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Rhodium-Catalyzed Direct *Ortho* C−H Arylation Using Ketone as Directing Group with Boron Reagent

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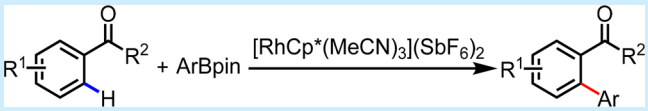
Supporting Information

ABSTRACT: A general method for selective *ortho* C−H arylation of ketone, with boron reagent enabled by rhodium complexes with excellent yields, is developed. The transformation is characterized by the use of air-stable Rh catalyst, high monoarylation selectivity, and excellent yields of most of the substrates.



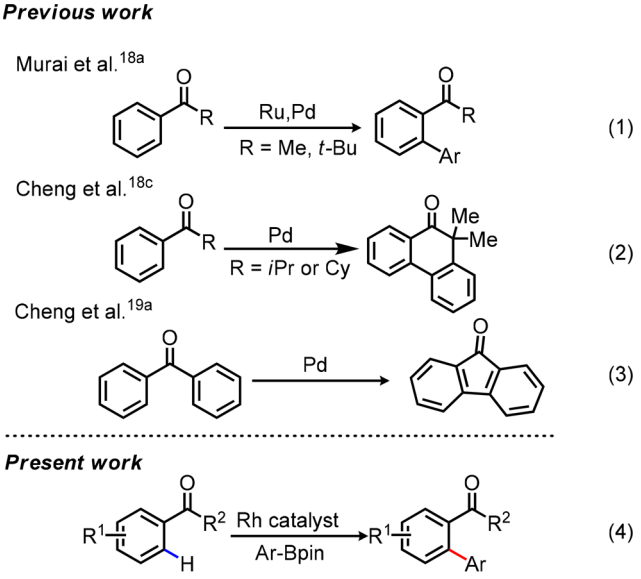
The biaryl structural motif plays an increasingly important role in biologically active molecules and photonic materials.[1] However, biaryl compounds have mainly been synthesized by using aryl halides and aryl metal compounds, releasing equivalent byproducts.[2] Due to the ubiquitous nature of C−H bonds, transition-metal-catalyzed C−H functionalization has emerged as a useful method to build aryl−aryl stocks.[3]

Inspired by the pioneering work of Murai and co-workers,[4] direct synthesis of carbon−carbon and carbon−heteroatom bonds using transition-metal-catalyzed C−H functionalization has attracted increasing attention.[5] As a result, a wide range of coordinating moieties have been utilized to efficiently activate the C−H bonds. Among these directing groups, pyridyl,[6] amino,[7] azo,[8] and amide groups[9] have been applied to facilitate various reactions described in the literature; however, other functional groups, such as thio,[10] hydroxy,[11] carbonyl,[12] ester,[13] aldehyde,[14] and carboxy groups,[15] were less reported.

Ketone-assisted C−H functionalization (e.g., alkylation, amination, hydroxylation, and olefination) catalyzed by Ru, Pd, Rh, and Ir has been well-documented.[16,17] However, arylation of aromatic C−H bonds assisted by ketone has seldom been described.[18] Murai et al. have reported *ortho* arylation of aromatic ketones catalyzed by Ru and Pd (Scheme 1, eq 1).[18a] Cheng et al. have reported Pd catalyzed ketone assisted arylation with relatively low yield (Scheme 1, eq 2).[18c] In addition, they have reported ketone-assisted dual C−H functionalization (Scheme 1, eq 3).[19] Inspired by our previous study on weak coordinating group amide directed C−H arylation catalyzed by Rh catalyst,[20] as well as others concerning Rh-catalyzed olefination and hydroxylation directed by ketones,[21] we aimed to establish a more efficient and site-selective synthetic method to build decorated biphenyl derivatives catalyzed by Rh catalyst using ketone as the directing group, with moderate to high yields. Herein, we report an interesting synthesis of biaryl derivatives from *sec*-alkyl aryl ketones and boron reagent by Rh-catalyzed C−H activation.

At the outset of our studies, we tested various reaction parameters for the envisioned Rh-catalyzed C−H arylation of

Scheme 1. C−H Arylation Assisted by Ketone



ketone (Table 1). Among silver salts, copper salts, and other organic oxidants, only AgF, AgOAc, and Ag_2O were effective (Table 1, entries 5, 8, 9, and 10), and Ag_2O gave the highest yield (Table 1, entry 9). As to the solvents, DCE gave the desired products with high yield (85%) in 3 h (Table 1, entry 9), while the other solvents, such as methanol and toluene, afforded no desired products (Table 1, entries 11 and 12). The yield was further elevated to 95% when the reaction time was prolonged to 6 h (Table 1, entry 13). Unfortunately, adding ligands, bases, or acids lowered the yield dramatically (see the Supporting Information). In addition, catalysts also evidently affected the reaction (see Table S5). The reaction of 1-(2-methoxyphenyl)-2-

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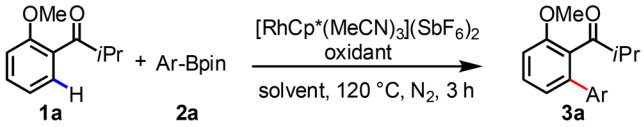
Table 1. Optimization of Reaction Conditions[a]



entry	oxidant	solvent	yield[b] (%)
1	BQ	DCE	NR
2	O_2	DCE	NR
3	$PhI(OAc)_2$	DCE	NR
4	$Cu(OAc)_2$	DCE	NR
5	AgF	DCE	52
6	Ag_2CO_3	DCE	NR
7	Ag_3PO_4	DCE	NR
8	AgOAc	DCE	53
9	Ag_2O	DCE	85
10	Ag_2O	DCM	65
11	Ag_2O	MeOH	NR
12	Ag_2O	toluene	NR
13[c]	Ag_2O	DCE	95

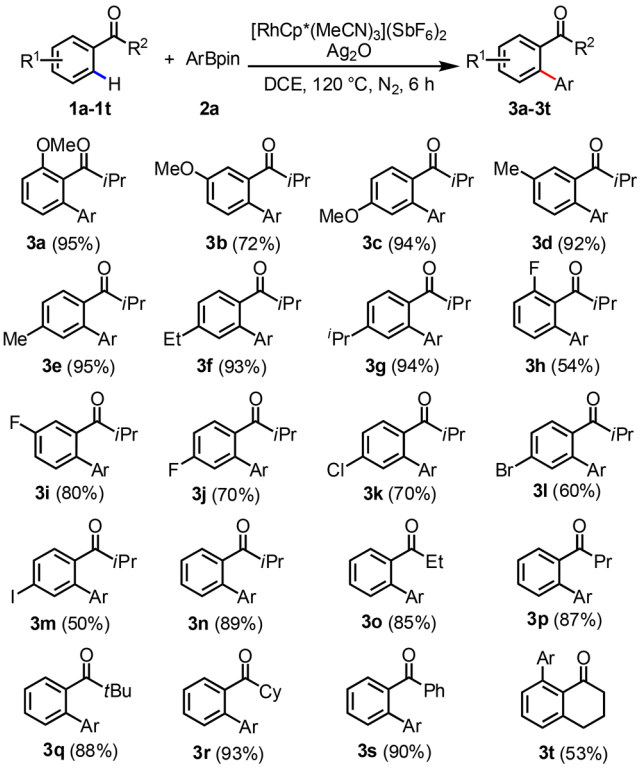
[a]Conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), $[RhCp^*(MeCN)_3](SbF_6)_2$ (10 mol %), oxidant (0.2 mmol), solvent (2 mL), N_2, 3 h, 120 °C. [b]The yield was determined by ^1H NMR analysis of crude product using CH_2Br_2 as an internal standard. [c]Reaction time 6 h.

methylpropan-1-one (**1a**) with 4-methoxycarbonylphenylboronic acid pinacol ester (4-CO_2Me-Ph-Bpin) (**2a**) in the presence of a more reactive Rh catalyst $[RhCp^*(MeCN)_3](SbF_6)_2$ (10 mol %) and Ag_2O (0.2 mmol) in DCE (2 mL) at 120 °C for 6 h generated a biphenyl derivative **3a** in 95% yield. Control experiments revealed that no desired product **3a** was obtained in the absence of Rh catalyst or silver salt (see Table S5).

Having identified these optimized conditions, we set out to evaluate the scope for this new reaction. A variety of substituted substrates were surveyed (Scheme 2). Various substrates were smoothly transformed into the corresponding *ortho*-arylated products in moderate to high yields. Substrates with electron-donating groups in the *ortho, meta,* and *para* sites afforded the desired products in excellent yields (**3a**–**g**) (Scheme 2). In particular, the regioselectivity was high, and only monosubstituted product was generated for each substrate. As demonstrated by the reaction of **1** bearing halogen groups, the functional group tolerance was high, although the yields were modest (**3h**–**m**) (Scheme 2), which allowed additional modification reactions in the halogenated positions. Moreover, reactions of other *sec*-alkyl aryl ketones, such as tertiary butyl, ethyl, propyl, cyclohexyl, and phenyl aryl ketones, afforded the desired products with excellent yields (**3n**–**s**) (Scheme 2). α-Tetralone gave moderate yield (53%), which can be attributed to its restricted structure (**3t**). Notably, benzophenone (**3s**) (Scheme 2) was also tolerated, which has rarely been reported until now.

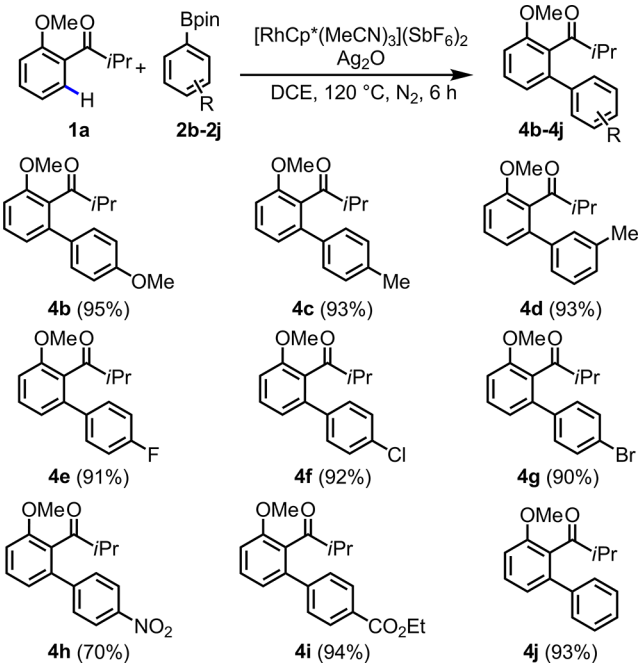
Afterward, this C–H bond functionalization reaction was successfully extended to various arylboronic acid pinacol esters with **1a** under the optimized conditions (Scheme 3). Non-substituted arylboronic acid pinacol ester (**2j**) (Scheme 3) gave the desired product with excellent yield (93%). Likewise, substrates with halogens in *para* positions (**2e**–**g**) (Scheme 3) also did so. In particular, arylboronic acid pinacol esters with a nitro group (**2h**) (Scheme 3) gave the desired products in 70% yield. We also prepared **3e** on gram scale to demonstrate the further application of this transformation (Scheme 4).

Scheme 2. Scope of Ketone Substrates.[a,b]



[a]Conditions: **1a**–**t** (0.1 mmol), **2a** (0.3 mmol), $[RhCp^*(MeCN)_3](SbF_6)_2$ (10 mol %), Ag_2O (0.2 mmol), DCE (2 mL), N_2, 6 h, 120 °C. [b]Isolated yield.

Scheme 3. Scope of Arylating Reagents[a,b]



[a]Conditions: **1a** (0.1 mmol), **2b**–**j** (0.3 mmol), $[RhCp^*(MeCN)_3](SbF_6)_2$ (10 mol %), Ag_2O (0.2 mmol), DCE (2 mL), N_2, 6 h, 120 °C. [b]Isolated yield.

To gain insights into the mechanism, deuterium-labeling experiments were conducted to determine the kinetic isotope

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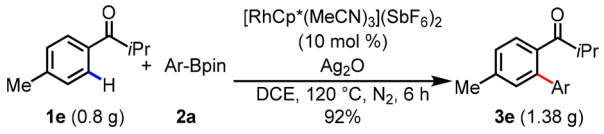
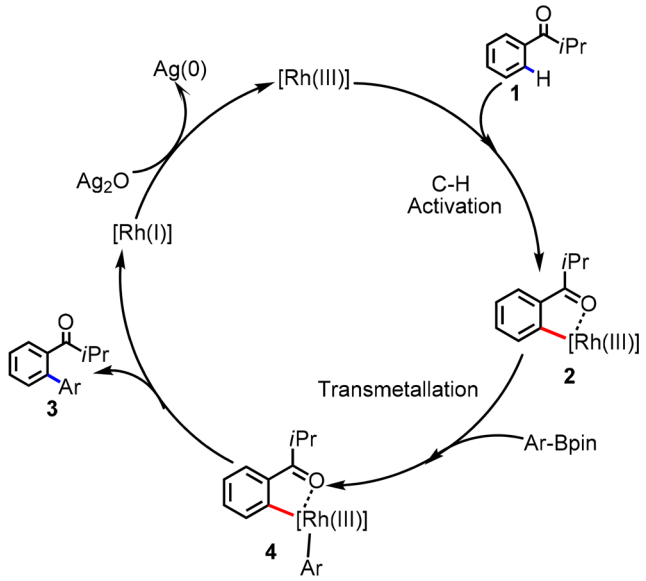
Scheme 4. Gram-Scale Synthesis



effect (KIE). The observed intermolecular KIE of 3.7 and parallel KIE of 2.3 revealed that the *ortho* C−H bond cleavage may be the rate-determining step (see the SI). On the basis of the results, a possible reaction mechanism was proposed for this catalytic reaction (Scheme 5). Coordination of the carbonyl of **1** to the Rh

Scheme 5. Proposed Reaction Mechanism



species followed by *ortho* metalation gives a five-membered intermediate **2**. Then coordinative insertion of Ar-Bpin into the Rh−aryl bond of metallacycle **2** provides the intermediate **4**, which undergoes reductive elimination to afford the *ortho* arylated product **3** and Rh(I) species. Subsequently, Rh(I) species are oxidized by Ag_2O to regenerate the reactive Rh(III) species for the next cycle.

In summary, we have developed a rhodium-catalyzed, chelation-assisted C−H functionalization reaction of aryl ketones and phenylboronic acid pinacol ester to afford biaryl derivatives in good to excellent yields. The catalytic reaction is highly regioselective, without disubstituted products. This procedure appears to be an effective and useful method to synthesize biaryl derivatives using ketone as directing group for C−H functionalization. Our group still endeavors to apply this method in natural product synthesis and to unravel the underlying mechanism.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02931.

Experimental details and characterization data of all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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