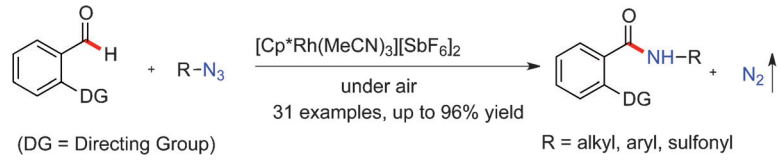

(DG = Directing Group)

R = alkyl, aryl, sulfonyl

C–H activation: A Rh^{III}-catalyzed direct aldehyde C–H amidation has been achieved with sulfonyl, aryl, and alkyl azides as the amine sources, and release of N_2 as the only byproduct (see scheme). More importantly, this catalytic reaction proceeds in the absence of external oxidants or additives, under mild conditions, at neutral pH under air. This reaction represents a new avenue for practical intermolecular C–N bond formation by aldehyde C–H bond activation. Cp* = 1,2,3,4,5-Pentamethylcyclopentadiene

Rhodium Catalysis

B. Zhou, Y. Yang, J. Shi, H. Feng, Y. Li** ..... ▮▮▮▮–▮▮▮▮

Rhodium-Catalyzed Synthesis of Amides from Aldehydes and Azides by Chelation-Assisted C–H Bond Activation

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Rhodium-Catalyzed Synthesis of Amides from Aldehydes and Azides by Chelation-Assisted C–H Bond Activation

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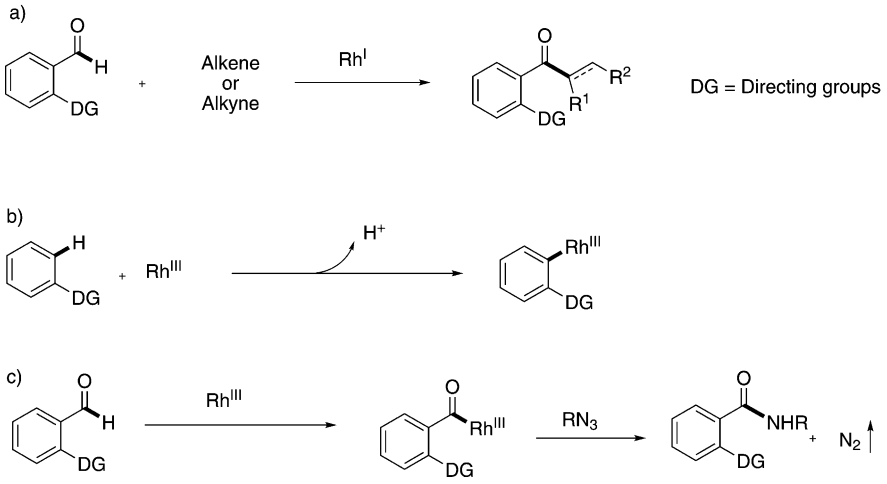
The amide bond is one of the most abundant functional groups in pharmaceuticals, agrochemicals, and natural products.[1] Amide bonds are routinely generated by condensation of carboxylic acids and amines through stoichiometric activation, under harsh conditions, or both.[2] A milder, atom-economic alternative approach is the direct amidation of aldehydes. Recent examples of this strategy include N-heterocyclic (NHC)-catalyzed,[3] metal-catalyzed,[4] or metal-free[5] oxidative amidation of aldehydes with amines, the Schmidt amidation of aldehydes with azides,[6] base-mediated amidation of aldehydes with azides,[7] direct organocatalytic oxidative amidation of aldehydes with amines through stoichiometric activation,[8] and cross-coupling of acyl and aminyl radicals.[9] Although significant progress has been made in this field, the development of catalytic and effective methods of amide bond formation under mild reaction conditions remains highly desirable.

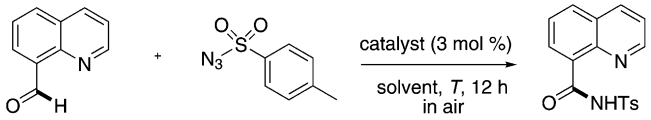
In addition, transition-metal-catalyzed aromatic C–H bond functionalization is currently a "hot topic" in organic chemistry.[10] In sharp contrast to arene C–H bonds, the selective functionalization of aldehyde C–H bonds is limited to coupling with alkenes and alkynes forming C–C bonds and yielding ketone derivatives through oxidative addition of low-valent transition-metal complexes (especially Rh^I) to aldehyde C–H bonds (Scheme 1 a).[11,12] To the best of our knowledge, direct catalytic C–N bond formation resulting from chelation-assisted aldehyde C–H bond activation remains undeveloped, with no examples reported to date.



Scheme 1. Coupling reactions involving C–C bond formation by C–H activation through a) an oxidative addition pathway, b) a deprotonation pathway, and c) C–N bond formation through a C–H activation pathway.

In this context, and attracted by recent successes in arene C–H bond amination reactions,[13] we surmised that an aldehyde C–H amidation by a C–H bond activation strategy

Table 1. Optimization of the Rh-catalyzed amide synthesis.[a]



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

	Catalyst ([mol %])	Solvent	T [°C]	Yield [%][b]
1	$[(Cp^*RhCl_2)_2]$ (3)	CH_2Cl_2	85	0
2	$[(Cp^*RhCl_2)_2]$ (3)/$AgSbF_6$ (12)	CH_2Cl_2	85	66
3	$[\{Ru(p\text{-cymene})Cl_2\}_2]$ (3)/$AgSbF_6$ (12)	CH_2Cl_2	85	14
4	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (3)	CH_2Cl_2	85	70
5	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (3)	DCE	85	77
6	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (3)	THF	85	60
7	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (3)	*tert*-amylOH	85	35
8	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (3)	PhMe	85	85
9	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (3)	PhMe	100	84
10	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (3)	PhMe	70	66 (83)
11[c]	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (3)	PhMe	85	84

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.22 mmol), catalyst (0.006 mmol), and solvent (1 mL) at the indicated temperature for 12 h. [b] yield of isolated product; Yield in parentheses is based on recovered starting material. [c] 1 g of **1a** was used. DCE = 1,2-dichloroethane.

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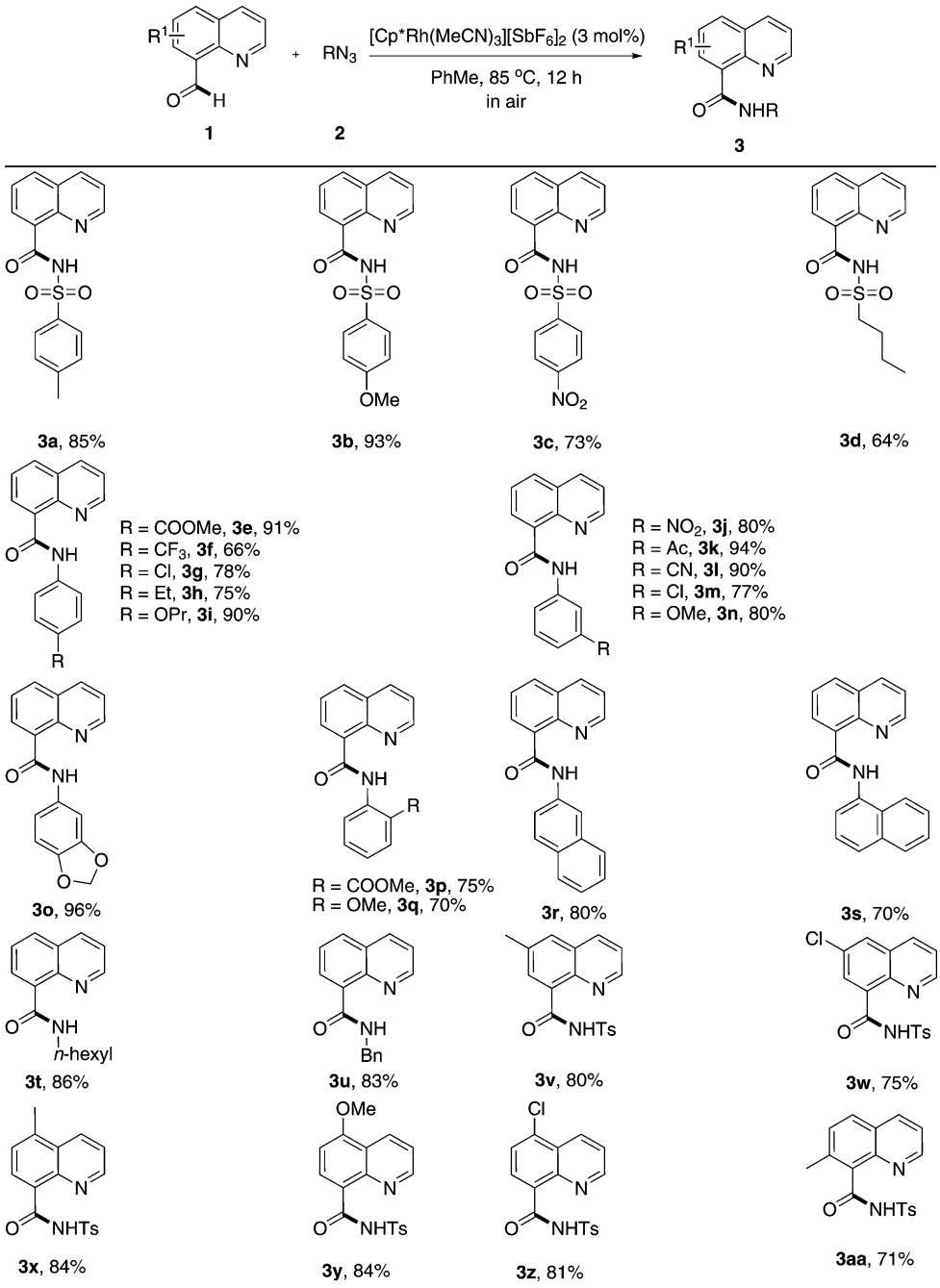
could provide a new approach to amide-bond synthesis. Recently, several investigations revealed that Rh^{III} complexes undergo chelation-assisted electrophilic metalation of *ortho* $C(sp^2)$–H bonds to form arylrhodium complexes,[14] which may be coupled to a variety of reagents such as aldehydes,[15] imines,[16] isocyanates,[17] diazomalonates,[18] azides,[19] alkenes, and alkynes (Scheme 1b).[20] Therefore, herein, we report the first example of Rh^{III}-catalyzed amidation of aldehydes with azides as an amine source in the presence of air (Scheme 1c). This catalytic aldehyde C–H amidation proceeds in the absence of external oxidants and additives, under mild and neutral reaction, conditions with high functional group tolerance, and releases N_2 as the single byproduct. Moreover, in addition to alkyl azides,[6,7] aryl and sulfonyl azides are tolerated, providing *N*-alkyl amides, acylsulfonamides, and *N*-aryl amides in excellent yields.

Initially, the reaction conditions were optimized by using 8-quinolinecarbaldehyde (**1a**) and *para*-toluenesulfonyl azide (**2a**) as cross-coupling partners (Table 1). Although 3 mol% of $[(Cp^*RhCl_2)_2]$ did not catalyze this reaction (Table 1, entry 1), $[(Cp^*RhCl_2)_2]$ (3 mol%) in the presence of $AgSbF_6$ (12 mol%)[21] in THF at 85°C provided the desired product, **3a**, in 66% yield (Table 1, entry 2). The ruthenium complexes known to be highly effective in direct C–H bond functionalization, was relatively ineffective in this reaction (Table 1, entry 3). The Rh^{III} precursor $[Cp^*Rh(MeCN)_3][SbF_6]_2$ led to similar reactivity to that observed with $[(Cp^*RhCl_2)_2]$ and $AgSbF_6$ (Table 1, entry 4). Therefore, $[Cp^*Rh(MeCN)_3][SbF_6]_2$ was used for all subsequent optimization studies. Solvent screening showed that an improved chemical yield could be obtained with toluene as the solvent, providing the product **3a** in 85% yield (Table 1, entry 8). Raising the temperature did not result in any reduction in yield (Table 1, entry 9) and lowering the temperature led to a slightly lower conversion (Table 1, entry 10). Finally, we were pleased to find that this reaction was scalable to gram amounts of substrate without decreasing the yield, and the product **3a** could be isolated by a simple purification process (recrystallization) with N_2 as the sole byproduct (Table 1, entry 11).

An array of azides and aldehydes were screened under the conditions established above (Table 2). Arenesulfonyl azides substituted with electron-donating groups, such as Me (**2a**) and MeO (**2b**), and -withdrawing groups, such as NO_2

Table 2. Substrate scope.[a]



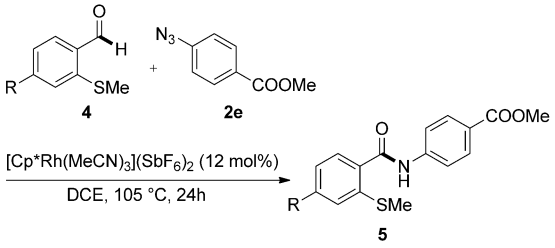
[a] Reaction conditions: **1** (0.2 mmol), **2** (0.22 mmol), Rh catalyst (0.006 mmol) and solvent (1 mL) at 85°C for 12 h. Yield of isolated product. Bn = Benzyl.

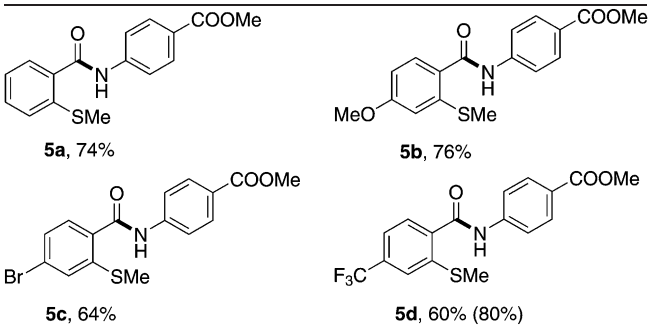
(**3c**), were tolerated, providing the desired amides in good to excellent yields. An aliphatic sulfonyl azide (**2d**) reacted equally well, giving the corresponding product (**3d**) in good yield. The substrate scope was further extended to a broad variety of aryl azides. Phenyl azides substituted with electron-withdrawing or -donating groups at the *para*-, *meta*- or *ortho*-position (**2e**–**2q**) were tolerated, with good to excellent yields of **3e**–**3q** obtained, irrespective of the electronic nature or position of the substituents on the phenyl ring. Moreover, the reaction showed good functional group compatibility. For example, phenyl azides with ester (**2e** and **2p**), nitro (**2j**), nitrile (**2l**), ketone (**2k**), ethyl (**2h**), methoxy (**2n** and **2q**), and chloro (**2g** and **2m**) groups were effective coupling partners under the optimized conditions. Notably, the tolerance of the ester, nitro, nitrile, ketone and chloro groups offers the opportunity for further functionalization. In addition, 2-naphthyl and 1-naphthyl azides (**2r** and **2s**) were readily converted to the corresponding products in good yields. Particularly remarkable is the participation of alkyl azides in this reaction, providing the corresponding *n*-hexyl and phenylmethane amide products (**3t** and **3u**, respectively) in excellent yields. It was found that the electronic nature of the substituents on the quinoline ring did not play a key role in this catalytic reaction. Aldehydes with either electron-donating or -withdrawing groups (**1v**–**1aa**) were readily converted to the corresponding products in good yields.

Encouraged by the successful amidation of 8-quinolinecarbaldehyde, we turned our attention to additional substrates bearing synthetically useful directing groups. To our delight, 2-(methylthio)benzaldehyde also underwent direct amidation with aryl azides (Table 3). Aromatic groups bearing electron-donating or -withdrawing groups were tolerated (**5a**–**d**) and good yields were obtained, despite the need for a relatively high catalyst loading.

To obtain further insight into this catalytic transformation, preliminary mechanistic experiments were carried out. When benzaldehyde (**6a**) was utilized as the substrate, the corresponding amide was not formed (Scheme 2a). Therefore, the presence of a directing group in the substrate seems to be critical to the initial C–H bond-functionalization event. No product formation was observed in the presence of $[(Cp^*RhCl_2)_2]$ or $AgSbF_6$ alone (Scheme 2b). The stable cyclometalated Rh^{III} complex **7** was obtained upon treatment of **1a** with $[(RhCp^*Cl_2)_2]$ and NaOAc (Scheme 2c). ^1H and ^{13}C NMR

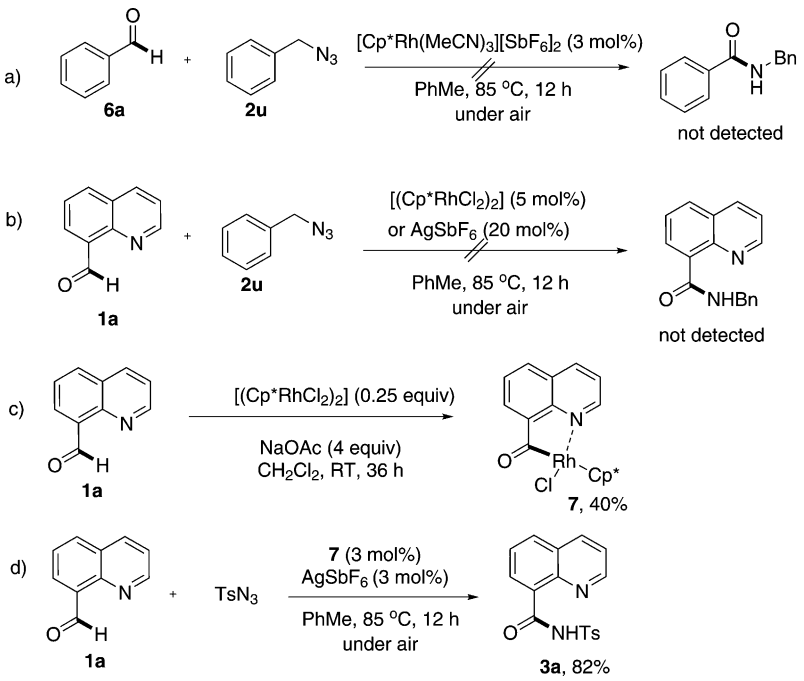
Table 3. 2-(Methylthio)benzaldehyde substrate scope.[a]



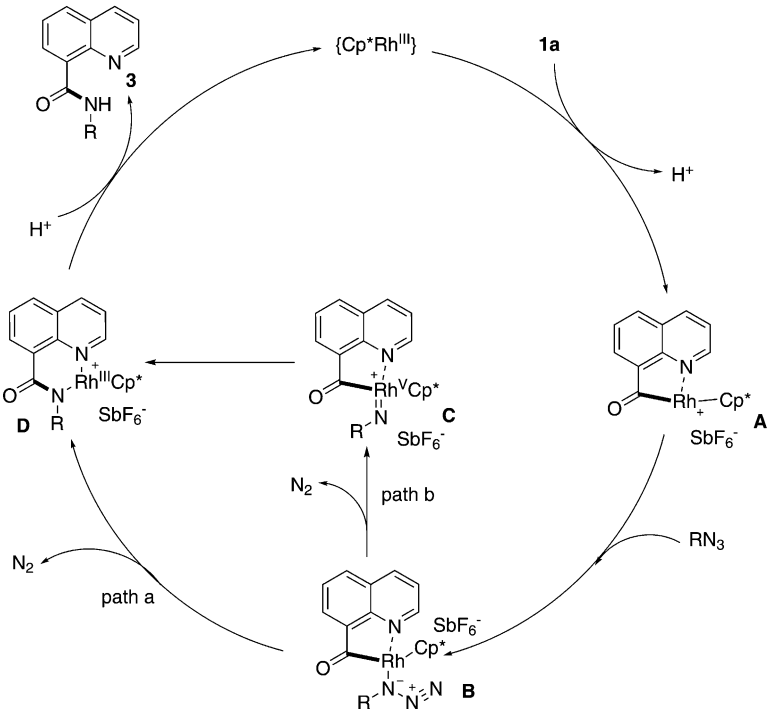


[a] Reaction conditions: **4** (0.2 mmol), **2e** (0.24 mmol), Rh catalyst (0.024 mmol), and solvent (0.3 mL) at 105 °C for 24 h under argon. Yield of isolated product; yield in parentheses is based on recovered starting material.

and mass spectrum analysis of **7** pointed to cyclometalation. Although a number examples of acyl–rhodium(III) complexes have been isolated by starting from Rh^I catalysts,[22] reports of stable isolated organorhodium(III) intermediates from Rh^{III} catalysts by deprotonation are still limited,[14c,16c,e,19a,23] particularly for acyl–rhodium(III) intermedi-



Scheme 2. Preliminary mechanistic studies.



Scheme 3. Proposed mechanism.

ates.[24] Complex **7** catalyzed the amidation reaction of **1a** to give **3a** in 82% yield (Scheme 2d), demonstrating the plausibility of **7** as an intermediate in the catalytic cycle. In addition, ruled out the possibility of involvement of a Schmidt-type rearrangement,[6] in which stoichiometric amounts of acid or Lewis acid are usually required and only alkyl azides are effective coupling partners.

Based on the aforementioned data, a plausible catalytic cycle is presented in Scheme 3. Coordination of the N atom of **1a** to Rh^{III} and the subsequent directed cyclorhodation affords a 5-membered rhodacycle intermediate **A**, which then binds an azide, leading to **B**. Subsequent concerted migratory insertion leads to the formation of a rhodium(III) amide species **D** (path a). Alternatively, species **D** can be formed by a stepwise nitrenoid pathway in which a high-valent rhodium(V) species **C** is involved (path b).[25] Finally, protonolysis of **D** provides the product **3**.

In summary, we have developed the first example of a Rh^{III}-catalyzed direct aldehyde C–H amidation with sulfonyl, aryl, and alkyl azides as an amine source in the presence of air. This catalytic aldehyde C–H amidation proceeds in the absence of external oxidants or additives, under mild, pH-neutral reaction conditions with high functional group tolerance, and release of N_2 as the sole byproduct, thus offering an environmentally benign method of amide synthesis that can be readily scaled up. *N*-Alkyl amides, acylsulfonamides, and *N*-aryl amides are accessible in good to excellent yields. Most importantly, this process may provide a new direction for direct C–N bond formation by aldehyde C–H bond activation. Further efforts to expand the scope of this methodology are currently underway in our laboratory.

Experimental Section

General procedure: $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (4.8 mg, 0.006 mmol), substrate **1** (0.2 mmol), **2** (0.22 mmol, 1.1 equiv), and toluene (1 mL) were added to a test tube in air. The reaction mixture was heated in an oil bath at 85 °C for 12 h. The resulting mixture was cooled to room temperature and purified directly on a silica gel column to give the product **3**.

Keywords: aldehydes · amides · azides · C–H activation · rhodium

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