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Arylation of Aldehydes To Directly Form Ketones via Tandem Nickel Catalysis

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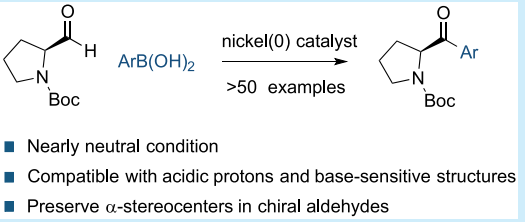
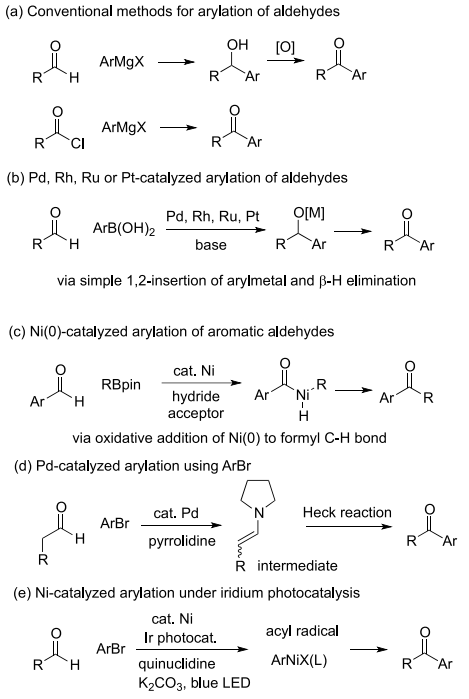
Supporting Information

ABSTRACT: A nickel-catalyzed arylation of both aliphatic and aromatic aldehydes proceeds with air-stable (hetero)arylboronic acids, with an exceptionally wide substrate scope. The neutral condition tolerates acidic hydrogen and sensitive polar groups and also preserves α-stereocenters of some chiral aldehydes. Interestingly, this nickel(0) catalysis does not follow common 1,2-insertion of arylmetal species to aldehydes and β-hydrogen elimination.

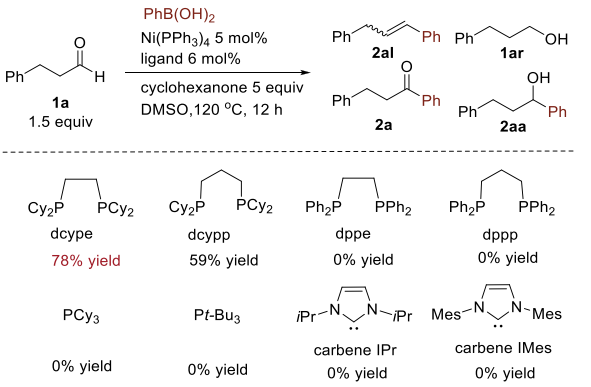


Arylation of aldehydes was traditionally performed by addition of Grignard reagents under basic conditions, followed by oxidation of the resulting carbinols (Scheme 1a). But carbinol oxidation often involves harsh acidic or basic conditions, which have poor compatibility with sensitive structures and acidic hydrogen. Alternatively, Grignard addition to acid chlorides can be performed to access ketones directly. Arylation of aldehydes with bench-stable organoborons to produce diaryl ketones is well documented with the assistance of homogeneous catalysts of Ru,[1] Rh,[2] Pd,[3] and Pt (Scheme 1b).[4] For example, Genet et al. reported Rh-catalyzed conversion of aryl aldehydes to biaryl ketones, using $ArBF_3K$ or $ArB(OH)_2$,[2] but the conditions cannot be applied to aliphatic aldehydes containing enolizable α-hydrogens. In particular, Gu et al. also reported arylation of aromatic aldehydes with RBpin esters catalyzed by nickel(0) and *N*-heterocyclic carbenes, which proceeded via a key step of nickel(0) oxidative addition

Scheme 1. Catalytic Arylation of Aldehydes for Preparation of Aryl Ketones



Scheme 2. Ligand Effect on Arylation of a Model Aldehyde (Yield of 2a Is Indicated)



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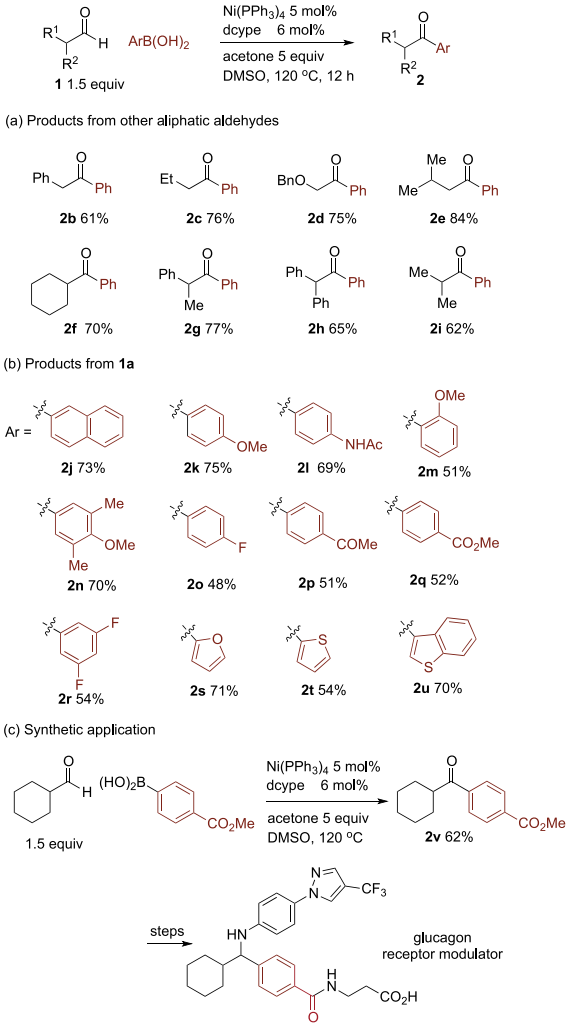
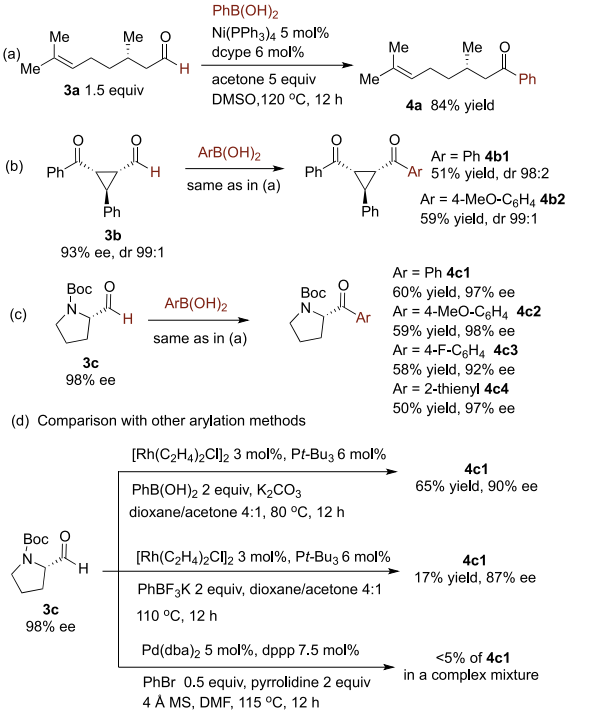
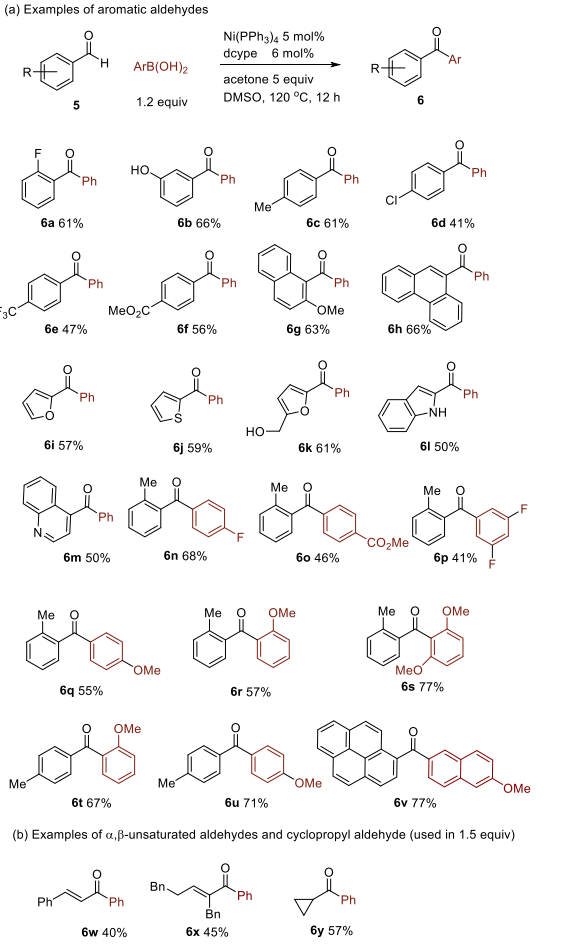
Scheme 3. Arylation of Aliphatic Aldehydes



Scheme 4. Arylation of Chiral Aldehydes and Comparison with Other Synthetic Methods



Scheme 5. Arylation of Aromatic Aldehydes and Enals



of formyl CH bonds (Scheme 1c).[5] Unfortunately, the examples were restricted to aryl aldehydes, while aliphatic aldehydes suffered from fast self-aldol condensation, a side reaction. Moreover, excess amounts of aldehydes, ketones, aryl iodides, and air or peroxides were needed as sacrificial oxidants to remove metal hydrides under these conditions.

Arylation of aldehydes with aryl electrophiles is another common approach to access ketones. For example, Hartwig et al. reported Pd-catalyzed arylation of *tert*-butyl hydrazones using aryl bromides, and a strong base, sodium *tert*-butoxide, was needed.[6] After acidic hydrolysis, aryl ketones were released. In another example, Xiao et al. reported Pd-catalyzed arylation of aliphatic aldehydes using aryl halides via a key step of arylation of in situ formed enamines (Scheme 1d),[7] but α-branched aldehydes cannot be used as substrates. Recently, MacMillan et al. reported nickel-catalyzed arylation of various aldehydes, including enolizable ones, using aryl bromides under blue LED irradiation (Scheme 1e).[8] Unfortunately, in all of the conditions above, bases-sensitive functional groups were incompatible. Recently, Newman et al. also disclosed arylation of both aromatic and aliphatic aldehydes with aryl triflates, but an example carrying an unprotected NH-indole resulted in poor yield.[9]

Finally, Cheng et al. disclosed nickel-catalyzed arylation of aryl aldehydes using aryl iodides with zinc powder as terminal

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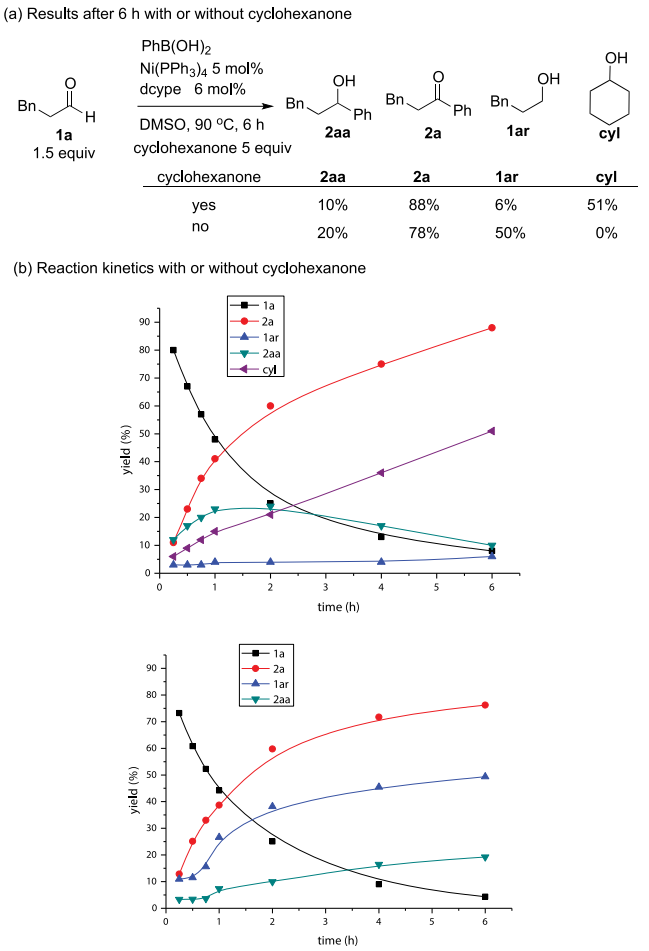


Figure 1. Phenylation kinetics of **1a** in the presence of cyclohexanone (top) and its absence (bottom).

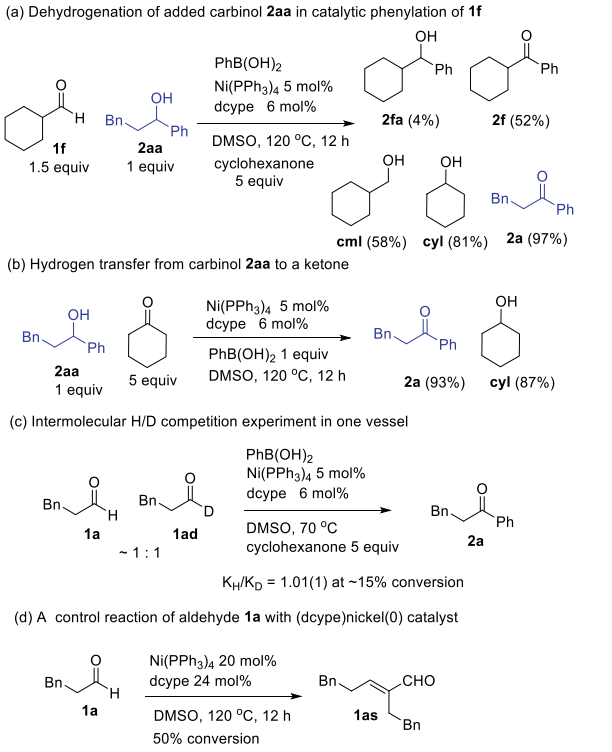
reductant, but aliphatic aldehydes gave poor yields.[10] Thus, efficient, general methods for arylation of aldehyde with good compatibility of sensitive functional groups are still desirable.[11]

Herein, we report a general arylation method that provides aryl ketones from aliphatic aldehydes, including enolizable ones, and (hetero)aryl aldehydes under nearly neutral conditions. We initiated our study by examining arylation of enolizable aldehyde **1a** and phenylboronic acid using a catalytic cocktail of $(PPh_3)_4Ni(0)$ and a bulky, strongly donating bisphosphine dcype as shown in Scheme 2. To our surprise, the reaction did not form aryl alkenes **2al** as we anticipated.[12] Instead, aryl ketone **2a** was produced under many conditions, along with side products derived from reduction of aldehyde (**1ar**) and phenyl addition (**2aa**).

The side reaction, reduction of aldehyde **1a**, clearly indicates that during the nickel catalysis a nickel hydride species is likely produced. Thus, we examined the effect of added hydride acceptors and found that addition of acetone or cyclohexanone remarkably improved the yield of ketone **2a**. In comparison, trifluoroacetone and acetophenone were less effective acceptors, giving 49% and 60% of **2a**, respectively.

The efficiency of the reaction was highly dependent on the nature of ancillary ligands on the nickel catalyst—only strongly donating, bulky bisphosphines, such as dcype and dcypp, generated active catalysts. Other diphosphines (binap, dppe, dppp, dppb, and dppf) and monophosphines (PPh_3, PCy_3, P*t*-Bu_3, Davephos, and XPhos) did not afford **2a** at all. DMSO

Scheme 6. Mechanistic Studies



was the best solvent for this transformation, while in DMA, THF, and toluene the yield of **2a** dropped to 74%, 54%, and 29%, respectively. Under similar conditions, palladium(0) complexes and nickel(II) salts gave no ketone **2a** at all (for details, see the Supporting Information).

When the model reaction of aldehyde **1a** and phenylboronic acid was carried out on a 2 mmol scale using 2 mol % nickel, 79% yield of **2a** was isolated. Phenylboroxine was also tested and afforded ketone **2a** in 57% yield. From other arylboron reagents, the yields of **2a** are 0% from PhBpin, 17% from PhBcat, 3% from PhBnep, and 21% from Ph_3B, respectively. Notably, aldol condensation of aldehyde **1a** was the main side reaction in these reactions.

Using the optimal conditions, a diverse set of aliphatic aldehydes smoothly reacted to give aryl ketones (Scheme 3). The main side reaction was reduction of aldehydes. *α*-Branched aldehydes were also well tolerated (**2f–i**). However, the reaction of hindered pivalaldehyde only afforded 10% of the desired ketone. In reactions of model aldehyde **1a**, electronically diverse arylboronic acids coupled smoothly. Notably, electron-deficient arylboronic acids usually gave moderate yields of aryl ketones (**2o–r**). Moreover, heteroaryl rings such as furan, thiophene, and benzothiophene were well tolerated (**2s–u**). Unfortunately, primary or secondary alkylboronic acids did not afford the desired ketones, while alkenyl ones furnished low yields; for example 1-cyclopentenyl boronic acid gave only <20% yield of the ketone. In those reactions, aldol condensation was the side reaction observed. As a demonstration of synthetic utility, arylation of aldehyde **1f** readily provided ketone **2v**, which was used as a synthetic intermediate toward a glucagon receptor modulator.[13]

(*S*)-Citronellal **3a** containing a *β*-tertiary stereocenter was also readily arylated to ketone **4a** in 84% yield (Scheme 4a). In reactions of a chiral cyclopropyl carboxaldehyde **3b** (Scheme 4b), three stereocenters were virtually unchanged during

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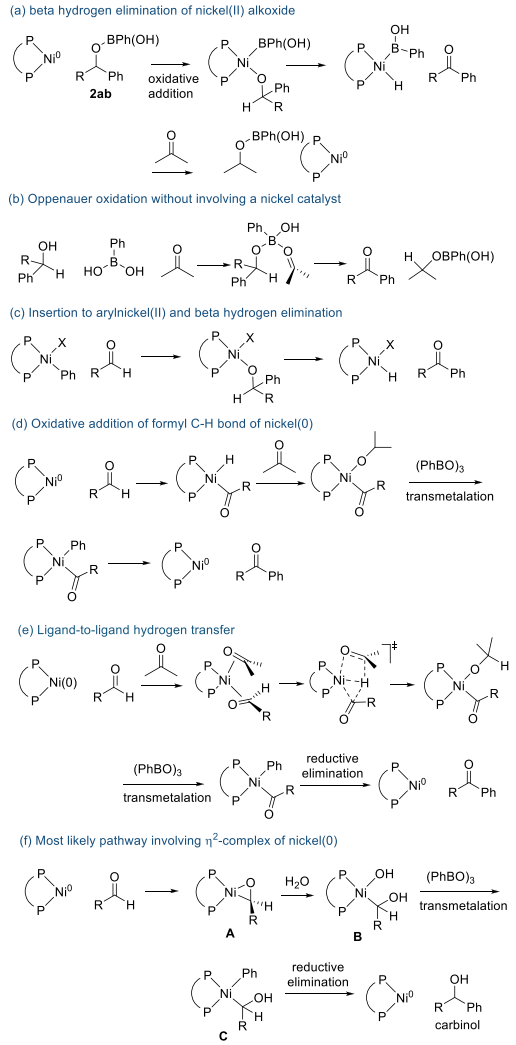
Scheme 7. Possible Reaction Pathways



arylation. In the third example, (*S*)-*N*-Boc-prolinal **3c** (98% ee) was smoothly arylated by both electron-rich and poor arylboronic acids as well as a thienylboronic acid (Scheme 4c), while the ee values of products were almost unchanged from the aldehyde. One exception was noticed in arylation using an electron-deficiency *p*-fluorophenyl ring (**4c3**), in which the ee dropped from 98% to 92%.

A comparison was made with Genet's Rh-catalyzed arylation using phenylboronic acid,[2b] which resulted in 65% yield of **4c1**, but the ee decreased to 90% even after we optimized the base, K_2CO_3 (Scheme 4d). Another procedure of Genet using $KArBF_3$ did not use any base,[2a] but it only afforded **4c1** in 17% yield and 87% ee, unfortunately. Furthermore, we noticed that Genet's methods only gave <10% yield of ketones when linear aldehyde **1a** was used. In a third comparison, Pd-catalyzed arylation of in situ formed enamines prefers aldehydes without α-branching as substrates,[7] so a reaction of **4c** resulted in a very complex mixture containing <5% of **4c1**.

Besides aliphatic aldehydes, the current arylation procedure was successfully applied to aromatic ones after adjusting the ratio of aldehydes to arylboronic acids to 1:1.2 (Scheme 5). Arylboronic acids of diverse electronic properties efficiently added to these aldehydes. Furthermore, heteroaryl aldehydes of thiophene, furan, indole, and quinoline also reacted well (**6i**–**m**). The conditions were compatible with esters (**6f** and **6o**), aryl fluorides (**6a**, **6n** and **6p**), and aryl chlorides (**6d**), while acidic protons of free phenols (**6b**), alcohols (**6k**) and unprotected indoles (**6l**) were compatible. The reactions of α,β-unsaturated aldehydes, however, gave moderate yields of the ketones **6w**–**x** owing to competitive reduction of the olefin and reduction of aldehydes. Finally, the reaction of cyclopropyl carboxaldehyde proceeded smoothly without ring opening (**6y**).

To understand the catalytic pathway, we monitored the phenylation kinetics of **1a** in the presence of cyclohexanone at 90 °C by GC. The conversion of aldehyde **1a** and yields of product **2a** and other byproducts are summarized in Figure 1. Several key observations were made. (a) Ketone **2a** was continuously formed and its yield reached 88% after 6 h, whereas the yield of carbinol **2aa** quickly reached plateau after 1 h (24% yield), which then slowly decreased to 10% after 6 h. (b) At the same time, cyclohexanol **cyl** progressively accumulated and reached 51% yield after 6 h, indicating that cyclohexanone was the main hydrogen acceptor. (c) A small amount of byproduct **1ar** was also detected (6% yield after 6 h). (d) To account for the formation of **2a**, some DMSO also served as a hydride scavenger because a distinct smell of Me_2S was noted after the reaction.[14] (e) In the absence of cyclohexanone, aldehyde **1a** was the main hydrogen acceptor giving **1ar** in 50% yield after 6 h. (f) In arylation with phenylboroxine, we found that 1 equiv of water significantly accelerated the formation of carbinol **2aa**, especially in the first hour (see the Supporting Information).

To gain additional support for the intermediacy of carbinols, carbinol **2aa** was then added to a catalytic phenylation of aldehyde **1f**. It almost fully converted to aryl ketone **2a** in 97% yield after 12 h (Scheme 6a). Moreover, when **2aa** was subjected to transfer hydrogenation with cyclohexanone, to our surprise, both (dcype)Ni(0) catalyst and 1 equiv $PhB(OH)_2$ were necessary. When $PhB(OH)_2$ was omitted, no dehydrogenation of **2aa** was detected, suggesting that the carbinol oxidation is mechanistically distinct from simple alcohol dehydrogenation (Scheme 6b).[15] Most likely, **2aa** reacted with $PhB(OH)_2$ to in situ form boronic ester **2ab**, which then underwent nickel(0)-catalyzed retro-hydroboration to produce ketone **2a** (Scheme 7a). The resulting borylnickel hydride was then trapped by cyclohexanone to complete the catalytic loop at the end (Scheme 7a).[16] The need for the nickel(0) catalyst also discounted an uncatalyzed Oppenauer-type oxidation (Scheme 7b).[17]

Furthermore, we have considered several possible pathways for the formation of carbinols. (a) The arylation can only be catalyzed by nickel(0) complexes, but not nickel(II) complexes at all. This rules out a simple pathway involving 1,2-insertion of arylnickel(II) to aldehydes (Scheme 7c).[10] (b) The intermediacy of aryl carbinols also precludes another pathway involving oxidative addition of formyl C–H bonds by nickel(0), followed by arylation[5,18] (Scheme 7d). Aryl esters, which are likely byproducts in this putative pathway, were never detected. Also consistent with this, a H/D competition experiment using a 1:1 mixture of **1a** and deuterated **1ad** resulted in an apparent k_H/k_D value of 1.0 (Scheme 6c). Furthermore, no decarbonylation of aldehydes[18,19] was detected after aldehydes were heated with 20 mol % (dcype)nickel(0) catalyst for 12 h at 120 °C. For example, **1a** only afforded only self-aldol condensation (**1as**) at 50% conversion, while heating 1-naphthlenealdehyde led to several side products at 10% conversion. (c) The participation of aryl

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carbinols also ruled out a pathway involving ligand-to-ligand hydrogen transfer[20] on the nickel center, directly between a bound aldehydes and a ketone acceptor as Gu et al. reported previously (Scheme 7e).

(Phosphine)nickel(0) complexes were known to form isolable η^2 complexes **A** with aldehydes (Scheme 7f),[21] which were implicated as key intermediates in several nickel-catalyzed processes,[22] including addition of alkylboranes and arylboron reagents to aldehydes that formed carbinols.[23] When aldehyde **1a** was added to an equimolar mixture of $Ni(PPh_3)_4$ and dcype, the solution quickly turned from red to light yellow, and two doublets were detected by $^{31}P\{^1H\}$ NMR spectroscopy at 66.8 and 56.3 ppm ($^2J_{P-P}$ = 67.4 Hz), characteristic of an η^2-complex.

We therefore propose in Scheme 7f that η^2-complex **A** is hydrolyzed by a trace amount of water, probably formed from dehydration of arylboronic acids under heating, to give coordinatively saturated hydroxonickel complex **B**. Complex **B** then undergoes fast transmetalation to afford phenylnickel **C**. Subsequent C−C reductive elimination results in the carbinol and regenerates the nickel(0) catalyst. Alternatively, η^2 complex **A** is ring-opened by an arylboronic acid to form a nickel boronate complex,[24] which undergoes direct β-aryl elimination for aryl transfer to nickel.

In summary, we report a general method to access aryl ketones from a wide range of aldehydes using easily available and bench-stable arylboronic acids. As a salient feature, the neutral conditions help to preserve α-stereocenters of chiral aldehydes and are compatible with acidic protons and sensitive structures. Mechanistically, this nickel-catalyzed arylation is distinct from other late transition metal catalyzed processes of aldehydes including nickel.[5]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01782.

Experimental procedures (PDF)

NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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