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Ligand-Promoted Rhodium(III)-Catalyzed *ortho*-C–H Amination with Free Amines

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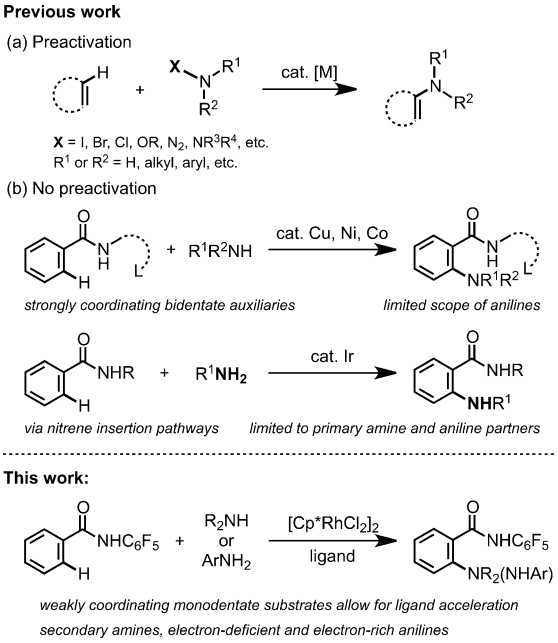
Abstract: *Ligand development for rhodium(III)-catalyzed C–H activation reactions has largely been limited to cyclopentadienyl (Cp) based scaffolds. 2-Methylquinoline has now been identified as a feasible ligand that can coordinate to the metal center of Cp*RhCl to accelerate the cleavage of the C–H bond of N-pentafluorophenylbenzamides, providing a new structural lead for ligand design. The compatibility of this reaction with secondary free amines and anilines also overcomes the limitations of palladium(II)-catalyzed C–H amination reactions.*

Aryl amines are privileged structural motifs in modern drug discovery.[1] Recently, transition-metal-catalyzed C–H activation/amination of arenes by an organometallic metal insertion approach has emerged as a significant area of research towards developing new methods for the synthesis of aryl amines.[2] A redox catalytic cycle proceeding through metal insertion and subsequent oxidation with chalcogenide-type (N–X species) N–O or N–halogen amino donors (such as *N*-benzoate alkylamines, *N*-chloroamines, *N*-hydroxycarbamates, *O*-acylhydroxylamines, nitrosobenzenes, azides, and 1,4,2-dioxazol-5-one) has been extensively explored with Pd^{II},[3,4] Ir^{III},[5] Rh^{III},[6] Ru^{II},[7] Cu^{II},[8] Co^{II},[9] and Fe^{II}[10] catalysts (Scheme 1 a). While these reactions have established the feasibility of the C–H insertion and C–N reductive elimination steps with a number of synthetically useful directing groups, the use of chalcogenide-type amino electrophiles is not ideal owing to the cost and limited scope of amino groups that can be introduced. Thus the development of a direct intermolecular coupling of arenes with free amines as nucleophiles is a significant task.



Scheme 1. Transition-metal-catalyzed C–H amination reactions.

Although C–H couplings with organometallic carbon nucleophiles by Pd^{II}/Pd^{0} catalysis have been developed,[11] analogous couplings using strongly coordinating free amines remain an unmet challenge. On the other hand, C–H amination reactions with secondary and primary amines have been made possible with Cu^{II}, Ni^{II}, and Co^{III} catalysts (Scheme 1 b).[12] Although the use of bidentate directing groups containing quinoline or oxazoline moieties substantially improved the scope of amine coupling partners, anilines, in particular, are poor coupling partners in general, with *N*-alkyl anilines being completely inactive. Significant progress has also been made with Ir^{III} catalysts to enable *ortho*-C–H aminations of benzamides with simple anilines and alkyl amines as coupling partners. However, the involvement of a nitrene insertion pathway excluded the use of secondary amines (Scheme 1 b).[13] Moreover, Rh^{III}-catalyzed intermolecular C–H amination is uniformly limited to preactivated amine coupling partners.[6] These limitations point to the need for new ligands for Rh^{III} catalysts. Herein, we report the identification of a new quinoline ligand that promotes Rh^{III}-catalyzed *ortho*-C–H amination reactions with free amines. Notably, both secondary amines and primary anilines are compatible with this newly developed catalytic system.

The combination of monodentate weakly coordinating amide substrates and ligands has enabled a great number of

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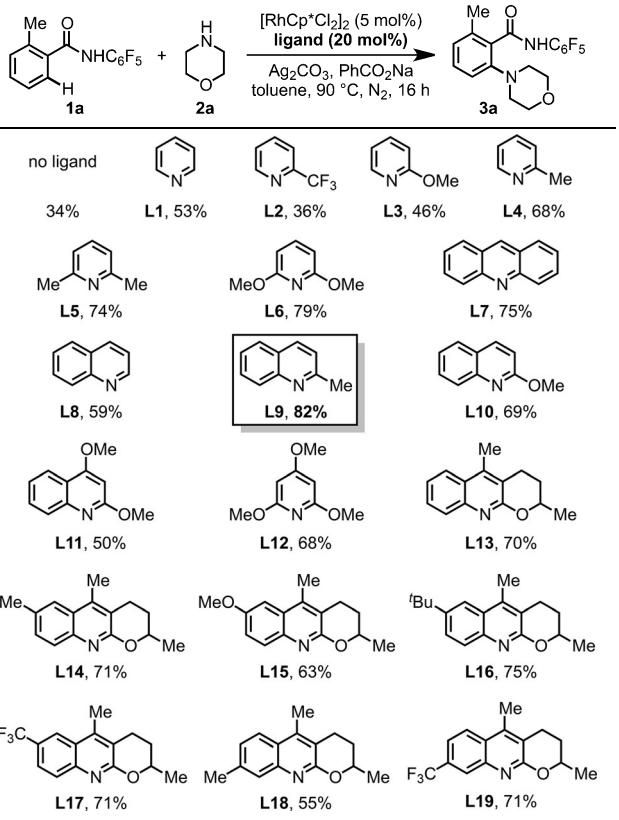
Pd^{II}-catalyzed C–H activation reactions. The synthetic utility and practicality of our *N*-pentafluorophenylbenzamide directing group has been demonstrated by an elegant synthetic route developed by a Novartis process team.[14] Inspired by the aforementioned progress on C–H amination, we began to investigate the possibility of achieving Rh^{III}-catalyzed C–H amination with morpholine using a simple monodentate amide directing group, anticipating potential ligand development. We commenced our investigation with *N*-aryl amide **1a** and morpholine (**2a**) using $[RhCp^*Cl_2]_2$ as the catalyst (see the Supporting Information, Table S1). We found that the addition of Ag_2CO_3 and NaOAc in MeCN afforded the aminated product **3a** in 8% yield (Table S1, entry 1). We further optimized various reaction parameters by screening oxidants, solvents, and bases, and found that the presence of $PhCO_2Na$ increased the yield to 34% (Table S1, entry 7).

Considering the impact of ligand development on Pd^{II}-catalyzed C–H amination reactions,[3c,d] it is reasonable to assume that the use of proper ligands could accelerate $C(sp^2)$–H cleavage and promote the subsequent C–N bond formation step by potentially tuning the steric and electronic properties of the active catalyst. Notably, ligand scaffolds for Rh^{III} catalysts are largely limited to cyclopentadienyl (Cp) motifs. To identify new ligand scaffolds for Rh^{III} catalysts, a series of simple pyridine-based ligands were tested for their efficiency of promoting amination (Table 1). Encouragingly, the addition of pyridine (**L1**) gave the desired product in 54% yield. Further ligand screening showed that an electron-withdrawing substituent (**L2**) had a slightly negative impact on the reaction while electron-donating ones (**L3**–**L7**) significantly improved the yield of the desired product (46–79%). We further investigated quinoline-based ligands (**L8**–**L19**) and found that 2-methylquinoline (**L9**) possesses an optimal balance of steric and electronic properties to provide **3a** in the highest yield (82%). Reducing the catalyst loading to 2.5 and 5 mol% decreased the yield to 45 and 67%, respectively. To elucidate the role of the ligand, we examined the influence of **L9** on the rate profile (Figure S2), which revealed that the ligand significantly increases the rate of this C–H amination reaction. Mono-N-protected amino acid (MPAA) and phosphine ligands have been studied for this reaction as well, and we found that MPAAs can also accelerate this $C(sp^2)$–H amination reaction to some extent (Table S2).

With the optimized conditions in hand, we examined the scope of *N*-pentafluorophenylbenzamides (**1b**–**1t**) with morpholine **2a** (Table 2). To our delight, substrates bearing various substituents were compatible with the reaction system, affording the desired products in moderate to good yields (56–88%). In general, the reactivity of electron-rich substrates (**1a**–**1h**) was higher than that of electron-deficient substrates (**1k**–**1r**). Unsubstituted benzamide **1i** afforded the desired product in good yield (77%). Notably, only mono-aminated products were formed in all cases. Moreover, for *meta*-substituted benzamides (**1b**, **1d**, and **1l**), C–H functionalization occurred exclusively at the less hindered position, showing good regioselectivity in this reaction system. Gratifyingly, 2-naphthamide **1j** was also applicable under the standard conditions, affording the desired product **3j** in reasonable yield. This transformation also tolerates halogenated substituents, especially the iodo group, which is apt to participate in cross-coupling reactions. In addition, we were pleased to find that heterocyclic amides, including furan **1s** and thiophene **1t**, are suitable substrates, and were also aminated in moderate yields (**3s** and **3t**, 56 and 68%, respectively). We also prepared **3g** on gram scale to demonstrate the preparative utility of this transformation. The auxiliary can be readily removed by treatment of the aminated products with $BF_3{\cdot}Et_2O$ in methanol, to convert these compounds into the corresponding methyl esters in good yields (see the Supporting Information).

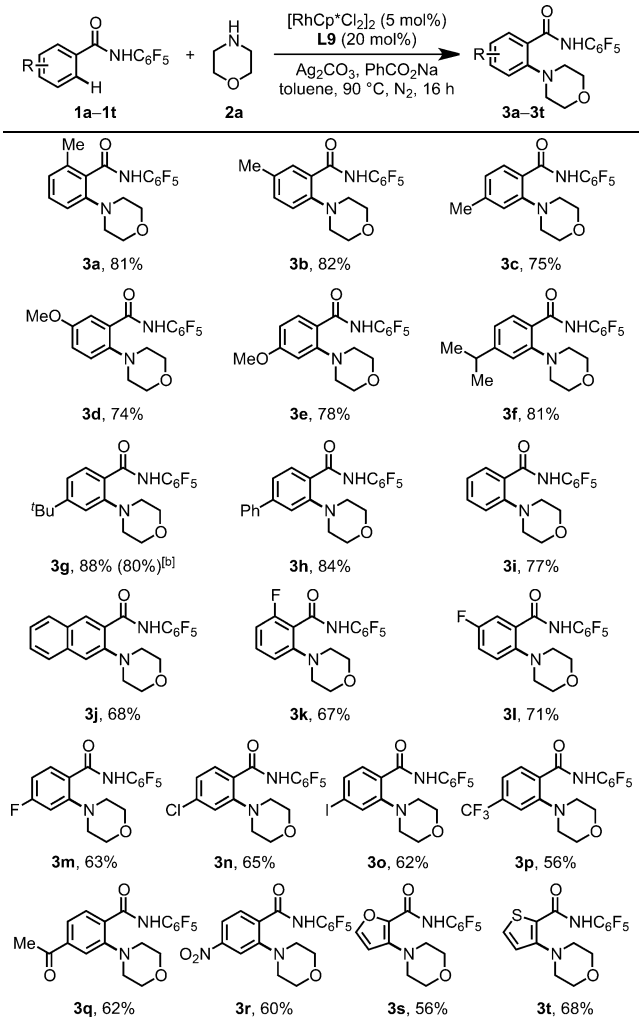
To further explore the scope of this amination reaction, various secondary amines were tested. As shown in Table 3, the reaction of substrate **1a** with a series of six-membered-ring secondary amines, such as piperidine, 4-methylpiperidine, ethyl isonipecotate, 4-cyanopiperidine, 1,4-dioxa-8-azaspiro[4.5]decane, and Boc-protected 4-aminopiperidine, under the optimized conditions afforded the corresponding aminated products in 62–80% yield (**4b**–**4g**). Moreover, the coupling of **1a** with several simple secondary amines, such as *N*-methylpropan-1-amine and diethylamine, also gave the aminated products **4h** and **4i** in 72 and 52% yield, respec-

Table 1: Ligand screening.[a]



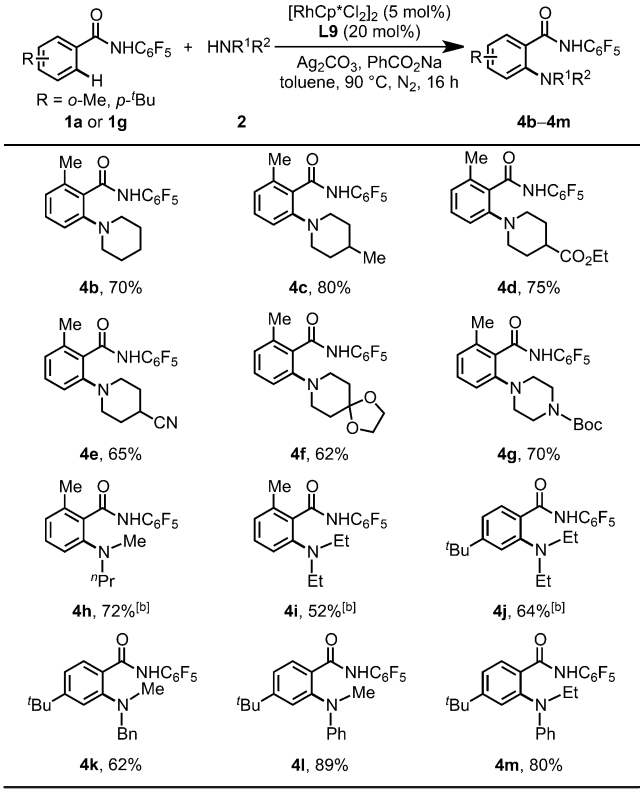
[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), Ag_2CO_3 (0.2 mmol), ligand (20 mol%), $PhCO_2Na$ (0.2 mmol), and dry toluene (2 mL) under N_2, 16 h, 90°C. The yields were determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard. Cp* = pentamethylcyclopentadienyl.

Table 2: Scope with respect to benzamide substrates.[a]



[a] Reaction conditions: **1a–1t** (0.1 mmol), **2a** (0.2 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), Ag_2CO_3 (0.2 mmol), **L9** (20 mol%), $PhCO_2Na$ (0.2 mmol), and dry toluene (2 mL) under N_2, 16 h, 90°C. Yields of isolated products are given. [b] On 3 mmol scale.

Table 3: Scope with respect to secondary amines.[a]



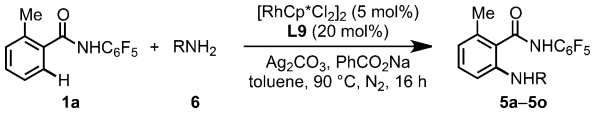
[a] Reaction conditions: **1a** or **1g** (0.1 mmol), **2** (0.2 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), Ag_2CO_3 (0.2 mmol), **L9** (20 mol%), $PhCO_2Na$ (0.2 mmol), and dry toluene (2 mL) under N_2, 16 h, 90°C. Yields of isolated products are given. [b] Alkyl amine (4 equiv).

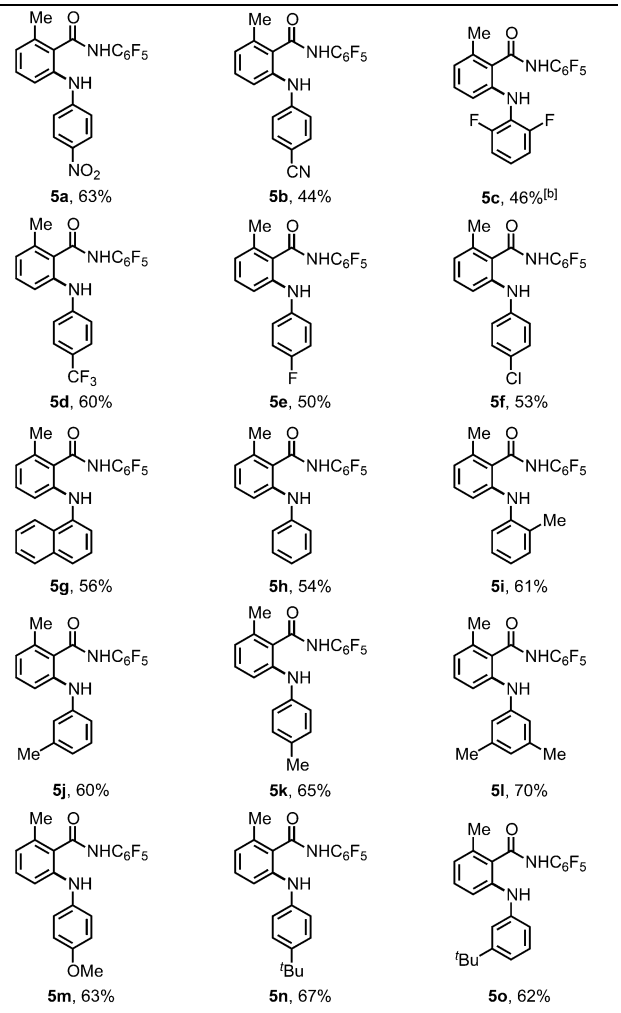
tively. Notably, with respect to **1a**, 4-*tert*-butylbenzamide **1g** afforded a higher yield (**4i** vs. **4j**). Meanwhile, the reaction of substrate **1g** with *N*-methylbenzylamine afforded the desired product **4k** in moderate yield. The reaction conditions are also suitable for aminations with N-substituted anilines. To the best of our knowledge, few examples of arene aminations with N-substituted anilines as the coupling partners have been reported thus far. Gratifyingly, we found that the coupling of **1g** with N-substituted anilines, such as *N*-methylaniline and *N*-ethylaniline, afforded the corresponding products **4l** and **4m** in excellent yields (89 and 80%, respectively).

The successful use of *N*-alkyl anilines prompted us to examine the compatibility of this reaction with free anilines. Transition-metal-catalyzed aminations of arenes with primary amines have been developed using several systems.[12k,l,13] However, only few examples with electron-rich anilines have been reported. The groups of Daugulis[12k] and Jana[12l] recently disclosed copper-mediated, bidentate-auxiliary-directed aminations with electron-rich anilines. We were pleased to observe that the present amination conditions were compatible with a wide range of anilines in the reaction of **1a** (Table 4). Anilines bearing electron-withdrawing substituents, such as nitro, nitrile, trifluoromethyl, and halogen moieties, afforded the desired products **5a–5f** in moderate yields (44–63%). Interestingly, 1-naphthylamine also reacted to furnish the corresponding aminated product **5g** in moderate yield (56%). Gratifyingly, the reactivity of aniline and its derivatives with electron-donating functional groups was observed to be good under the present conditions. Simple aniline also reacted with **1a**, providing the desired product **5h** in moderate yield (54%). Anilines possessing a methyl substituent afforded the aminated products **5i–5k** in good yields (60–65%). 3,5-Dimethylaniline gave **5l** in the highest yield of 70%. Importantly, anilines with electron-donating substituents, such as methoxy and *tert*-butyl groups, also furnished the desired products **5m–5o** in good yields (62–67%).

We next carried out extensive mechanistic investigations to gain further insight into this ligand-promoted C–H amination reaction. To test the possibility that the amines are converted in situ into electrophilic/reactive amines, we monitored the quantity of the free aniline (4-methoxyaniline) and the corresponding amination product **5m** by NMR spectroscopy throughout the reaction. Only unreacted aniline was observed. Although we observed that a large proportion of free aniline was oxidized to diazene species (see the

Table 4: Scope with respect to primary amines.[a]

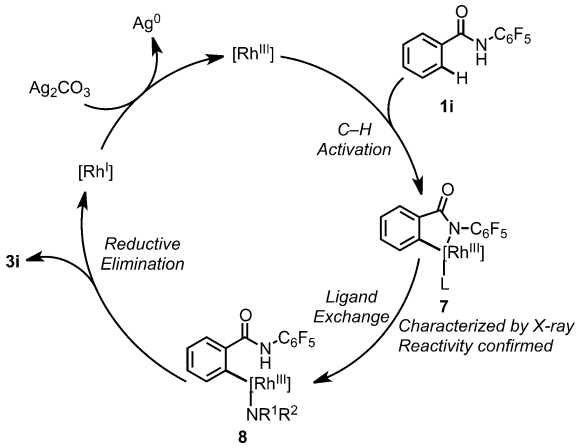




[a] Reaction conditions: **1a** (0.1 mmol), **6** (0.2 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), Ag_2CO_3 (0.2 mmol), **L9** (20 mol%), $PhCO_2Na$ (0.2 mmol), and dry toluene (2 mL) under N_2, 16 h, 90°C. Yields of isolated products are given. [b] Primary amine (4 equiv).

Supporting Information) in the absence of the benzamide substrate, control experiment showed that such diazene species are not reactive in this amination reaction. Competition experiments with free anilines (4-(trifluoromethyl)aniline and *p*-toluidine) also revealed that the electron-rich aniline with higher nucleophilicity was more reactive in this reaction (see the Supporting Information).

To probe whether C–H activation is the rate-determining step in this catalytic cycle, we performed a series of experiments to determine the kinetic isotope effect (KIE). The observed intermolecular KIE of 1.87 and the parallel KIE of 1.70 revealed that the *ortho*-C–H bond cleavage may be the rate-determining step (see the Supporting Information). The key C–H insertion intermediate was also characterized (rhodacycle **7′**; see the Supporting Information), and trans-



Scheme 2. Proposed reaction mechanism.

formed into the desired product **5m** (isolated in 46% yield) under the standard reaction conditions (see the Supporting Information), supporting the involvement of this intermediate. Based on the reaction conditions, a plausible reaction mechanism for this transformation is proposed in Scheme 2. The reaction is initiated by the coordination of amide **1i** to a Rh^{III} species bound to the quinoline ligand (L), which is followed by C–H activation to give the corresponding five-membered rhodacycle intermediate **7**. Subsequent ligand exchange at the Rh^{III} center leads to intermediate **8**, which undergoes C–N reductive elimination to give the *ortho*-aminated product **3i** and a Rh^{I} species. Such a ligand exchange process has also been observed with phosphine ligands.[15] The oxidation of Rh^{I} by Ag_2CO_3 completes the catalytic cycle.

In summary, we have developed a ligand-promoted Rh^{III}-catalyzed amination reaction of aryl C–H bonds with free secondary alkyl amines as well as a variety of anilines using a readily removable *N*-pentafluorophenylamide auxiliary. This transformation exhibits a broad substrate scope and tolerates various functional groups. The significant enhancement observed with the quinolines also provides a new lead for ligand design in Rh^{III}-catalyzed C–H activation reactions.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: amination · amines · ligand design · quinolines · rhodium

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