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Ruthenium(0)-Catalyzed C−H Arylation of Aromatic Imines under Neutral Conditions: Access to Biaryl Aldehydes

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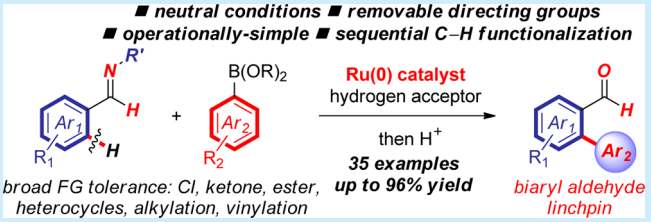
Supporting Information

ABSTRACT: The first ruthenium(0)-catalyzed C−H bond arylation of aromatic imines with arylboronates under neutral conditions is reported. This versatile method provides rapid access to a wide range of biaryl aldehydes that are difficult to assemble using traditional methods with high atom economy. A new hydrogen acceptor for Ru(0) arylation has been identified. This atom-economical strategy has potential for an array of direct applications in Ru(0)-catalyzed C−H bond arylations using removable directing groups. An indole synthesis by a sequential one-pot, multiple C−H activation protocol is reported.



In the past decade, selective C−H functionalization has revolutionized the field of organic synthesis; however, significant challenges in the synthesis of common building blocks using practical, atom-economical conditions still remain.[1] Recently, notable progress has been achieved in the development of ruthenium-catalyzed C−H functionalization fueled by the economic advantages of ruthenium.[2] In this context, the majority of recent advances focused on versatile Ru(II) catalysts.[2a] However, the development of robust methods using this catalytic manifold might be complicated by less favorable atom economy.[3] An alternative strategy involving C−H activation by a Ru(0)/Ru(II) cycle offers several advantages, including (i) operationally simple conditions, (ii) C−H activation in the absence of inorganic oxidants and/or bases, and (iii) mild neutral conditions for C−H functionalization.[4] Ru(0)-catalyzed C−H arylation of aromatic ketones was achieved using a $RuH_2(CO)(PPh_3)_3$ catalyst and pinacolone as a hydrogen acceptor; however, this method is limited to sterically hindered ketones to prevent diarylation.[5] Moreover, other carbonyl groups such as esters and ketones are incompatible with the $RuH_2(CO)(PPh_3)_3$ catalyst.[4,5] Recently, Snieckus significantly extended this activation manifold by employing amides as the regioselectivity controlling directing group.[6] Due to the amide bond planarity, only a single isomer was observed in a range of C−X (X = N, O) activation reactions. Unfortunately, the amide-directed C−H activation was reported to occur only with electron-rich heterocycles.[6a]

While direct ortho-arylation of aromatic aldehydes is currently beyond the scope of C−H activation manifolds due to weak coordination and low stability under the conditions required for C−H activation, we hypothesized that the atom-economical Ru(0)-catalyzed C−H arylation[7] directed by imines[8,9] as versatile aldehyde equivalents[10,11] could provide a general route to nitrogen-containing biaryls as well as to functionalized biaryl aldehydes that are high-value motifs in pharmaceuticals[10] and could serve as powerful synthetic linchpins.[11] The development of a broadly applicable Ru(0)-catalyzed C−H arylation using imines as versatile aldehyde equivalents is challenging for several reasons: (i) an efficient acceptor for the Ru−H species must be found that would be accommodated under the reaction conditions;[12] (ii) the imine can undergo competing reduction with Ru−H species;[13] (iii) the imine should be stable under the reaction conditions to prevent formation of Ru-amine complexes;[14] (iv) the imine should be electronically balanced to facilitate Ru coordination/C−H activation steps under mild conditions.[14] Finally, the formation of dialkoxyborane, a poison for Ru(0), must be avoided.[5]

Within our program on metal catalysis,[15] herein, we report the first Ru(0)-catalyzed C−H bond arylation of aromatic imines with arylboronates (Figure 1).[7−9] This atom-economical Ru(0)-catalyzed C−H activation/cross-coupling has two major advantages: (i) in a Ru(0)/Ru(II) cycle, inorganic oxidant and base are not required, leading to an inorganic waste-minimized protocol;[1−3] (ii) rationally designed, hemilabile, carbonyl-based directing groups[16] modulate the selectivity of C−H cross-coupling under thermodynamic C−H cleavage[4] that can be applied to a wide range of available carbonyl substrates. Moreover, we demonstrate that ketimines provide an unprecedented controlling factor for highly selective Ru(0)-catalyzed monoarylation;[17] note that Ru(0)-catalyzed, ketone-directed arylation is limited to sterically hindered ketones to prevent diarylation.[5] The functional-group-tolerant $Ru_3(CO)_{12}$ catalyst delivers the products in high yields and with broader compatibility than $RuH_2(CO)(PPh_3)_3$.[5,6] We have identified a new hydride acceptor that may find applications beyond this work.[18] Our strategy holds a potential for direct applications in Ru(0)-catalyzed C−H bond functionalization using removable directing groups.

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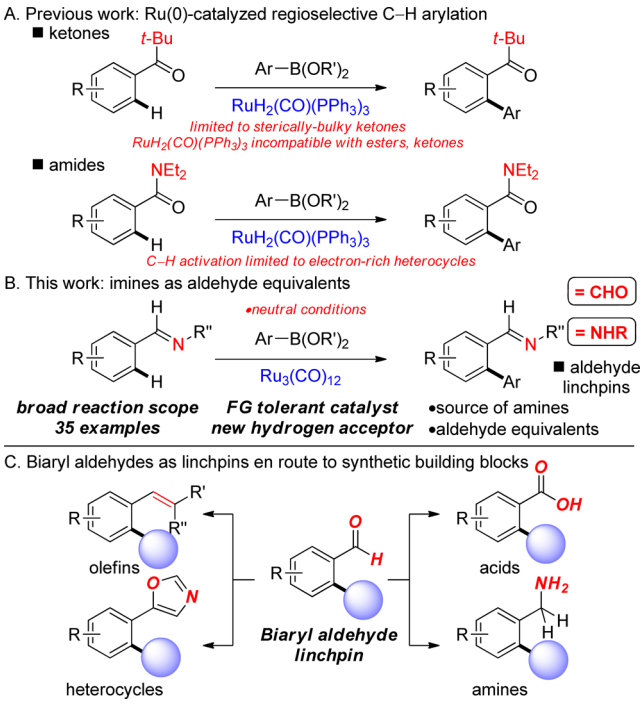
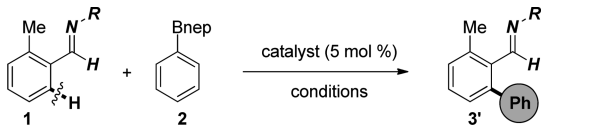


Figure 1. (A) Ru(0)-catalyzed C–H arylation of ketones and amides using $RuH_2(CO)(PPh_3)_3$. (B) This work: functional-group-tolerant Ru(0)-catalyzed C–H arylation of imines as synthetic aldehyde equivalents using $Ru_3(CO)_{12}$. (C) Biaryl aldehyde linchpins.

We started by studying the coupling of various imines of *o*-tolualdehyde with phenylboronate esters in the presence of Ru(0) catalysts and hydride acceptors. Selected results are outlined in Table 1. Complex mixtures were formed in absence of the acceptor. After extensive optimization, we found that the proposed arylation is indeed feasible in the presence of $Ru_3(CO)_{12}$ catalyst, benzylideneacetone (BA) as Ru–H acceptor, *N*-aryl imine (**1**) as C–H functionalization substrate, and neopentyl aryl boronate (**2**), providing the desired C–H arylation product in excellent 98% yield with no observable side reactions (entries 1–19). $RuH_2(CO)(PPh_3)_3$ employed for ketone arylation[5] and various Rh(I) and Ru(II) conditions (not shown) failed to provide the desired product. The nature of Ru–H acceptor is critical, with strained and aromatic olefins providing inferior results (entries 6–13). Coordination of the carbonyl to Ru might facilitate hydride transfer.[19] Phosphine ligands had a deleterious effect (entry 14). Other imines (entries 15–17), organometallic reagents, and conditions tested (entries 18–19) afforded the product in lower yields.

Next, the preparative scope was evaluated (Scheme 1). All C–H arylation products were obtained directly as aldehydes after mild hydrolysis.[11] Aryl boronates containing electron-rich (**3b**,**c**) and electron-poor (**3d**) functional groups afforded the desired products in excellent yields. Electrophilic functional groups, such as *p*-fluoro- (**3e**), *p*-chloro- (**3f**), *p*-ester (**3g**), *p*-ketone (**3h**), and *p*-olefin (**3i**), are perfectly accommodated. Reductive dechlorination was not observed under the reaction conditions,[6a] albeit the product was obtained in lower yield due to low conversion. Highly electron-donating (**3j**) and electron-withdrawing substituents (**3k**), polyarenes (**3l**), and electrophilic heterocycles (**3m**–**3o**) are well-tolerated. The protocol could be extended to vinyl (**3p**) and even alkyl nucleophiles (**3q**) under the standard conditions. Of note is the facility with which ketone and ester-containing nucleophiles can be employed, outperforming the $RuH_2(CO)(PPh_3)_3$-catalyzed protocol.[5,6] Evaluation of additional functional group tolerance is currently underway.

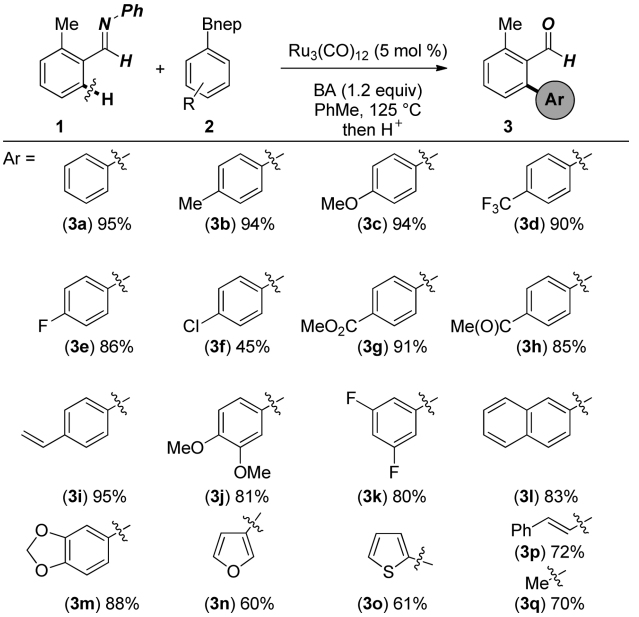
Table 1. Ru(0)-Catalyzed C–H Arylation of Imines[a]



entry	catalyst	acceptor	solvent	yield[b] (%)
1	$RuH_2(CO)(PPh_3)_3$	BA	toluene	8
2	$RuH_2(PPh_3)_4$	BA	toluene	11
3	$RhCl(PPh_3)_3$	BA	toluene	9
4	$[Rh(COD)Cl]_2$	BA	toluene	6
5	$Ru_3(CO)_{12}$	BA	toluene	98
6	$Ru_3(CO)_{12}$	BA	acetone	57
7	$Ru_3(CO)_{12}$	BA	dioxane	82
8	$Ru_3(CO)_{12}$	BA	pinacolone	91
9	$Ru_3(CO)_{12}$	BA	*i*-PrOH	33
10	$Ru_3(CO)_{12}$	styrene	toluene	74
11	$Ru_3(CO)_{12}$	norbornene	toluene	64
12	$Ru_3(CO)_{12}$	dec-1-ene	toluene	55
13	$Ru_3(CO)_{12}$	acrylonitrile	toluene	<2
14[c]	$Ru_3(CO)_{12}$	BA	toluene	5
15[d]	$Ru_3(CO)_{12}$	BA	toluene	61
16[e]	$Ru_3(CO)_{12}$	BA	toluene	80
17[f]	$Ru_3(CO)_{12}$	BA	toluene	93
18[g]	$Ru_3(CO)_{12}$	BA	toluene	90
19[h]	$Ru_3(CO)_{12}$	BA	toluene	88

[a]Imine (0.20 mmol), PhBnep (1.5 equiv), acceptor (2 equiv), catalyst (5 mol %), solvent (1.0 M), 125 °C, 15 h. [b]Determined by ^1H NMR and GC. [c]PPh_3 (5 mol %). [d]*N*-Me instead of *N*-Ph. [e]*N*-*t*-Bu. [f]*N*-2,6-$Me_2C_6H_3$. [g]PhBnep (1.0 equiv). [h]PhBpin (1.5 equiv). BA = benzylideneacetone. Bnep = 5,5-dimethyl-1,3,2-dioxaborolane.

Scheme 1. Ru(0)-Catalyzed C–H Arylation: Scope of Nucleophiles[a,b]



[a]Imine (0.20 mmol), PhBnep (0.30 mmol), BA (0.24 mmol), catalyst (5 mol %), PhMe (1.0 M), 125 °C, 1–15 h. [b]All yields are isolated yields of the corresponding aldehyde after hydrolysis. See SI for details.

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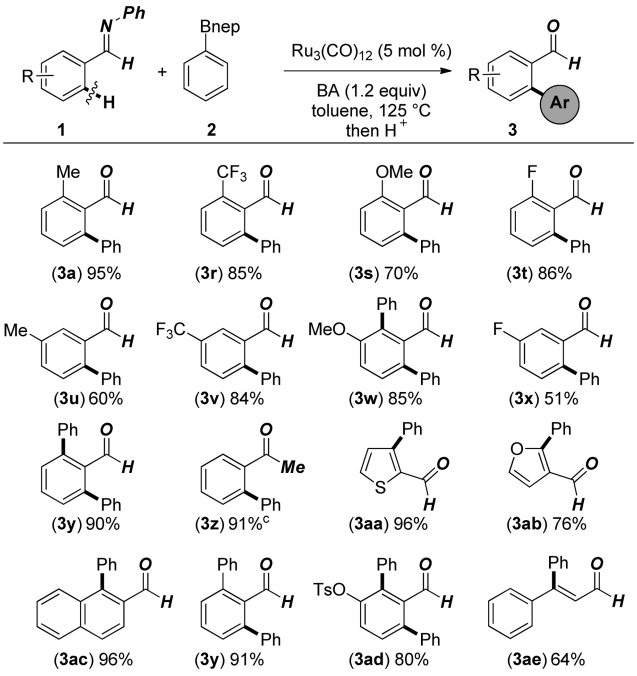
This new Ru(0)-catalyzed method enables access to a broad range of aldehydes with unconventional selectivity (Scheme 2). First, significant steric and electronic effects of substituents are observed (**3r**–**3x**). Ortho-substituted imines were found to be excellent substrates (**3r**–**3t**).

Scheme 2. Ru(0)-Catalyzed C–H Arylation: Scope of Imines[a,b]



[a,b]See Scheme 1. ArBnep (1–3 equiv). [c]Ketimine substrate.

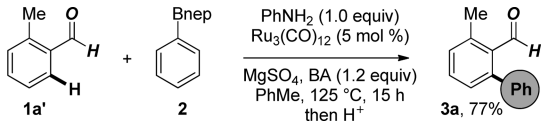
Excellent regioselectivity was observed in the arylation of electron-poor meta-substituted imines (**3v**, >50:1). Electron-rich substituents resulted in double arylation (**3w**). This reactivity is complementary to the monoarylation under Pd(II)/(0) catalysis.[8a] A plot of $\log_{(\text{meta-selectivity})}$ versus σ^* gives Hammett correlation ($\rho = 1.37$; $R^2 = 0.93$), indicating that electronic effects determine the reaction outcome. While the unsubstituted imine substrate afforded the valuable diarylated aldehyde (**3y**), the corresponding ketimine enabled high regiocontrol (**3z**, >12:1).[17] This reactivity represents a significant bonus compared to Ru(0)-catalyzed ketone-directed arylation, in which steric hindrance (e.g., *t*-Bu) was required to prevent diarylation.[5] Heteroatom-containing imines (**3aa**,**3ab**) and polyarenes (**3ac**) are well-tolerated. Arylation via a six-membered metalacycle was not observed (**3y**). The reaction also tolerates removable alcohol protecting groups (**3ad**). Furthermore, vinyl groups undergo sp^2-arylation (**3ae**).

Importantly, due to the mild, waste-minimized conditions, the reaction sequence can be readily performed by starting directly from aldehyde by an in situ imine synthesis/post-C–H arylation hydrolysis (Scheme 3). We determined that the method for an in situ arylation is general and preferred when less stable imines are used.

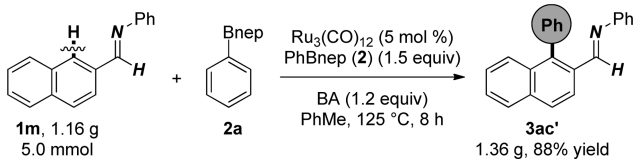
The C–H arylation was carried out on a gram scale, demonstrating scalability of our protocol (Scheme 4).

Studies were performed to gain preliminary insight into the reaction mechanism (see SI). (1) Intermolecular competition experiments between differently substituted imines revealed that electron-deficient substrates are inherently more reactive,

Scheme 3. In Situ Aldehyde Arylation



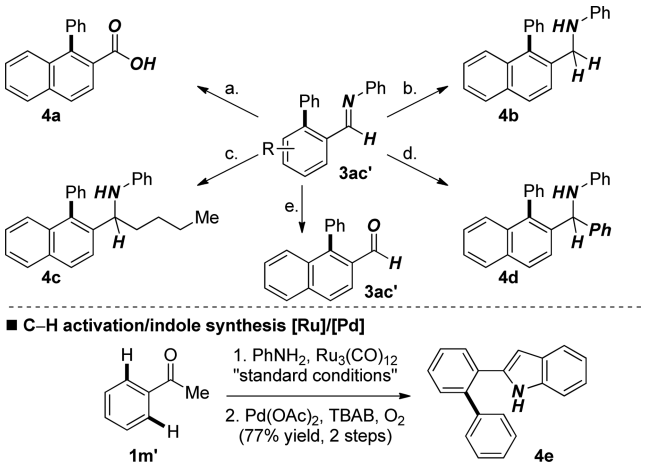
Scheme 4. Gram Scale Synthesis



consistent with reductive elimination via a migration π–π coupling mechanism.[4] (2) Experiments with electronically diverse boronates revealed that the electronic nature of the nucleophile does not significantly affect the yield, consistent with the nitrogen-assisted B–Ru transmetalation.[20] (3) Quantitative reduction of BA to 4-phenylbutan-2-one is observed.[18,19] (4) Electronic effects in the mono/diarylation selectivity of meta-substituted imines (**3v**,**w**) are consistent with imine coordination to the Ru center during the cycle. We have not detected products resulting from carbonyl reduction in the acceptor.[19] Likewise, the formation of dialkoxyborane was not observed.[21] Further studies to elucidate the mechanism are ongoing.

We demonstrated the utility of products in the synthesis of a diverse set of building blocks (Scheme 5). The in situ Ru(0)-

Scheme 5. Product Transformations[a]



[a]Reagents and conditions: (a) $NaClO_2$, MeCN, H_2O, rt, 18 h, 76%; (b) $NaBH_4$, *p*-TsOH, EtOH, rt, 2 h, 81%; (c) *n*-BuLi, THF, 78 °C to rt, 2 h, 85%; (d) $NaBPh_4$, $[RhCl(cod)]_2$, xylenes, 160 °C, 24 h, 70%; (e) HCl, Et_2O, rt, 3 h, quant.

catalyzed C–H arylation/Pd(II)-catalyzed indole synthesis underscores the potential of our mild protocol in the synthesis of biologically active heterocycles via multiple C–H functionalizations.[22]

In conclusion, we have reported the first Ru(0)-catalyzed C–H arylation of aromatic imines with organoboranes under neutral conditions. This strategy provides rapid access to functionalized biaryl aldehydes that are important building blocks in organic synthesis. We expect that this method will lead to the

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development of new C−H activation protocols with versatile Ru(0) catalysts.

■ ASSOCIATED CONTENT

Supporting Information

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Procedures and analytical data (PDF)

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Notes

The authors declare no competing financial interest.

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