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Palladium-Catalyzed Heck-Type Reaction of Oximes with Allylic Alcohols: Synthesis of Pyridines and Azafluorenones

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We describe herein a palladium-catalyzed Heck-type reaction of *O*-acetyl ketoximes and allylic alcohols to pyridines. This protocol allows robust synthesis of pyridines and azafluorenones in good to excellent yields with tolerance of ¹⁰ various functional groups under mild conditions. The reaction is supposed to go through an oxidative addition of oximes to palladium(0) complexes generating alkylideneamino-palladium(II) species, which is utilized as a key intermediate to capture the nonbiased alkenes for ¹⁵ carbon–carbon bond formation.

The N-heterocycles are some of the most important building blocks in organic chemistry.¹ Among that, pyridines are one of the most significant building blocks, which not only exist extensively in pharmaceuticals, agrochemicals, and functional ²⁰ materials, but also serve as useful synthetic intermediates in modern organic synthesis.² Considering the large spectrum of fascinating applications, the synthesis of pyridine derivatives has long been an area of intense interest, and a number of different methods have been devised for their preparation.³ However, ²⁵ challenges still remains in the scope of group tolerance and equivalent usage of catalysts. Therefore, the development of methodologies for a more direct and efficient access to different substituted and specifically functionalized frameworks is always a great challenge in modern synthetic organic chemistry.

- ³⁰ The development of catalytic C-C bond-forming reactions remains one of the main challenges in organic chemistry.⁴ Among the transition metal-catalyzed reactions known to form C-C bonds, the palladium-catalyzed oxidative coupling by Mizoroki-Heck stands out as one of the most valuable synthetic tools.⁵ Since its
- ³⁵ first report in 1970s, lots of efforts have been devoted to its utilization, and it is now fully recognized as one of the most significant methods for carbon–carbon bond formations.⁶ Given that most of the oxidative Heck reaction was limited to active alkenes or styrenes due to the poor reactivity of unactivated
- ⁴⁰ olefins⁷ and the dilemma of selective β -H elimination⁸ (Scheme 1, a), therefore, transition metal-catalyzed olefination of nonbiased allylic alcohols, without the prior functionalization, is even more environmentally friendly and versatile (Scheme 1, b).⁹ According to previous reports, oximes and their derivatives can be used as ⁴⁵ "internal oxidant" towards transition metal-catalyzed oxidative C-
- H functionalization and cleavage of the N-O bond by the

participation transition metals form of to activ. alkylideneaminopalladium(II) species, which tautomerized to th key iminylpalladium(II) intermediates, making the following 50 alkylpalladium-catalyzed oxidative Heck-type reaction poss (Scheme 1, c).^{10,11} In this regard, based on our previous work on oximes¹² and allylic alcohols as alkyl ketone resourses¹³, design the possible [3 + 3] type cyclization with these two substrates and suppose the reaction to go through a palladium 55 catalyzed Heck-Type coupling of oximes with alkenes, with high efficiency under mild reaction conditions.





With the ability of palladium to reduce oxime N-O bonds, w 60 chose 3,4-dihydronaphthalen-1(2H)-one O-acetyl oxime (1a) an but-3-en-2-ol (2a) as model substrates and screened different additives and other reaction conditions (Table 1). To our delight the desired product 3aa could be detected in 56% yield when the model reaction was conducted in CH₃CN with CuBr₂ as additiv-65 in the presence of Pd(OAc)₂ catalyst under dioxygen atmosphere at 80 °C for 24 h (entry 1). The screening of different additive: including Cu(OAc)₂, KI, and AgNO₃, revealed that 3aa could also be formed in lower yields (entries 2-4). And $Cu(OAc)_2$ as found to be the best additive and the yield of **3aa** could re. h 70 87% (entry 2). However, with other additives, such as LiBr NH₄Br, Bu₄NBr, and AgOAc, only trace amount of 3aa wa detected (entries 5-8). The model reaction was then tested usin, other palladium catalytic system, and Pd(OAc)₂ was found to be the most suitable catalyst system for the target reaction (entries 9 75 11). No reaction was observed in the absence of palladium

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catalyst (entry 12), while with the absence of $Cu(OAc)_2$, the reaction could give 10% yield of product **3aa** (entry 13). The yield was unsatisfactory with the decrease of the reaction temperature (entry 14), while raising the temperature to 100 °C s improved the yield to 91% (entry 15). When the reaction was carried out in N₂ atmosphere, only trace amount of **3aa** was detected by GC-MS (entry 17).

Table 1 Screening for optimal reaction conditions^a

NOAc + 1a 2		$(Pd] 5 mol\%$ additive 20 mol% OH base 1.5 equiv. $O_2(1 \text{ atm}), \text{ solvent}$			N Jaaa
entry ^a	catalyst	additive	base	solvent	yield ^b (%)
1	$Pd(OAc)_2$	CuBr ₂	K_2CO_3	CH ₃ CN	56
2	Pd(OAc) ₂	Cu(OAc) ₂	K_2CO_3	CH ₃ CN	87 (87)
3	Pd(OAc) ₂	KI	K_2CO_3	CH ₃ CN	10
4	Pd(OAc) ₂	AgNO ₃	K_2CO_3	CH ₃ CN	25
5	Pd(OAc) ₂	LiBr	K_2CO_3	CH ₃ CN	trace
6	Pd(OAc) ₂	NH ₄ Br	K_2CO_3	CH ₃ CN	trace
7	Pd(OAc) ₂	Bu ₄ NBr	K_2CO_3	CH ₃ CN	trace
8	Pd(OAc) ₂	AgOAc	K_2CO_3	CH ₃ CN	trace
9	PdCl ₂	Cu(OAc) ₂	K_2CO_3	CH ₃ CN	57
10	$Pd(OTf)_2$	Cu(OAc) ₂	K_2CO_3	CH ₃ CN	63
11	Pd ₂ (dba) ₃	Cu(OAc) ₂	K_2CO_3	CH ₃ CN	trace
12		Cu(OAc) ₂	K_2CO_3	CH ₃ CN	n.d.
13	Pd(OAc) ₂		K_2CO_3	CH ₃ CN	10
14 ^c	Pd(OAc) ₂	Cu(OAc) ₂	K_2CO_3	CH ₃ CN	35
15 ^d	$Pd(OAc)_2$	Cu(OAc) ₂	K_2CO_3	CH ₃ CN	91
16 ^e	$Pd(OAc)_2$	Cu(OAc) ₂	K_2CO_3	CH ₃ CN	78
17 ^f	$Pd(OAc)_2$	Cu(OAc) ₂	K_2CO_3	CH ₃ CN	trace

^a Reaction conditions: Unless otherwise noted, the reaction was carried out with 1a (0.2 mmol), 2a (0.4 mmol), Pd catalyst (5 mol %), additive (20 mol %) and base (1.5 equiv) in solvent (1 mL) at 80 °C for 24 h. ^b Yield determined by GC-MS with dodecane as internal standard, and isolated yield in the parentheses. ^c The reaction was carried out at 60 °C. ^d
¹⁵ The reaction was carried out at 100 °C. ^e The reaction was carried out in the open air. ^f The reaction was carried out in N₂ atmosphere.

With the optimal reaction conditions in hand, we subsequently explored the reaction scope. The oxime substrates derived from other aryl ketones such as tetralones, propiophenones and 2-²⁰ phenylacetophenones could afford the products **3aa-3na** in good to excellent yields, respectively. Besides, oximes derived from aliphatic ketones afforded the pyridine derivatives **3oa-3ra** in moderate to good yields. To be specific, chroman-4-one oxime

- could afford **3da** in 59% yield. The formation of **3da** and **3ea** ²⁵ were inert under these conditions, indicating that the palladium catalyst preferentially reacts with the N-O bond of the oxime acetate over the carbon-halogen bonds. Other aryl functionalized amides could also undergo the pathway well. The 2-furansubstituted and 3-furan-substituted oximes could be tolerated in
- ³⁰ this transformation, generating **3ia** and **3ja** in 56% and 74% yields, respectively. It is noteworthy that alkyl-substituted oximes were also suitable substrates in this reaction with good yields (**3oa** to **3ra**). For example, propone oximes that contained short alkyl chains gave the products 2,6-dimethylpyrudine in moderate

35 yield (3qa). Notably, L(-)-carvone derived oximes could transfer to 3ra in 43% yield.

 Table 2 Pd-catalyzed synthesis of substituted pridited from affections and oximes^a



^a Reaction conditions: Unless otherwise noted, the reaction was carried out with 1 (0.5 mmol), 2a (1.0 mmol), Pd(OAc)₂ (5 mol %), Cu(OAc)₂ (20 mol %) and K₂CO₃ (1.5 equiv) in CH₃CN (1 mL) at 80 °C for 16-24 h.

We next focused our attention on the scope and generality of the olefin substrates in the oxidative coupling with oxime **1a**. ⁴⁵ This transformation displayed high functional group tolerance and proved to be a quite general method. Both aliphatic and aromatic allylic alcohols could undergo the protocol with good to excellent yields (Table 3). Alkyl-substituted allyl alcohols were found to be suitable substrates for this transformation and a transformed to the desired products in good wields (200 the 20 the

⁵⁰ transferred to the desired products in good yields (**3aa** to **3ad** Even the bulky aromatic allylic alcohols with methyl, methoxy and fluoro on aryl rings all gave good to excellent yields of the corresponding pyridines (**3af-3ah**). To be specifically, **3ah** could be obtained in 35% yield, which implied the steric hindrance had ⁵⁵ no much effect on this transformation. And the substrate with aryl substitution of 1-(thiophen-3-yl)prop-2-en-1-ol underwent the Heck reaction smoothly and gave the corresponding product **3ak**

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in 66% yield. As for the application of hexa-1,5-dien-3-ol in this reaction, hydrogen immigration product **3aj** was obtained in 45% yield, which may further support the role of palladium in the β -H elimination. Besides, with the application of 2-⁵ methylenepropane-1,3-diol as the coupling reagent, the yield of the desired product **3al** sharply decreased to 14% and 50% yield of **3ai** was obtained.¹⁴

Table 3 Pd-catalyzed synthesis of substituted pyridines from different ${}_{10}$ allylic alcohols^{*a*}



^{*a*} Reaction conditions: Unless otherwise noted, the reaction was carried out with **1a** (0.5 mmol), **2** (1.0 mmol), $Pd(OAc)_2$ (5 mol %), $Cu(OAc)_2$ (20 mol %) and K_2CO_3 (1.5 equiv) in CH₃CN (1 mL) at 80 °C for 16-24 h.

¹⁵ Furthermore, with 1-indanone oximes as substrate, different azafluorenones could be obtained in this system.¹⁵ For example, the reaction of 2,3-dihydro-1*H*-inden-1-one *O*-acetyl oxime (**1w**) afforded the corresponding 4-azafluorenones in good yield. Pleasingly, when 5,6-dihydro-7*H*-cyclopenta[*b*]pyridin-7-one *O*-²⁰ acetyl oxime (**1x**) was applied, 39% yield of 4,5-diazafluorenone

Table 4 Synthesis of azafluorenones^a

was obtained.¹⁶



^a Reaction conditions: Unless otherwise noted, the reaction was carried ²⁵ out with **1** (0.5 mmol), **2** (1.0 mmol), Pd(OAc)₂ (5 mol %), Cu(OAc)₂ (2[^] mol %) and K₂CO₃ (1.5 equiv) in CH₃CN (1 mL) at 80 °C for d fract to online

Based on the experimental results¹⁷ and previous reports, plausible mechanism is proposed in Scheme 2. Firstly, the oxidative addition of the oxime N-O bond to Pd(0) species easily transformed to palladium enamide intermediate **A**. Subsequer tautomerization affords the enamine-derived amido-Pd(II) species **B**.¹¹ Further isomerization of this species results in the conversio of this N-bound enamido-Pd(II) **B** species to its C-bound isomer **C**.¹⁸ Followed by Mizoroki-Heck reaction of allylic alcohol **2** inserting into the carbon-palladium bond of alkylpalladium species **C** forms intermediate species **D**.¹⁹ Then, intermediate **b** undergoes β -H elimination to give intermediate **E** and regenerate. the active palladium catalyst.¹⁴ The intramolecular condensatio

of the amine and ketone moieties of intermediate **E** forms **F** ⁴⁰ Finally, the dehydrative oxidation gives the pyridine product **3aa**.²⁰ Alternative mechanism is shown in the Supportin Information.



Scheme 2 Possible mechanism

- ⁴⁵ In summary, we have successfully developed a palladium, catalyzed strategy to construct pyridines from *O*-acetyl oxime and nonbiased alkenes. This protocol provides a possible pathway for the insertion of alkenes to oximes. With the operationa simplicity, efficiency and functional group compatibility, thi ⁵⁰ protocol will expand the scope of pyridine derivatives Furthermore, the present method also enables the direct construction of a diverse array of azafluorenone cores, which ma find applications in natural product synthesis and medicinal chemistry.
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