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Rh(III)–catalyzed synthesis of isoquinolines from *N*-hydroxyoximes and alkynes in γ-valerolactone

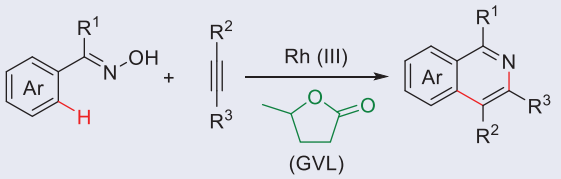
Kuan-Chang Jiang[a], Liang Wang[a,b], Qun Chen[a], Ming-Yang He[a], Ming-Gui Shen[c], and Zhi-Hui Zhang[a]

[a]School of Petrochemical Engineering, Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou, China; [b]School of Chemical and Pharmaceutical Engineering, Changzhou Vocational Institute of Engineering, Changzhou, China; [c]National Engineering Laboratory for Biomass Chemical Utilization, Key and Open Laboratory on Forest Chemical Engineering, Key Laboratory of Biomass Energy and Material, Institute of Chemical Industry of Forest Products, Nanjing, China

ABSTRACT

A Rh (III)–catalyzed synthesis of isoquinoline derivatives from *N*-hydroxyoximes and alkynes *via* C–H activation/annulation process in biomass-derived γ-valerolactone (GVL) has been developed. A series of functional groups were well tolerated, affording the desired products in good to excellent yields.

GRAPHICAL ABSTRACT



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Introduction

Isoquinoline derivatives are very important heterocycles that have found wide applications in natural products and pharmaceuticals.[1] They also serve as useful ligands in synthetic organic chemistry.[2] Traditionally, synthesis of isoquinolines required the use of functionalized starting materials or strong acids.[3] These approaches usually suffered from some drawbacks including poor yields, poor regioselectivity and harsh reaction conditions.

In recent years, transition-metal-catalyzed C–H bond activation has emerged as a practical and useful method for the construction of complex molecular scaffolds.[4] Particularly, the C–H activation/annulation strategy is appealing from a synthetic perspective since it allows the rapid formation of highly valuable cyclic products from

CONTACT Liang Wang lwcczu@126.com School of Petrochemical Engineering, Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, China; School of Chemical and Pharmaceutical Engineering, Changzhou Vocational Institute of Engineering, Changzhou 213164, China; Zhi-Hui Zhang zhangzh@cczu.edu.cn School of Petrochemical Engineering, Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, China.

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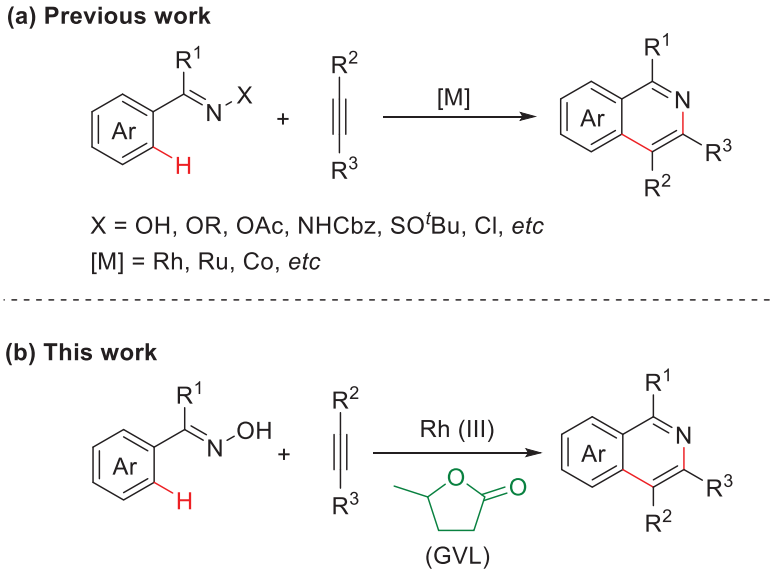


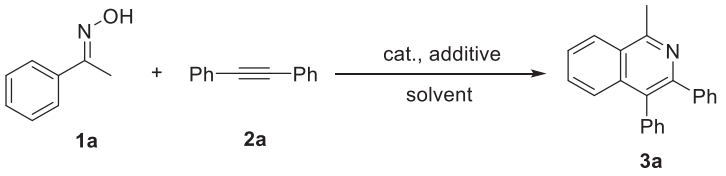
Scheme 1. Transition-metal-catalyzed synthesis of isoquinolines. (a) Previous work. (b) This work.

readily available substrates.[5] In this context, the synthesis of isoquinoline derivatives using such strategy has been widely reported and great advance has been achieved. Previously, such reactions proceeded under oxidative conditions, thus stoichiometric amount of external oxidants were required for the regeneration of active catalytic species.[6–10] To overcome these drawbacks, oxidizing directing groups such as N–O,[11–31] N–N,[32–37] N–S[38] and N–Cl[39] were employed. They could served as internal oxidants, thereby enabling the reaction proceed under redox-neutral conditions (Scheme 1a).

Despite these significant advances, there are still some issues need to be addressed. For example, although various oxidizing directing groups have been developed, the use of oxime as the directing group undoubtedly has some advantages since oximes are cheap, readily available, and water is generated as the byproduct in such reaction. Moreover, the reported protocols were usually conducted in volatile and toxic organic solvents, making them environmentally unfriendly. Finally, only a handful of reports exist using 1,3-diynes as the substrates in the synthesis of isoquinolines. Regioselectivity (3-alkynylation or 4-alkynylation) and chemoselective (mono- and difunctionalization) are also big challenges.[29,30]

Considering these facts, it is still highly desirable to develop a protocol for the synthesis of isoquinolines using simple substrates in green solvent. Recently, the use of γ-valerolactone (GVL) as reaction medium has become a hot field.[40] GVL is recognized as a sustainable solvent due to its advantages such as high boiling and flash points, good chemical stability and low toxicity. To our best knowledge, reports on the C–H activation reactions in GVL are few. Herein, we report a Rh(III)-catalyzed synthesis of isoquinoline derivatives from oximes and alkynes in GVL. Different oximes survived well under the reaction conditions, and good regioselectivity and chemoselective was observed when 1,3-diynes were utilized as the substrates (Scheme 1b).

Table 1. Optimization of reaction conditions.[a]



1a **2a** **3a**

Entry	Catalyst	Additive 1	Additive 2 (equiv.)	Solvent	Yield (%)[b]
1	$[RhCp^*Cl_2]_2$	$AgSbF_6$	–	GVL	80
2	$[RhCp^*Cl_2]_2$	–	–	GVL	0
3	$[RhCp^*Cl_2]_2$	$AgBF_4$	–	GVL	63
4	$[RhCp^*Cl_2]_2$	$AgSbF_6$	$Cu(OAc)_2•H_2O$	GVL	84
5	$[RhCp^*Cl_2]_2$	–	$Cu(OAc)_2•H_2O$	GVL	55
6	$[RhCp^*Cl_2]_2$	–	$CuCl_2•H_2O$	GVL	0
7	$[RhCp^*Cl_2]_2$	–	CsOAc	GVL	56
8	$[RhCp^*Cl_2]_2$	–	KOAc	GVL	61
9	$[RhCp^*Cl_2]_2$	–	NaOAc	GVL	46
10	$[RhCp^*Cl_2]_2$	$AgSbF_6$	KOAc	GVL	88
11	$[RhCp^*Cl_2]_2$	$AgSbF_6$	KOAc	DMF	58
12	$[RhCp^*Cl_2]_2$	$AgSbF_6$	KOAc	CH_3CN	46
13	$[RhCp^*Cl_2]_2$	$AgSbF_6$	KOAc	DMSO	15
14	$[RhCp^*Cl_2]_2$	$AgSbF_6$	KOAc	DCE	60
15	$[RhCp^*Cl_2]_2$	$AgSbF_6$	KOAc	THF	36
16	$[RhCp^*Cl_2]_2$	$AgSbF_6$	KOAc	HFIP	73
17	$[RhCp^*Cl_2]_2$	$AgSbF_6$	KOAc	H_2O	20
18	$[RhCp^*Cl_{2]2}$	$AgSbF_6$	KOAc	GVL	45[c], 77[d]

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst (2 mol%), additive 1 (8 mol%), additive 2 (0.2 equiv.), solvent (2 mL), 80 °C for 12 h in a sealed tube.
[b]Isolated yields.
[c]At 60 °C.
[d]At 100 °C.

Results and discussion

At the outset of our studies, we chose acetophenone oxime **1a** and 1,2-diphenylethyne **2a** as the model substrates to screen the reaction conditions in the presence of $[RhCp^*Cl_2]_2$ (2 mol%) and $AgSbF_6$ (8 mol%) in GVL (2 mL) at 80 °C for 12 h (Table 1, entry 1).

Encouragingly, the desired product **3a** was obtained in 80% yield under above reaction conditions. The reaction did not occur in the absence of any additive (entry 2). Switching $AgSbF_6$ to $AgBF_4$ gave the desired product in relative lower yield (63%, entry 3). The addition of $Cu(OAc)_2•H_2O$ slightly improve the yield, indicating an external oxidant was not necessary (entry 4). It was also worth noting that a moderate yield of **3a** could be obtained in the presence of $Cu(OAc)_2•H_2O$, while no product was observed when $CuCl_2•H_2O$ was used as the additive. It was assummed that OAc anion might promote the reaction (entries 5 and 6). A series of additives including CsOAc, KOAc and NaOAc were then tried alone, however, only moderate yields were obtained (entries 7–9). Instead, the combination of $AgSbF_6$/KOAc afforded **3a** in 88% yield (entry 10). Other solvents were also evaluated. Reactions in *N*,*N*-dimethylformamide (DMF), acetonitrile, dimethyl sulfoxide (DMSO), 1,2-dichloroethane (DCE) and tetrafuran (THF) gave unsatisfactory yields (entries

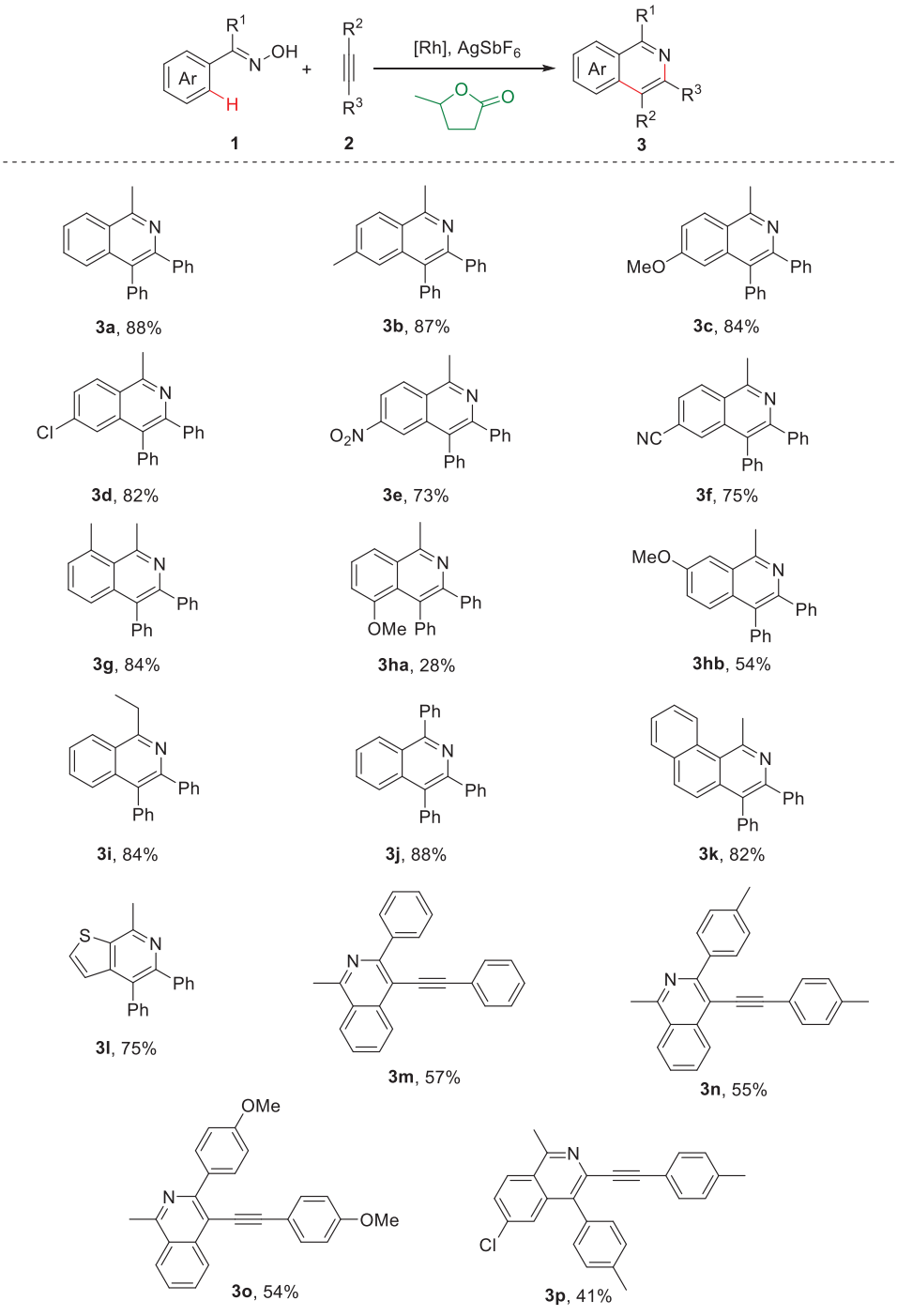
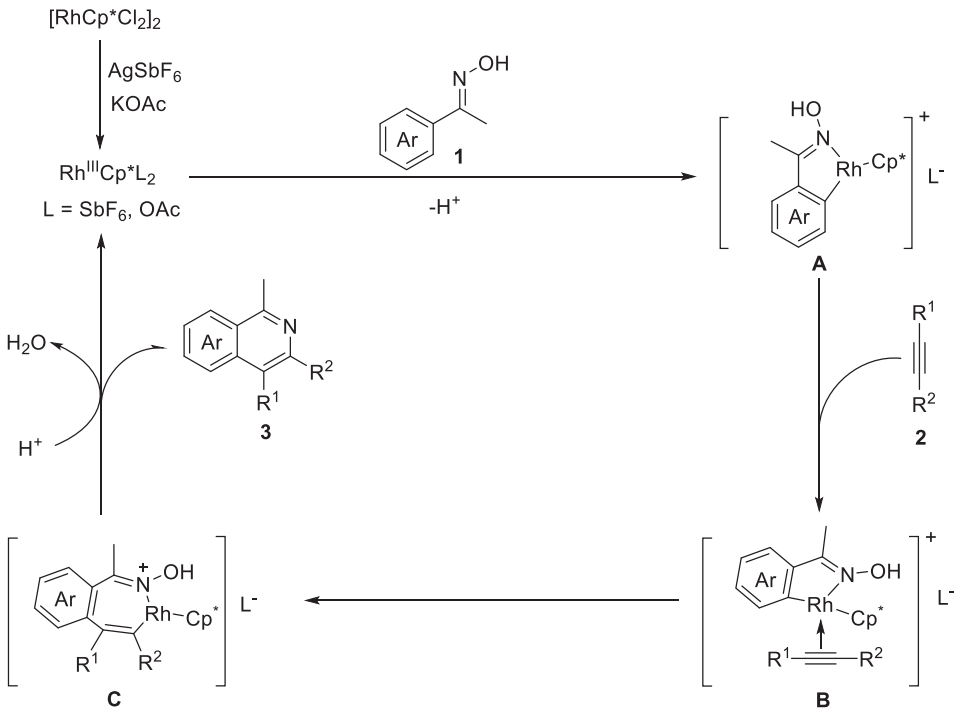


Figure 1. Reaction scope. Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), $[RhCp^*Cl_2]_2$ (2 mol%), $AgSbF_6$ (8 mol%), KOAc (0.2 equiv.), GVL (2 mL), 80 °C for 12 h in a sealed tube, isolated yields.



Scheme 2. Plausible mechanism.

11–15). On the contrary, reaction in hexafluoroisopropanol (HFIP) provided **3a** in 73% yield (entry 16). We also tried the reaction in water, while only 20% yield was obtained (entry 17). Other reaction parameters were also checked. It was found that the reaction was performed efficiently at 80 °C, while the yield dropped to 45% at 60 °C and 77% at 100 °C, respectively (entry 18).

Next, the scope of the substrates under the optimized reaction conditions was explored. Initially, a series of ketoximes were evaluated (Figure 1). Generally, acetophenone oximes containing both electron-withdrawing groups and electron-donating groups reacted with 1,2-diphenylethyne **2a** smoothly to give the desired products in good to excellent yields (**3a–3h**). For the *para*-substituted acetophenone oximes, a series of functional groups including alkyl, methoxy, chloro, nitro and cyano were tolerated well. No obvious steric hindrance effect was observed for 2-methyl-substituted acetophenone oxime. In the case of *meta*-substituted oxime, regioisomeric mixtures were obtained. The reaction occurred preferentially at the less hindered site (**3ha** and **3hb**). Other ketoximes derived from ketones such as propiophenone, benzophenone and 1-(naphthalen-1-yl)ethan-1-one also showed good reactivities, affording the corresponding products **3i–3k** in good yields. In addition, ketoxime of heterocyclic ketone also reacted smoothly to give the desired product **3l** in 75% yield. Finally, we extended the substrate **2** to 1,3-diynes. To the best of our knowledge, the formation of 3-alkynylated heterocycles from 1,3-diynes has been well documented,[41] while only one report gave the 4-alkynylated isoquinolines.[29] In the present protocol, reactions between **1a** and 1,4-diphenylbuta-1,3-diyne, 1,4-di-*p*-tolylbuta-1,3-diyne or 1,4-bis(4-methoxyphenyl)buta-1,3-diyne provided the 4-alkynylated isoquinolines **3m**, **3n** and **3o** in moderate yields

(57%, 55% and 54%, respectively). In the sharp contrast, 3-alkynylated isoquinolines **3p** was observed as the major product for 1-(4-chlorophenyl)ethan-1-one oxime.

Based on the above literatures, we proposed a mechanism for this transformation. As shown from Scheme 2, initially, rhodium catalyst coordinates to the nitrogen of the ketoxime **1**, then C–H activation occurs, presumably facilitated by OAc anion, to give the 5-membered rhodacycle **A**. The rhodacycle **A** coordinates to an equivalent of alkyne **2**, followed by migratory insertion of an alkyne to give **C**. Finally, reductive elimination delivers product **3**. Meanwhile, the catalytically active species are regenerated by the internal oxidant *via* N−O bond cleavage.

Conclusion

In summary, we have developed a Rh (III)-catalyzed synthesis of isoquinolines derivatives from *N*-hydroxyoximes and alkynes *via* C–H activation/annulation process in γ-valerolactone. The present C–H activation/annulation reaction allows the rapid formation of isoquinolines from readily available substrates. The reaction conditions are mild, and a series of functional groups were tolerated well, providing the desired products in good to excellent yields. 1,3-Diynes also show good reactivities and regioselectivities. Moreover, GVL is derived from lignocellulosic biomasses and is highly soluble in water. Thus, the use of GVL instead of conventional organic solvents as the reaction medium can ease its biodegradation and reduce its environmental impact.

Experimental

General remarks

All reagents were obtained from local commercial suppliers and used without further purification. The reaction was monitored by TLC using analytical-grade silica gel plates (GF254) under UV light. ^{1}H NMR, ^{13}C NMR and spectra were recorded at ambient temperature on a 300 NMR spectrometer (75 MHz for ^{13}C). Chemical shifts are given in parts per million (δ, ppm) and were referenced to $CDCl_3$ (7.26 or 77.0 ppm). The coupling constants J are given in Hz. Mass spectrometry was performed on an LCMS-2010 EV (Shimadzu) instrument with an ESI source. High-resolution mass spectrometry (HRMS) was performed on an Agilent 6540 Q-TOF MS instrument with an ESI source. Melting points (m.p.) are determined with an Optimelt MPA 100 apparatus and are not corrected.

General procedure for synthesis of isoquinolines

In a 10 mL of Schlenk tube equipped with a stir bar was charged with ketoxime **1** (0.2 mmol, 1.0 equiv), alkyne **2** (0.2 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (2 mol%), $AgSbF_6$ (8 mol%), KOAc (0.2 equiv.) in GVL (2 mL). The tube was sealed and the reaction mixture was stirred at 80 °C for 12 h in oil bath. After the completion of the reaction, the mixture was extracted by EtOAc and washed with water for several times. The organic layer was then dried over anhydrous Na_2SO_4, concentrated in vacuum, and the residue

was purified by flash column chromatography on silica gel with petroleum ether and EtOAc as the eluent to give the pure acridine products.

Selected data: 1-Methyl-3,4-diphenylisoquinoline (**3a**).[28] Yellow solid; m.p. 156–158 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20–8.16 (m, 1H), 7.65 (dt, $J = 6.9$, 3.5 Hz, 1H), 7.59–7.54 (m, 2H), 7.37 (d, $J = 7.4$ Hz, 2H), 7.35–7.28 (m, 3H), 7.24–7.20 (m, 2H), 7.21–7.13 (m, 3H), 3.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 149.2, 140.9, 137.4, 135.8, 131.2, 130.1, 129.8, 129.0, 128.0, 127.4, 127.0, 126.8, 126.4, 126.1, 126.0, 125.34, 22.6; MS (ESI) *m/z* 296 $[M + H]^+$.

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