ORGANIC LETTERS

2012
Vol. 14, No. 16
4166–4169

Rhodium(III)- and Ruthenium(II)-Catalyzed Olefination of Isoquinolones

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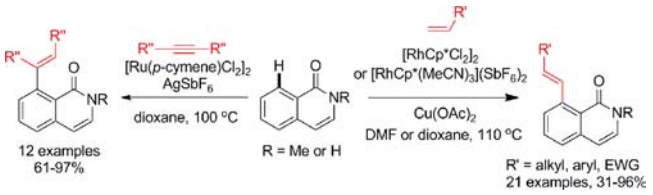
Received July 5, 2012

ABSTRACT



NH and N-protected isoquinolones undergo Rh(III)-catalyzed oxidative olefination at the 8-position. Complementary redox-neutral olefination of such isoquinolones using internal alkynes was achieved under ruthenium catalysis.

Transition-metal-catalyzed C−H bond activation followed by oxidative functionalization with alkenes (the Fujiwara−Moritani reaction) has emerged as a powerful alternative to the traditional Heck coupling for a new C−C bond formation.[1] The power of this reaction has been elegantly demonstrated in many new reactions as well as in the total synthesis of natural products.[2] Palladium catalysts undoubtedly predominate among the transition metals for this type of transformation,[3] although other metals such as ruthenium have also been reported.[4] In the olefination of aryl C−H bonds, two categories of arene substrates have been reported. Electron-rich (hetero)arenes (such as indoles)[5] and arenes bearing acidic C−H bonds (such as polyfluoronated benzenes)[6] are reactive and undergo C−H olefination without chelation assistance. In contrast, when the arene ring is not activated, a directing group is usually necessary to assist the C−H activation.[7] In addition to oxidative olefination, redox-neutral olefination

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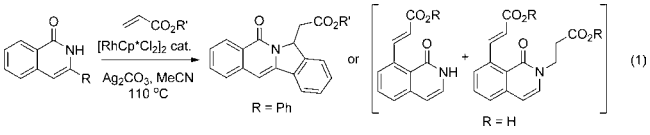
10.1021/ol3018352
Published on Web 07/31/2012

of C−H bonds under chelation assistance via hydroarylation of internal alkynes have also been developed using ruthenium,[8] rhodium,[9] iridium,[10] rhenium,[11] and palladium[12] catalysts. This represents a green process that can complement the oxidative C−H olefination process because no oxidant is needed and trisubstituted olefin products are generated. Despite the success, the substrate scope remains limited and it is necessary to develop new catalyst systems in both the oxidative and redox-neutral olefination of C−H bonds.

Recently, rhodium(III)-catalyzed C−H activation leading to C−E (E = C, O, and N) bond formation has attracted much attention due to the high efficiency, selectivity, and functional group tolerance.[13] In most cases, Rh(III)-catalyzed C−H olefination requires substrates bearing nitrogen and oxygen directing groups as in pyridines,[14] amides,[15] oximes,[16] sulfonamides,[17] carboxylic acids,[18] ketones,[19] aldehydes,[20] carbamates,[21] and esters.[20,22] While in most cases terminal olefins have been applied, active internal olefins are occasionally viable substrates.[23]

We recently reported the oxidative olefination of NH isoquinolones bearing a 3-aryl group catalyzed by $[RhCp^*Cl_2]_2$.[23a] The olefination using acrylates occurred at the *ortho* position of the 3-aryl group, followed by intramolecular aza-Michael cyclization, leading to γ-lactams (eq 1). However, both substrates are limited and poor selectivity was achieved for simple NH isoquinolones. For example, the oxidative coupling of acrylates with simple NH isoquinolones afforded a mixture of olefination and olefination−aza-Michael addition products.[15b] Thus it is necessary to develop a more general method for the olefination of isoquinolones using alkenes and alkynes.



(1)

We initiated our studies with the screening of the olefination of NH isoquinolone **1a** using simple styrene. Although essentially no coupling occurred under our previously employed conditions (eq 1), efficient olefination at the 8- position was achieved even under a slightly lower loading of the $[RhCp^*Cl_2]_2$ (3 mol %) catalyst when the oxidant was switched to $Cu(OAc)_2 \cdot H_2O$ in DMF. Under these conditions (Conditions A, Scheme 1), product **2aa** was isolated in 75% yield.

The scope and limitations of this olefination reaction were next explored (Scheme 1). Different olefins were first allowed to react with NH isoquinolone **1a** under the optimized conditions. Styrenes bearing electron-donating and -withdrawing *para* substituents such as Me, Cl, and OMe are viable coupling partners, and products **2aa**−**2ae** were isolated in 71−85% yield. In addition, 2-vinylnaphthlene reacted with **1a** in comparably high yield. In contrast, 1-vinylnaphthlene showed a somewhat lower reactivity (**2ag**), likely due to steric hindrance. Simple aliphatic olefins are much less reactive; thus essentially no coupling proceeded between **1a** and 1-hexene. However, vinylcyclohexane gave a reactivity lying between styrenes and 1-hexene, and product **2ai** was isolated in 41% yield. The C=C unit in the olefin is not limited to C-substitution, and *N*-vinylphthalimide reacted with **1a** to give **2ah** in 61% yield.

We reasoned that since the 3- and 4-substituents in the isoquinolone ring are distal to both the C(8)−H bond and to the oxygen directing group, substituents at these positions should be tolerated. Indeed, when different 3-alkyl, -cyclopropyl, and -silyl groups were introduced into the isoquinolone ring, the coupling with styrene proceeded with high efficiency and products **2ba**−**2ea** were isolated in high yields (83−96%). In contrast, when NH isoquinolones bearing dialkyl substituents at the 3- and 4- positions were applied as substrates, somewhat sluggish couplings with simple styrene were observed, and **2fa** was isolated in 46% yield.

Introduction of a 3-subsitituent in an NH isoquinolone should offer steric protection and suppress an aza-Michael reaction (eq 1), leading to higher selectivity. To prove this hypothesis, the coupling of 3-*n*-propylisoquinolone with *n*- and *tert*-butyl acrylates was carried out. Indeed, products

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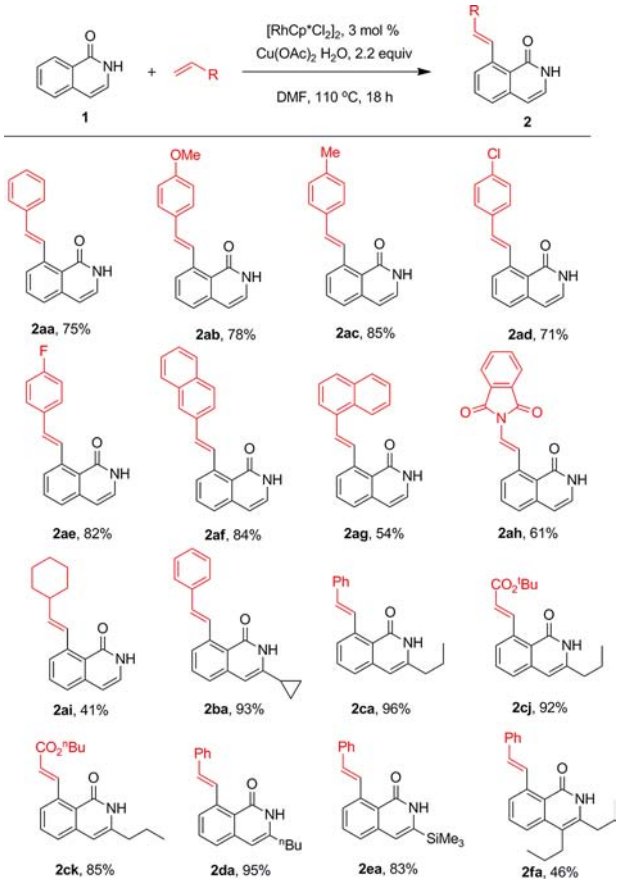
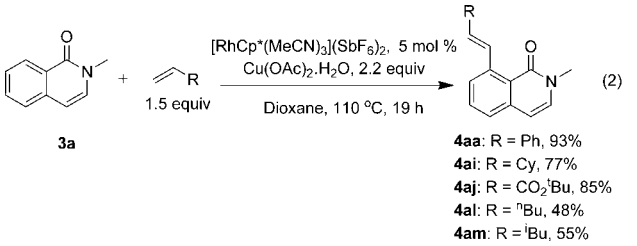
2cj and **2ck** were isolated in high yields. Surprisingly, no clean reaction and no identifiable product were obtained when the acrylate ester was extended to methyl and benzyl acrylates. It is possible that these two acrylates bear a more reactive ester group and side reactions such as nucleophilic attack of the NH group impede this coupling system.

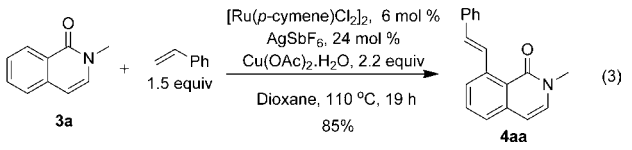
Scheme 1. Oxidative Olefination of Isoquinolones[a,b]



[a] Conditions: isoquinolone (0.30 mmol), olefin (0.45 mmol), $[RhCp^*Cl_2]_2$ (3 mol %), DMF (2 mL), under nitrogen, 110 °C, 18 h. [b]Isolated yield.

To expand the scope of the isoquinolone substrate, *N*-protected isoquinolones such as *N*-methylisoquinolone (**3**) were next applied. In contrast to the facile olefination of NH isoquinolones, the coupling of **3** with styrene failed under Conditions A. By switching to a cationic catalyst $[RhCp^*(MeCN)_3](SbF_6)_2$ (6 mol %) in 1,4-dioxane (Conditions B), product **4aa** was isolated in high yield (eq 2). This observation agrees with previous reports, where, in the olefination of arenes bearing a protic directing group, neutral $[RhCp^*Cl_2]_2$ suffices, while, for arenes bearing neutral nitrogen or oxygen directing groups, cationic Rh(III) catalysts are often the choice.[14−23] Under these new conditions, the olefin substrates were extended to less reactive ones. In contrast to the low-yielding coupling of NH isoquinolone with vinylcyclohexane (Conditions A), switching to the *N*-methyl protected one allowed efficient coupling under Conditions B and product **3ai** was isolated in 77% yield. Although 1-hexene and 4-methyl-1-pentene are much less reactive in olefination reactions, their coupling with *N*-methylisoquinolone was still achieved in 48% and 55% yield, respectively. In all cases, no isomerization of the C=C bond in the product was observed. It should be noted that only a few reports documented the rhodium(III)-catalyzed olefination of arenes using unactivated alkenes.[15a,17,24] Recent examples have shown that ruthenium(II) catalysts can compliment or parallel rhodium catalysts in the oxidative C−H functionalization of arenes.[25] Our studies on the coupling of *N*-methyl isoquinolone with styrene showed that an efficient coupling could be achieved but only with a rather high loading of the $[Ru(p\text{-cymene})Cl_2]_2/AgSbF_6$ catalyst (6 mol %/24 mol %), under which conditions product **4aa** was isolated in 85% yield (eq 3). These results suggest that the rhodium catalyst is more efficient for oxidative olefination of isoquinolones.





To further probe the C−H activation process, H/D exchange studies were carried out. When **1a** was subjected to the conditions with the $[RhCp^*(MeCN)_3](SbF_6)_2$ catalyst and a stoichiometric amount of $Cu(OAc)_2 \cdot H_2O$ in methanol-d_4 (110 °C, 16 h), the starting material is 73% deuterated at the C(8) position, indicative of reversible C(8)−H activation.

In addition to oxidative C—H olefination, redox-neutral olefination using alkynes has also been explored. While olefination of **3a** with PhC≡CPh catalyzed by $[RhCp^*Cl_2]_2/AgSbF_6$ in the presence of HOAc only afforded products **5aa** in 45% isolated yield, a high yield of **5aa** was obtained when the catalyst was switched to an iridium(III) or a ruthenium(II) catalyst (eq 4). Given the low cost of the ruthenium catalyst, the $[Ru(p\text{-cymene})Cl_2]_2/AgSbF_6$ system was retained for further studies and

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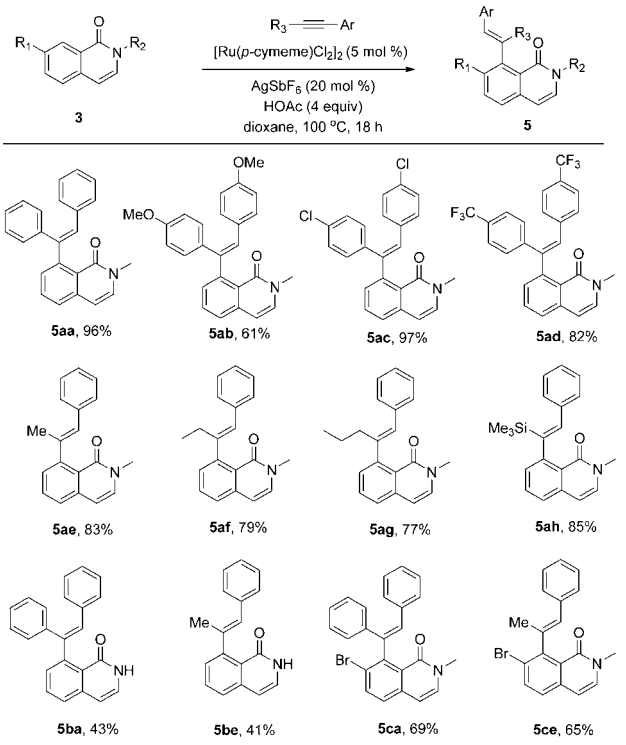
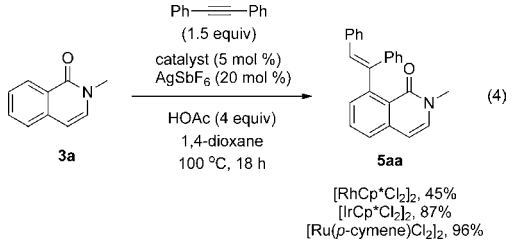
Scheme 2. Hydroarylation of Alkynes[a,b]



[a] Conditions: isoquinolone (0.3 mmol), alkyne (0.45 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %), $AgSbF_6$ (0.06 mmol, 20 mol %), HOAc (1.2 mmol), dioxane (3 mL), 100 °C, 16 h. [b] Isolated yield.

this catalyst system has been reported in the olefination of tertiary amides.[8e]



(4)

Under these optimized conditions, **3a** smoothly coupled with a series of aryl-substituted internal alkynes, and the corresponding products **5aa**–**5ag** were isolated in good to high yields (61–97%, Scheme 2), although electron-rich alkynes tend to give a lower reactivity (**5ab**). In the case of aryl- and alkyl-substituted nonsymmetrical alkynes, in the ^{1}H NMR spectra of these products derived from nonsymmetrical alkynes, the olefinic CH resonates as a single signal, consistent with the distal trans orientation of the olefinic CH and the alkyl group as given in Scheme 2, and this regioselectivity is in line with literature reports[8e] where the aryl group is distal to the C(8) position. Of note, the coupling of a sterically hindered alkyne PhC≡C$SiMe_3$ is also well-tolerated and the regiochemistry of the product **5ah** was confirmed by NOESY spectroscopy. Steric hindrance and a halogen group in the isoquinolone are also tolerated as indicated by the isolation of **5ca** and **5ce** in good yields. In addition to *N*-protected isoquinolones, NH isoquinolones can be olefinated albeit with lower efficiency. In contrast, no coupling was achieved when dialkyl substituted alkynes were applied.

In summary, we have achieved the effective oxidative olefination of both NH and *N*-methyl isoquinolones at the 8- position via a rhodium(III)-catalyzed C–H activation pathway using copper acetate as a convenient oxidant. A neutral RhCp* complex is an efficient catalyst for the olefination of NH isoquinolones, while a cationic RhCp* complex proved necessary for the olefination of *N*-methylisoquinolone. A broad scope of both coupling partners has been established, and unactivated olefins are viable coupling partners in some cases. Furthermore, ruthenium-catalyzed efficient C–H olefination of the same isoquinolones has been realized using internal alkynes. These methods may find applications in the synthesis of useful complex heterocycles.

Acknowledgment. We thank the Dalian Institute of Chemical Physics, Chinese Academy of Sciences for financial support.

Supporting Information Available. Detailed synthetic procedures and characterization data of all new products. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.