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# Access to 1-amino-3,4-dihydroisoquinolines *via* palladium-catalyzed C–H bond aminoimidoylation reaction from functionalized isocyanides†

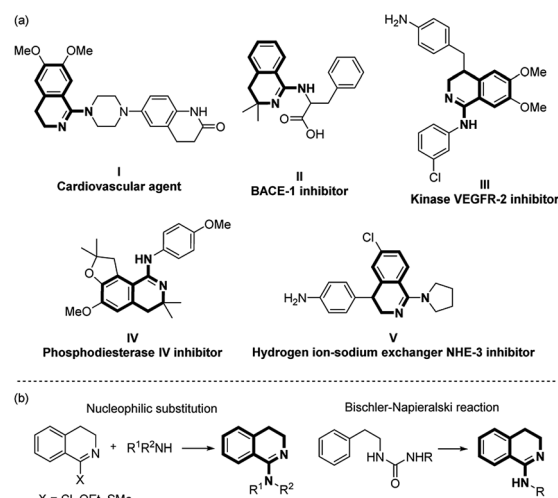
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Efficient access to 1-amino-3,4-dihydroisoquinolines, through palladium-catalyzed intramolecular C–H bond aminoimidoylation of  $\alpha$ -benzyl- $\alpha$ -isocyanoacetates, has been developed. Consecutive isocyanide insertion and C–H bond activation were realized with C–N and C–C bonds formation in one step under redox neutral conditions, employing *O*-benzoyl hydroxylamines as electrophilic amino sources.

As a class of cyclic amidine compounds, 1-amino-3,4-dihydroisoquinolines are essential six-membered heterocycles which can be found in numerous natural products, functional chemicals and pharmaceutical agents (Scheme 1).<sup>1</sup> For example, piperazine tethered dihydroisoquinoline and benzocyclic amide I was found to be an efficient cardiovascular agent.<sup>1a</sup> Phenylalanine-derived and arylamine or cyclic aliphatic-amine-containing 1-amino-3,4-dihydroisoquinolines (II–V) show outstanding BACE-1 inhibition, kinase VEGFR-2 inhibition, phosphodiesterase IV inhibition and hydrogen ion-sodium exchanger NHE-3 inhibition activities, respectively.<sup>1b–e</sup> Traditional preparation of such 1-amino-3,4-dihydroisoquinoline scaffolds is mainly based on nucleophilic substitution of readily prepared 3,4-dihydroisoquinolines<sup>2</sup> and Bischler-Napieralski reaction starting from urea.<sup>3</sup> Most of these methods suffer from multiple-step synthesis, harsh conditions or the use of toxic reagents. Thus, developing an efficient and practical method for the construction of 1-amino-3,4-dihydroisoquinoline derivatives remain an attractive synthetic task.

In recent decades, isocyanides have been extensively studied in multicomponent reactions,<sup>4</sup> imidoyl radical-involved transformations<sup>5</sup> and transition-metal-catalyzed insertion reactions<sup>6</sup> due to their diverse and unique reactivities. A variety of acyclic imine derivatives were synthesized *via* palladium-catalyzed imidoylation reactions.<sup>7</sup> For the construction of biorelevant nitrogen-containing heterocycles *via* Pd-catalyzed non-functionalized isocyanide insertion reactions, a nucleophilic group is usually preinstalled to the substrates containing C–X

(C–H) bonds, followed by Pd-catalyzed oxidative addition (C–H bond activation)/isocyanide insertion/ligand substitution/reductive elimination sequence.<sup>8</sup> For example, Maes and coworkers developed an efficient palladium-catalyzed synthesis of 4-aminoquinazolines from *N*-(2-bromoaryl)amidines using amidine as an internal nucleophile.<sup>8a</sup> Access to the same scaffold through palladium-catalyzed amidine-directed C–H bond imidoylation/cyclization reaction was reported by Zhu group.<sup>8c</sup> Isocyanide acted as a C1 synthon in these cyclization reactions, with the terminal carbon of isocyanide being used in the ring formation.<sup>9</sup> Considering the diversity of R group on the nitrogen atom of isocyanide, the so-called functionalized isocyanide strategy was widely developed as well, with various *N*-heterocycles such as oxazoles,<sup>10</sup> indoles,<sup>11</sup> phenanthridines,<sup>12</sup> 9*H*-pyrido [3,4-*b*]indoles<sup>13</sup> and nonaromatic azepines<sup>14</sup> being synthesized



**Scheme 1** (a) Representative bioactive molecules containing the 1-amino-3,4-dihydroisoquinoline moiety. (b) Traditional synthetic methods.

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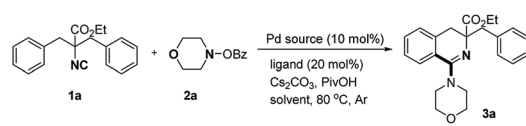
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efficiently. Zhu and coworkers developed the first asymmetric C–H bond imidoxylation reaction from easily accessible  $\alpha,\alpha$ -dibenzyl- $\alpha$ -isocyanoacetates with chiral quaternary-carbon-containing 3,4-dihydroisoquinolines being generated (Scheme 2a).<sup>15</sup> Recently, a catalytic system controlled regioselective C–H bond imidoxylation was realized for the selective synthesis of 5 or 6-membered cyclic imines (Scheme 2b).<sup>16</sup> Aryl halides were mostly used in these transformations while N–O compounds were rarely reported as electrophiles in Pd-catalyzed isocyanide insertion reactions.<sup>17</sup> Zhu group reported the synthesis of phenanthridin-6-amine derivatives from *O*-benzoyl hydroxylamines and commonly used biaryl isocyanides.<sup>17c</sup> However, a methyl or methoxyl carbonyl group was needed at the ortho position of isocyano group, which critically limited the application of the reaction. Herein, we developed an efficient and practical synthesis of 1-amino-3,4-dihydroisoquinolines, through palladium-catalyzed intramolecular C–H bond amino-imidoxylation reaction of  $\alpha$ -benzyl- $\alpha$ -isocyanoacetates. Consecutive isocyanide insertion and C–H bond activation were realized with C–N and C–C bonds being constructed in one step, employing *O*-benzoyl hydroxylamines as electrophilic amino sources.

The reaction conditions were optimized with ethyl 2-benzyl-2-isocyano-3-phenylpropanoate (**1a**) and morpholino benzoate (**2a**) as model substrates, and ethyl 3-benzyl-1-morpholino-3,4-dihydroisoquinoline-3-carboxylate (**3a**) was obtained in 34% yield in the presence of Pd(OAc)<sub>2</sub> (1.5 equiv.), PPh<sub>3</sub> (20 mol%), Cs<sub>2</sub>CO<sub>3</sub> (1.0 equiv.) and PivOH (0.6 equiv.) in toluene at 80 °C (entry 1, Table 1). Dioxane was proven to be the best choice after screening of solvents and the product was generated in 76% yield (entries 2–6). The reaction was totally suppressed in high polar solvents such as MeCN and DMSO (entries 5–6). The yield decreased sharply when the catalyst was changed to Pd(OPiv)<sub>2</sub>, Pd(TFA)<sub>2</sub>, PdCl<sub>2</sub>(MeCN)<sub>2</sub> or Pd(PPh<sub>3</sub>)<sub>4</sub> (entries 7–10). And no better results were detected by using other phosphine ligands (entries 12–17). Fortunately, the yield of **3a** was increased to 84% at 110 °C (entry 18). Control experiments revealed that palladium catalyst and additives (Cs<sub>2</sub>CO<sub>3</sub>/PivOH) were essential and the reaction was much less efficient when using other bases such as CsOPiv, K<sub>2</sub>CO<sub>3</sub>, and Na<sub>2</sub>CO<sub>3</sub> (entries 19–24). The yield

Table 1 Optimization of the reaction conditions<sup>a</sup>

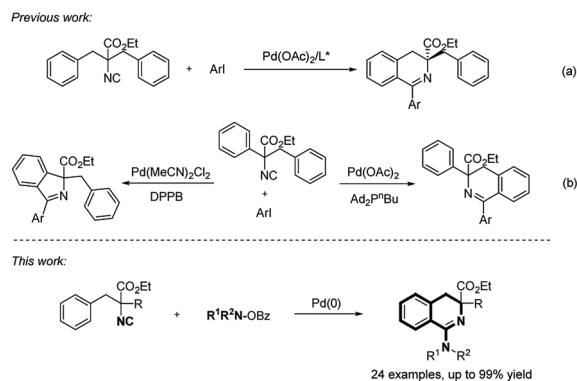
				
Entry	Catalyst	Ligand	Solvent	Yield <sup>b</sup>
1	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	Toluene	34
2	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	THF	Trace
3	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	DCE	29
4	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	Dioxane	76
5	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	MeCN	Trace
6	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	DMSO	Trace
7	Pd(OPiv) <sub>2</sub>	PPh <sub>3</sub>	Dioxane	31
8	Pd(TFA) <sub>2</sub>	PPh <sub>3</sub>	Dioxane	26
9	PdCl <sub>2</sub> (MeCN) <sub>2</sub>	PPh <sub>3</sub>	Dioxane	38
11	Pd(PPh <sub>3</sub> ) <sub>4</sub>		Dioxane	56
12	Pd(OAc) <sub>2</sub>	BINAP	Dioxane	30
13	Pd(OAc) <sub>2</sub>	dppb	Dioxane	26
14	Pd(OAc) <sub>2</sub>	dppp	Dioxane	28
15	Pd(OAc) <sub>2</sub>	XantPhos	Dioxane	42
16	Pd(OAc) <sub>2</sub>	SPhos	Dioxane	34
17	Pd(OAc) <sub>2</sub>	XPhos	Dioxane	24
18 <sup>c</sup>	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	Dioxane	84 (80) <sup>d</sup>
19 <sup>c</sup>	None	PPh <sub>3</sub>	Dioxane	0
20 <sup>c</sup>	Pd(OAc) <sub>2</sub>	None	Dioxane	56
21 <sup>c,e</sup>	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	Dioxane	0
22 <sup>c,f</sup>	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	Dioxane	41
23 <sup>c,g</sup>	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	Dioxane	24
24 <sup>c,h</sup>	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	Dioxane	31
25 <sup>c,i</sup>	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	Dioxane	61

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), Pd-catalyst (0.01 mmol, 10 mol%), ligand (0.02 mmol, 20 mol%), Cs<sub>2</sub>CO<sub>3</sub> (0.1 mmol, 1.0 equiv.), PivOH (0.06 mmol, 0.6 equiv.), 80 °C, Ar. A solution of **1a** was added *via* a syringe pump within 1 h. <sup>b</sup> NMR yield with 1-iodo-4-methoxybenzene as an internal standard. <sup>c</sup> *T* = 110 °C.

<sup>d</sup> Isolated yield. <sup>e</sup> Without Cs<sub>2</sub>CO<sub>3</sub> and PivOH. <sup>f</sup> CsOPiv was used as the base. <sup>g</sup> K<sub>2</sub>CO<sub>3</sub> was used as the base. <sup>h</sup> Na<sub>2</sub>CO<sub>3</sub> was used as the base. <sup>i</sup> 5 mol% of catalyst was used.

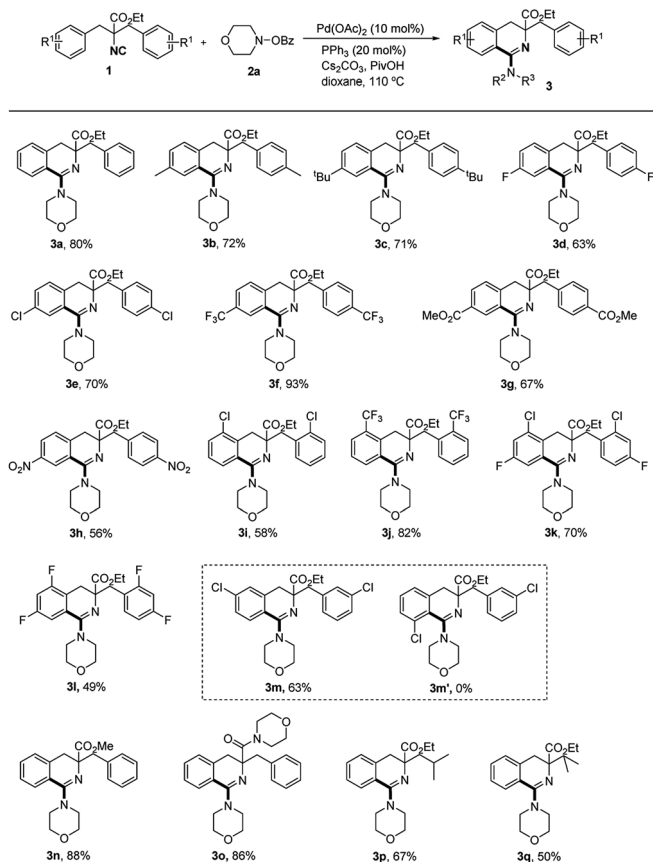
decreased sharply to 61% when the catalyst loading was reduced to 5 mol% (entry 25).

With the optimized conditions in hand, the scope of functionalized isocyanide was investigated first, using morpholino benzoate **2a** as the coupling partner (Scheme 3). Both electron rich and withdrawing substituents such as Me, *t*-Bu, F, Cl, CF<sub>3</sub>, CO<sub>2</sub>Me and NO<sub>2</sub> at the *para* position of aromatic ring can tolerate the reaction conditions, and generate the corresponding products in good to excellent yields (**3a–3h**). Isocyanides bearing ortho substituents on the phenyl ring underwent the reaction smoothly, generating the products **3i** and **3j** in 58% and 82% yields respectively. Even substrates bearing two substituents were well suited to the reaction conditions, affording the amino-imidoxylation products without loss of efficiency (**3k–3l**). Compound **3m** was delivered with excellent regioselectivity in 63% yield when *m*-Cl substituted starting material was employed in the reaction, which indicated the hindrance sensitivity of this reaction. Modifying the ester moiety in **1** to a methyl ester or an amide did not impede the reaction, giving **3n** and **3o** with



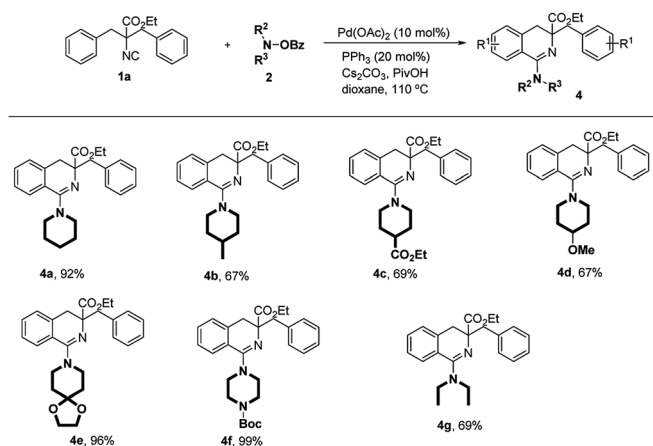
Scheme 2 Palladium-catalyzed imidoxylation cyclization of  $\alpha$ -benzyl-ethylacetates.





**Scheme 3** Scope of isocyanides. Reaction conditions: **1** (0.1 mmol), **2a** (0.15 mmol), Pd(OAc)<sub>2</sub> (0.01 mmol, 10 mol%), PPh<sub>3</sub> (0.02 mmol, 20 mol%), Cs<sub>2</sub>CO<sub>3</sub> (0.1 mmol, 1.0 equiv.), PivOH (0.06 mmol, 0.6 equiv.), 110 °C, Ar. A solution of **1** was added via a syringe pump within 1 h. Isolated yields.

excellent yields. Changing one of the benzyl groups to alkyl substituents didn't decrease the reaction efficiency, generating products **3p** and **3q** in moderate yields.

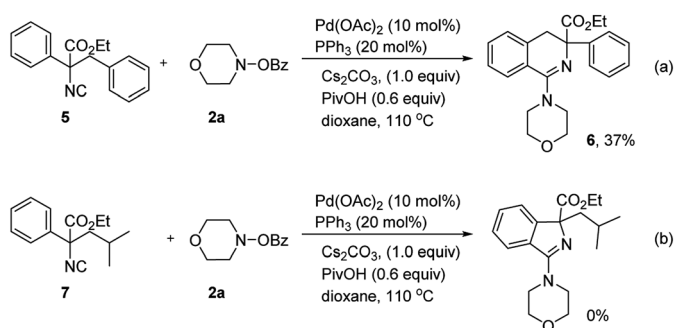


**Scheme 4** Substrate scope of aminating agents. Reaction conditions: **1a** (0.1 mmol), **2** (0.15 mmol), Pd(OAc)<sub>2</sub> (0.01 mmol, 10 mol%), PPh<sub>3</sub> (0.02 mmol, 20 mol%), Cs<sub>2</sub>CO<sub>3</sub> (0.1 mmol, 1.0 equiv.), PivOH (0.06 mmol, 0.6 equiv.), 110 °C, Ar. A solution of **1a** was added via a syringe pump within 1 h. Isolated yields.

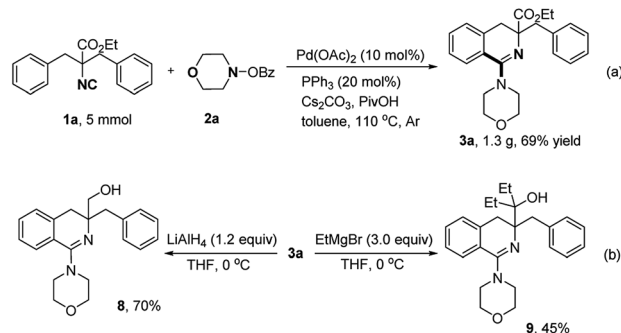
Then we moved our attention to the investigation of substrate scope of aminating partners (Scheme 4). It was found that various *O*-benzoyl hydroxylamines derived from piperidines could be smoothly employed in the reaction (**4a–4e**). Substituents such as Me, CO<sub>2</sub>Et, OMe and ketal group on the piperidines were well tolerated (**4b–4e**). Aminating reagent derived from Boc-protected piperazine was also compatible with this reaction, generating the product **4f** in 99% yield. Fortunately, acyclic aminated product **4g** was obtained as well in moderate yield.

When ethyl 2-isocyano-2,3-diphenylpropanoate was conducted in the reaction with **2a**, the 3,4-dihydroisoquinoline product **6** was generated exclusively, albeit in only 37% yield (Scheme 5a). To examine if isoindoline could be afforded by this aminoimidoylation reaction, ethyl 2-isocyano-4-methyl-2-phenylpentanoate (**7**) was selected as the substrate with **2a** (Scheme 5b). However, no desired product was generated under the standard conditions, showing different site-selectivity with the previous imidoylation reaction developed by Zhu and coworkers.<sup>16</sup>

Gram-scale preparation of **3a** was carried out smoothly under standard conditions (Scheme 6a). The reduction reaction of **3a** was carried out using LiAlH<sub>4</sub> and the corresponding product **8** was generated in 70% yield (Scheme 6b). The ester group was successfully transformed to tertiary alcohol (**9**) in moderate yield with Grignard reagent.

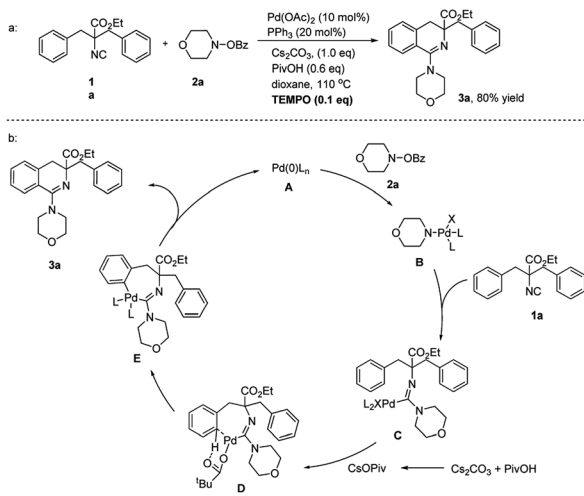


**Scheme 5** Reaction conditions: **5(7)** (0.1 mmol), **2a** (0.15 mmol), Pd(OAc)<sub>2</sub> (0.01 mmol, 10 mol%), PPh<sub>3</sub> (0.02 mmol, 20 mol%), Cs<sub>2</sub>CO<sub>3</sub> (0.1 mmol, 1.0 equiv.), PivOH (0.06 mmol, 0.6 equiv.), 110 °C, Ar. A solution of **5(7)** was added via a syringe pump within 1 h. Isolated yields.



**Scheme 6** Gram-scale preparation and diversifications of **3a**.





Scheme 7 Proposed mechanism.

In order to get further insight into the reaction mechanism, a radical trapping reaction with 0.1 equivalents of TEMPO was carried out (Scheme 7a). The product **3a** was generated without loss of efficiency, which indicated that the radical-involved pathway could be ruled out. A plausible mechanism was then proposed in Scheme 7b. The reaction was initiated with oxidative addition of *O*-benzoyl hydroxylamine **2a** to the *in situ* generated Pd(0) species. Migratory isocyanide insertion to intermediate **B** afforded aminoimidoyl Pd(II) intermediate **C**. The following intramolecular C–H bond activation and reductive elimination *via* **E** yielded the final product **3a** and regenerated Pd(0) to complete the catalytic cycle.

In conclusion, we have developed an efficient and practical method to prepare 1-amino-3,4-dihydroisoquinolines *via* palladium-catalyzed intramolecular C–H bond aminoimidoylation of  $\alpha$ -benzyl- $\alpha$ -isocyanoacetates under redox-neutral conditions. Consecutive isocyanide insertion and C–H bond activation were realized with C–N and C–C bonds formation in one step, employing *O*-benzoyl hydroxylamines as electrophilic amino sources. A broad range of substrates were applicable to the reaction in good to excellent yields.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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