Rhodium(III)-Catalyzed Synthesis of Pyridines from α,β-Unsaturated Ketoximes and Internal Alkynes

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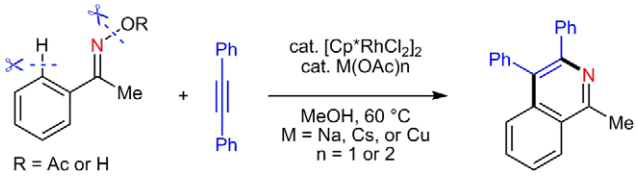
Abstract: A method for the synthesis of highly substituted pyridines from α,β-unsaturated oximes and internal alkynes has been developed using [Cp*RhCl$_2$]$_2$–CsOPiv as the catalyst system. The present transformation is carried out by a redox-neutral sequence of vinylic C–H rhodation, alkyne insertion, and C–N bond formation of the putative vinyl rhodium intermediate with the oxime nitrogen, where the N–O bond of oxime derivatives could work as an internal oxidant to maintain the catalytic cycle.

Key words: pyridines, oximes, alkynes, rhodium, C–H activation

Among nitrogen-containing heterocycles (azaheterocycles),[1] pyridines are one of the most prevalent motifs in numerous natural products, potent pharmaceutical drugs, and synthons for functional materials. Although diverse approaches toward synthesis of pyridines have been developed,[2,3] there remains a demand for versatile methodologies to construct pyridines with selective control of substitution patterns from readily accessible building blocks.

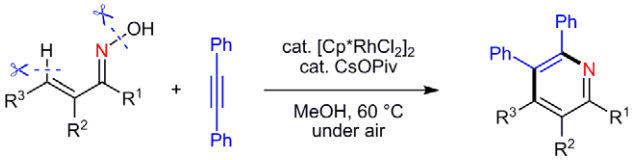
Synthetic transformation via C–H bond functionalization by transition-metal catalysts is an ideal process in organic synthesis in terms of atom- and step-economical points of view.[4] Commonly, suitable heteroatoms are utilized as a directing group to activate the specific proximal C–H bond, where an sp^2-imino/amido nitrogen atom has been employed in numerous examples of the C–H bond activation.[5]

Recently, redox-neutral catalytic strategies using the N–O bond attached in the nitrogen directing group have been developed for the synthesis of azaheterocycles via the sequence of *ortho* C–H activation and C–N bond formation, where the N–O bond works as an internal oxidant to maintain catalytic turnover.[6,7] For example, Guimond and Fagnou disclosed the synthesis of isoquinolones from benzhydroxamic acid derivatives and internal alkynes catalyzed by the [Cp*RhCl$_2$]$_2$–CsOAc system.[7a,g,8,9] It was also reported by us that the N–O bond of aryl ketoximes could be used for the rhodium(III)-catalyzed synthesis of isoquinoline derivatives with internal alkynes (Scheme 1).[7c,e,f]



Scheme 1

Based on these backgrounds, our attention has been drawn to the use of readily available α,β-unsaturated ketoximes for vinylic C–H fission/functionalization. Herein we wish to report rhodium(III)-catalyzed synthesis of highly functionalized pyridines from α,β-unsaturated ketoximes and internal alkynes under mild reaction conditions (Scheme 2).[10]



Scheme 2

First, we screened the reaction conditions for synthesis of pyridine **3aa** from (*E*)-4-phenylbut-3-ene-2-one oxime derivatives **1a** and diphenyl acetylene (**2a**, 1.2 equiv) using 2.5 mol% of [Cp*RhCl$_2$]$_2$ and 30 mol% of metal carboxylates as an additive in MeOH (Table 1). As expected, the reactions of *O*-acetyloxime **1a** (Table 1, entries 1–3) proceeded to give desired pyridine **3aa**, the highest yield of which was provided by running with CsOPiv as an additive (10 h, 77% yield, Table 1, entry 3). The reaction with Cu(OAc)$_2$,[7c] however, did not give the desired pyridine **3aa**, resulting in decomposition of oxime acetate **1a** (Table 1, entry 4). Using the [Cp*RhCl$_2$]$_2$–CsOPiv system, the effect of the substituent X was next examined. Although the yield of pyridine **3aa** from oxime pivalate **1a′** was moderate (Table 1, entry 5), the reactions of oxygen-free oxime **1a″** resulted in the smooth reaction, affording pyridine **3aa** in 79% yield within seven hours (Table 1, entry 6). The reaction under a N$_2$ atmosphere

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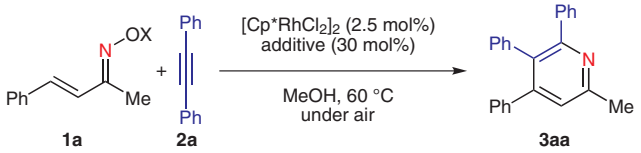
was found to be sluggish, indicating that the presence of air (oxygen) has a crucial role to maintain and accelerate the catalytic turnover (Table 1, entry 7). Use of 1.5 equivalents of oxime **1a**" with diphenyl acetylene (**2a**) gave 86% yield of pyridine **3a** (based on acetylene **2a**), while longer reaction time (24 h) was required (Table 1, entry 8).

Table 1 Optimization of Reaction Conditions[a,b]

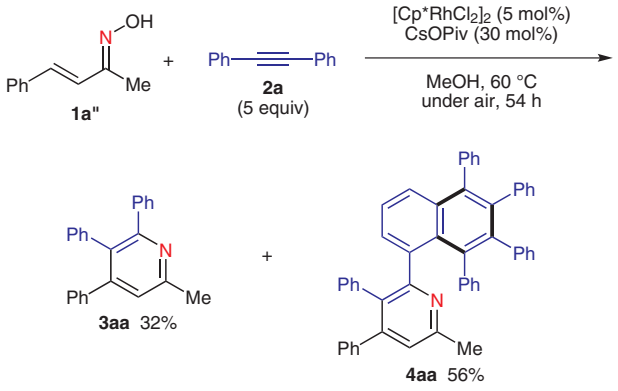


Entry	X	Additive	Time (h)	Yield of **3aa** (%)[b]
1	**1a** X = Ac	NaOAc	24	49
2	**1a** X = Ac	CsOAc	24	62
3	**1a** X = Ac	CsOPiv	10	77
4	**1a** X = Ac	$Cu(OAc)_2$	14	0
5	**1a**′ X = Piv	CsOPiv	19	55
6	**1a**″ X = H	CsOPiv	7	79
7[c]	**1a**″ X = H	CsOPiv	24	78
8[d]	**1a**″ X = H	CsOPiv	24	86

[a] Unless otherwise noted, reactions were carried out using 0.5 mmol of oxime **1a** and 1.2 equiv of alkyne **2a** with 2.5 mol% of $[Cp^*RhCl_2]_2$ and 30 mol% of additive in MeOH at 60 °C under an air atmosphere.
[b] Isolated yields were recorded above.
[c] The reaction was conducted under a N_2 atmosphere.
[d] The reaction was conducted using 0.5 mmol of alkyne **2a** and 1.5 equiv of oxime **1a**″, and the yield of **3aa** was calculated based on alkyne **2a**.

During optimization of the reaction conditions (Table 1), in addition to the desired pyridine **3aa** generated via 1:1 coupling of oxime **1a** and alkyne **2a**, the formation of 2-naphthylpyridine **4aa** (1:3 coupling of **1a** and **2a**) was observed as a minor side product (less than 10% yield) in most of the entries. The naphthyl moiety of **4aa** was presumably constructed from **3aa** via catalytic multiple C–H bond cleavage and insertion of two more equivalents of alkyne **2a**.[11,12] Indeed, treatment of oxime **1a**″ with excess amounts (5 equiv) of alkyne **2a** under the present reaction conditions delivered 2-naphthylpyridine **4aa** in 56% yield after 54 hours along with 32% yield of **3aa** (Scheme 3).

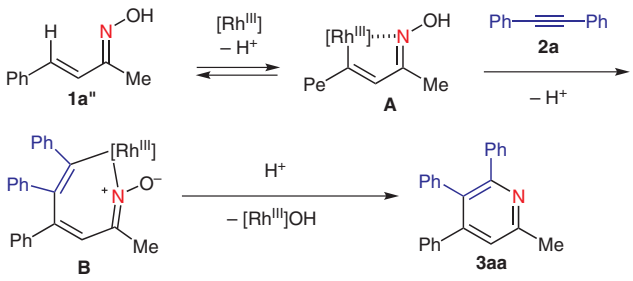
With the optimized reaction conditions using oxygen-free oxime **1a**″ (Table 1, entry 6), generality of the substituents on internal alkynes **2** was investigated (Table 2). Symmetrical diaryl acetylenes **2** bearing various substituents reacted smoothly, affording the corresponding pyridines **3** in good yields (Table 2, entries 1–3). Similarly, the reactions of dialkyl acetylenes **2e** and **2f** also proceeded smoothly (Table 2, entries 4 and 5). Insertion of unsymmetrical alkynes **2g–i** occurred somehow in regioselective manner, albeit in moderate selectivity (Table 2, entries 6–8).



Scheme 3

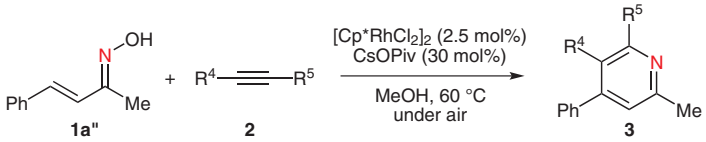
The present process showed wide substrate tolerance with α,β-unsaturated oxime derivatives **1** by the reactions with alkynes **2a** or **2e** (Table 3). By varying the substituent on the β-carbon, benzene rings bearing electron-donating groups (Table 3, entries 1–3) and a bromine atom (Table 3, entry 4) as well as naphthyl and thienyl groups (Table 3, entries 5–8) could be introduced, leading to the formation of the corresponding pyridines **3** in good to moderate yields. The reaction of dibenzylideneacetone oxime (**1i**) with diphenyl acetylene (**2a**) proceeded smoothly to give 6-styrylpyridine **3ia** in 81% yield (Table 3, entry 9). When the substituent of R^1 of oxime **1a**″ was replaced from methyl to isopropyl, the stereochemistry of the N–O bond of oxime **1j** became a mixture of *E*- and *Z*-isomers in a 55:45 ratio. The reaction of oxime **1j** afforded pyridine **3ja** in 40% yield with 25% recovery of *Z*-isomer (Table 3, entry 10).[13] Pentasubstituted pyridines **3ka** and **3la** could be synthesized smoothly in good yields (Table 3, entries 11 and 12). When 3-benzylbut-3-en-2-one oxime (**1m**) without the β-substituent was employed, the reaction took place in a shorter reaction time (2 h), affording 2,3,5,6-tetrasubstituted pyridine **3ma** in 88% yield (Table 3, entry 13).

A proposed catalytic reaction pathway of the present pyridine formation was outlined in Scheme 4. It commences with vinylic C–H activation of α,β-unsaturated oxime **1a**″ with the aid of the oxime sp^2-nitrogen to give vinyl rhodium intermediate **A**. Insertion to alkynes **2a** with **A** affords seven-membered-ring rhodacyclic iminium cation intermediate **B**, which undergoes concerted redox processes of C–N reductive elimination and regeneration of rhodium(III) species to give pyridine **3aa**.



Scheme 4 A proposed catalytic pathway

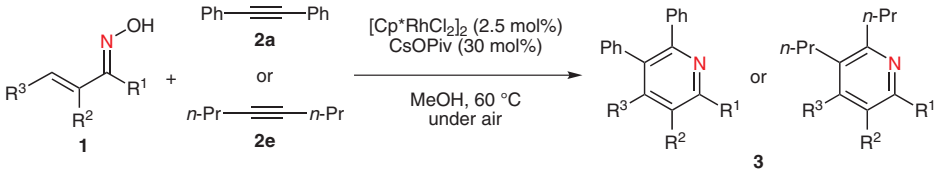
Table 2 Scope of Internal Alkynes[a]



Entry	Alkyne	R^4	R^5	Time (h)	Yield of **3** (%)[b]	
1	**2b**	4-$MeOC_6H_4$	4-$MeOC_6H_4$	24	**3ab**	61
2	**2c**	4-$TMSC_6H_4$	4-$TMSC_6H_4$	10	**3ac**	60[c]
3	**2d**	3-BrC_6H_4	3-BrC_6H_4	10	**3ad**	77
4	**2e**	*n*-Pr	*n*-Pr	8	**3ae**	75
5	**2f**	$TBSOCH_2$	$TBSOCH_2$	30	**3af**	69
6	**2g**	Me	Ph	8	**3ag**	97 (60:40)
7	**2h**	CO_2Et	Ph	24	**3ah**	45 (60:40)
8	**2i**	4-$MeOC_6H_4$	4-$F_3CC_6H_4$	24	**3ai**	87 (70:30)

[a] Unless otherwise noted, reactions were carried out using 0.5 mmol of oxime **1a″** and 1.2 equiv of alkyne **2** with 2.5 mol% of $[Cp^*RhCl_2]_2$ and 30 mol% of CsOPiv in MeOH at 60 °C under an air atmosphere.
[b] Isolated yields were recorded above.
[c] Oxime **1a″** was recovered in 32% yield.

Table 3 Scope of α,β-Unsaturated Oximes[a]



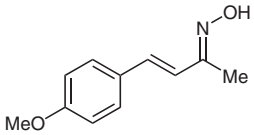
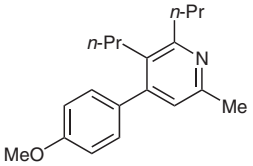
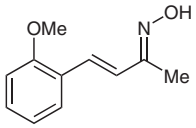
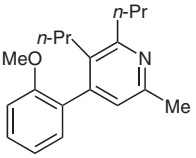
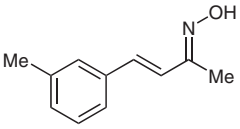
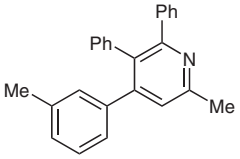
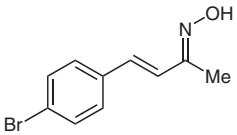
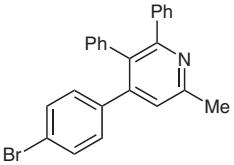
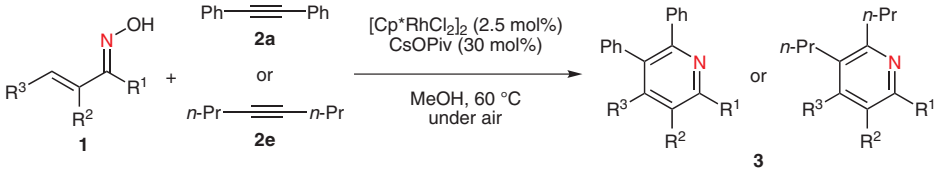
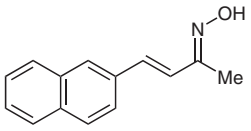
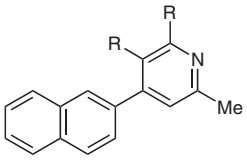
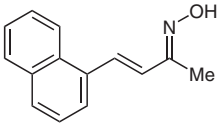
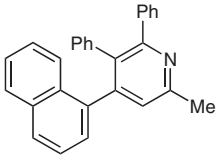
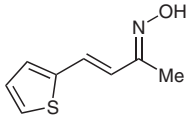
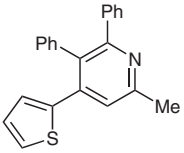
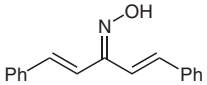
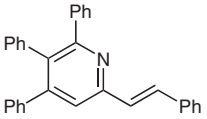
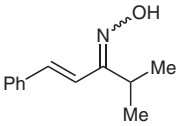
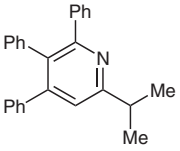
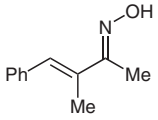
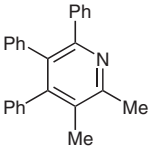
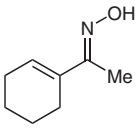
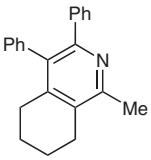
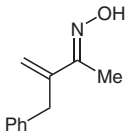
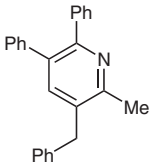
Entry	Oximes **1**	Alkynes **2a** or **2e**	Time (h)	Pyridines **3**	Yield (%)[b]
1	 **1b**	**2e**	20		**3be** 60
2	 **1c**	**2e**	30		**3ce** 63
3	 **1d**	**2a**	30		**3da** 68
4	 **1e**	**2a**	12		**3ea** 87

Table 3 Scope of α,β-Unsaturated Oximes[a] (continued)



Entry	Oximes **1**	Alkynes **2a** or **2e**	Time (h)	Pyridines **3**	Yield (%)[b]
5	 **1f**	**2a**	24		**3fa** R = Ph, 87
6		**2e**	24		**3fe** R = *n*-Pr, 77
7	 **1g**	**2a**	24		**3ga** 74
8	 **1h**	**2a**	24		**3ha** 53
9[c]	 **1i**	**2a**	7		**3ia** 81
10	 **1j** *E*/*Z* = 55:45	**2a**	24		**3ja** 40[d]
11	 **1k**	**2a**	7		**3ka** 66
12	 **1l**	**2a**	10		**3la** 68
13	 **1m**	**2a**	2		**3ma** 88

[a] Unless otherwise noted, reactions were carried out using 0.5 mmol of oxime **1** and 1.2 equiv of alkyne **2** with 2.5 mol% of $[Cp^*RhCl_2]_2$ and 30 mol% of CsOPiv in MeOH at 60 °C under an air atmosphere.
[b] Isolated yields were recorded above.
[c] The reaction was conducted using 1 equiv of alkyne **2a**.
[d] The *Z* isomer of oxime **1j** was recovered in 25% yield.

In summary, we have developed a synthetic method of highly substituted pyridines from α,β-unsaturated oximes and internal alkynes using $[Cp^*RhCl_2]_2$–CsOPiv as the catalyst system.[14] Further investigation on application of this methodology for the synthesis of other types of heterocycles are currently under way.

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(12) The formation of **4aa** could result in generation of rhodium(I) species, which should be re-oxidized to rhodium(III) by air (O_2) to maintain the catalytic turnover.

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(14) **General Procedure (Table 1, Entry 6)**
To a MeOH solution (2.5 mL) of (2*E*,3*E*)-4-phenylbut-3-en-2-one oxime (**1a**, 80.5 mg, 0.50 mmol) and diphenylacetylene (**2a**, 106.9 mg, 0.60 mmol) were added $[Cp^*RhCl_2]_2$ (7.7 mg, 0.0125 mmol) and CsOPiv (35.1 mg, 0.15 mmol), and the reaction mixture was stirred at 60 °C under air for 7 h. After cooled to r.t., the solvent was removed in vacuo, and the resulting crude material was subjected to flash column chromatography (hexane–EtOAc = 90:10) to afford 6-methyl-2,3,4-triphenylpyridine (**3aa**, 126.4 mg, 0.393 mmol) in 79% yield.