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Pd-catalyzed assembly of phenanthridines from aryl ketone *O*-acetyloximes and arynes through C–H bond activation

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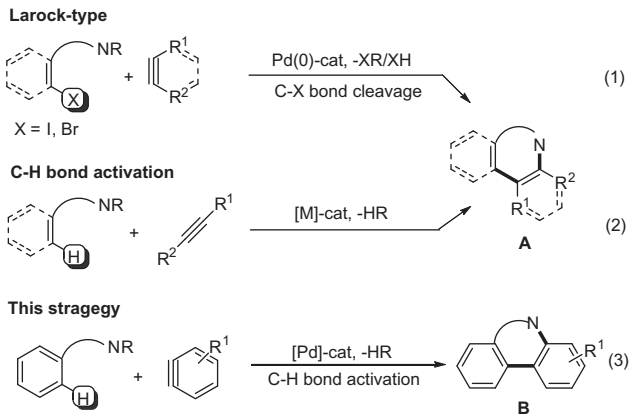
ABSTRACT

Pd-catalyzed annulation of aryne and aryl ketone *O*-acetyloxime via C–H bond activation was realized. Through the C–H bond activation/insertion/cyclization/elimination reaction sequence, phenanthridines are successfully constructed, providing an attractive strategy to approach substituted heterocycle without preactivation of starting materials.

Transition-metal catalyzed annulation reaction represents a powerful methodology for the assembly of complex polycyclic skeletons in organic chemistry.[1] For example, Larock-type heterocycle synthesis has been well developed to construct indoles, isoquinolines, and other heterocycles (**A**, Scheme 1, Eq. 1).[2] However, the application is limited by the availability of the preactivated substrates since most of these methodologies start from the oxidation addition of metal to C–X bond. In contrast, the C–H bond activation strategy utilizing a directing group to aid the *ortho* C–H metalation can be a perfect solution due to its highly atom- and step-economic property.[3] During the last decade, the C–H activation involving alkynes and aromatics with directing groups has been significantly developed.[4] Pyridine[4a–g,5] and pyrrole[4h–j] derivatives could be successfully obtained by following the C–H activation/insertion/cyclization sequence (Scheme 1, Eq. 2).

Similar with ordinary alkynes, arynes are highly reactive and easily available molecules and have been applied in transition-metal catalyzed annulation reactions to approach various polycyclic aromatic hydrocarbons,[2a,6,7] such as phenanthrene[6] and fluorenone derivatives.[7] In most of the known approaches, however, the utilization of preactivated aryl or vinylic halides and triflates is inevitable. Inspired by the previous work,[8,7c] we envisioned that if the C–H activation strategy can be introduced to realize the annulation of aryne, desirable fused rings would be formed from easily accessible starting materials (Scheme 1, Eq. 3). Herein, we report a Pd-catalyzed C–H activation of aryl ketone *O*-acetyloximes and arynes to synthesize phenanthridines.

Initially, the reaction of acetophenone *O*-acetyl oxime (**1a**) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a**) was carried out in the presence of $PdCl_2$, $CuCl_2$, Cs_2CO_3, and CsF in mixed solvent toluene/CH_3CN (v/v 2:1) at 80 °C. Desired product phenanthridine **3a** was obtained in 21% yield (Table 1, entry 1). Then we tried to optimize the reaction conditions (Table 1). After an initial screening of several palladium catalysts, $Pd(OAc)_2$ was found to be the best choice, giving product **3a** in 45% yield (entry 4). Effects of



Scheme 1. Heterocycle formation via transition-metal catalyzed annulation reactions.

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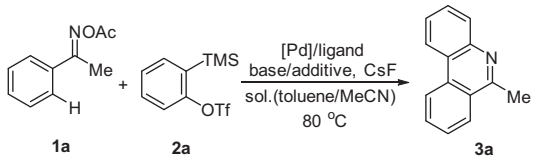
Table 1
Optimization of the reaction conditions[a]



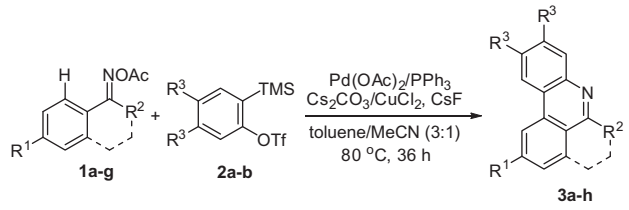
1a 2a 3a

Entry	[Pd]/ligand[b]	Base/additive	Sol.[c]	Time (h)	Yield[d]
1	$PdCl_2$	$Cs_2CO_3/CuCl_2$	2:1	24	21%
2	$Pd(MeCN)_2Cl_2$	$Cs_2CO_3/CuCl_2$	2:1	24	23%
3	$Pd(PPh_3)_2Cl_2$	$Cs_2CO_3/CuCl_2$	2:1	24	Trace
4	$Pd(OAc)_2$	$Cs_2CO_3/CuCl_2$	2:1	36	45%
5	$Pd(OAc)_2$	$Cs_2CO_3/CuCl_2$	3:1	36	50%
6[e]	$Pd(OAc)_2$	$Cs_2CO_3/CuCl_2$	1:0	36	0%
7	$Pd(OAc)_2$	$Cs_2CO_3/Cu(OTf)_2$	3:1	36	Trace
8	$Pd(OAc)_2$	$Cs_2CO_3/Cu(OAc)_2$	3:1	36	23%
9	$Pd(OAc)_2$	$K_2CO_3/CuCl_2$	3:1	36	21%
10	$Pd(OAc)_2$	$Na_2CO_3/CuCl_2$	3:1	36	13%
11	$Pd(OAc)_2$	$Li_2CO_3/CuCl_2$	3:1	36	Trace
12	$Pd(OAc)_2$	DBU/$CuCl_2$	3:1	12	0%
13	$Pd(OAc)_2$	CsOAc/$CuCl_2$	3:1	24	Trace
14	$Pd(OAc)_2$	*t*-BuOK/$CuCl_2$	3:1	12	0%
15	$Pd(OAc)_2$	$K_3PO_4/CuCl_2$	3:1	36	10%
16	$Pd(OAc)_2$/bipy	$Cs_2CO_3/CuCl_2$	3:1	36	Trace
17	$Pd(OAc)_2$/dppe	$Cs_2CO_3/CuCl_2$	3:1	36	54%
18	$Pd(OAc)_2$/dppp	$Cs_2CO_3/CuCl_2$	3:1	36	44%
19	$Pd(OAc)_2$/dppf	$Cs_2CO_3/CuCl_2$	3:1	36	49%
20	$Pd(OAc)_2$/binap	$Cs_2CO_3/CuCl_2$	3:1	36	50%
21	$Pd(OAc)_2/PPh_3$	$Cs_2CO_3/CuCl_2$	3:1	36	59%
22[f]	$Pd(OAc)_2/PPh_3$	$Cs_2CO_3/CuCl_2$	3:1	36	30%
23[g]	$Pd(OAc)_2/PPh_3$	Cs_2CO_3/—	3:1	36	Trace
24[h]	—/PPh_3	$Cs_2CO_3/CuCl_2$	3:1	36	0%
25[i]	$Pd(OAc)_2/PPh_3$	$Cs_2CO_3/CuCl_2$	3:1	36	0%
26[j]	$Pd(OAc)_2/PPh_3$	$Cs_2CO_3/CuCl_2$	3:1	36	38%
27[k]	$Pd(OAc)_2/PPh_3$	$Cs_2CO_3/CuCl_2$	3:1	36	0%

[a] Reaction conditions: 1.0 equiv of **1a** (0.3 mmol), 2.0 equiv of **2a**, 8 mol % of [Pd], 16 mol % of ligand, 2.1 equiv of additive, 2.0 equiv of base and 4.0 equiv of CsF in 3.6 mL of solvent at 80 °C.
[b] Abbreviations: bpy = 2,2′-bipyridine; dppe = 1,2-bis(diphenylphosphino) ethane; dppf = 1,1′-bis(diphenylphosphino)ferrocene; dppp = 1,3-bis(diphenylphosphino) propane; binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.
[c] The ratio of mixed solvent (v/v).
[d] Isolated yields.
[e] The reaction was carried out utilizing 3.6 mL of toluene.
[f] The reaction was carried out utilizing 4 mol % of $Pd(OAc)_2$ and 8 mol % of PPh_3.
[g] The reaction was carried out utilizing 100 mol % of $Pd(OAc)_2$ and 200 mol % of PPh_3 without $CuCl_2$.
[h] The reaction was carried out without $Pd(OAc)_2$.
[i] Performed at 60 °C.
[j] The reaction was carried out utilizing 0.9 mL of DMSO and 2.7 mL of toluene at 105 °C.
[k] The reaction was carried out utilizing *O*-benzoyloxime **1a′** instead of *O*-acetyloxime **1a**.

solvents, additives, bases, ligands, and reaction temperature were then examined. Employing the mixed solvent toluene/CH_3CN (v/v 3:1) could slow down the generation of the benzyne, resulting **3a** in a higher yield (50% vs 45%, compare entry 5 with 4). However, when the reaction was carried out by using only toluene as solvent, no desired product **3a** was obtained (entry 6). Utilization of other additives $Cu(OTf)_2$, $Cu(OAc)_2$ (entries 7 and 8) or other bases (entries 9–15) did not give better yields. Ligands bpy, dppe, dppp, dppf, binap, and PPh_3 were also examined (entries 16–21) with PPh_3 giving a better yield of **3a** (entry 21). The reactions conducted with different loads of $Pd(OAc)_2$ and PPh_3 furnished lower yields of **3a** (entries 22–24). Notably, $Pd(OAc)_2$ and $CuCl_2$ are inevitable in this reaction (entries 23 and 24). Trials under different temperatures gave no better results (entries 25 and 26). In addition, reaction with the employment of *O*-benzoyloxime **1a′** instead of *O*-acetyloxime **1a** was also conducted and no product **3a** was

Table 2
Synthesis of phenanthridines **3** from aryl ketone *O*-acetyloximes **1** and aryne precursors **2**[a]



1a-g 2a-b 3a-h

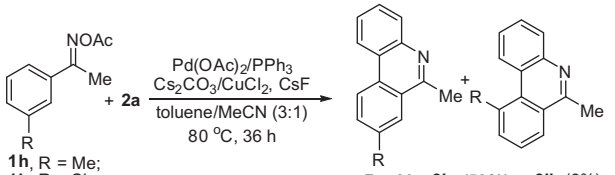
Entry	1		2	Yield[b] (%)
	R^1	R^2	R^3	
1	H	Me (**1a**)	H (**2a**)	59 (**3a**)
2	OMe	Me (**1b**)	**2a**	62 (**3b**)
3	Me	Me (**1c**)	**2a**	60 (**3c**)
4	Cl	Me (**1d**)	**2a**	40 (**3d**)
5	F	Me (**1e**)	**2a**	61 (**3e**)
6	OMe	1b	Me (**2b**)	55 (**3f**)
7	H	Et (**1f**)	**2a**	41 (**3g**)
8	H	$-(CH_2)_3-$ (**1g**)	**2a**	39 (**3h**)

[a] Reaction conditions: 1.0 equiv of **1** (0.3 mmol), 2.0 equiv of **2**, 8 mol % of $Pd(OAc)_2$, 16 mol % of PPh_3, 2.1 equiv of $CuCl_2$, 2.0 equiv of Cs_2CO_3 and 4.0 equiv of CsF in 0.9 mL of MeCN and 2.7 mL of toluene at 80 °C for 36 h.
[b] Isolated yield of **3** based on **1**.

observed (entry 27). Thus, the optimal reaction conditions were confirmed as that described in entry 21.

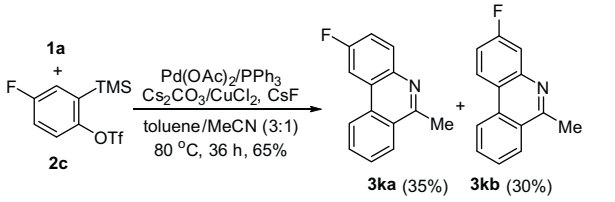
With the optimized conditions in hand, we next explored the application scope of this reaction with a series of aryl ketone *O*-acetyloximes **1** and aryne precursors **2** (Table 2). Reactions of *O*-acetyloximes **1a**–**e** with the symmetrical arynes (from **2a**–**b**) proceeded smoothly, giving corresponding phenanthridines **3a**–**f** in 40–62% yields (entries 1–6). Employment of **1f** bearing the ethyl group (R^2) gave product **3g** in a relatively lower yield (41%, entry 7). Moreover, α-tetralone *O*-acetyloxime **1g** could also be successfully applied to construct the tetracyclic phenanthridine **3h** in 39% yield (entry 8).

When **1h** bearing *m*-tolyl was introduced, isomeric products **3ia**[9] and **3ib** were obtained in 50% and 6% yields, respectively (Eq. (4)). The observed regiochemistry may be explained by the steric hindrance of the methyl substituent. On the contrary, **1i** with *m*-chloro phenyl afforded regioisomers **3ja**[9] and **3jb** in 25% and 20% yields, respectively.



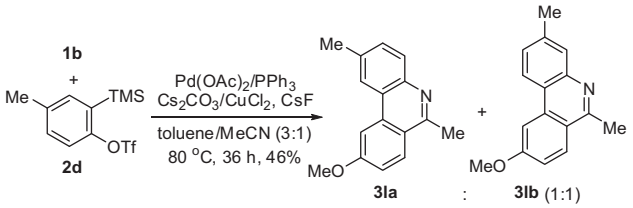
(4)

Regioselectivity of this Pd-catalyzed annulation reaction was examined by employing the non-symmetric arynes. Introduction of aryne precursor **2c** gave regioisomers **3ka**[9] and **3kb** in 35% and 30% yields, respectively (Eq. (5)).



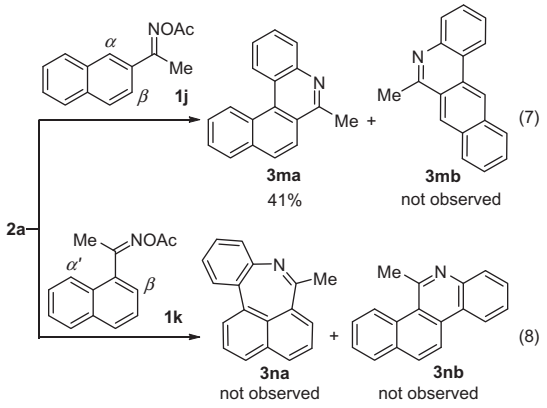
(5)

When aryne precursor **2d** was applied, a 1:1 mixture of regioisomers **3la** and **3lb** was observed in 46% combined yield (Eq. (6)). The ratio of isomers was determined by the ^{1}H NMR analysis of the crude product.



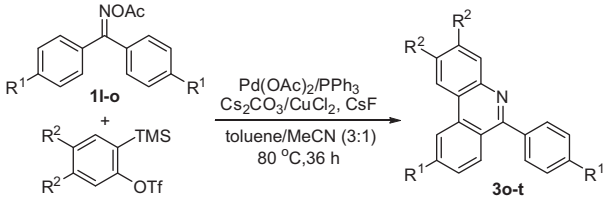
(6)

Moreover, we are interested in investigating the different C–H bond reactivities of naphthalene at the α- and β-positions. The reaction of naphthalenylethanone *O*-acetyloxime **1j** with **2a** provided phenanthridine **3ma**[9] in 41% yield as the sole isomer, with no regioisomer **3mb** observed (Scheme 2, Eq. 7). This result indicated that the C–H bond at the α-position was more reactive. However, the reaction utilizing **1k** did not afford the preconceived product **3na**, which may lie in the high strain of the seven-membered ring and the long distance between the α′-position and the directing group; **3nb** was not observed either due to the low C–H reactivity at the β-position (Scheme 2, Eq. 8).[10]



Scheme 2. Reactions of naphthalenylethanone *O*-acetyloximes **1j** and **1k** with benzyne.

Table 3
Synthesis of 6-aryl phenanthridines **3** from diarylmethanone *O*-acetyloximes **1** and **2**[a]

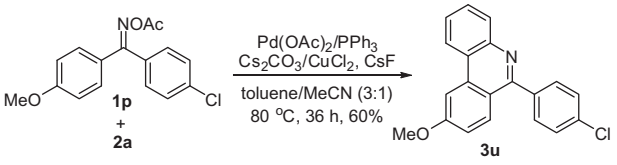


Entry	1	2	Yield[b] (%)
	R^1	R^2	
1	H (**1l**)	H (**2a**)	72 (**3o**)
2	OMe (**1m**)	**2a**	79 (**3p**)
3	Cl (**1n**)	**2a**	66 (**3q**)
4	F (**1o**)	**2a**	81 (**3r**)
5	**1m**	Me (**2b**)	71 (**3s**)
6	**1o**	**2b**	80 (**3t**)

[a] Reaction conditions: 1.0 equiv of **1** (0.3 mmol), 2.0 equiv of **2**, 8 mol % of $Pd(OAc)_2$, 16 mol % of PPh_3, 2.1 equiv of $CuCl_2$, 2.0 equiv of Cs_2CO_3 and 4.0 equiv of CsF in 0.9 mL of MeCN and 2.7 mL of toluene at 80 °C for 36 h.
[b] Isolated yield of **3** based on **1**.

Notably, phenanthridine derivatives are important core structures found in natural products and biologically active compounds.[11] Especially, 6-aryl-substituted phenanthridines are widely applied in material science and as DNA-intercalating agents.[12] Thus, the scope of the reaction was further explored (Table 3). A series of 6-aryl phenanthridines could be synthesized in good yields. Equipped with a strong electron-donating group –OMe, **1m** furnished corresponding product **3p** in higher yield (79% vs 66%, compare entry 2 with entry 3). Interestingly, up to 81% yield of product **3r** was observed with the employment of fluoro substituted **1o**. In addition, other aryne precursor **2b** could also be successfully applied, giving corresponding products **3s** and **3t** in good yields.

Interestingly, the reaction of non-symmetric diarylmethanone *O*-acetyloxime **1p** with benzyne (from **2a**) gave 60% of **3u** as the sole product (Eq. (9)).



(9)

The structure of **3u** was established by the ^{1}H NMR analysis and NOESY study (Fig. 1). The annulation occurred on the -OMe substituted aryl ring, indicating that the C–H bond on the electron-rich aryl ring is more likely to be activated.

According to our knowledge of Pd-catalyzed reaction,[13] the insertion may occur on two sites of *O*-acetyloxime **1**: the oxidative addition may occur to the N–O bond;[13c] on the other hand, *N*-containing functional group may act as the directing group to aid the C–H bond activation at the *ortho* position,[4c] leading to a Pd-contained cyclic specie to undergo the subsequent insertion with aryne. To shed light on the mechanism of this Pd-catalyzed annulation, control experiments were conducted. As shown in Eq. (10), we tried to trap the intermediate by adding H_2O to the reaction. Other than heterocyclic product **3a** (24% yield), compounds **4** and **5**, both with benzyne inserting to the C–H bond at the *ortho* position of the oxime group, were isolated in 31% and 7% yields. Meantime, the decomposed product **6** from **1a** was also observed in 20% yield. The reaction of CH_3OD and **1a** was explored under the optimal reaction conditions (Eq. (11)) and the product **1a–d** was isolated in 92% yield in 65% deuterated ratio as detected by the ^{1}H NMR analysis. We believe that the above observation supports the hypothesis that the Pd-catalyzed reaction starts from the C–H bond activation at the *ortho* position by the direction of the oxime group.

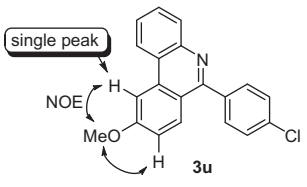
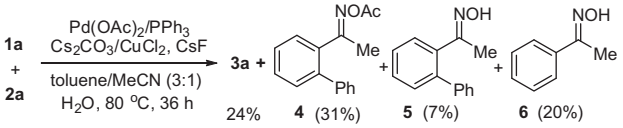
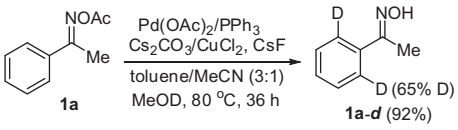


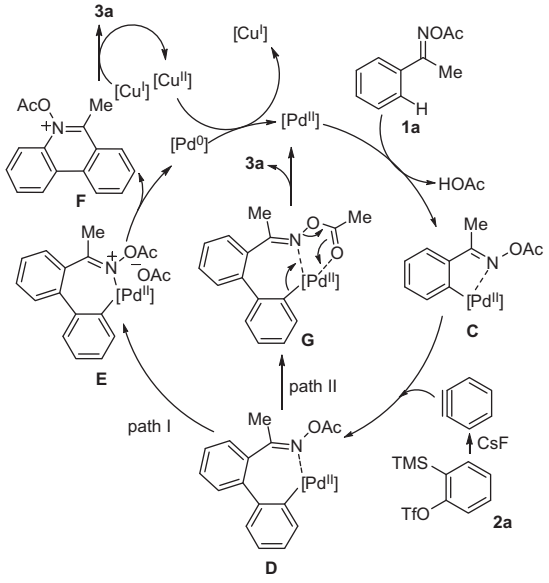
Figure 1. NOESY study of **3u**.



(10)



(11)



Scheme 3. Proposed mechanism.

On the basis of the above experimental facts and the known chemistry of arynes,[2a,14] the possible mechanism of this transformation was proposed (Scheme 3). With the aid of the sp^2 oxime nitrogen atom, the activation of *ortho*-C–H leads to intermediate **C**, which then inserts to the aryne generated in situ from 2-(trimethylsilyl)aryl triflate **2** to afford palladium specie **D**. The final product **3** may be furnished through two possible reaction paths (path I and path II) via path I,[4c,15] seven-membered ring palladacyclic iminium cation intermediate **E** may be formed. Following C–N reductive elimination would provide *N*-acetoxyphenanthridinium cation **F**, along with regeneration of the Pd(II) catalyst by the oxidation of Cu(II). The resulting Cu(I) species would take part in the reduction of **F** to furnish final product **3**. Alternatively, the concerted C–N bond formation/N–O bond cleavage sequence via the transient intermediate **G** may occur as the direct formation of phenanthridine **3** (path II).

In summary, we have developed a Pd-catalyzed reaction of aryl ketone *O*-acetyloximes and arynes to construct phenanthridines. Our strategy of Pd-catalyzed C–H bond activation is successfully realized in the aryne participated heterocycle construction. Therefore, preactivation of starting materials could be avoided, providing a novel and efficient approach to synthesize substituted phenanthridines. Due to the potential utilization of the products and the easy availability of the starting materials, this methodology may be of great potential value.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.12.075.

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