C–H Activation

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Rhodium(I)-Catalyzed Redox-Economic Cross-Coupling of Carboxylic Acids with Arenes Directed by N-Containing Groups**

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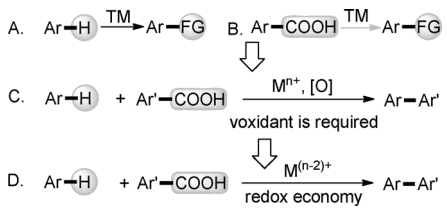
Traditional cross-couplings were considered to be the most powerful and accurate tools for constructing C–C bonds, and was recognized with the Nobel Prize in 2010.[1] For more efficient and greener methods to construct C–C bonds, much attention has been paid to direct C–H functionalization, starting from arenes (Scheme 1 A), in the past several



Scheme 1. Rational design of cross-coupling of arenes and aryl carboxylic acids. TM = transition metal.

decades.[2] Among these modern couplings, the coupling partners can be organic halides/pseudohalides,[3] organometallic reagents,[4] and even another arene.[5] Carboxylic acids are considered another important carbon source because of its ready availability, stability, and nontoxicity.[6] Although decarboxylation as well as cross-coupling with aryl halides are well known, decarboxylative oxidative coupling with arenes is relatively underexplored (Schemes 1 B and C).[7,8] Following the first example of the decarboxylative oxidative coupling by Myers et al.,[9] Crabtree and co-workers extended this concept to the coupling of benzoic acids with unactivated arenes.[6j] Then Glorius and co-workers developed intramolecular annulations to synthesize dibenzofuran and its derivatives.[10] All these methods have advantages but also have relatively complicated catalytic systems, require harsh reaction conditions, and have limited substrate scopes. Another drawback is the requirement of large amounts of oxidants in these reactions. Recently, Yu and co-workers made significant progress by using the decarbonylation of acyl chlorides and benzoic anhydrides to realize direct arylation in the absence of any oxidants.[11] In this article, we reported a new method to carry out the pseudo-decarboxylative coupling of carboxylic acids with arenes in the absence of heavy metal oxidants, thus offering a new convenient pathway for the construction of C_{sp^2}–C_{sp^2} bonds of biaryls and C_{sp^3}–C_{sp^2} bonds of alkyl aryls, which are potentially useful for the synthesis of a vast number of nature products and bioactive compounds.[12]

In general, different strategies have been proposed to facilitate the C–H activation to form C–M intermediates.[13] For oxidative decarboxylative coupling with arenes, previous efforts indicated that high-valent transition-metal species are efficient catalysts, and derive from an electrophilic metalation with relatively electron-rich arenes. To facilitate the catalytic cycle, the oxidant is required to oxidize the low-valent transition metal, generated from the reductive elimination at the final step of C–C formation, to the active species, thus called oxidative coupling (Scheme 1 C).[14] Another powerful pathway to realize C–H activations is through oxidative addition, which also produces C–M intermediates that might also undergo the decarboxylative coupling with carboxylic acids (Scheme 1 D).[15] The advantage of this design is to avoid a large amount of oxidant, especially toxic late-transition-metal salts, since the arene itself can oxidize the regenerated low-valent transition-metal complexes through oxidative addition after the catalytic cycle. Thus, we started searching for a solution to a desirable decarboxylative coupling.

A directing strategy was considered owing to its broad applications in promoting C–H activation and regioselectivity control in previous studies.[16] According to our recent successful development of an approach to C–H/C bond cleavage and decarbonylation by rhodium catalysis,[17] we initially chose 2-(*m*-tolyl)pyridine (**1a**) as the substrate and a rhodium(I) catalyst to test our idea (see Table S1 in the Supporting Information). We first carried out the reaction of **1a** with 4-methoxybenzoic acid (**2a**) under rhodium(I) catalysis and to our delight, $[\{Rh(CO)_2(acac)\}_2]$ served as a catalyst in the presence of Ac_2O to afford the desired arylation product **3a** (see Table 1 for structure) in 20% yield, as determined by NMR spectroscopy using benzyl methyl ether as an internal standard. In this reaction different

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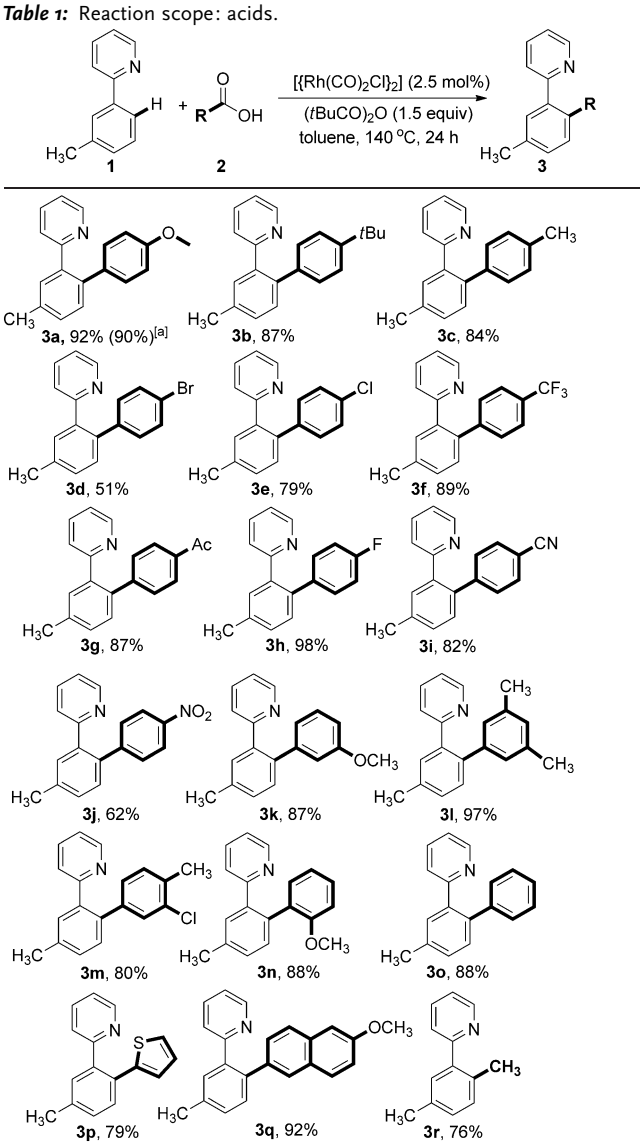
additives seem play key roles to promote the efficacy. PivCl and Boc_2O were tested and to our delight, Boc_2O gave much better results (59%). Various catalysts were screened and we found that $[\{Rh(CO)_2Cl\}_2]$ exhibited the best efficiency. To inhibit the formation of the biarylated product, the amount of the acid was reduce to 1.5 equivalents. With 5.0 mol% of $[\{Rh(CO)_2Cl\}_2]$ as the catalyst, investigations with regard to the solvents indicated that toluene is better than others, and afforded the product in an 85% yield upon isolation. Interestingly, when the catalyst loading and the amounts of the anhydride additives were reduced, the best yield (92%) was obtained, and even a reduction of the catalyst loading to 1.0 mol% did not reduce the yield notably. The reaction can also be run on a 1 mmol scale, thus allowing a remarkable reduction in both the amount of rhodium (from 2.5 mol% to 1 mol%) and the solvent (from 0.1M to 0.2M) with almost the same product yield.

With optimized reaction conditions in hand, we set out to test different carboxylic acids as coupling partners (Table 1). Gratifyingly, a variety of aryl carboxylic acids successfully coupled with **1a**. Different functionalities on the phenyl ring of the carboxylic acids, whether they were electron-withdrawing or electron-donating groups, are compatible. For example, bromo (**3d**), chloro (**3e**), trifluoromethyl (**3f**), acetyl (**3g**), fluoro (**3h**), cyano (**3i**), and nitro (**3j**) substituents on the benzoic acids survived and the desired products were obtained in good to excellent yields. These results implied that the electronic effect is not critical for this transformation. The *ortho*-substituted acids, such as *ortho*-methoxylbenzoic acid, can also afford a good product yield (**3n**), thus showing steric hindrance has little effect on the reaction. Heteroaromatic acids, such as 2-thiophenecarboxylic acid were tolerated, albeit with a slightly decreased yield (**3p**). It is noteworthy that when the α-ketophenylacetic acid was present, the product **3o** was produced through double decarbonylation albeit in a relatively low yield. Most importantly, an alkyl group can also be introduced onto the arene in good yield (**3r**), and might be a complementary method of the Friedel–Crafts reaction for the alkylation of arenes.

Taking into consideration that different substituents with distinct electronic and steric features may greatly influence the reactivity of substrates, we tested numerous functionalized 2-phenylpyridine derivatives (Table 2). To our delight, different substituents did not significantly affect the efficiency of the reaction under the optimized reaction conditions, thus further expanding the scope. Notably, the chloro substituent on the pyridinyl moiety did not affect the yields of the desired product **4h**, and offers the potential for orthogonal transformations.[18] Reaction of 3-methyl-2-(*m*-tolyl)pyridine resulted in a lower yield, which may arise from the steric hindrance thus forcing both aryl groups out of the plane (**4g**).

Moreover, we tested different aryl substituents to replace the 3-methylphenyl group. Replacing the methyl group with other functional groups at the *meta* position, such as phenyl (**4a**), sulfide methyl (**4b**), acetyl (**4c**), fluoro (**4f**), methoxyl (**4d**), also gave good to excellent product yields. The naphthyl group also worked well and the desired product was produced in an excellent yield (**4i**). To explore the application of this method, we tried other N-containing directing groups.

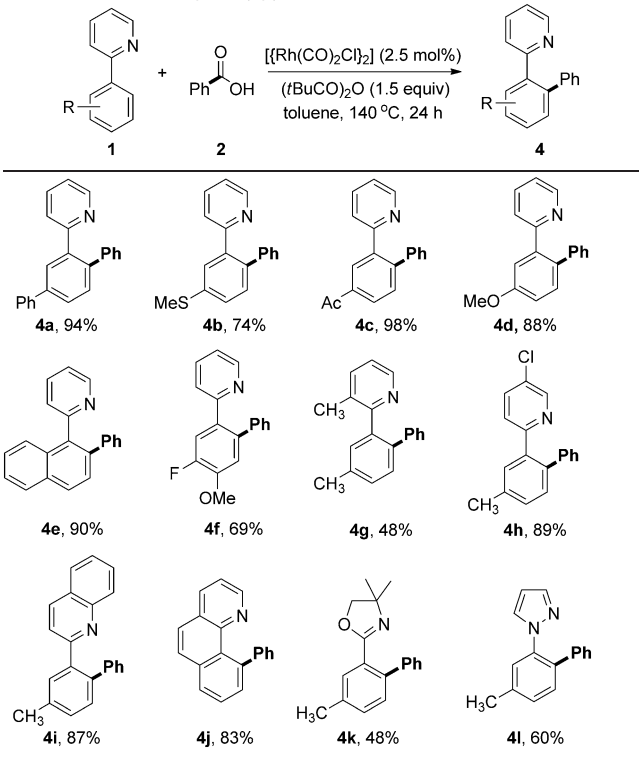
Table 1: Reaction scope: acids.



Reaction conditions: **1a** (0.2 mmol), acids (0.3 mmol) and anhydride (0.3 mmol), $[\{Rh(CO)_2Cl\}_2]$ (2.5 mol%) in toluene (2.0 mL) at 140°C for 24 h. [a] The reaction was scaled up to 1.0 mmol.

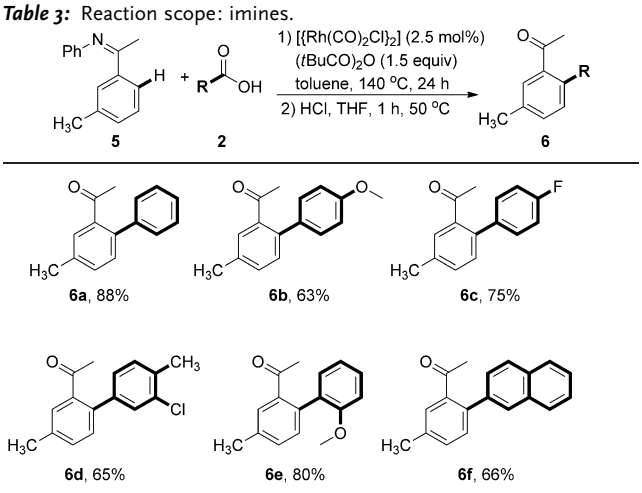
Benzo[h]quinolone, oxazole, and pyrazolyl groups all demonstrated reactivity and the products were isolated in good yield (**4j**, **4k**, **4l**), thus extending the potential applications of the method. Most importantly, in addition to the pyridinyl group, an imine (Table 3) could also serve as a directing group to afford the desired products. Different substitued benzoic acids, such as methoxy (**6b** and **6e**), fluoro (**6c**), chloro (**6d**), naphthyl (**6f**), gave moderate to excellent yields, with the ketone as the final product after the simple hydration. This development has potential in organic synthesis. To further explore the application of this method, the ketone products were subsequently converted into esters and amides through the Beckmann rearrangement as well as the Baeyer–Villiger oxidation (Scheme 2).

Table 2: Reaction scope: arylpyridines.



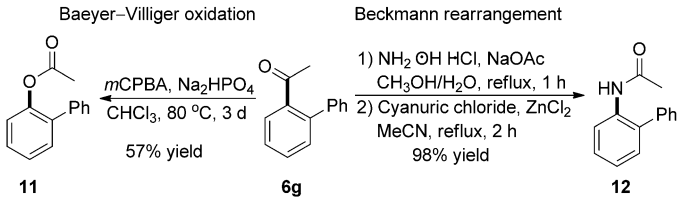
Reaction conditions: **1** (0.2 mmol), acids (0.3 mmol) and anhydride (0.3 mmol), [{Rh(CO)$_2$Cl}$_2$] (2.5 mol%) in toluene (2.0 mL) at 140 °C for 24 h.

Table 3: Reaction scope: imines.

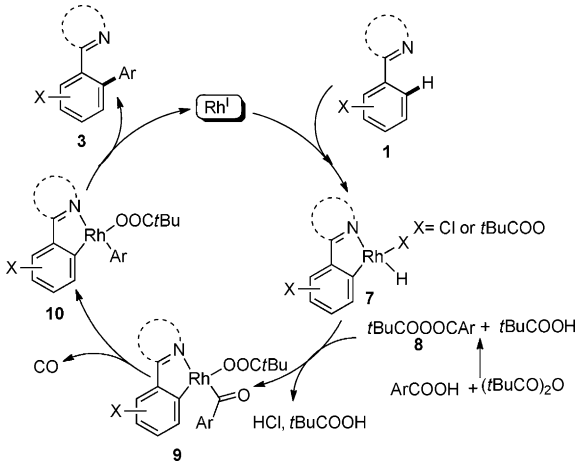


Reaction conditions: **5** (0.2 mmol), acids (0.3 mmol), anhydride (0.3 mmol) [{Rh(CO)$_2$Cl}$_2$] (2.5 mol%) in toluene (2.0 mL) at 140 °C for 24 h, then added 0.5 mL concentrated HCl and 0.5 mL THF. THF = tetrahydrofuran.

To probe the catalytic pathway, additional investigations were conducted. First of all, we investigated the gas phase of the reaction mixture and we found that carbon monoxide (CO) was detected by GC/MS (please see the Supporting Information). By testing the by-product of the reaction mixture, more than two equivalents of pivalic acid were



Scheme 2. Versatile transformations of the ketone product. *m*CPBA = 3-chloroperoxybenzoic acid.



Scheme 3. Proposed mechanism for decarbonylative C–H bond arylation of arenes.

detected. Based on our investigations and previous observations by Yu and co-workers, the catalytic pathway is considered to proceed as shown in Scheme 3.[11] The rhodium(I) species reacts with **1** to generate the complex **7** through C–H bond oxidative addition with the assistance of the N-containing group. The mixed anhydride **8** reacts with **7** to generate the complex **9**,[19] accompanied by the production of the first molecule of acid. A previous report on the use of anhydrides for a decarbonylative Heck-type reaction supports this hypothesis.[20] The complex **10** is generated through decarbonylation of **9**, and finally, reductive elimination produces the desired product **3** with the regeneration of the rhodium(I) catalyst to facilitate the catalytic cycle.

In conclusion, we have reported the first example of a cross-coupling between aryl carboxylic acids and arenes through the decarbonylation of the acid and direct C–H bond activation. Thus biaryls/alkyl aryls could be constructed by direct arylation of the arene with inexpensive, readily available, and nontoxic benzoic acids as arylating reagents. This protocol exhibits broad substrate scope with respect to benzoic acids and the yields are good to excellent, thus providing an attractive alternative to the arylation of arenes. Mechanistic studies indicate a new pathway of cross-coupling initiated by the oxidative addition of C–H bond to a rhodium(I) species. Expensive and toxic oxidants are avoided in this pseudo-oxidative decarboxylative coupling. These studies provide a new concept for the further development of C–C bond formations.

Experimental Section

$[\{Rh(CO)_2Cl\}_2]$ (0.005 mmol, 1.9 mg), 2-(*m*-tolyl)pyridine **1a** (0.2 mmol, 33.8 mg), $(tBuCO)_2O$ (0.3 mmol, 55.9 mg), and anisic acid (0.3 mmol, 30.4 mg) were added to a Schlenk flask. And then 2 mL of anhydrous toluene was added to the mixture. The reaction mixture was subsequently heated at 140 °C in a Wattecs parallel reactor for the indicated time (see the Supporting Information) with stirring. After cooling to room temperature, 1 mL of a concentrated ammonia solution was added to the solvent and the mixture was directly purified on silica gel chromatography with petroleum ether/EtOAc (12:1→5:1) to afford the desired product **3a** in 92% yield.

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