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Cp*Rh(III)-Catalyzed Mild Addition of C(sp^3)−H Bonds to α,β-Unsaturated Aldehydes and Ketones

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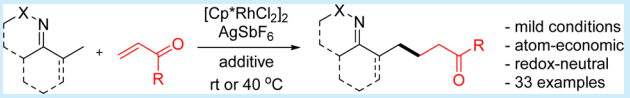
Supporting Information

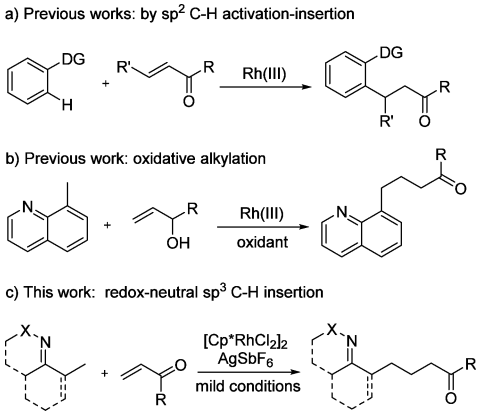
ABSTRACT: A Rh(III)-catalyzed addition of benzylic C(sp^3)−H bond to α,β-unsaturated ketones/aldehydes has been realized, leading to efficient synthesis of γ-aryl ketones/aldehydes. This atom-economic reaction proceeded under mild and redox-neutral conditions with a broad substrate scope. Besides benzylic C−H, allylic C−H bonds are also applicable when assisted by *O*-methyl ketoxime directing groups.



Transition-metal-catalyzed C−H bond activation and functionalization has become one of the most powerful strategies for construction of new chemical bonds, with broad applications in synthesis of organics, natural products, and materials.[1] In the past decade, a large number of synthetic methods have been developed on the basis of Cp*Rh(III)-catalyzed C−H activation systems, which stand out with high efficiency, good selectivity, functional group compatibility, and diverse synthetic applicability.[2] Among those systems, much attention has been directed to the direct addition of Rh(III)-catalyzed addition of sp^2 C−H bonds to polar unsaturated bonds,[3] as in the reports by Ellman,[4] Shi,[5] Kim,[6] Li,[7] and others.[8] The polar unsaturated compounds usually contain useful synthetic functional groups, which makes the addition reactions powerful and useful in the construction of drug-related alcohols, amines, amides, and heterocycles by C−H addition to aldehydes, imines, isocyanates, and other polar unsaturated compounds. α,β-Unsaturated carbonyl compounds exhibit good coordinating capacity and high reactivity, and they represent important coupling partners to C−H substrates for C−C bond formation. Remarkable advances in Rh(III)-catalyzed C−H bond addition to these compounds have been made (Scheme 1a).[4h−j,7f,9] However, these addition reactions generally require arene substrates. Thus, although C−H activation of sp^3 C−H bonds leading to hetero-functionalization and arylation have been recently reported using Cp*Rh(III) and Cp*Ir(III) catalysts,[10] redox-neutral addition of the sp^3 C−H bond to C═C bonds has been rarely reported, most likely because of the low reactivity of the Rh−C(alkyl) species. Recently, Kim et al. reported this type of addition of sp^3 C−H bonds to maleimides;[11] however, the substrate scope is narrow, and only maleimides have been demonstrated.

Our group is interested in Rh(III)-catalyzed C(sp^3)−H bond activation and diverse functionalization with carbon- and nitrogen-centered coupling partners.[12] Among the sp^3 C−H substrates, 8-methylquinolines are particularly reactive.[10a−i] 8-Methylquinolines are known to couple with ketenes[12d] under

Scheme 1. Rh(III)-Catalyzed C−H Addition Leading to Alkylation



redox-neutral conditions, and we also briefly reported the oxidative coupling with cyclopropanols.[12a] In the latter reaction, we found that the reaction did not occur via an enone intermediate. On the other hand, during the submission of this paper, Kim and co-workers reported the oxidative C(sp^3)−H alkylation of 8-methylquinolines with allylic alcohols to deliver the same γ-aryl ketone products (Scheme 1b).[13] Given the ready availability of enones and analogues and the concept of atom-economy and green processes, we herein report C−H activation of benzylic and allylic C−H bonds and their addition to α,β-unsaturated aldehydes/ketones under mild conditions in the absence of any stoichiometric amounts of oxidants.

We initiated our investigation by screening the reaction conditions of the addition of 8-methylquinoline (**1a**) to acrolein (**2a**) under Rh(III) catalysis. As given in Table 1, coupling of **1a** (0.2 mmol) with **2a** (0.2 mmol) in the presence of [Cp*Rh-

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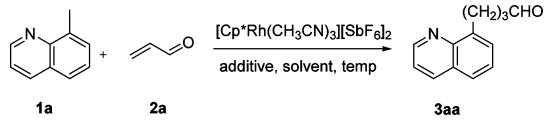
Table 1. Optimization Studies[a]



entry	temp (°C)	1a/2a	solvent	additive (equiv)	yield[b] (%)
1	80	1:1	DCE		<3
2	80	1:1	DCE	AgOAc (0.5)	46
3	80	1:1	DCE	AgOAc (0.2)	26
4	80	1:1	DCE	AgOAc (1.0)	38
5	80	1:1	DCE	$Cu(OAc)_2·H_2O$ (0.5)	30
6	80	1:1	DCE	NaOAc (0.5)	24
7	80	1:1	dioxane	AgOAc (0.5)	25
8	80	1:1	CH_3CN	AgOAc (0.5)	trace
9	80	1:1	DMF	AgOAc (0.5)	<5%
10	80	1:1	PhCl	AgOAc (0.5)	40
11	40	1:1	DCE	AgOAc (0.5)	58
12	80	1:2	DCE	AgOAc (0.5)	55
13[c]	80	1:2	DCE	AgOAc (0.5)	84
14[c]	40	1:2	DCE	AgOAc (0.5)	90
15[c]	rt	1:2	DCE	AgOAc (0.5)	90
16[d]	rt	1:2	DCE	AgOAc (0.5)	85

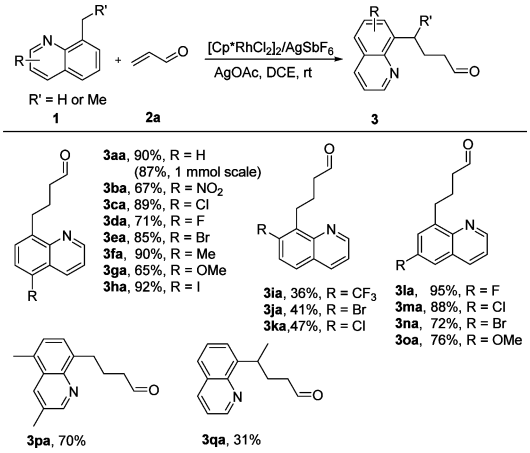
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 or 0.4 mmol), $[Cp*Rh(CH_3CN)_3][SbF_6]_2$ (8 mol %), additive, solvent (2.0 mL), 12 h, under Ar. [b]Isolated yield. [c]$[Cp*RhCl_2]_2/AgSbF_6$ (4 mol %/16 mol %) was used. [d]$[Cp*RhCl_2]_2/AgSbF_6$ (2 mol %/8 mol %) was used.

$(CH_3CN)_3][SbF_6]_2$ (8 mol %) and AgOAc (0.1 mmol) in DCE (2 mL) at 80 °C afforded the desired product in 46% yield (entry 2). Only traces of product were detected without the use of AgOAc (entry 1). Charging of the amount of AgOAc led to lower yield (entries 3 and 4). Screening of several other solvents revealed that DCE was optimal (entries 7−11). Screening of additives revealed that both $Cu(OAc)_2·H_2O$ and NaOAc were less ineffective (entries 5 and 6). Then effects of the reaction temperature were examined, and 40 °C or room temperature all gave better results (entries 14−16). By switching to a $[Cp*RhCl_2]_2/AgSbF_6$ catalyst, we were pleased to reach a higher yield (entry 15). Finally, we chose the condition in entry 15 as the standard reaction conditions.

With the optimal reaction conditions in hand, various substituted 8-methylquinolines (**1a−q**) were allowed to couple with acrolein (**2a**, Scheme 2). Various 8-methylquinolines bearing NO_2 (**1b**), halogen groups (**1c**, **1d**, **1e**, **1h**, **1l−1n**), methyl (**1f**), and methoxy (**1g**, **1o**) at the 5- and 6-positions all reacted with moderate to excellent yields (65−92%). 7-Substituted substrates (**1i−1k**) also reacted with **2a** but with lower yields (36−47%). A multisubstituted substrate can also react smoothly in the reaction system (**1p**). The C−H activation was not limited to a methyl substrate. Thus, the methylene C−H bond of 8-ethylquinoline (**1q**) was alkylated in 31% yield.

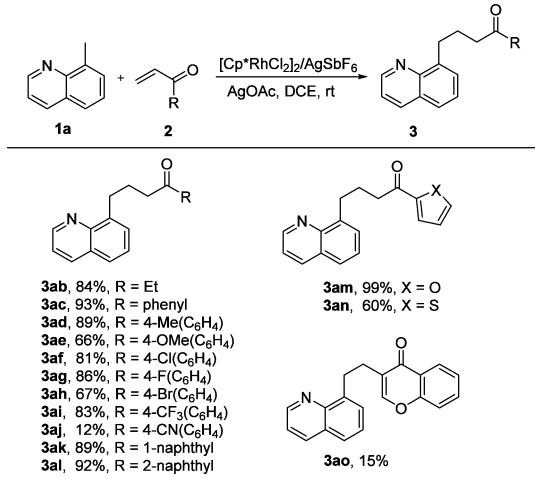
The scope of the *α,β*-unsaturated acceptors is also broad, and the catalytic system allowed the efficient transformation of various alkyl/aryl vinyl ketones (Scheme 3). For example, coupling of aliphatic enone **2b** gave the desired product with similar reactivity (**3ab**, 84%). Furthermore, a variety of substituted aryl enones bearing electron-donating and -with-drawing groups have also been examined. Most of the enones coupled with **1a** in good to excellent yield (**3ac−3ai**) except for that bearing a CN group (**3ja**, 12%). Furthermore, naphthylvinyl

Scheme 2. Scope of 8-Methylquinolines[a,b]



[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), $[Cp*RhCl_2]_2/AgSbF_6$ (4 mol %/ 16 mol %), and AgOAc (0.5 equiv) in DCE (2.0 mL) at room temperature for 12 h. [b]Isolated yield.

Scheme 3. Scope of *α,β*-Unsaturated Acceptors[a,b]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), $[Cp*RhCl_2]_2/AgSbF_6$ (4 mol %/ 16 mol %), and AgOAc (0.5 equiv) in DCE (2.0 mL) at room temperature for 12 h. [b]Isolated yield.

ketones were also viable, furnishing the desired products in excellent yields (**3ga** and **3ha**). The reaction also proceeded well for heteroaryl vinyl ketones, affording the products in 99 and 60% yields, respectively (**3am** and **3an**). An exocyclic enone substrate, 3-methylenechroman-4-one, was also examined, but oxidative coupling occurred (**3ao**).

To further define the scope and limitations of this reaction, coupling of the oxime ether of L-(−)-carvone (**4a**) with acrolein (**2a**) was examined (Scheme 4). Traces of product were observed under our standard conditions. By simple optimization, the desired product (**5aa**) was obtained in moderate yield upon switching to $Zn(OAc)_2$ additive with TFE as the solvent (51%). Another oxime ether, **4b**, also reacted to afford the corresponding product in 46% yield.

To demonstrate the synthetic utility of the addition products, derivatization reactions were carried out. The formyl group in product **3aa** was selected to be reduced by $NaBH_4$, and both the formal and the pyridine ring were reduced when using $NaBH_4/NiCl_2·6H_2O$ (Scheme 5a).

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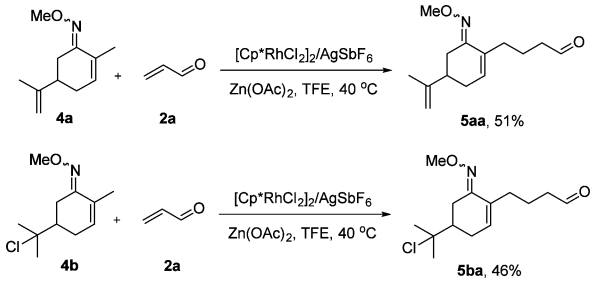
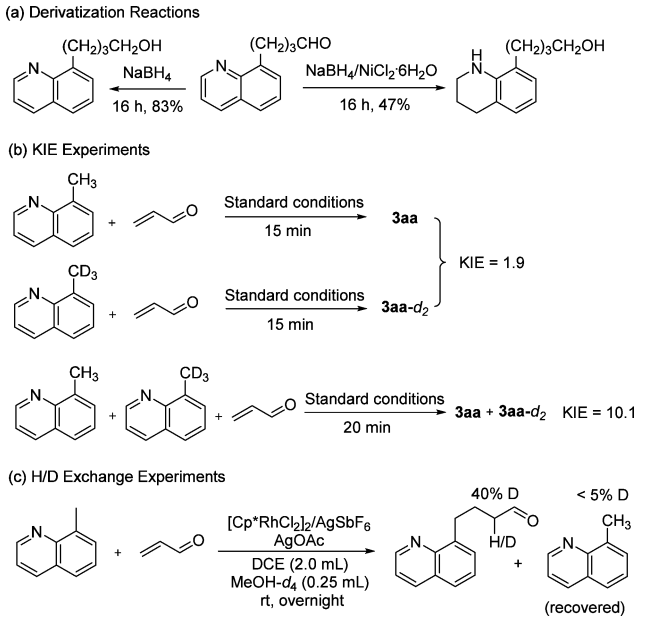
Scheme 4. Allylic C−H Addition to Acrolein



Scheme 5. Derivatization, KIE, and H/D Exchange Reactions

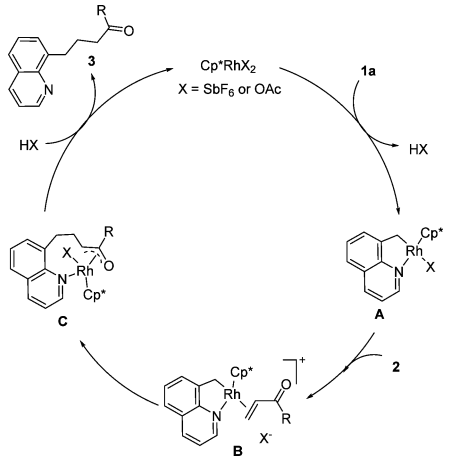


To gain some insight into the mechanism of this reaction, KIE experiments were conducted in both parallel and one-pot measurements. The KIE values of 1.9 in parallel reactions and 10.1 in competition experiments indicated that the cleavage of the methyl C−H bond is probably involved in the turnover-determining step (Scheme 5b).[14] H/D exchange was not observed at the methyl position of **1a** in the presence of MeOH-d_4 and in the absence of acrolein **2a**. No deuteration was detected, either, for recovered **1a** when it was allowed to couple with **2a** in the presence of MeOH-d_4. However, the proton at the α-position of the aldehyde group was deuterated (40% D, Scheme 5c). These results indicate that the C−H activation in the catalytic system is irreversible, and the catalytic cycle may involve protonolysis of a Rh−C bond.

Based on the above results and precedents of Rh(III)-catalyzed C(sp^2)−H bond addition reactions, a likely mechanism is given in Scheme 6. Cyclometalation of 8-methylquinoline affords a five-membered rhodacyclic intermediate **A**. Coordination of α,β-unsaturated carbonyl compound to the rhodium center (**B**) is followed by insertion into the Rh−C(sp^3) bond to give an enolate intermediate **C**. Finally, protonolysis of **C** gives the addition product and regenerates the active rhodium species.

In summary, we have demonstrated Rh(III)-catalyzed C-(sp^3)−H bond addition to α,β-unsaturated aldehydes and ketones under mild and redox-neutral reaction conditions. The reactions are highly efficient and atom-economical. Two types of directing groups proved to be viable, and the scope of the

Scheme 6. Proposed Mechanism



catalytic system was investigated and found to be quite decent. Given the mild and oxidant-free conditions, broad scope, and high catalytic efficiency, this method may find applications in the synthesis of related complex structures.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00690.

Detailed experimental procedures, characterization of new compounds, and copies of NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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