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Easy Access to Isoquinolines and Tetrahydroquinolines from Ketoximes and Alkynes via Rhodium-Catalyzed C−H Bond Activation

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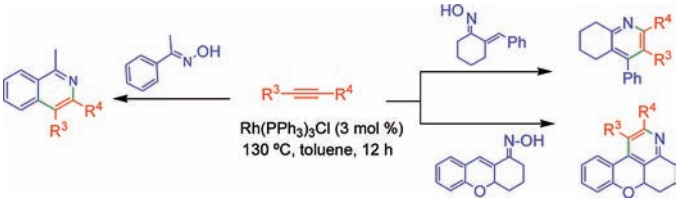

Described herein is a convenient and highly regioselective synthesis of substituted isoquinoline derivatives from various aromatic ketoximes and alkynes via a one-pot, rhodium-catalyzed C−H bond activation. In addition, tetrahydroquinoline derivatives are formed in good yields from 2-arylidene-1-cyclohexanone oximes possessing an exocyclic double bond and from tetrahydroxanthone oximes. A possible mechanism is proposed that involves chelation-assisted C−H activation via oxidative addition of Rh(I) to an *ortho*-C−H bond, insertion of the alkyne, reductive elimination, intramolecular electrocyclization, and aromatization. This mechanism is supported by isolation of the *ortho*-alkenylation products **7p** and **7q**. Also described herein is an example of an iridium-catalyzed activation of an sp^3 C−H bond.

Introduction

Isoquinoline derivatives are an important class of heterocycles and are found in many naturally occurring compounds that exhibit a variety of biological activities such as antitumor, analgesic, antihistaminic, and antifertility activities.[1] Furthermore, some isoquinoline derivatives are useful ligands in the synthesis of phosphorescent emitters for organic light-emitting diodes (OLEDs).[2] Although a number of classical methods are available for the synthesis of isoquinoline derivatives, including Bischler−Napieralski, Pomeranz−Fritsch, and Pictet−Spengler reactions,[3] these methods often suffer from tedious reaction procedures and harsh reaction conditions.

The transition-metal-catalyzed annulation reaction of 2-iodobenzaldimine or aromatic 2-iodoketimines with carbon−carbon multiple bonds is a promising method for the synthesis of isoquinoline derivatives. Initially, Heck[4] and co-workers reported a synthesis of an isoquinolinium salt from cyclopalladated benzaldimines and alkynes. Larock[5] developed a palladium-catalyzed iminoannulation of internal alkynes that leads to isoquinoline compounds, and other related catalytic reactions have been described, as well.[6] We reported an efficient nickel-catalyzed isoquinoline synthesis from alkynes and 2-iodobenzaldimines.[7] Mechanistically, this catalytic reaction proceeds via a five-membered metallacycle intermediate, and these metallacycles are further converted into various useful heterocyclic compounds.[8] In most

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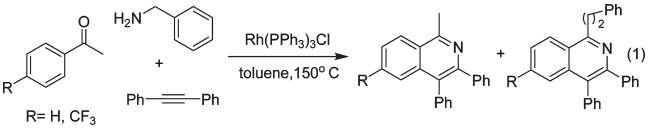
of these reactions, a carbon−halogen moiety is used to generate the reactive species. If an unreactive C−H bond could participate in such a reaction, the overall transformation would fit well with the principles of green chemistry since the use of a halogen would be avoided and less organic waste would be produced.

An alternative method for constructing the metallacycle intermediate involves the direct chelation-assisted activation of a C−H bond.[9] In these similar types of reactions, aldehyde, ketone, imine, alcohol, amine, carboxylic acid, and nitrile groups have been used as directing groups to activate an *ortho* aromatic or olefinic C−H bond.[10] Recently, several examples of using oxime as a directing group for the catalytic activation of aromatic or olefinic C−H bonds for organic synthesis catalyzed by palladium complexes were reported. In this context, Ryabov employed an oxime as a directing group for the activation of an *ortho* aromatic C−H bond using a palladium complex,[11] and Sanford described a palladium-catalyzed *O*-methyl oxime-directed activation of sp^2 and sp^3 C−H bonds followed by oxygenation with ozone and $PhI(OAc)_2$.[12] In 2006, Che reported the *ortho* amidation of an *O*-methyl oxime via a palladium-catalyzed C−H activation and subsequent nitrene insertion.[13] Recently, Yu developed a palladium-catalyzed oxidative ethoxycarbonylation of *O*-methyl oxime benzaldehyde with DEAD.[14]



In 2003, Jun demonstrated the synthesis of isoquinoline derivatives via a transition-metal-catalyzed chelation-assisted strategy.[15] In the presence of a rhodium catalyst, an aromatic ketimine reacted with an alkyne, and subsequent intramolecular electrocyclization led to an isoquinoline compound. However, the reaction was complicated by the formation of two different isoquinoline derivatives (eq 1). Recently, Ellman et al. reported the synthesis of pyridines from imines and alkynes via C−H bond activation. However, this reaction requires two steps: the formation of dihydropyridine (DHP) and the oxidation of the DHP using 10% Pd/C and air in acetic acid.[16] Very recently, Jones and co-workers described the formation of polycyclic isoquinoline salts from arylaldimines or benzo[*h*]quinoline and alkynes via C−H bond activation with rhodium complexes.[17] The reaction intermediates were isolated and well-characterized.

Our continued interest in the metal-catalyzed synthesis of heterocycles[18] via metallacycles prompted us to explore the possibility of constructing such metallacycles by the strategy of chelation-assisted C−H activation. Recently, we reported a palladium-catalyzed synthesis of functionalized fluoren-9-one derivatives from an aldoxime ether and an aryl iodide. This reaction involved two distinct steps—C−H activation and Heck-type cyclization—in one pot.[19] We also reported a rhodium-catalyzed chelation-assisted β-C−H bond activation of α,β-unsaturated ketoximes and the subsequent reaction with alkynes to afford substituted pyridine derivatives in good to excellent yields.[20] Herein, we describe the extension of this work to various oxime substrates, including aromatic ketoximes and exocyclic α,β-unsaturated cyclic ketone oximes. The present catalytic reaction provides a convenient method for the synthesis of various isoquinoline derivatives in one step in good to excellent yields without further dehydrogenation or oxidation. In addition, the ketoxime substrates are readily prepared from the corresponding ketones and hydroxyamine and are relatively stable when compared with the corresponding ketimines.

Results and Discussion

Treatment of acetophenone oxime (**1a**) with diphenylacetylene **2a** in the presence of 3 mol % of $Rh(PPh_3)_3Cl$ in toluene at 130 °C for 12 h gave isoquinoline product **3a** in 89% isolated yield. The structure of **3a** was confirmed by ^1H NMR, ^{13}C NMR, and mass spectral analysis.

To evaluate the effect of catalyst on the isoquinoline formation reaction, various rhodium complexes were investigated in the reaction of **1a** with **2a**. First, we examined the reaction in the absence of a metal catalyst. Compounds **1a** and **2a** were stirred in toluene at 130 °C for 24 h, and no **3a** was observed. Under similar reaction conditions,

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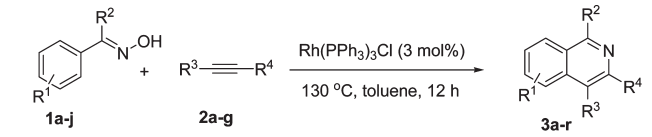
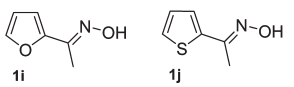
TABLE 1. Results of the Reaction of Aromatic Oximes with Alkynes[a]



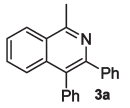
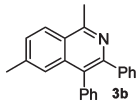
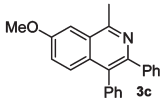
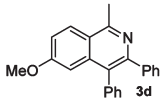
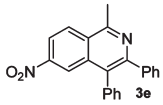
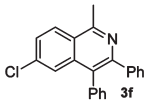
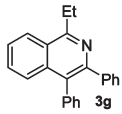
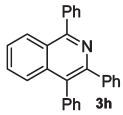
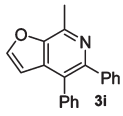
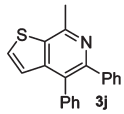
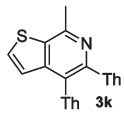
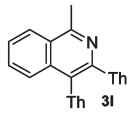
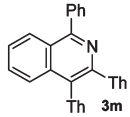
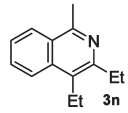
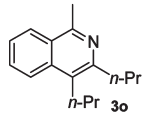
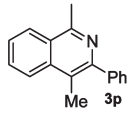
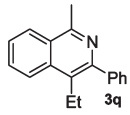
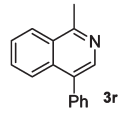
1a-j 2a-g 3a-r

1a: R^1 = H, R^2 = Me
1b: R^1 = 4-Me, R^2 = Me
1c: R^1 = 3-OMe, R^2 = Me
1d: R^1 = 4-OMe, R^2 = Me
1e: R^1 = 4-NO_2, R^2 = Me
1f: R^1 =4-Cl, R^2 = Me
1g: R^1 = H, R^2 = Et
1h: R^1 = H, R^2 = Ph

2a: R^3 = Ph, R^4 = Ph
2b: R^3 = Th, R^4 = Th
2c: R^3 = Et, R^4 = Et
2d: R^3 = *n*-Pr, R^4 = *n*-Pr
2e: R^3 = Me, R^4 = Ph
2f: R^3 = Et, R^4 = Ph



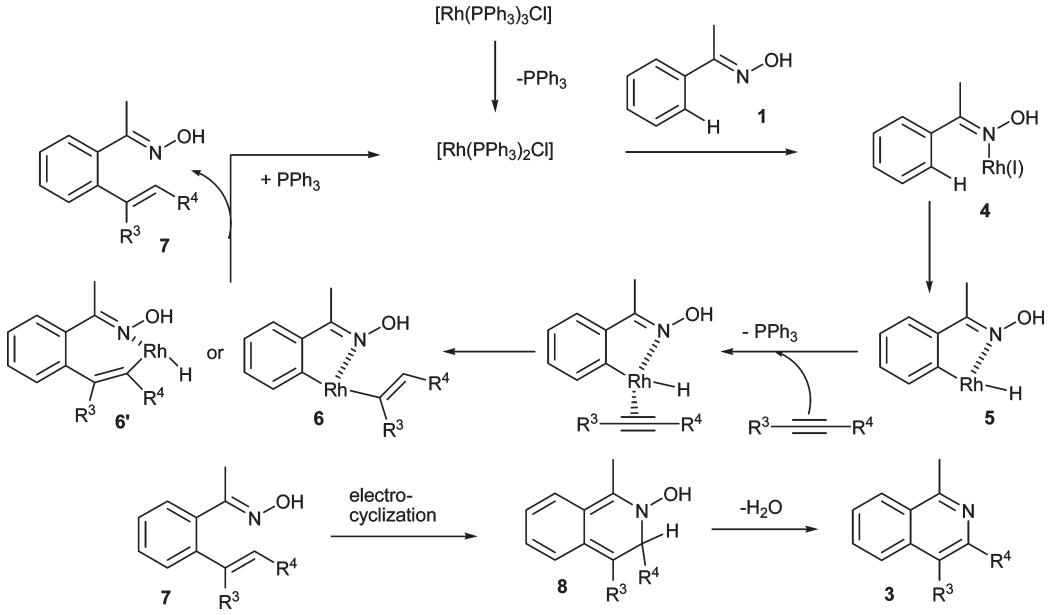
1i **1j**

Entry	Oxime **1**	Alkyne **2**	Product **3**	Yield (%)[b]
1	**1a**	**2a**	 **3a**	89
2	**1b**	**2a**	 **3b**	83
3	**1c**	**2a**	 **3c**	81
4	**1d**	**2a**	 **3d**	86
5	**1e**	**2a**	 **3e**	68
6	**1f**	**2a**	 **3f**	81
7	**1g**	**2a**	 **3g**	87
8	**1h**	**2a**	 **3h**	84
9	**1i**	**2a**	 **3i**	79
10	**1j**	**2a**	 **3j**	90
11[c]	**1j**	**2b**	 **3k**	83
12[c]	**1a**	**2b**	 **3l**	80
13[c]	**1h**	**2b**	 **3m**	78
14[d]	**1a**	**2c**	 **3n**	74
15[d]	**1a**	**2d**	 **3o**	77
16[d]	**1a**	**2e**	 **3p**	78
17[d]	**1a**	**2f**	 **3q**	74
18[d]	**1a**	 **2g**	 **3r**	45

[a]All reactions were carried out using substituted acetophenone oximes **1** (1.0 mmol), alkynes **2** (1.1 mmol), $Rh(PPh_3)_3Cl$ (3 mol %), and toluene (3.0 mL) at 130 °C for 12 h. [b]Isolated yields. [c]Th = di(2-thienyl)acetylene. [d]Reaction was carried out at 130 °C for 16 h.

$[RhCl(COD)]_2$ was an effective catalyst for the present reaction only when a monodentate phosphine ligand was employed. The use of bidendate phosphines (dppm, dppe, dppp, and dppf) or bipyridine as ligands for rhodium was unsuccessful, as were phosphine-free conditions. Of the catalyst systems with a monodentate phosphine ligand,

SCHEME 1. Proposed Mechanism for the Formation of Isoquinoline Derivatives



$[RhCl(COD)]_2/4P(Cy)_3$ gave **3a** in 38% yield, while $[RhCl(COD)]_2/4P(furyl)_3$, and $[RhCl(COD)]_2/4PPh_3$ afforded **3a** in 16 and 57% yields, respectively. Wilkinson's catalyst ($Rh(PPh_3)_3Cl$) proved to be the most effective, forming isoquinoline product **3a** in 89% isolated yield.

To evaluate the scope of the present catalytic isoquinoline formation, we examined the reactions of several substituted acetophenone oximes (**1b**−**j**) with various alkynes (**2b**−**h**) under optimized reaction conditions (Table 1). 4-Methylacetophenone oxime **1b** underwent C−H activation and the subsequent electrocyclization reaction effectively with **2a**, affording isoquinoline derivative **3b** in 83% yield (entry 2). Interestingly, electron-donating 3-methoxy- and 4-methoxyacetophenone oximes **1c** and **1d** reacted nicely with **2a** to give **3c** and **3d** in 81 and 86% yields (entries 3 and 4). In the reaction of 3-methoxyacetophenone oxime, there are two possible C−H bond activation sites at C2 and C6 of **1c**, but the C−H activation occurs only at C6 likely due to the steric effect of the methoxy group at C3. In a similar manner, 4-nitro- and 4-chloroacetophenone oximes **1e** and **1f** gave isoquinoline derivatives **3e** and **3f** in 68 and 81% yields, respectively (entries 5 and 6). The effect of changing the methyl group in acetophenone oxime **1a** to other substituents on the product yield was also investigated. Thus, propiophenone oxime **1g** and benzophenone oxime **1h** reacted with **2a** to provide **3g** and **3h** in 87 and 84% yields, respectively (entries 7 and 8).

The scope of the catalytic reaction was extended to heterocyclic ketoximes **1i** and **1j**. Treatment of 2-acetylfuran oxime **1i** with alkyne **2a** gave furo[2,3-*c*]pyridine derivative **3i** in 79% yield (entry 9). Similarly, reaction of 2-acetylthiophene oxime **1j** with **2a** or with **2b** afforded thieno[2,3-*c*]-pyridine derivatives **3j** and **3k** in 90 and 83% yields, respectively (entries 10 and 11).

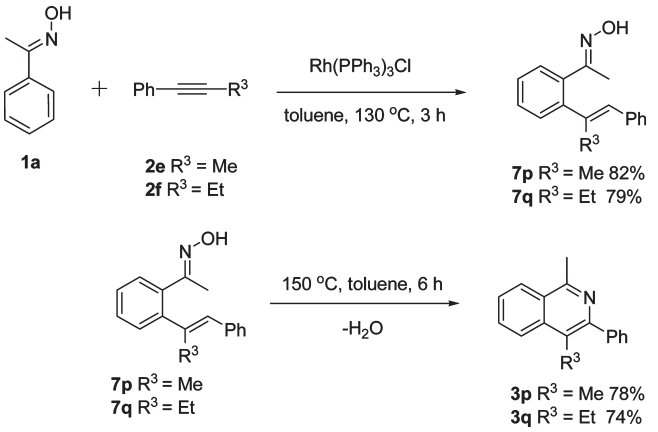
In addition to **2a**, other symmetrical alkynes (**2b**−**d**) were also tested for the C−H activation and electrocyclization reaction. Thus, the reaction of di(2-thienyl)acetylene **2b** with **1a** and **1f** gave 3,4-di(2-thienyl)isoquinoline derivatives **3l** and **3m** in 80 and 78% yields, respectively (entries 12 and 13). Likewise, treatment of hex-3-yne (**2c**) and oct-4-yne (**2d**) with **1a** provided the corresponding isoquinoline products **3n** and **3o** in 74 and 77% yields, respectively (entries 14 and 15). It is noteworthy that the reaction of benzaldoxime with diphenylacetylene in the presence of 3 mol % of $Rh(PPh_3)_3Cl$ in toluene at 130 °C for 12 h did not give the expected isoquinoline product. Further studies are required to understand the reaction.[21]

This cyclization appears to be highly regioselective, and to understand this regioselectivity, unsymmetrical alkynes were used as substrates for the reaction with **1a**. Thus, 1-phenyl-1-propyne (**2e**) underwent cyclization with **1a** at 130 °C for 16 h to give **3p** in 78% yield (entry 16), and no other regioisomeric product was detected in the reaction mixture. The regiochemistry of product **3p** was confirmed by NOE experiments. Similar regioselectivity was observed in the reaction between 1-phenyl-1-butyne (**2f**) and **1a**, forming product **3q** in 74% yield (entry 17). Encouraged by these results, terminal alkyne **2g** was tested in the reaction with **1a**, and product **3r** was isolated in 45% yield. Although the reaction gave a relatively low yield of the expected product (due to the competitive cyclotrimerization of **2g**), we observed only the regioisomer in which the phenyl substituent is located at C-4 of the isoquinoline moiety (entry 18). The regiochemistry of product **3r** was established by comparing its ^1H NMR spectrum with that of the other regioisomer of **3r** prepared according to a previous method.[7] The observed different regiochemistry of products **3p**−**r** from **1a** and unsymmetrical alkynes is interesting but difficult to explain. It is likely related to the selection of insertion of alkyne into Rh−H or Rh−C bonds and the subsequent reductive elimination (see Scheme 1).

On the basis of known metal-catalyzed, directing-group-assisted C−H bond activation and cyclization reactions,[1,4,7,8]

(21) Park, S.; Choi, Y.-A.; Han, H.; Yang, S. H.; Chang, S. *Chem. Commun.* **2003**, 1936.

SCHEME 2. Synthesis and Electrocyclization of Addition Products 7



a plausible mechanism for the present rhodium-catalyzed cyclization of acetophenone oxime (**1a**) with alkyne **2** is outlined in Scheme 1. The first step likely involves coordination of the nitrogen atom of oxime group of **1a** to the rhodium metal center, followed by oxidative addition of an *ortho* aromatic C−H bond to the metal to form hydrometallacycle **5**. Coordinative *syn* insertion of alkyne **2** to the rhodium−hydride or rhodium−carbon bond of intermediate **5** gives **6** or **6′**, respectively. Subsequent reductive elimination of **6** or **6′** gives the addition product **7** and regenerates the catalyst. Compound **7** then undergoes 6π-electrocyclization and elimination of water to give product **3**.

The proposed formation of intermediate **7** is strongly supported by the isolation of reaction intermediates **7p** and **7q** from the reactions of acetophenone oxime with 1-phenyl-1-propyne and 1-phenyl-1-butyne, respectively (Scheme 2). Intermediate **7p** was isolated in 82% yield from the reaction of **1a** with **2e** in the presence of 3 mol % of $Rh(PPh_3)_3Cl$ in toluene at 130 °C for 3 h. The *E* stereochemistry of the *ortho*-alkenylation products **7p** and **7q** was confirmed by NOE experiments. In addition, the structure of **7p** was determined by single-crystal X-ray diffraction. Furthermore, reaction intermediate **7p** underwent electrocyclization and elimination of water in toluene at 150 °C for 6 h to give **3p** in 78% yield (Scheme 2). In a similar manner, **7q** also underwent electrocyclization and elimination of water to afford **3q** in 74% yield.

The C−H activation of α-tetralone oxime also proceeded smoothly (Scheme 3). Thus, the reaction of α-tetralone oxime **1k** with diphenylacetylene (**2a**) in the presence of 3 mol % of $Rh(PPh_3)_3Cl$ in toluene at 130 °C for 12 h provided the cyclization product **3s** in 94% yield.

The scope of the present rhodium-catalyzed C−H activation reaction can also be applied to ketoximes possessing an exocyclic double bond and to tetrahydroxanthone oximes. The results are summarized in Table 2. Treatment of 2-arylidene-1-cyclohexanone oxime (**4a**) with diphenylacetylene (**2a**) in the presence of 3 mol % of $Rh(PPh_3)_3Cl$ in toluene at 130 °C for 5 h afforded tetrahydroquinoline derivative **5a** in 83% yield (entry 1). Under similar reaction conditions, **4a** reacted with hex-3-yne (**2c**) to give tetrahydroquinoline **5b** in 74% yield (entry 2). However, the reaction of unsymmetrical alkyne 1-phenyl-1-propyne (**2e**) with **4a** provided two regioisomeric products **5c** and **5c′** in 43 and

SCHEME 3. C−H Activation of α-Tetralone Oxime

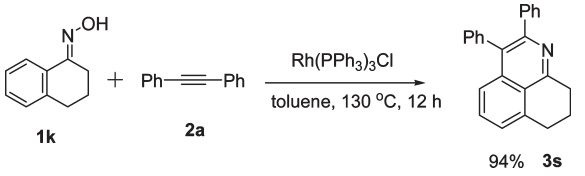
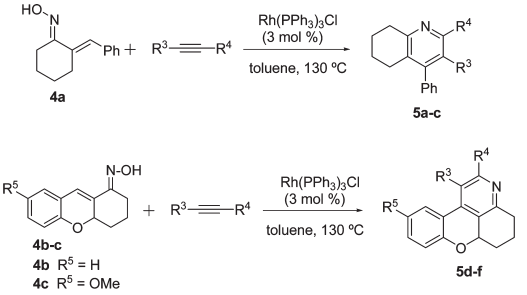
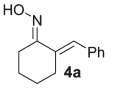
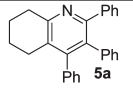
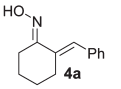
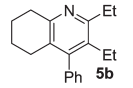
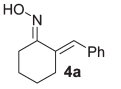
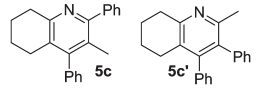
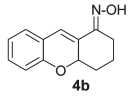
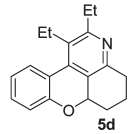
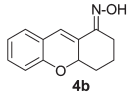
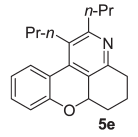
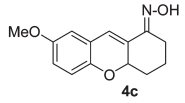
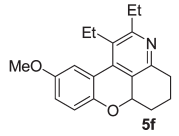


TABLE 2. Results of the Reaction of Ketoximes Possessing an α-Exocyclic Double Bond with Alkynes[a]



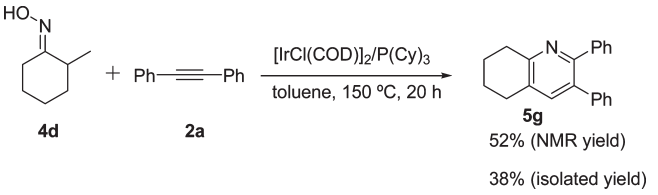
Entry	Oxime **1**	Alkyne **2**	Product **3**	Yield (%)[b]
1		**2a**		83
2[c]		**2c**		74
3[c]		**2e**		43/41
4		**2c**		76
5[c]		**2d**		72
6[c]		**2c**		70

[a]All reactions were carried out using oximes **4** (1.0 mmol), alkynes **2** (1.1 mmol), $Rh(PPh_3)_3Cl$ (3 mol %), and toluene (3.0 mL) at 130 °C for 6 h. [b]Isolated yields. [c]Reaction was carried out at 130 °C for 8 h.

41% yield, respectively (entry 3). The result contrasts with the high regioselectivity that is observed in the formation of isoquinoline **3n** from oxime **1a** and alkyne **2e** but is similar to the regiochemistry observed in the reaction of α,β-unsaturated ketoxime with alkyne **2e**.[20]

Tetrahydroxanthone oxime **4b** also undergoes C−H activation by $Rh(PPh_3)_3Cl$ at the β-carbon of the exocyclic

SCHEME 4. Result of the sp^3 C−H Bond Activation of 2-Methylcyclohexanone Oxime (4d)



double bond. Oxime **4b** reacted with alkynes **2c** and **2d** in the presence of $Rh(PPh_3)_3Cl$ to give the expected cyclization products **5d** and **5e** in 76 and 72% yields, respectively (entries 4 and 5). Similarly, tetrahydroxanthone oxime **4c**, which bears a methoxy group on the aromatic ring, reacted smoothly with **2c** to afford **5f** in 70% yield (entry 6).

In addition to the oxime-assisted sp^2 C−H bond activation by rhodium complexes, we also investigated the activation of sp^3 C−H bonds by rhodium and iridium complexes. However, when 2-methylcyclohexanone oxime (**4d**) was treated with diphenylacetylene (**2a**) in the presence of $Rh(PPh_3)_3Cl$ (3 mol %) in toluene at 150 °C for 20 h, only a trace amount of cyclization product **5g** was observed. After extensive optimization studies that examined different metal complexes (see the Supporting Information), we identified $[IrCl(COD)]_2/P(Cy)_3$ as an effective catalyst for the sp^3 C−H activation of **4d** under the same reaction conditions (toluene at 150 °C for 20 h) used above. The tetrahydropyridine derivative **5g** was obtained in 52% yield by ^1H NMR and was isolated in 38% yield (Scheme 4). While the mechanism for the formation of **5g** is not clear, it is likely that oxime-group-assisted sp^3 C−H activation by the iridium complex is involved, followed by dehydrogenation and other catalytic steps similar to those shown in Scheme 1. It should be noted that examples of sp^3 C−H activation by metal complexes are abundant,[22] but the application of such methodologies to give useful organic compounds catalytically is less common.

Conclusion

We have successfully developed a novel and convenient method for the synthesis of isoquinoline and tetrahydroquinoline derivatives via a sequence that involves rhodium-catalyzed C−H activation followed by 6π-electrocyclization and aromatization in one pot. The catalytic reaction is highly regioselective with unsymmetrical alkynes. The approach was also used for the sp^3 C−H activation and cyclization catalyzed by an iridium complex. Further studies toward the sp^3 C−H activation and the formation of different carbon−heteroatom bonds are in progress as is application of this methodology in the context of total synthesis.

Experimental Section

A few representative experimental procedures are listed below. Full experimental procedures and spectroscopic data for all compounds can be found in the Supporting Information.

General Procedure for the Synthesis of Isoquinoline Derivatives. A sealed tube containing $Rh(PPh_3)_3Cl$ (0.030 mmol, 3.0 mol %) was evacuated and purged with nitrogen gas three times. Freshly distilled toluene (2.0 mL), ketoxime (1.00 mmol), and alkyne (1.10 mmol) were sequentially added to the system, and the reaction mixture was allowed to stir at 130 °C for 12 h. The mixture was filtered through a short Celite pad and washed with dichloromethane several times. The filtrate was concentrated, and the residue was purified on a neutral silica gel column using hexanes/ethyl acetate as eluent to afford the isoquinoline derivative **3**.

1-Methyl-3,4-diphenylisoquinoline (3a):. White solid; mp 174−176 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20−8.18 (m, 1 H), 7.65−7.56 (m, 3 H), 7.37−7.16 (m, 10 H), 3.06 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 149.4, 141.0, 137.5, 136.0, 131.3, 130.2, 129.9, 129.1, 128.1, 127.5, 127.0, 126.9, 126.5, 126.2, 126.1 125.5, 22.7; HRMS calcd for $C_{22}H_{17}N$ 295.1361, found 295.1355.

1,6-Dimethyl-3,4-diphenylisoquinoline (3b):. Pale yellow solid; mp 158−160 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 9.0 Hz, 1 H), 7.41 (s, 1 H), 7.39 (d, J = 9.0 Hz, 1 H), 7.33−7.31 (m, 5 H), 7.20−7.14 (m, 5 H), 3.03 (s, 3 H), 2.41 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 149.3, 140.8, 140.3, 137.6, 136.2, 131.4, 130.2, 128.7, 128.1, 127.5, 127.0, 126.8, 125.5, 125.0, 124.5, 22.5, 22.1; HRMS calcd for $C_{23}H_{19}N$ 309.1517, found 309.1520.

1-Methyl-4-phenylisoquinoline (3r):. Brownish viscous oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1 H), 8.17 (d, J = 7.6 Hz, 1 H), 7.88 (d, J = 7.6 Hz, 1 H), 7.64−7.59 (m, 2 H), 7.52−7.44 (m, 5 H), 3.00 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 141.5, 137.3, 134.3, 131.9, 130.1, 130.0, 128.5, 127.7, 126.8, 125.8, 125.4, 22.5; HRMS calcd for $C_{16}H_{13}N$ 219.1048, found 219.1042.

Acknowledgment. We thank the National Science Council of Republic of China (NSC 95-2119-M-007-005) for support of this research.

Supporting Information Available: General experimental procedure and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

(22) Metal-catalyzed sp^3 C−H bond activation: (a) Lin, M.; Sen, A. *Nature* **1994**, *368*, 613. (b) Jun, C.-H.; Hwang, D.-C.; Na, S.-J. *Chem. Commun.* **1998**, 1405. (c) Jun, C.-H.; Lee, H.; Park, J.-B.; Lee, D.-Y. *Org. Lett.* **1999**, *1*, 2161. (d) Chatani, N.; Asaumi, T.; Ikeda, T.; Yorimitsu, S.; Ishii, Y.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **2000**, *122*, 12882. (e) Kalyani, D.; Deprez, N. R.; Desai, L. V.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 7330. (f) Li, Z.; Li, C.-J. *J. Am. Chem. Soc.* **2005**, *127*, 3672. (g) Catino, A.; Nichols, J. M.; Nettles, B. J.; Doyle, M. P. *J. Am. Chem. Soc.* **2006**, *128*, 5648. (h) Requejo, M. M. D.; Disalvo, D.; Brookhart, M. *J. Am. Chem. Soc.* **2003**, *125*, 2038. (i) Ray, A.; Zhu, K.; Kissin, Y. V.; Cherian, A. E.; Coates, G. W.; Goldman, A. S. *J. Am. Chem. Soc.* **2006**, *128*, 5648. (j) Alt, H. G.; Bohmer, I. K. *Angew. Chem., Int. Ed.* **2008**, *47*, 2619.