

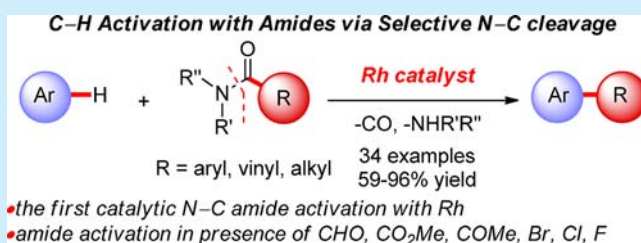
Rhodium-Catalyzed C–H Bond Functionalization with Amides by Double C–H/C–N Bond Activation

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Supporting Information

ABSTRACT: The first C–H bond functionalization with amides as the coupling partners via selective activation of the amide N–C bond using rhodium(I) catalysts under highly chemoselective conditions is reported. Notably, this report constitutes the first catalytic activation of the amide N–C(O) bond by rhodium. We expect that this concept will have broad implications for using amides as coupling partners for C–H activation beyond the work described herein.



In the past decade, tremendous advances have been made in the field of transition metal catalyzed direct C–H bond functionalization.¹ Site-selective functionalization of arene C–H bonds provides ready access to C–C,² C–O,³ C–N,⁴ and C–X⁵ products with high atom economy.^{1–5} In this context, the formation of C–C bonds constitutes a cornerstone of organic synthesis.⁶ The utility of the C–H activation technology to forge C–C bonds is ultimately limited by the availability of new coupling partners and the development of generic activation manifolds.⁷ Chelation-assisted arene C–H functionalization with a number of coupling partners, including aryl halides,^{8a–d} pseudohalides,^{8e–g} organometallic reagents,⁹ and arenes¹⁰ have been developed. However, the majority of these methods require the use of complex catalyst systems, oxidants, or have limited substrate scope. Recent progress was achieved by the use of acyl chlorides¹¹ and aldehydes¹² under Rh(I)/(III) catalysis to form C–C bonds after decarbonylation. Elegant approaches to the development of chelation-assisted coupling of C–H bonds with imines,^{13a,b} aldehydes,^{13c} and ketones^{13c} via Rh(III) and Co(I)/(III)^{13d} catalytic cycles have been reported. In contrast, transition metal catalyzed C–H bond functionalization with significantly more challenging amides (amide bond resonance of 15–20 kcal/mol)¹⁴ has so far proved elusive, despite the fundamental role of amide bonds as building blocks in chemistry and biology,¹⁴ and the urgent need to develop new coupling partners for generic C–H activation methods under base-free, oxidant-free conditions, which would additionally show a wide substrate scope and be amenable to rational method development.¹⁵

We report herein the first site-selective arene C–H bond functionalization with amides as the coupling partners via selective cleavage of the amide N–C bond, which proved viable with highly discriminating Rh(I) catalysts.¹⁶ This report constitutes the first example of a rhodium-catalyzed activation of the amide N–C bond.¹⁷ The following features are noteworthy: (1) The method provides functionalized biaryls¹⁸ from bench-stable, readily available amide precursors. (2) The reaction shows excellent functional group tolerance, including halides and aldehydes. (3) The Rh(I) catalyst shows high

specificity for the chelation-directed insertion into the amide N–C bond, overriding the inherent decarbonylation/dehalogenation. (4) The reaction is characterized by operational simplicity and is conducted in the presence of ambient air and moisture. This work demonstrates that typically inert, electronically neutral amides can be exploited for C–C bond-forming reactions via C–H activation.¹⁹ Given the utility of Rh(I) as highly useful C–H activation catalysts¹⁶ and the importance of amides in organic synthesis,¹⁴ we expect that this concept will have broad implications for using amides as coupling partners for C–H activation in ways beyond the coupling described herein.

We have recently discovered the first Suzuki^{20a,b} and Heck^{20b} reactions of nonplanar amides²¹ under Pd(0)/(II) catalysis. Independently, Garg^{20c} and Zou^{20d} demonstrated the use of nonplanar imides²¹ in the Suzuki reaction using Ni^{20c,d} and Pd catalysis (Figure 1).^{20d} Altogether, these reactions represent the first examples of the elusive class of transition metal catalyzed

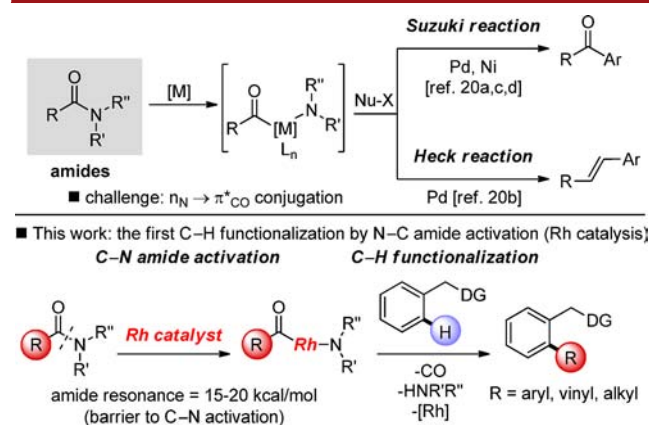


Figure 1. Transformations of amides via C–N activation.

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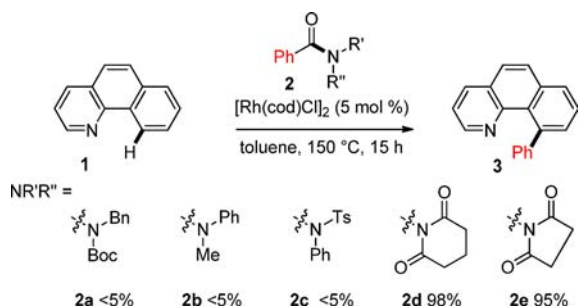
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amide bond N–CO insertion/cross-coupling reactions for the formation of C–C bonds proceeding via selective N–C activation,²² where it is believed that the $n_N \rightarrow \pi^*_{CO}$ amide bond resonance is disrupted by ligand coordination to nitrogen.²³ While ground-state distortion^{24a} and electronic activation^{24b} contribute to the observed reactivity, these transformations exploit selective transition metal catalyzed activation of the classically inert N–C amide bonds.¹⁴ It is important to note that all of these methods employ bench-stable, readily available amide precursors²⁵ as acylating or even arylating reagents, thus enabling a new powerful transition metal catalyzed amide disconnection via acyl-metal intermediates.²⁶

On the basis of our previous studies,^{20a,b,23c,d} we hypothesized that bench-stable amides could be employed as arylating C–H functionalization partners with arenes by identifying an appropriate amide precursor and catalyst system. A critical feature of our design is the capacity of a low-valent metal catalyst to insert into the inert amide N–C bond under mild conditions¹⁷ that would be compatible with the C–H activation cycle.^{11–13} At the outset of our studies, only two metals, Pd(0) and Ni(0), had been known to activate amide N–C bonds catalytically, operating under the conditions that are incompatible with C–H activation manifolds.^{1–5} The development of C–H functionalization with amides would require identifying an appropriate catalyst system to insert into the amide N–C bond and control the relative reactivity of the intermediates.

Evaluation of the C–H bond functionalization strategy with amides was first examined by the coupling of benzo[*h*]quinoline **1** with amides **2** under various conditions (Scheme 1). For our initial studies, we selected 2-phenylpyridine directing groups because of their well-known capacity to undergo cyclometalation

Scheme 1. Rh-Catalyzed C–H Arylation with Amides: The Effect of Different N-Substituents^a



^aConditions: **1** (0.1 mmol), amide (1.5 equiv), [Rh(cod)Cl]₂ (5 mol %), PhMe (0.25 M), 150 °C. See Supporting Information for full details.

under mild conditions,^{2a} and the importance of pyridine-containing biaryls in medicinal chemistry.¹⁸ Although the C–H functionalization products were not detected using Pd and Ni as catalysts, the proposed C–H functionalization was indeed possible using Rh(I)-catalysts and sterically distorted amide **2d**. Importantly, less distorted anilides **2a–2c**²¹ resulted only in trace quantities of the C–H activation product, consistent with the facility of metal insertion into the amide N–CO bond.¹⁷ Interestingly, the coupling of **1** with a significantly less distorted amide **2e**²¹ gave an excellent yield of the cross-coupling product, indicating the high activity of the Rh(I) catalyst for the N–CO insertion. Importantly, ketone products were not detected, consistent with the high capability of the Rh(I) catalyst to facilitate decarbonylation.¹⁶ The arylation process occurred

exclusively at the less electrophilic 10-position of benzo[*h*]quinoline, consistent with nitrogen-directed cyclometalation.^{2a}

Key optimization results with amide **2d** are shown in Table 1. Various catalysts were tested, and [Rh(cod)Cl]₂ showed the best catalytic activity (entries 1–6). Control experiments in the absence of a metal catalyst resulted in full recovery of **2d**. The use

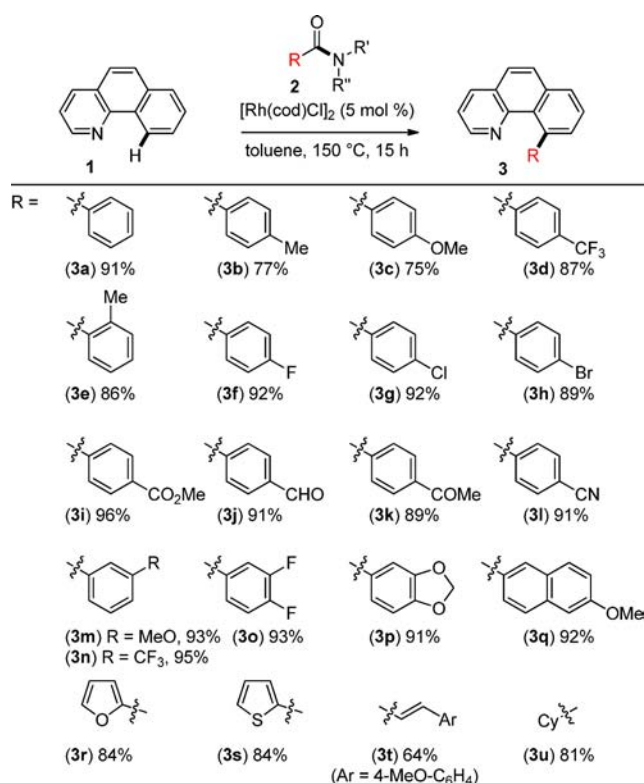
Table 1. Optimization of Regioselective Arylation of Benzo[*h*]quinoline with Amides^a

entry	catalyst	additive	solvent	yield (%)
1	[Rh(cod)Cl] ₂	–	toluene	>98
2	[Rh(CO) ₂ Cl] ₂	–	toluene	30
3	[Rh(cod) ₂]BF ₄	–	toluene	98
4	RhCl(PPh ₃) ₃	–	toluene	9
5	[Rh(C ₂ H ₄) ₂ Cl] ₂	–	toluene	69
6	[RhCp*Cl] ₂	–	toluene	<5
7 ^b	[Rh(cod)Cl] ₂	CuI	toluene	39
8 ^c	[Rh(cod)Cl] ₂	O ₂	toluene	47
9 ^d	[Rh(cod)Cl] ₂	PPh ₃	toluene	30
10 ^d	[Rh(cod)Cl] ₂	DPPF	toluene	54
11 ^d	[Rh(cod)Cl] ₂	DPPP	toluene	<5
12	[Rh(cod)Cl] ₂	Na ₂ CO ₃	toluene	75
13	[Rh(cod)Cl] ₂	KF	toluene	77
14	[Rh(cod)Cl] ₂	K ₂ CO ₃	toluene	<5
15	[Rh(cod)Cl] ₂	–	dioxane	16
16	[Rh(cod)Cl] ₂	–	PhCl	<5
17	[Rh(cod)Cl] ₂	–	DCE	<5
18 ^e	[Rh(cod)Cl] ₂	–	toluene	30
19 ^f	[Rh(cod)Cl] ₂	H ₂ O	toluene	>98

^aConditions: **1** (0.1 mmol), **2d** (1.5 equiv), catalyst (5 mol %), solvent (0.25 M), additive (1.5 equiv), 150 °C. ^bAdditive (1.0 equiv). ^c1 atm. ^dAdditive (0.1 equiv). ^e120 °C. ^fH₂O (1.5 equiv). See Supporting Information for details.

of Rh(III) precatalysts resulted in recovery of **2d**. The use of oxidants resulted in low yields, consistent with a Rh(I)/(III) cycle (entries 7–8). Strongly coordinating ligands provided **3** in lower yields (entries 9–11). Bases had a deleterious effect on the reaction efficiency (entries 12–14). Molecular sieves were not required for the reaction.^{11a} The reaction could ensue at lower temperatures (entry 18); however, the process was less efficient. Finally, we note that the reaction is highly practical; the reaction tolerates water and can be conducted in the presence of ambient air with no decrease in yields (entry 19). This stands in sharp contrast to C–H arylation with more electrophilic acyl precursors, which require careful control of the reaction conditions and moisture.^{11a–d} To our knowledge, this transformation represents the first example of both: (i) transition metal catalyzed C–H arylation with amides; (ii) catalytic activation of an amide N–CO bond by a rhodium catalyst.¹⁷

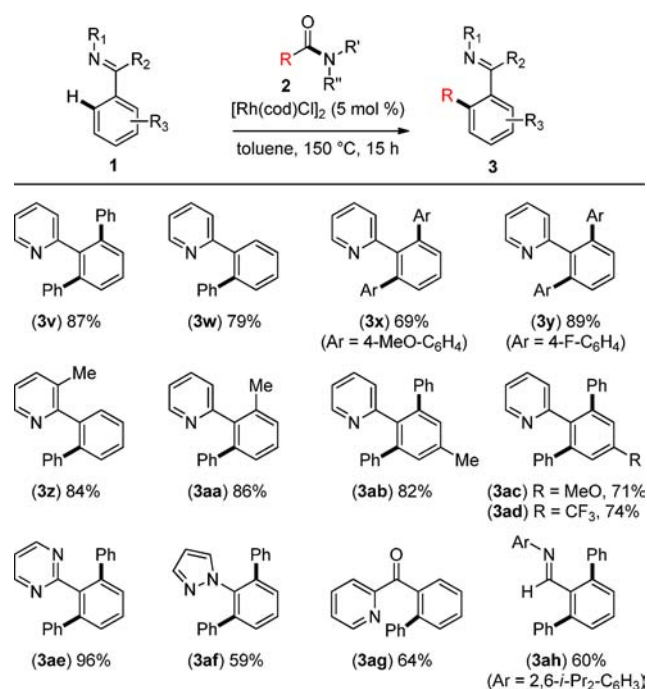
With optimal conditions in hand, we explored the preparative scope of our Rh(I)-catalyzed C–H arylation with respect to the amide component (Scheme 2). The reaction tolerates a remarkably broad range of functional groups. Amides containing neutral, electron-donating and electron-withdrawing groups afforded the desired products in excellent yields (entries 1–4).

Scheme 2. C–H Functionalization of Benzo[*h*]quinoline with Amides: Structural Variation of Amide^a

^a1 (1.0 equiv), amide (1.5 equiv), [Rh(cod)Cl]₂ (5 mol %), toluene (0.25 M), 150 °C, 15 h. R'R'' = (2d). See [Supporting Information](#) for details.

Steric hindrance was well-tolerated (entry 5). *p*-Fluoro, *p*-chloro, and even *p*-bromo groups gave the arylation product in high yields (entries 6–8), providing functional handles for further functionalization. Notably, the arylation with amide was accomplished in the presence of more reactive carbonyl functional groups such as esters and aldehydes (entries 9–10), which illustrates the strategic advantage of using typically inert amide bonds for transition metal catalyzed C–H activation. Other sensitive groups such as ketones and nitriles are also tolerated (entries 11–12). Meta-substitution (entries 13–14) and strongly electron-donating/withdrawing functional afforded the products in high yields (entries 15–16). This protocol could be further applied to naphthalene rings (entry 17). Moreover, heterocycles are compatible with the reaction conditions (entries 18–19). Most importantly, the reaction is not limited to sp²–sp² biaryl coupling, as vinyl (entry 20) and even alkyl groups (entry 21) can be successfully coupled in high yields. The latter provide an alternative to Friedel–Crafts alkylation. Overall, this reaction shows the highest functional group tolerance of all previously reported transition metal catalyzed transformations of amides via C–N activation,^{17,20} which highlights the high specificity of Rh(I) catalysts.

Next, we investigated the effect of electronic and structural modifications of the directing group component (Scheme 3). Typically, an excess of the amide precursor (3 equiv) was used for these reactions, resulting in double C–H activation.¹¹ However, the example with a stoichiometric amount (3w) illustrates that monoarylation is possible with high selectivity. The reaction is successful for electron-withdrawing and -donating substrates

Scheme 3. C–H Functionalization of Arenes with Amides: Structural Variation of 2-Phenylpyridine^a

^aSee Scheme 2. Amide (1–3 equiv). R'R'' = (2d). See [Supporting Information](#) for details.

(3x–3y). Moreover, monoarylation is selectively achieved with substrates bearing ortho-substituents on the pyridine ring (3z). The sterically demanding ortho-methyl substrate coupled in high yield (3aa). Substrates bearing electron-withdrawing and -donating groups at the para-position are well-tolerated (3ab–3ad). Furthermore, substrates bearing other directing groups such as pyrimidines (3ae), pyrazoles (3af), 2-acetylpyridines (3ag), and imines (3ah) were successfully functionalized to furnish the biaryl products in good yields. Notably, the inherently difficult 6-membered metalacycles (3ag) can be accommodated.^{3c} In this case, monoarylation product was formed, consistent with slower cyclometalation. Importantly, the coupling of imines provides rapid access to synthetically valuable biaryl aldehydes after hydrolysis.

Studies were conducted to shed light on the mechanism (see [Supporting Information](#), SI). Stoichiometric ESI-MS measurements with amide 2d indicated the presence of Rh-aryl intermediates, consistent with amide activation by Rh(I). A remarkably high TON for N–C activation of 1000 in the arylation of 1a with 2d demonstrates highly efficient catalysis (see SI). A possible mechanism is presented in Scheme 4.

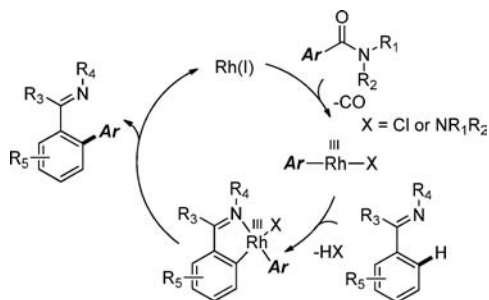
In conclusion, this report describes the first C–H arylation using amides by the N–C activation of the amide bond. Given the importance of amides and advantages of C–H activation manifolds, we expect that this concept will have a broad impact in using amides as coupling partners for C–H bond activation. Furthermore, our studies provide the first example of Rh(I)-catalysts for activation of inert N–C amide bonds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00058.

Scheme 4. Proposed Mechanism



Procedures and analytical data (PDF)

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Notes

The authors declare no competing financial interest.

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