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Oxidative Alkenylation/Annulation of Benzimidates *via* Ruthenium(II)-Catalyzed C–H Activation to Generate 3-Methyleneisoindolin-1-ones

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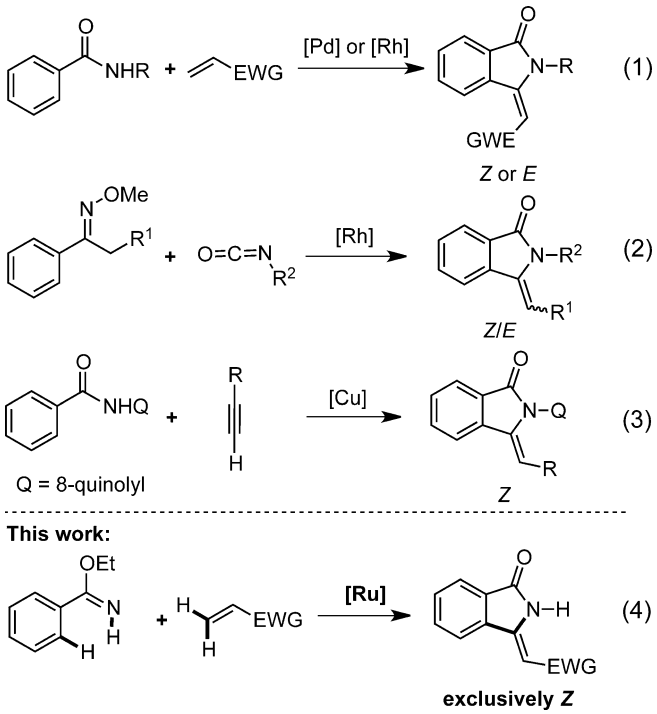
Abstract: A novel ruthenium-catalyzed oxidative alkenylation/annulation cascade reaction is described for synthesizing 3-methyleneisoindolin-1-ones. In the protocol, the *N*–H imidate is applied efficiently as a directing group in ruthenium-catalyzed C–H activation, generating various 3-methyleneisoindolin-1-ones with high regio- and stereoselectivity in moderate to good yields.

Keywords: alkenes; annulation; cascade reaction; C–H activation; ruthenium

The oxidative alkenylation/annulation cascade reaction involving transition metal-catalyzed C–H activation has emerged as a highly attractive tool for constructing useful heterocycles because it avoids the need for prefunctionalized starting materials.[1,2] Reactions based on this transformation type usually require appropriate directing groups, transition metals as the catalysts and stoichiometric amounts of external oxidants in order to achieve C–H regioselectivity and good reactivity.[1,2] A broad range of directing groups, including amides,[3] carboxy,[4] hydroxy,[5] triflamide,[6] amidine[7] and acetophenone moieties,[8] have been tested in these reactions. The *N*–H imidate was reported by Glorius in 2013 as a novel directing group in C–H activation,[9] but it has not yet to be tested in the oxidative alkenylation/annulation cascade reaction.

The 3-methyleneisoindolin-1-one nucleus is a key structural motif found in various natural products, pharmaceutically relevant molecules and intermediates in the synthesis of complex molecules.[10] The diverse biological properties of molecules containing a 3-methyleneisoindolin-1-one nucleus, including antihypertensive,[11] antipsychotic,[12] anesthetic,[13] sedative,[14] antiulcer,[15] antiviral,[16] and antileukemic[17] activities, have made 3-methyleneisoindolin-1-ones of great interest in synthetic organic chemistry.[18]

Of the various methods to synthesize 3-methyleneisoindolin-1-ones,[18] the Rh- or Pd-catalyzed oxidative alkenylation/annulation cascade reaction is often used to convert aromatic amides into 3-methyleneisoindolin-1-one derivatives [Scheme 1, Eq. (1)].[19,20] In 2013, Li developed an Rh(III)-catalyzed annulation of aryl ketone *O*-methyl oximes and isocyanates to generate



Scheme 1. Methods for synthesizing 3-methyleneisoindolin-1-ones based on C–H activation.

3-methyleneisoindolin-1-ones with moderate stereoselectivity [Scheme 1, Eq. (2)].[21] More recently, the copper-mediated tandem coupling/annulation of arenes and terminal alkynes with the assistance of 8-aminoquinoline has been disclosed by You [Scheme 1, Eq. (3)].[22]

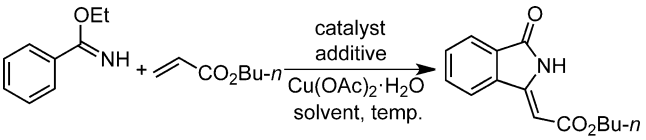
Using an *N*–H imidate as the directing group, we report here the Ru(II)-catalyzed oxidative alkenylation/annulation cascade reaction between benzimidates and alkenes *via* C–H activation.[23] This new protocol generates 3-methyleneisoindolin-1-ones with high regio- and stereoselectivity [Scheme 1, Eq. (4)].

Initially, ethyl benzimidate (**1a**) was treated with *n*-butyl acrylate (**2a**) in the presence of $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%) and $Cu(OAc)_2{\cdot}H_2O$ (2.2 equiv.) in toluene at 80 °C for 6 h. We were pleased to obtain the desired 3-methyleneisoindolin-1-one product **3a** in 16% isolated yield (Table 1, entry 1). Numerous other ruthenium catalysts, including $RuH_2(CO)(PPh)_3$, $RuCl_2(PPh_3)_3$, $Ru(OAc)_2(PPh_3)_3$, and $CpRuCl(PPh_3)_2$ showed little or no activity in this transformation (entries 2–5). Therefore we used $[RuCl_2(p\text{-cymene})]_2$ as the catalyst to investigate various solvents (entries 6–10). DCE and $CHCl_3$ performed well, while $(CHCl_2)_2$ gave the highest product yield of 54%. Extending the reaction time to 12 h improved the yield to 61% (entry 11). Using $AgSbF_6$ or NH_4PF_6 as additive reduced the yield of product **3a**, whereas using AgOAc increased the yield to 67% (entries 12–14). Replacing AgOAc with KPF_6 further increased the yield to 73% (entry 15), but the reason for this cation effect is not clear at the current stage. Scaling up the reaction proved straightforward (entry 16). Lowering the temperature or reducing the catalyst loading sharply reduced the yield (entries 17 and 18).

Once we had established the optimal reaction conditions for this Ru-catalyzed oxidative alkenylation/annulation cascade reaction, we explored the scope of the substrates (Table 2). For alkenes **2**, various acrylates bearing a range of different alkyl groups (1°, 2° and 3°) worked well in this reaction to produce the corresponding products **3a–3g** in moderate to good yield (61–74%). In fact, using phenyl acrylate gave an acceptable 56% yield of the corresponding product **3h**. Methyl vinyl ketone also reacted well in the cascade reaction, giving the product **3i** in 59% yield. To our delight, treating **1a** with *N*-benzylacrylamide furnished the corresponding product **3j**, albeit in relatively low yield. Moreover, diethyl vinylphosphonate could also be successfully employed in this transformation and gave the annulated product **3k** in 55% yield. However, terminal alkenes such as 1-octene, allylbenzene, styrene and methyl methacrylate showed no reactivity towards **1a** under the current conditions.

To further evaluate the scope of the cascade process, a broad range of substituted benzimidates **1** were reacted with methyl acrylate (**2b**) to form various 3-methyleneisoindolin-1-one products. Ethyl benzimidates with electron-donating or electron-withdrawing groups such as OPh, F and CF_3 in the *para* position reacted well, affording the corresponding products **3l–3n** in moderate to good yield. Note that the structure of the product **3l** was further confirmed by single crystal X-ray analysis.[24] The reaction of **2b** with **1** bearing a F at the *ortho* or *meta* position also proceeded well, giving **3o** in 41% yield and **3p** in 62% yield. The different yields of **3o** and **3p** might reflect steric effects on the benzene ring of **1**. Reaction of ethyl 3-fluorobenzimidate and **2b** gave only product **3p** and no another potential product of alkenylation/annulation adjacent to the F, suggesting a strong steric effect. Such an effect was also observed in the reaction of ethyl 3-methylbenzimidate and **2b**, which gave the desired product **3q** in 84% yield. Substrates bearing two substituents at the *meta* positions of the benzene ring reacted smoothly with **2b** to furnish **3r** and **3s** in moderate yields. Moreover, 3,4-disubstituted

Table 1. Optimization of conditions for reaction of **1a** and **2a**.[a]

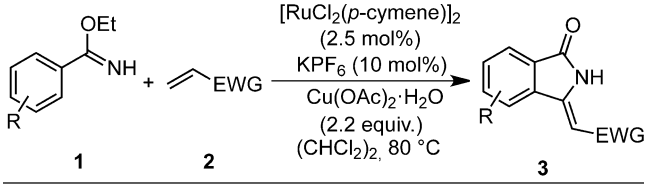


1a **2a** **3a**

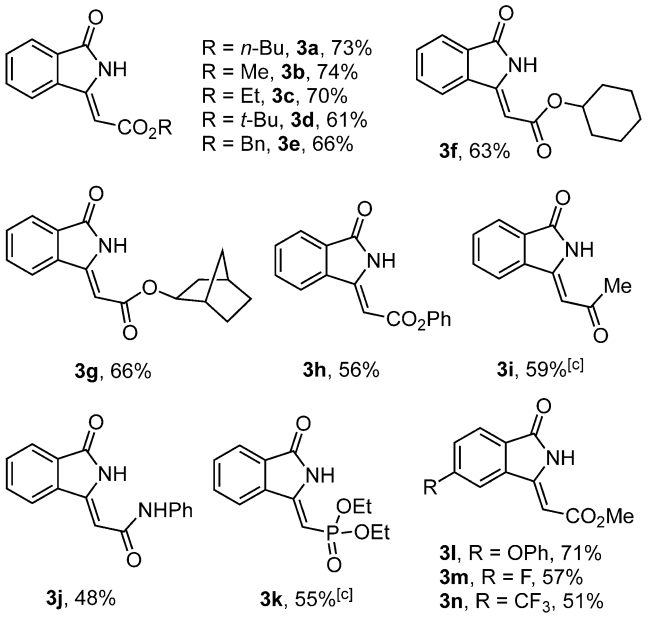
Entry	Catalyst	Additive	Solvent	Yield [%][b]
1	$[RuCl_2(p\text{-cymene})]_2$	–	toluene	16
2	$RuH_2(CO)(PPh)_3$	–	toluene	0
3	$RuCl_2(PPh_3)_3$	–	toluene	0
4	$Ru(OAc)_2(PPh_3)_3$	–	toluene	trace
5	$CpRuCl(PPh_3)_2$	–	toluene	trace
6	$[RuCl_2(p\text{-cymene})]_2$	–	dioxane	21
7	$[RuCl_2(p\text{-cymene})]_2$	–	CH_3CN	29
8	$[RuCl_2(p\text{-cymene})]_2$	–	$CHCl_3$	40
9	$[RuCl_2(p\text{-cymene})]_2$	–	DCE	41
10	$[RuCl_2(p\text{-cymene})]_2$	–	$(CHCl_2)_2$	54
11[c]	$[RuCl_2(p\text{-cymene})]_2$	–	$(CHCl_2)_2$	61
12[c]	$[RuCl_2(p\text{-cymene})]_2$	$AgPF_6$	$(CHCl_2)_2$	40
13[c]	$[RuCl_2(p\text{-cymene})]_2$	NH_4PF_6	$(CHCl_2)_2$	44
14[c]	$[RuCl_2(p\text{-cymene})]_2$	AgOAc	$(CHCl_2)_2$	67
15[c]	**$[RuCl_2(p\text{-cymene})]_2$**	**KPF_6**	**$(CHCl_2)_2$**	**73**
16[c,d]	$[RuCl_2(p\text{-cymene})]_2$	KPF_6	$(CHCl_2)_2$	67
17[c,e]	$[RuCl_2(p\text{-cymene})]_2$	KPF_6	$(CHCl_2)_2$	21
18[c,f]	$[RuCl_2(p\text{-cymene})]_2$	KPF_6	$(CHCl_2)_2$	10

[a] *Reaction conditions:* **1a** (0.4 mmol), **2a** (0.8 mmol), catalyst (0.01 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.88 mmol), additive (0.04 mmol), solvent (2 mL), 80 °C, 6 h, under N_2.
[b] Isolated yield.
[c] 12 h.
[d] The reaction was scaled up to 2 mmol of substrate (**1a**).
[e] At 60 °C.
[f] 0.004 mmol catalyst was used.

Table 2. Scope of alkenes and benzimidates in the oxidative alkenylation/annulation cascade reaction.[a,b]



1 2 3



[a] *Reaction conditions:* **1** (0.4 mmol), **2** (0.8 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.01 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.88 mmol), KPF_6 (0.04 mmol), $(CHCl_2)_2$ (2 mL), 80 °C, 12 h, under N_2, unless otherwise noted.

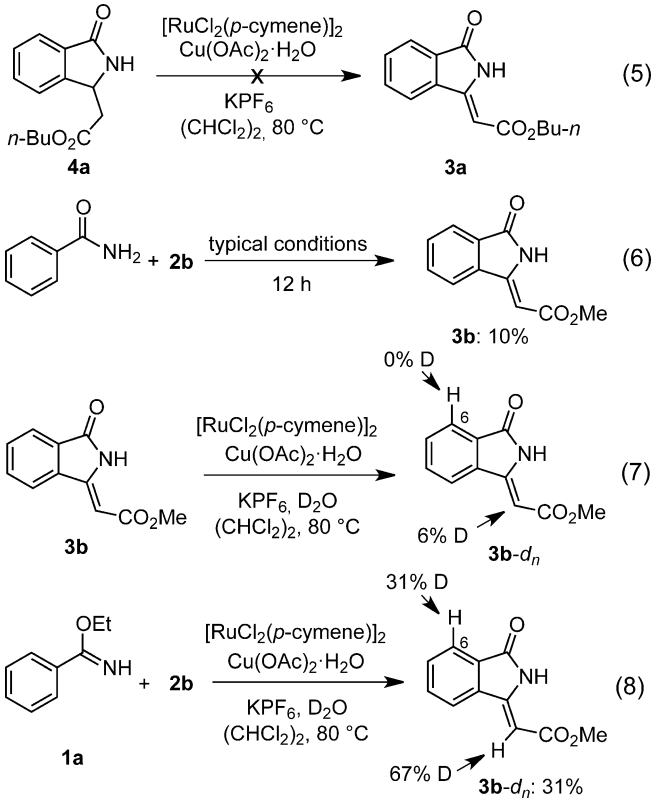
[b] Isolated yield.

[c] 2.0 mmol of **2** were used.

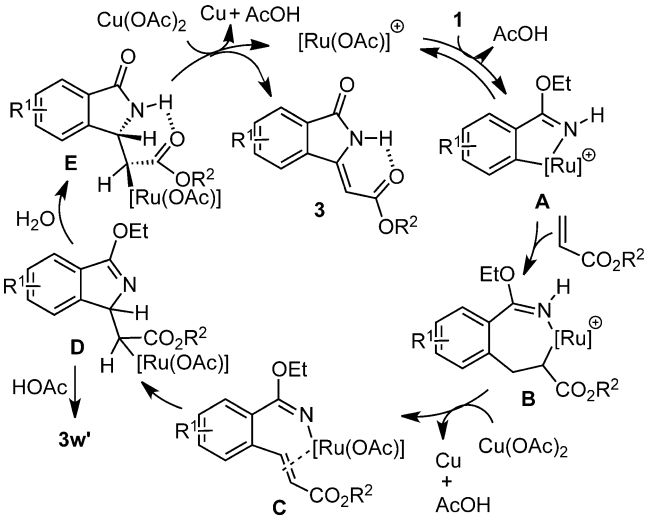
[d] A 9% yield of the unisolable 5,6-difluorosubstituted product **3u′** was also produced.

derivatives could also be employed in this transformation to give products **3t** and **3u** with moderate yields and excellent stereoselectivity. Unexpectedly, when the phenyl was replaced by a thienyl group, the reaction only gave the alkenylated product **3v′** in 41% yield instead of an annulated product, which might be caused by the immediate hydrolysis after the alkenylation step. Interestingly, the reaction of ethyl 2-naphthimidate with **2b** proceeded differently through alkenylation and annulation, producing **3w′** in 40% yield.

Next we performed several experiments to gain insights into the mechanism of the Ru-catalyzed oxidative alkenylation/annulation cascade reaction. The isoindolin-1-one **4a** was inert under the typical conditions and no product **3a** was observed [Scheme 2, Eq. (5)]. This suggested that compound **4a** might not be an intermediate in the catalytic cycle. In addition, treating benzamide with **2b** under the typical conditions gave **3b** in only 10% yield, which indicated that benzamide might not be the key starting material in this reaction [Scheme 2, Eq. (6)]. When product **3b** was exposed to D_2O (0.2 mL) under catalytic conditions, 6% deuterium was observed on the α-position of the ester carbonyl group and no deuterium was founded on the *ortho*-position of the imidate group [Scheme 2, Eq. (7)]. However, reaction of **1a** and **2b** under the same conditions [Scheme 2, Eq. (8)] in the presence of D_2O (0.2 mL) led to significant H/D scrambling (31% D) at the C-6 site in **3b**-d_n, indicating reversible C–H metalation in the catalytic cycle. At the same time, 67% D was observed on the α-posi-



Scheme 2. Mechanistic studies of the oxidative alkenylation/annulation cascade reaction.



Scheme 3. Plausible catalytic pathway for the Ru(II)-catalyzed oxidative alkenylation/annulation cascade reaction.

tion relative to the ester carbonyl group, raising the possibility of rapid H/D exchange on the NH-acidic imidate group before subsequent intramolecular addition.

Based on our mechanistic studies and the literature data,[1,2,19] a plausible mechanism for this oxidative alkenylation/annulation cascade reaction is proposed (Scheme 3). Initially, a reversible C–H metalation of the ruthenium(II) complex and **1** produces the five-membered ruthenacycle **A**, followed by insertion with alkene to give the intermediate **B**. Then, β-hydride elimination of intermediate **B** followed by deprotonation provides the alkenylated intermediate **C**. Next, intramolecular coordinative insertion of N–Ru bond of intermediate **C** into the C=C bond *via* aza-Michael addition gave intermediate **D**, which might provide the intermediate **E** after the hydrolysis or the product **3w′** *via* the direct protonation. Finally, in the presence of $Cu(OAc)_2$, β-hydride elimination of intermediate **E** possessing an intramolecular hydrogen bond affords the *Z*-configured product **3** and regenerates the ruthenium catalyst species.[19a,23]

In summary, we have developed a Ru(II)-catalyzed oxidative alkenylation/annulation cascade reaction for the synthesis of 3-methyleneisoindolin-1-ones. In this strategy, the *N*–H imidate functions efficiently as the directing group of C–H activation, leading the substrates to undergo intramolecular C–N bond formation. A wide range of substrates have been applied in this transformation to produce various 3-methyleneisoindolin-1-ones with high regio- and stereoselectivity in moderate to good yields. Further studies on the detailed mechanism and applications of the reaction are ongoing in our laboratory.

Experimental Section

Typical Experimental Procedure for Product 3a

1a (0.4 mmol), **2a** (0.8 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.01 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.88 mmol), KPF_6 (0.04 mmol), and $(CHCl_2)_2$ (2 mL) were mixed in an oven-dried reaction vessel. The vessel was sealed and heated at 80 °C for 12 h. The resulting mixture was cooled to room temperature and the solvent evaporated under vacuum. The crude product was purified by column chromatography on silica gel using 10:1 PE/EA as eluent to afford the product **3a**.

Acknowledgements

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[24] CCDC 1014386 contains the supplementary crystallographic data compound **3l** in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

