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# Synthesis of 3-(aminomethylene)-2-oxoindolines by palladium-catalyzed annulation of 3-chloro-2-iodo-*N*-arylacrylamides with amides or amines†

**Guo-Bo Deng,[a] Zhi-Qiang Wang,[a] Ren-Jie Song,[a] Ming-Bo Zhou,[a] Wen-Ting Wei,[a] Peng Xie[a] and Jin-Heng Li*[b]**

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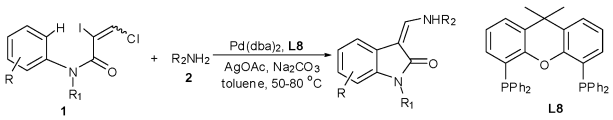
**A new palladium-catalyzed C–H bond activation–annulation–amination tandem method was presented for selectively synthesizing 3-(aminomethylene)-2-oxoindolines. In the presence of $Pd(dba)_2$, xantphos (L8), AgOAc and $Na_2CO_3$, a variety of 3-chloro-2-iodo-*N*-arylacrylamides underwent the reaction with amides or amines to afford the corresponding 3-(aminomethylene)-2-oxoindolines in moderate to good yields.**

3-Methyleneindolin-2-ones,[1–7] particularly 3-(aminomethylene)-2-oxoindolines,[2] are pharmacologically important components of numerous biologically active natural products and medicinally significant compounds.[1] The common classical methods used for the construction of the 3-methyleneindolin-2-one framework are the intermolecular condensation of oxindoles with diaryl ketones, and often they are limited due to nonavailability of suitably substituted starting precursors and unsatisfactory selectivity.[3] Therefore, considerable effort has been made on the development of efficient metal-catalyzed methods for selectively synthesizing 3-methyleneindolin-2-ones.[4–6] Among these methods, palladium-catalyzed reactions that involve the arene C–H bond functionalization are particularly attractive[4,5] because they can avoid the use of expensive 2-haloanilide or 2-(alkynyl)phenylisocyanate reagents.[6] Zhu and co-workers have disclosed Pd(0)-catalyzed arene C–H bond activation domino reactions of *N*-arylpropiolamides with aryl halide electrophilic reagents leading to the corresponding 3-(diarylmethylenyl)oxindoles under basic conditions.[4] Our group also found that *N*-arylpropiolamides could react with a wide range of nucleophilic reagents, such as phthalimide, acids, $ArI(OAc)_2$ and alcohols, through a Pd(II)-catalyzed oxidative C–H bond functionalization process with the aid of oxidants.[5] However, only an amide, phthalimide, was employed to react with *N*-arylpropiolamides leading to (*E*)-(2-oxindolin-3-ylidene)phthalimides.[5a] In view of the importance of 3-(aminomethylene)-2-oxoindolines,[2] the development of new methods involving the C–H bond activation strategy for their preparation is desirable.[5a,6j] Here, we report a novel route to (*Z*)-3-(aminomethylene)-2-oxoindolines by palladium-catalyzed C–H bond activation–annulation–amination of 3-chloro-2-iodo-*N*-arylacrylamides with amides or amines (Scheme 1).[8,9]




**Scheme 1** A new route to 3-(aminomethylene)-2-oxoindolines.

Our investigation began with the reaction of 3-chloro-2-iodo-*N*-methyl-*N*-phenylacrylamide (**1a**) with benzamide (**2a**) to determine the optimal reaction conditions (Table 1).[10] Initially, a series of ligands **L1–L10** were examined, and xantphos (**L8**) gave the best results (entries 1–12). While the reaction of substrate **1a** with **2a**, $Pd(OAc)_2$, AgOAc and $Cs_2CO_3$ afforded a trace of the desired product **3** without ligands (entry 1), the yield of **3** was increased to 20% in the presence of $PPh_3$ (**L1**) (entry 2). Gratifyingly, the yield was enhanced to 45% using xantphos (**L8**) (entry 10). Notably, $Na_2CO_3$ was more effective than $Cs_2CO_3$ (entries 8 and 9). Subsequently, a number of other Pd catalysts, such as $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_4$ and $Pd(dba)_2$, were tested, and they were more efficient than $Pd(OAc)_2$ (entries 13–16). The results showed that the Ag effect affected the reaction (entries 16–22). The activities of other Ag salts, such as $CF_3CO_2Ag$, $Ag_2O$ or $Ag_2CO_3$, were lowered slightly in terms of yields (entries 16–19). We found that the amount of AgOAc has a fundamental influence on the reaction (entries 20–22): the best results were obtained at 2 equiv. AgOAc. From the reaction temperature examination, it turned out that the reaction at 50 °C gave the highest yield after prolonging the reaction time (entries 23 and 24). However, the yield of **3** was reduced to 58% in the presence of 5 mol% $Pd(dba)_2$ (entry 25).

As shown in Table 2, the scope of both 3-chloro-2-iodo-*N*-arylacrylamides **1** with amides **2** was explored under the optimal conditions. The results demonstrated that substrate **1b** with a *N*-Bn group was reacted with amide **2a**, $Pd(dba)_2$, **L8**, AgOAc and $Na_2CO_3$ smoothly to afford the target product **4** in 60% yield (entry 1), which was less active than

[a] *Key Laboratory of Chemical Biology & Traditional Chinese Medicine Research (Ministry of Education), Hunan Normal University, Changsha 410081, China*
[b] *State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China. E-mail: jhli@hunnu.edu.cn; Fax: +86731 8887 2531; Tel: +86731 8887 2576*

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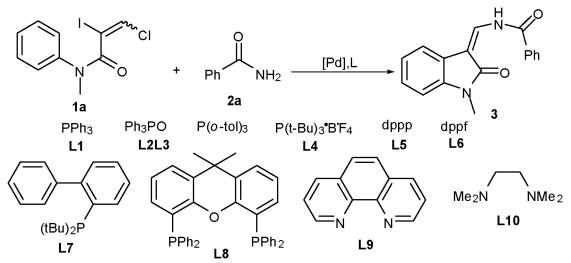
**Table 1** Screening optimal conditions[a]

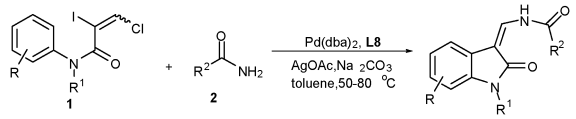



| Entry | [Pd] (mol%) | Ligand | [Ag] (equiv.) | Base | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 | $Pd(OAc)_2$ | — | AgOAc (1) | $Cs_2CO_3$ | Trace |
| 2 | $Pd(OAc)_2$ | **L1** | AgOAc (1) | $Cs_2CO_3$ | 20 |
| 3 | $Pd(OAc)_2$ | **L2** | AgOAc (1) | $Cs_2CO_3$ | Trace |
| 4 | $Pd(OAc)_2$ | **L3** | AgOAc (1) | $Cs_2CO_3$ | 30 |
| 5 | $Pd(OAc)_2$ | **L4** | AgOAc (1) | $Cs_2CO_3$ | 21 |
| 6 | $Pd(OAc)_2$ | **L5** | AgOAc (1) | $Cs_2CO_3$ | Trace |
| 7 | $Pd(OAc)_2$ | **L6** | AgOAc (1) | $Cs_2CO_3$ | Trace |
| 8 | $Pd(OAc)_2$ | **L7** | AgOAc (1) | $Cs_2CO_3$ | 30 |
| 9 | $Pd(OAc)_2$ | **L7** | AgOAc (1) | $Na_2CO_3$ | 35 |
| 10 | $Pd(OAc)_2$ | **L8** | AgOAc (1) | $Na_2CO_3$ | 45 |
| 11 | $Pd(OAc)_2$ | **L9** | AgOAc (1) | $Na_2CO_3$ | 25 |
| 12 | $Pd(OAc)_2$ | **L10** | AgOAc (1) | $Na_2CO_3$ | Trace |
| 13 | $PdCl_2$ | **L8** | AgOAc (1) | $Na_2CO_3$ | 67 |
| 14 | $Pd(PPh_3)_2Cl_2$ | **L8** | AgOAc (1) | $Na_2CO_3$ | 65 |
| 15 | $Pd(PPh_3)_4$ | **L8** | AgOAc (1) | $Na_2CO_3$ | 66 |
| 16 | $Pd(dba)_2$ | **L8** | AgOAc (1) | $Na_2CO_3$ | 68 |
| 17 | $Pd(dba)_2$ | **L8** | $CF_3CO_2Ag$ (1) | $Na_2CO_3$ | 46 |
| 18 | $Pd(dba)_2$ | **L8** | $Ag_2O$ (1) | $Na_2CO_3$ | 56 |
| 19 | $Pd(dba)_2$ | **L8** | $Ag_2CO_3$ (1) | $Na_2CO_3$ | 50 |
| 20 | $Pd(dba)_2$ | **L8** | AgOAc (1.5) | $Na_2CO_3$ | 79 |
| 21 | $Pd(dba)_2$ | **L8** | AgOAc (2) | $Na_2CO_3$ | 85 |
| 22 | $Pd(dba)_2$ | **L8** | AgOAc (3) | $Na_2CO_3$ | 80 |
| 23[c] | $Pd(dba)_2$ | **L8** | AgOAc (1) | $Na_2CO_3$ | 86 |
| 24[d] | $Pd(dba)_2$ | **L8** | AgOAc (1) | $Na_2CO_3$ | 72 |
| 25[c,e] | $Pd(dba)_2$ | **L8** | AgOAc (1) | $Na_2CO_3$ | 58 |

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), [Pd] (10 mol%), ligand (10 mol%), [Ag] (1 equiv.) and base (2 equiv.) in the solvent (2 mL) at 80 °C for 8 h. [b] Isolated yield. [c] At 50 °C for 13 h. [d] At room temperature for 96 h. [e] 5 mol% of $Pd(dba)_2$ was added.

*N*-Me-substituted substrate **1a** (entry 23 in Table 1). Consequently, a number of *N*-Me-substituted substrates **1c–1f** were tested (entries 2–5). To our delight, substrates **1c–1f**, bearing electron-donating or electron-deficient groups on the *N*-aryl ring, were compatible under the optimal conditions. Substrate **1d** with an *o*-Me group, for instance, underwent the reaction with amide **2a** in 60% yield (entry 3). Good yield was still achieved from substrate **1f** with a *p*-$CF_3$ group (entry 5). Subsequently, a variety of amides **2b–2l** were evaluated under the standard conditions (entries 6–16). Screening disclosed that the annulation had a wide range of amides compatibility, including arylamides, vinylamides, alkylamides and carbamates. Moreover, several functional groups, such as Me, MeO, Cl or Br, on the aryl ring were tolerated well (entries 6–11). It was noted that amide **2g** with an *o*-Br group was successfully annulated with substrate **1a**, $Pd(dba)_2$, **L8**, AgOAc and $Na_2CO_3$, furnishing the desired Br-containing product **14** in 78% yield (entry 11), which provides a route to introduction of a new group at the Br-substituted position. Gratifyingly, heteroarylamide **2h** was also suitable for the reaction (entry 12). In the presence of $Pd(dba)_2$, **L8**, AgOAc and $Na_2CO_3$, acrylamide (**2i**) or acetamide (**2j**) could react

**Table 2** Palladium-catalyzed tandem reactions of 3-chloro-2-iodo-*N*-arylacrylamides (**1**) with amides (**2**)[a]



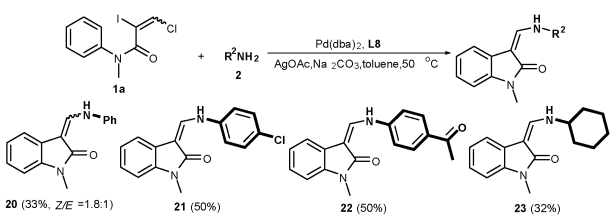

| Entry | $R/R^1$ in substrate **1** | $R^2$ in amide **2** | $T$/°C | Yield[b] (%) |
|---|---|---|---|---|
| 1 | H/Bn (**1b**) | $C_6H_5$ (**2a**) | 50 | 60 (**4**) |
| 2 | *p*-MeO/Me (**1c**) | $C_6H_5$ (**2a**) | 50 | 74 (**5**) |
| 3[c] | *o*-Me/Me (**1d**) | $C_6H_5$ (**2a**) | 80 | 60 (**6**) |
| 4 | *p*-Cl/Me (**1e**) | $C_6H_5$ (**2a**) | 50 | 73 (**7**) |
| 5 | *p*-$CF_3$/Me (**1f**) | $C_6H_5$ (**2a**) | 50 | 79 (**8**) |
| 6 | H/Me (**1a**) | *p*-$MeC_6H_4$ (**2b**) | 50 | 74 (**9**) |
| 7 | H/Me (**1a**) | *m*-$MeC_6H_4$ (**2c**) | 50 | 60 (**10**) |
| 8 | H/Me (**1a**) | *p*-$MeOC_6H_4$ (**2d**) | 80 | 68 (**11**) |
| 9 | H/Me (**1a**) | *o*-$MeOC_6H_4$ (**2e**) | 50 | 73 (**12**) |
| 10 | H/Me (**1a**) | *p*-$ClC_6H_4$ (**2f**) | 50 | 93 (**13**) |
| 11 | H/Me (**1a**) | *o*-$BrC_6H_4$ (**2g**) | 50 | 78 (**14**) |
| 12 | H/Me (**1a**) | 5-Mepyridin-2-yl (**2h**) | 50 | 61 (**15**) |
| 13 | H/Me (**1a**) | Vinyl (**2i**) | 80 | 51 (**16**) |
| 14 | H/Me (**1a**) | Me (**2j**) | 50 | 65 (**17**) |
| 15 | H/Me (**1a**) | OMe (**2k**) | 50 | 75 (**18**) |
| 16 | H/Me (**1a**) | OBn (**2l**) | 50 | 80 (**19**) |

[a] Reaction conditions: **1** (0.3 mmol), **2** (0.45 mmol), $Pd(dba)_2$ (10 mol%), **L8** (10 mol%), AgOAc (2 equiv.) and $Na_2CO_3$ (2 equiv.) in toluene (2 mL) for 13 h. [b] Isolated yield. [c] For 24 h.

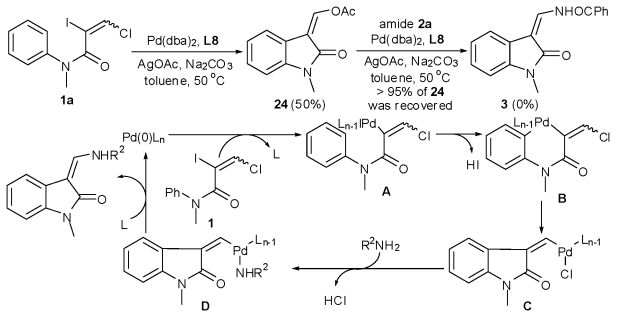
with substrate **1a** leading to the corresponding products **16** and **17** in moderate yields (entries 13 and 14). It is noteworthy that annulation of substrate **1a** with carbamates **2k** or **2l** is successful under the same conditions (entries 15 and 16).

In light of the above results, a variety of amines were employed for the annulation reaction with 3-chloro-2-iodo-*N*-methyl-*N*-arylacrylamide (**1a**) under the optimal conditions (Scheme 2). However, the reaction between substrate **1a** and aniline gave a mixture of *Z*/*E*-isomers **20** in a low total yield. To our delight, amines with a *para*-substituent on the aryl ring were selectively treated with substrate **1a**, providing the corresponding products **21** and **22** in moderate yields. Cyclohexanamine reacted with substrate **1a**, $Pd(dba)_2$, **L8**, AgOAc and $Na_2CO_3$ in 32% yield.

To our surprise, an acetoxypalladation product **24**, not (*Z*)-3-(chloromethylene)-1-methylindolin-2-one, was obtained exclusively without amides **2**. However, product **24** could not be converted into product **3** under the present optimal conditions (Scheme 3). Therefore, a possible mechanism as outlined in Scheme 3 was proposed.[2e,4,5,8,9] Oxidative addition of Pd(0) to the C–X bond of substrate **1** yields intermediate **A**, followed by arene C–H bond activation affording intermediate **B**.[4,5,8] Sequential reductive elimination and oxidative addition of intermediate **B** results in intermediate **C**, which is supported




**Scheme 2** Annulation of substrate (**1a**) with amines (**2**).




**Scheme 3** Possible mechanism.

by the formation of acetoxypalladation product **24**. Insertion of intermediate **C** with an amine forms intermediate **D**.[9] Finally, intermediate **D** undergoes reductive elimination to furnish the desired product and regenerate the active Pd(0) species. The role of Ag salts is to activate the arene C–H bond.[8]

In summary, we have described a new palladium-catalyzed tandem protocol for the synthesis of (*Z*)-3-(aminomethylene)-2-oxoindolines. This method allows two new bonds, a C–C bond and a C–N bond, formation in one-step by a sequential C–H bond activation/annulation/amination tandem process. Importantly, this method displays high substrates compatibility, which makes it more attractive for organic synthesis and industry.

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10 See the detailed data in ESI.† The stereochemistry of the products was assigned as the (*Z*)-isomer on the basis of the chemical shift of the olefinic proton according to the authoritative $^1$H NMR spectra (see ref. 1*j*, 2*a* and 2*b*) and the X-ray single-crystal diffraction analysis of product **3**. (The CCDC number is 822997.).