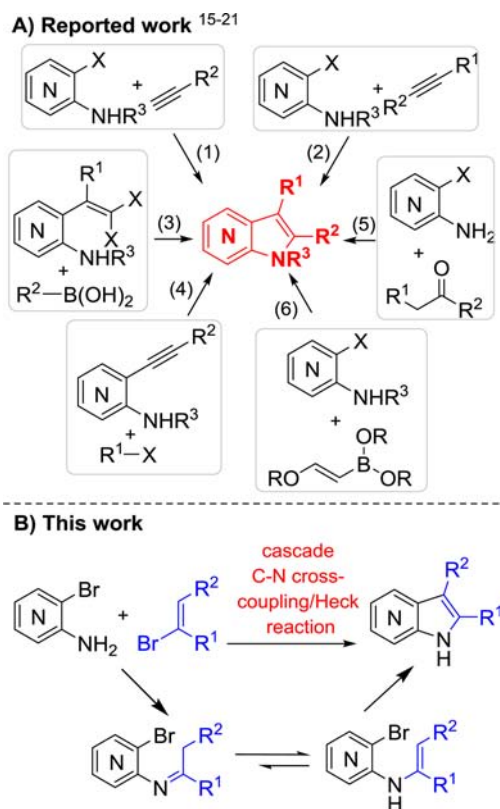
To our knowledge, the reported cascade methods toward the azaindole nucleus involving amino-*ortho*-halogenated pyridines rely on reaction with ketones via formation of an imine intermediate followed by Heck reaction of the corresponding enamine.^{16,17} However, azaindoles are only attained in good yields when either cyclic ketones under microwave conditions, pyruvate derivatives, or activated aromatic ketones are used. Strategies to obtain imine/enamine from deactivated ketones and amino-*ortho*-halogenated pyridines are scarce; they generally require harsh reaction conditions; they possess low functional group tolerance; and chemo- and stereoselectivity are compromised.^{16,24} Furthermore, these imine intermediates are very prone to hydrolysis. Consequently, metal-catalyzed approaches toward imines and enamines have been developed.^{25,26} Simultaneously to our work, Nolan and co-workers reported the α -arylation of stable preformed imines from 3-amino-*o*-chloropyridines to achieve the corresponding 4- and 6-azaindoles, yet for 5- and 7-azaindoles the method proved to be unsuitable.²²

Our group has been employing metal-catalyzed cross-coupling reactions for the preparation of bioactive heterocycles such as indole and benzimidazole.^{27,28} Herein, we report a practical method to synthesize azaindoles, indole bioisosteres, from amino-*o*-bromopyridines and alkenyl bromides via a Pd-catalyzed cascade amination/Heck coupling (Scheme 1B). Our initial intent was to achieve substituted azaindoles using imines/enamines as key intermediates, obtained from commercially available amino-*o*-bromopyridines and aryl ketones. We turned our attention to the preparation of imine/enamine

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Scheme 1. (A) Reported Synthetic Routes for the Preparation of Azaindoles from Aminopyridines. (B) Cascade Alkenyl Amination/Heck Reaction Involving Amino-*o*-Bromopyridines



derivatives via Pd catalysis using Buchwald ligands (Figure 1). In the designed strategy, the first synthetic step consisted of a

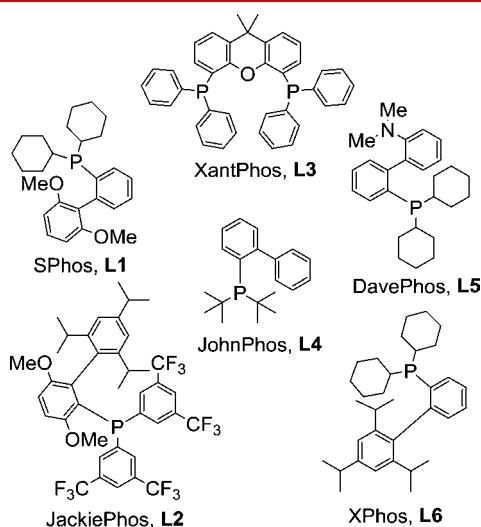


Figure 1. Buchwald ligands studied (L).

Buchwald–Hartwig amination of alkenyl bromides that has been reported to involve in situ imine/enamine formation.²⁹

It was expected that primary aminobromopyridines would give the corresponding imine products that are in tautomeric equilibrium with the less stable enamine (Scheme 1B). Gratifyingly, the azaindole nucleus could be observed when

amino-*o*-bromopyridines were chosen as starting materials. Prompted by the bromine positioned *ortho* to the amine group, a cascade C–N/Heck reaction seems to occur, consisting of an efficient route toward the challenging azaindole core.

In order to establish the reaction conditions, 4-amino-3-bromopyridine (**1a**) and α -bromostyrene (**2a**) were used as models and *t*-BuONa as base³⁰ (Table 1). After confirmation of

Table 1. Influence of Pd/Ligand (L) and Solvent in the Cascade Alkenyl Amination/Heck Reaction

entry	cat. (mol %)	L	base (equiv)	solvent	time (h)	3a/4a (yield, %) ^b
1 ^a	Pd(OAc) ₂ (5)	L1	<i>t</i> -BuONa (2)	toluene	24	3a
2 ^a	Pd ₂ (dba) ₃ (5)	L1	<i>t</i> -BuONa (2)	toluene	24	4a ^c /3a
3 ^a	Pd ₂ (dba) ₃ (5)	L2	<i>t</i> -BuONa (2)	toluene	24	3a
4 ^a	Pd ₂ (dba) ₃ (5)	L3	<i>t</i> -BuONa (2)	toluene	96	3a
5 ^a	Pd ₂ (dba) ₃ (5)	L4	<i>t</i> -BuONa (2)	toluene	48	3a
6 ^d	Pd ₂ (dba) ₃ (4)	L5	<i>t</i> -BuONa (3)	toluene	24	4a (29) ^e
7 ^d	Pd ₂ (dba) ₃ (4)	L5	<i>t</i> -BuONa (3)	<i>t</i> -BuOH	24	4a (26) ^e
8 ^d	Pd ₂ (dba) ₃ (4)	L5	<i>t</i> -BuONa (3)	<i>t</i> -BuOH	48	4a (27) ^e
9 ^d	Pd ₂ (dba) ₃ (4)	L6	<i>t</i> -BuONa (3)	toluene	24	4a (34) ^e
10 ^f	Pd ₂ (dba) ₃ (10)	L6	<i>t</i> -BuONa (3)	toluene	24	4a (50) ^e
11 ^d	Pd ₂ (dba) ₃ (4)	L6	<i>t</i> -BuONa (3)	dioxane	24	4a (29) ^e
12 ^d	Pd ₂ (dba) ₃ (4)	L6	NaHMDS (3)	dioxane	24	4a (42) ^e
13 ^d	Pd ₂ (dba) ₃ (4)	L6	<i>t</i> -BuONa (3)	<i>t</i> -BuOH	24	4a (57)
14 ^f	Pd ₂ (dba) ₃ (10)	L6	<i>t</i> -BuONa (3)	<i>t</i> -BuOH	24	4a (69)
15 ^d	Pd ₂ (dba) ₃ (4)	L6	<i>t</i> -BuONa (3)	toluene: <i>t</i> -BuOH (1:1)	24	4a (35) ^e
16 ^d			<i>t</i> -BuONa (3)	<i>t</i> -BuOH	24	

^aConditions: **1a** (1 equiv), **2a** (1 equiv), a 1:2 molar ratio of Pd/ligand, *c* = 0.25 M, temp = 105–110 °C. ^bImine **3a** and azaindole **4a** were detected by TLC and ¹H NMR; yield after isolation. ^cTraces. ^d**1** (1 equiv), **2** (1.5 equiv), a 1:2 molar ratio of Pd/ligand, base (3 equiv), *c* = 0.1 M, temp = 105–110 °C. ^eTraces of imine. ^f10 mol % of Pd₂(dba)₃ and 20 mol % of L6 were used.

the imine **3a** formation, the first attempts on the synthesis of azaindole **4a** consisted of a search for the best catalytic system (Table 1, entries 1–5). When Pd(OAc)₂ was used as palladium source, SPhos (**L1**) as ligand, and *t*-BuONa as base in toluene, only the imine **3a** was observed (Table 1, entry 1). Under the same reaction conditions but with Pd₂(dba)₃ as catalyst, traces of the azaindole **4a** were detected (Table 1, entry 2). On pursuing the best Pd/ligand system, different Buchwald ligands^{31,32} were tested (Figure 1), e.g., bulky electron-rich biphenyl phosphines (DavePhos, **L5**; SPhos, **L1**; JohnPhos, **L4**;

JackiePhos, L2; and XPhos, L6) and a bidentate ligand (XantPhos, L3).

When L2, L3, and L4 were employed, only the imine product **3a** was observed (Table 1, entries 3, 4 and 5, respectively). Furthermore, longer reaction times did not promote the formation of **4a** (Table 1, entries 4 and 5). The use of L5 (Table 1, entry 6) led to the formation of azaindole **4a**, but the reaction was still not complete, and after isolation a 29% yield was achieved. At this point, we decided to investigate *t*-BuOH as solvent in combination with L5, but without significant improvements (Table 1, entries 7 and 8). Subsequently, L6 was considered as ligand and a 34% yield of **4a** was achieved (Table 1, entry 9). The catalyst loading was explored, and increasing the amount of the catalytic system to 10 mol % of Pd₂(dba)₃ and 20 mol % of L6 led to 50% yield (Table 1, entry 10).

Next we investigated the use of dioxane as solvent, and a slightly lower yield was observed when *t*-BuONa was used as base (Table 1, entries 9 vs 11). When a stronger base such as NaHMDS was used, **4a** was isolated in 42% yield (Table 1, entry 12).

Surprisingly, L6 in *t*-BuOH gave azaindole **4a** as the only product in 57% yield (Table 1, entry 13). Best results were obtained using the previous conditions with a higher catalyst loading (10 mol % of Pd₂(dba)₃ and 20 mol % of L6, Table 1 entry 14) with 69% of **4a**. A mixture of toluene/*t*-BuOH (1:1) was also tested (Table 1, entry 15), although it was shown to be less efficient than *t*-BuOH alone. Moreover, no reaction occurred in the absence of the catalyst (Table 1, entry 16).

With the optimized reaction conditions in hand, the scope of the reaction was studied with respect to the four types of commercially available amino-*o*-bromopyridines: 4-amino-3-bromopyridine (**1a**); 3-amino-2-bromopyridine (**1b**); 3-amino-4-bromopyridine (**1c**); and 2-amino-3-bromopyridine (**1d**) with various alkenyl bromides **2** (Scheme 2).

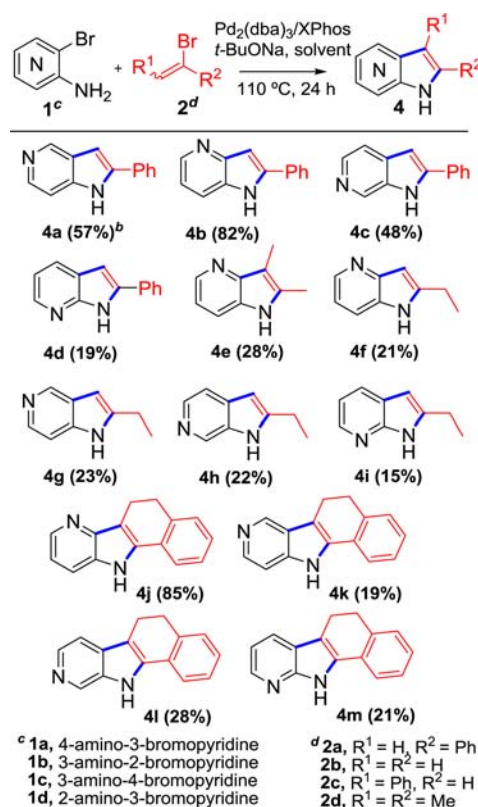
Initial experiments were carried with amino-*o*-bromopyridines **1** and α -bromostyrene **2a**. The 3-amino-2-bromopyridine (**1b**) gave the best result with 82% yield, followed by **1a** (57%), **1c** (48%) and **1d** (19%), as a consequence of the differences of aminopyridines reactivity.

The results obtained for **1b** with **2a** encouraged us to explore this aminopyridine with some other alkenyl bromides. Thus, 2-bromo-2-butene (*cis/trans*) (**2b**) was reacted with **1b** to furnish 2,3-dimethyl-4-azaindole (**4e**) in 28% yield. β -Bromostyrene (*cis/trans*) **2c** was also tested under the selected reaction conditions to attain 3-phenyl-4-azaindole, but in trace amounts, isolated from a very complex mixture, detected by ¹H NMR (see the SI). These results suggest that beyond **1b** electronics alkenyl bromide substitution also influences the cascade reaction success.

Furthermore, 2-bromo-1-butene (**2d**) was used with the four amino-*o*-bromopyridines **1**, and the azaindoles **4f–i** were obtained in moderate yields. In the expectation that cyclic alkenyl bromides would afford more stable imines/enamines, the bromide **2e** was also reacted with the different aminopyridines **1**. Gratifyingly, azaindole **4j** was obtained in 85% yield, and the other azaindoles **4k–m** were also obtained in moderate yields.

Vinyl bromide **2f** was reacted with **1a–d**; however, only 7-azaindole was observed in 9% yield (see the SI). Once again, the results obtained suggest that the presence of an alkyl/aryl substituent geminal to the bromine at the alkenyl moiety might favor azaindole formation. These observations indicate that the

Scheme 2. Scope of Cascade Alkenyl Amination/Heck Reaction with Amino-*o*-bromopyridines **1**^a



^a Conditions: **1** (1 equiv), **2** (1.5 equiv), Pd₂(dba)₃ (4 mol %), XPhos (8 mol %), *t*-BuONa (3 equiv), 0.1 M *t*-BuOH. ^b A 69% yield was achieved with 10 mol % of Pd₂(dba)₃ and 20 mol % of L6.

present method is suitable for the preparation of 2-substituted and 2,3-disubstituted azaindoles, representing a direct and regioselective approach.

It was anticipated that *N*-substituted aminobromopyridines would provide the corresponding enamine, promoting the intramolecular Heck reaction (Scheme 1B). Due to the interest in a straightforward access to 1,2-diarylazaindoles, this approach would consist of a simple route, avoiding, for example, the *N*-arylation of 2-substituted azaindoles, that has been shown to be difficult for the 2-substituted azaindoles.^{12,33,34} Thus, we efficiently prepared *N*-phenylamino-*o*-bromopyridines (**5a–d**) by reacting **1** with iodobenzene³⁵ in high to excellent yields (79–99%) using Pd₂(dba)₃ (4 mol %) L3 (8 mol %) and *t*-BuONa (2 equiv) (see the SI).

In the first attempts, the reaction of *N*-phenylaminobromopyridines **5a–d** with **2a** did not seem to occur under the previous conditions. The same result was observed when the reaction was performed with **2b**. These results did not surprise us, given that *N*-arylated aminopyridines **5** are more sterically hindered than the corresponding primary aminopyridines, even though when DavePhos L5 was employed as ligand the 1,2-diphenyl-4-azaindole was isolated in low yield (see the SI). This result suggests that this route might indeed furnish 1,2-diarylated azaindoles; however, a careful Pd/ligand optimization is required. Currently, the *N*-arylation of the azaindole nucleus can be performed according to the reported procedures.^{33,34,36–39}

In summary, we have developed a novel straightforward synthesis of substituted 4-, 5-, 6-, and 7-azaindoles using a

$\text{Pd}_2(\text{dba})_3/\text{XPhos}/t\text{-BuONa}$ system. This is the first example of a cascade amination/Heck reaction of alkenyl bromides with amino-*o*-bromopyridines. The cascade approach proved to be successful when readily available primary aminopyridines were used. Lastly, several alkenyl bromides were employed, allowing access to various substituted azaindoles. Therefore, this route constitutes a novel platform for ready access to the indole bioisostere core, an important scaffold in medicinal chemistry and material science.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.orglett.6b01500](https://doi.org/10.1021/acs.orglett.6b01500).

Experimental details, compound characterization data for all isolated compounds, and NMR spectra (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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