Advanced Synthesis & Catalysis

## Accepted Article

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**To be cited as:** *Adv. Synth. Catal.* 10.1002/adsc.201801162

**Link to VoR:** http://dx.doi.org/10.1002/adsc.201801162

10.1002/adsc.201801162

UPDATE

**DOI: 10.1002/adsc.201**((will be filled in by the editorial staff))

# Pd-catalyzed One-pot Insertion Reaction of Cyclic *C*-acylimines into Carbon–carbon σ-Bonds for the Synthesis of Polyfunctional Indolin-3-ones from 2-Alkynyl Arylazides and Aryl Ketones

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Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

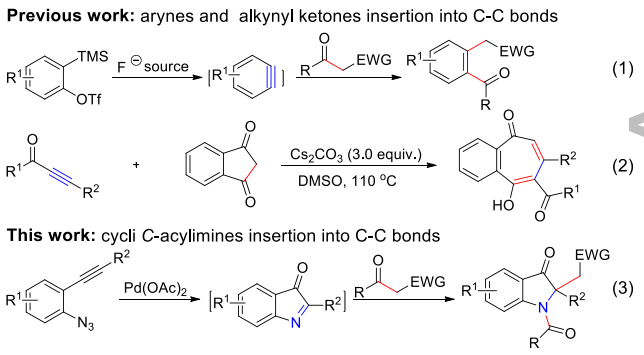
**Abstract.** A method to prepare polyfunctional indolin-3-ones by Pd-catalyzed one-pot insertion reaction of cyclic *C*-acylimines into carbon-carbon σ-bonds is described. The reaction was accomplished in good to excellent yields under mild reaction conditions.

**Keywords:** Pd-catalyzed; insertion reaction; cyclic *C*-acylimines; polyfunctional indolin-3-ones

The development of carbon-carbon σ-bonds insertion reactions is of considerable very important in organic chemistry.[1] The mild and selective insertion methods provide an efficient synthetic strategy for the construction of polyfunctional molecules, which are found particularly high significance in bioactive product synthesis,[2] molecular recognition,[3] drug design[4] and novel materials preparation.[5] Among the reported reactions in this area, the insertion of arynes into C-C σ-bonds is a powerful method for the synthesis of polysubstituted arenes by introducing two functional groups into triple bonds [Scheme 1, (1)].[6] In this type of reaction, a formal acyl-alkylated bifunctional product was obtained via a four-membered ring formation and followed by an acyl group migration process.[7] In these insertion reactions, malononitriles,[7a] *α*-cyanocarbonyls,[7b] acylated fluorenes,[7c] *β*-ketosulfones,[7d] *β*-ketoesters[7e] or *β*-ketophosphonates[7f] were normally employed as the precursors of C-C σ-bonds. And the key intermediates arynes, due to their high activity, were generated in situ from *ortho*-silyl aryltriflates in the presence of $F^-$ source. While the synthesis of *ortho*-silyl aryltriflates has been reported to need multi-steps and often harsh conditions.[8] Recently, Li group[9] reported the ring expansion reactions of indene-1,3-dione for the synthesis of functionalized benzoannulated seven-membered ring compounds. In this work, the alkyne functional groups were inserted into the indene-1,3-dione [Scheme 1, (2)].

In this context, we envisioned that the development of novel alternatives generated from easily accessible substrates for the insertion reaction of C-C σ-bonds would be particularly attractive.

Indolin-3-ones are versatile synthetic building blocks and utilized as core structures in the preparation of various natural products,[10] such as austamide, [10a] halichrome **A**, [10b] cephalinone, [10c] and fluorocurine.[10d] Especially, polyfunctional indolidin-3-ones are of considerable useful intermediates for the construction of natural products.[11]




**Scheme 1** Insertion reactions of functional groups into C-C σ-bonds.

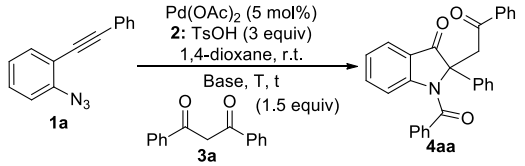
While this has led to many efficient synthetic methods,[12] those that describe the preparation of

10.1002/adsc.201801162

polyfunctional indolin-3-ones via insertion of cyclic *C*-acylimines into C-C σ-bonds process have not been reported [Scheme 1, (3)].

Recent reports have shown the use of 2-alkynyl arylazides as efficient substrates in many nitrogen-containing heterocycles formation reactions via α-imino metal carbenes intermediates.[13] For instance, we recently reported [14] Pd-catalyzed one-pot synthesis of C2-quaternary indolin-3-ones from 2-alkynyl arylazides and aryl ketones. [14a] To our surprise, we later found that substitution with strongly electron-withdrawing groups at α-position of aryl ketones resulted in the formation of polyfunctional compounds via unexpected insertion reaction of cyclic *C*-acylimines into C-C σ-bonds. To our knowledge, however, approaches to polyfunctional indolin-3-ones from 2-alkynyl arylazides via pd-catalyzed one-pot insertion process have not been reported. As part of an ongoing examining the utility of 2-alkynyl arylazides in heterocycles synthesis, we report herein the facile insertion reaction of cyclic *C*-acylimines generated in situ into carbon–carbon σ-bonds for the synthesis of polyfunctional indolin-3-ones.

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




| Entry | Base | T (℃) | Time (h) | Yield/%[b] |
|---|---|---|---|---|
| 1 | $Cs_2CO_3$ | 90 | 0.8 | 95 |
| 2 | $Cs_2CO_3$ | r.t. | 24 | 20 |
| 3 | $Cs_2CO_3$ | 60 | 7 | 94 |
| 4 | $K_2CO_3$ | 90 | 12 | 95 |
| 5 | $K_3PO_4$ | 90 | 24 | 56 |
| 6 | *t*-BuOK | 90 | 0.5 | 65 |
| 7 | DBU | 90 | 0.5 | 46 |
| 8 | ---- | 90 | 24 | trace[c] [d] |
| 9 | $Cs_2CO_3$ | 90 | 0.8 | 74[e] |

[a] Reaction conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (5 mol%), **2a** (3 equiv), 1,4-dioxane (1 mL), base (3.5 equiv), and **3a** (1.5 equiv).
[b] Isolated yield.
[c] Without base.
[d] Checked using TLC and $^1$H NMR measurements from the crude mixture.
[e] 2.5 equiv of $Cs_2CO_3$ was used.

At the outset of this study, we chose 1-azido-2-(phenylethynyl)benzene **1a** and 1,3-diphenylpropane-1,3-dione **3a** as model substrates to explore the optimal conditions (Table 1). This revealed that treating a solution of reaction containing **1a** (1 equiv) and TsOH (3 equiv) with 5 mol % of $Pd(OAc)_2$ at room temperature for 10 min and then added $Cs_2CO_3$ (3.5 equiv) and **3a** (1.5 equiv) at 90 ℃ for 40 min gave the best result (entry 1). Under these conditions, 1-benzoyl-2-(2-*oxo*-2-phenylethyl)-2-phenylindolin-3-one **4aa** was obtained in 95 % yield, which was confirmed by $^1$H NMR analysis and X-ray crystal structure determination (Fig. 1).

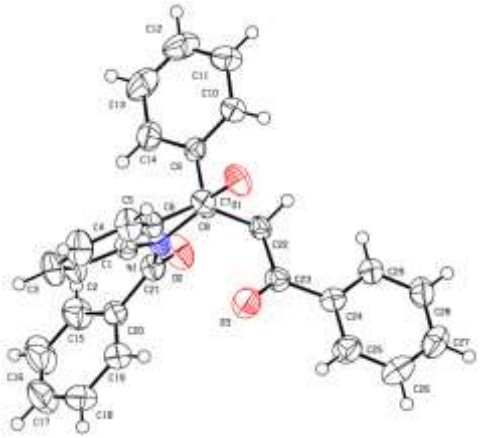


**Figure 1** ORTEP drawing of **4aa** with thermal ellipsoids at 50% probability.

Repeating this reaction at room temperature was found to result in dramatically low yield of 20% and need longer reaction time (entry 2). when the temperature was decreased to 60 ℃, a similar yield was obtained after 7 hours (entry 3). In contrast, repeating the reaction in the presence of other bases at the same temperature was found to give different results. When $K_2CO_3$ was employed as a base, the desired product was obtained in high yield of 95%, but need a longer time (entry 4). However, either $K_3PO_4$, *t*-BuOK or DBU was used as the base, low products yields of 46-65% were obtained (entries 5-7). It was noted that the reaction was completed in relatively short time when stronger or organic base was employed. On the other hand, some unknown compounds were observed by checking the crude mixture of the reaction using *t*-BuOK or DBU as the base, which could not be analyzed by $^1$H NMR analysis. Trace amount of the desired product **4aa** was also afforded without employing a base and the rest of the mixture solution were mainly 2-phenyl-1*H*-indol-3-yl 4-methylbenzenesulfonate **E** and 2-phenyl-3*H*-indol-3-one **G** checked by TLC and $^1$H NMR analysis (entry 8). A relatively low product yield of 74% was also obtained when the amount of $Cs_2CO_3$ was decreased to 2.5 equiv (entry 9).

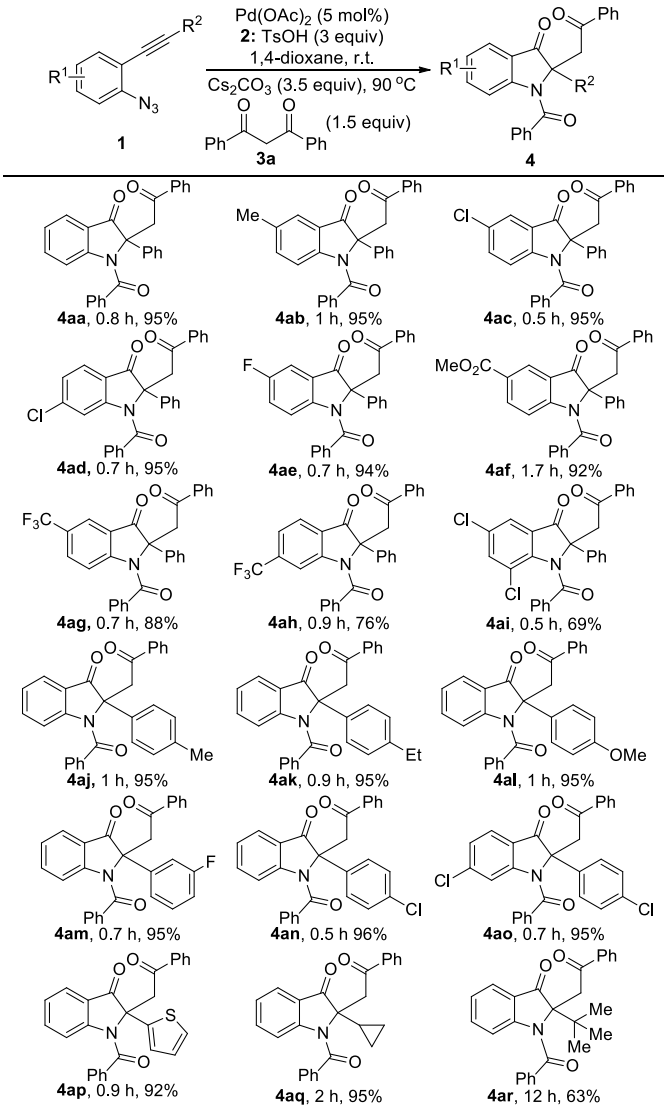
To define the scope of the pd-catalyzed one-pot insertion reactions, we applied this method to a series of 2-alkynyl arylazides **1** and aryl ketones with electron-withdrawing group at α-position **3** to define the scope of this one-pot protocol. The results are shown in Tables 2-3.

As shown in Table 2, we first examine the one-pot insertion reaction of 2-alkynyl arylazides bearing electron-withdrawing and electron-donating groups **1a-r** with 1,3-diphenylpropane-1,3-dione **3a**. Under

10.1002/adsc.201801162

the optimized reaction conditions, we found the reactions of 2-alkynyl arylazides **1** bearing an electron-withdrawing or electron-donating group on the aromatic ring ($R^1$ = Me, halide and ester) with **3a** to proceed in excellent yields of 92-95% (**4aa**-**4af**). When the substituted group $R^1 = CF_3$, slightly lower yields of 76-88% were obtained (**4ag**-**4ah**). On the other hand, the yield of the product **4ai** with dichloro substituted on the aromatic ring was decreased to 69%.

**Table 2** Substrates scope of the 2-alkynyl arylazides **1** [a][b]

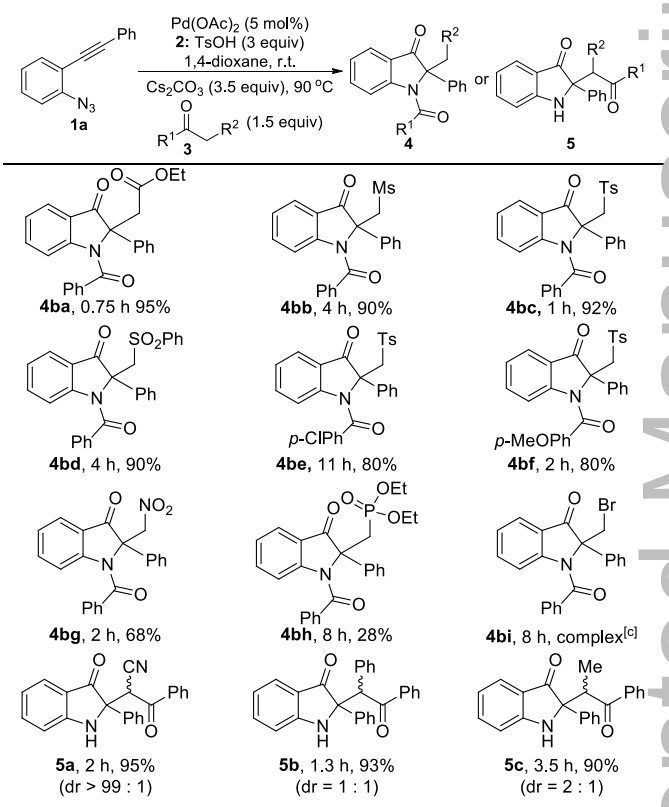



[a] Reaction conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (5 mol%), **2** (3 equiv), 1,4-dioxane (1 mL), $Cs_2CO_3$ (3.5 equiv), and **3a** (1.5 equiv).
[b] Isolated yield.

The present method was also shown to work well for the insertion reactions of 2-alkynyl arylazides **1** containing different substituted aryl or hetero aryl groups on the terminal alkyne carbon, which gave the desired products **4aj**-**4ap** in excellent yields of 92-96%. In addition, substrates **1** containing aliphatic pendant groups were also examined. Substrate with $R^2$ = cyclopropyl group provided the corresponding product **4aq** in 95% yield. However, only 63% yield of product **4ar** was obtained when the terminal substituted group $R^2$ = *t*-Bu, which might be the steric effects of substrates **1**.

To further examine the substrate scope of the present pd-catalyzed one-pot process, the insertion reactions of **1a** with different substituted ketones **3** were also investigated (Table 3). Under the standard reaction conditions, the desired products **4ba**-**4bf** were obtained in good to excellent yields of 80-95% when β-ketoester **3b** and β-ketosulfones **3c**-**3g** were employed.

**Table 3** Substrates scope of the aryl ketones **3** [a][b]

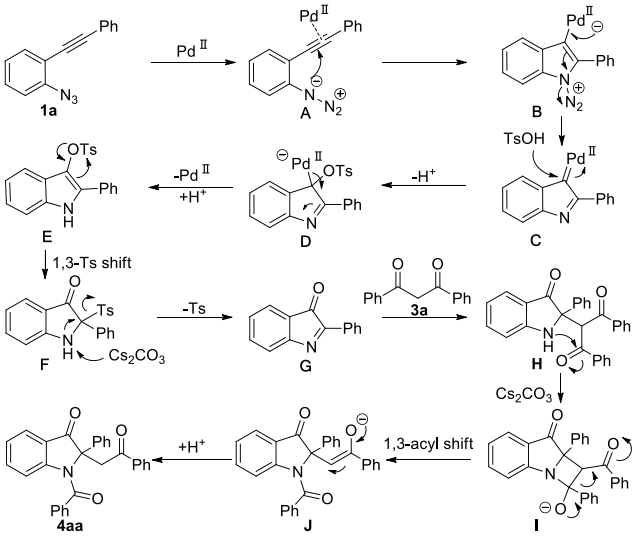



[a] Reaction conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (5 mol%), **2** (3 equiv), 1,4-dioxane (1 mL), $Cs_2CO_3$ (3.5 equiv), and **3** (1.5 equiv).
[b] Isolated yield.

Likewise, α-nitrocarbonyl **3h** and β-ketophosphonate **3i** were also employed to repeat the reactions, which led to lower product yields of 28-68% (**4bg**-**4bh**). Moreover, α-bromocarbonyl **3j** was also tested under the optimized reaction conditions but was found to give a mixture of decomposition compounds that could not be identified by the analysis of TLC and $^1$H NMR (**4bi**). Similarly, reaction of **1a** with α-cyanocarbonyl substrate **3k** was found to result in formation of Mannich-like addition adduct **5a** in 95% yield with diastereomers ratio of more than 99:1. No insertion reaction occurred could be due to the quite

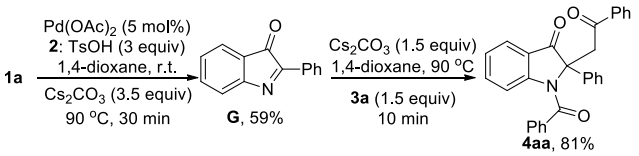
active carbon anion without sufficient stabilized groups, which was generated after 1,3-acyl shift step. In contrast, other substituted groups at the α-position of aryl ketones **3**, such as phenyl and methyl, were also examined. Under the standard reaction conditions, the direct addition products **5b** and **5c** were furnished in 90-93% yields as a mixture of inseparable diastereomers in ratios of 1:1 and 2:1, respectively.

Based on the above results, we tentatively propose a possible pathway in scheme 2 for converting **1a** to **4aa**, although it is highly speculative. This could involve activation of **1a** through coordination of the Pd catalyst with triple bonds. This delivers a pd-coordinated intermediate **A** which could undergo intramolecular cyclization to give species **B**. The newly formed α-imino palladium carbene **C** generated by releasing the $N_2$ would be attacked by TsOH to form complex **D**. Subsequent protodemetalation gave the aryl sulfonate **E**, which would further be transformed to active intermediate **F** after 1,3-Ts shift step.[15] Under basic reaction conditions, subsequent reductive desulfonation of α-amino sulfone **F** [16] led to the formation of another key intermediate 2-phenyl-3*H*-indol-3-one **G** [17], which would undergo Mannich-like addition to deliver the alkylated compound **H**. Intramolecular attacking of N to C gave a four-membered ring complex **I** followed by a carbon-carbon σ-bond cleavage process to 1,3-acyl shift complex **J**, which would further provide the insertion product **4aa** after protonation process.



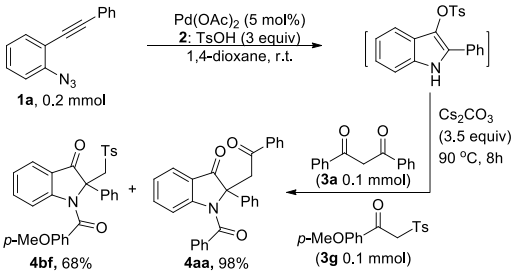

**Scheme 2** Proposed mechanism.

To further verify the mechanism, we conducted some control experiments and isolated successfully the key intermediate 2-phenyl-3*H*-indol-3-one **G**. When a solution of 1,4-dioxane containing **1a** was treated with 5 mol % of $Pd(OAc)_2$ at room temperature under the conditions shown in Scheme 3, 2-phenyl-3*H*-indol-3-one **G** was obtained in 59% yield after simple filtration through a pad of celite. Under basic conditions, the reaction was performed in 1,4-dioxane at 90 ℃ by employing the key intermediate **G** and **3a**, which provided the desired insertion product **4aa** in 81% yield.




**Scheme 3** Control experiments.

We later conducted a crossover experiment in order to understand the cleavage of C-C σ-bond. The reaction was repeated by employing two different ketones **3a** and **3g**, which provided non-crossover products **4aa** and **4bf** in yields of 98% and 68%, respectively. The result of crossover experiment suggested that the C-C σ-bond cleavage was an intramolecular process.




**Scheme 4** Crossover experiment.

## Conclusions

In conclusion, an efficient palladium-catalyzed one-pot insertion reaction of 3*H*-indol-3-ones into carbon–carbon σ-bonds has been reported. The desired products polyfunctional indolin-3-ones were obtained in good to excellent yields under mild reaction conditions.These results show that the reaction tolerates various 2-alkynyl arylazides and aryl ketones. Our studies show that the insertion reaction of cyclic *C*-acylimines generated in situ into carbon–carbon σ-bonds represents an attractive alternative synthetic method to polyfunctional indolin-3-ones. Further applications of this strategy are currently underway and will be reported in the future.

## Experimental Section

### General Procedure for the Preparation of Polyfunctional Indolin-3-ones 4 in One-pot Process

To a 10 ml of flask was added 2-alkynyl arylazides **1** (0.1 mmol, 1 equiv), TsOH (3 equiv.), $Pd(OAc)_2$ (5 mol%),

and 1,4-dioxane (1 mL). The reaction mixture was stirred at room temperature. After the 2-alkynyl arylazides **1** disappeared monitored by TLC (about 10 min for most of **1**), $Cs_2CO_3$ (0.35 mmol, 3.5 equiv) and aryl ketones **3** (0.15 mmol, 1.5 equiv.) were added to the reaction solution, which was then stirred at 90 ℃ and monitored by TLC analysis. On completion, the reaction mixture was directly subjected to purification by flash column chromatography on silica gel to give the desired **4**. (eluent: petrol ether: ethyl acetate = 40:1 to 8:1)

**General Procedure for the Preparation of 2-Phenyl-3*H*-indol-3-one G and Its Conversion to 1-Benzoyl-2-(2-*oxo*-2-phenylethyl)-2-phenylindolin-3-one 4aa**

To a solution of 1-azido-2-(phenylethynyl)benzene **1a** (0.2 mmol) in 1,4-dioxane (1 mL) was added $Pd(OAc)_2$ (5 mol%) and TsOH (0.6 mmol, 3 equiv.) in sequence at room temperature. The resulting solution was stirred and monitored by TLC analysis (10 min). On completion, $Cs_2CO_3$ (0.7 mmol, 3.5 equiv.) was added to the reaction solution. Then the reaction was stirred at 90 ℃ and monitored by TLC analysis. After 20 min, the reaction solution was then directly passed through a pad of celite and rinsed with eluent (petrol ether: ethyl acetate = 8: 1). The 2-phenyl-3*H*-indol-3-one G was obtained in 59% yield.

To a solution of 2-phenyl-3*H*-indol-3-one **G** (0.1 mmol) in 1,4-dioxane (1 mL) was added $Cs_2CO_3$ (0.15 mmol, 1.5 equiv.) and 1,3-diphenylpropane-1,3-dione **3a** (0.15 mmol, 1.5 equiv.) in sequence at room temperature. The resulting solution was stirred at 90 ℃ and monitored by TLC analysis. After 10 min, the reaction solution was then directly subjected to purification by flash column chromatography on silica gel to give the desired product **4aa** in 81% yield (eluent: petrol ether: ethyl acetate = 40:1 to 8:1)

## Supporting Information

Detailed descriptions of experimental procedures and their spectroscopic data are presented in the Supporting Information.

"CCDC for compound **4aa**: 1864448 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via. www.ccdc.cam.ac.uk/data_request/cif."

## Acknowledgements

*This work was supported by the National Natural Science Foundation of China Grants (21302096 and 21502093), Natural Science Foundation of Jiangsu Province Grants (BK20171449, and BK20150871), and the Project Fund from the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).*

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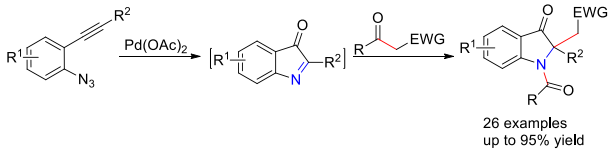
## COMMUNICATIONS

Pd-catalyzed One-pot Insertion Reaction of Cyclic C-acylimines into Carbon–carbon σ-bonds for the Synthesis of Polyfunctional Indolin-3-ones from 2-Alkynyl Arylazides and Aryl ketones




*Adv. Synth. Catal.* **Year**, *Volume*, Page – Page

Ping Li, Wanxiong Yong, Rong Sheng, Weidong Rao, Xinbao Zhu and Xiaoxiang Zhang*