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Ir(III)-catalyzed *ortho* C–H alkylations of (hetero) aromatic aldehydes using alkyl boron reagents†

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Transition-metal-catalyzed C–H alkylation reactions directed by aldehydes or ketones have been largely restricted to electronically activated alkenes. Herein, we report a general protocol for the Ir(III)-catalyzed *ortho* C–H alkylations of (hetero)aromatic aldehydes using alkyl boron reagents as the coupling partner. Featuring aniline as an inexpensive catalytic ligand, the method was compatible with a wide variety of benzaldehydes, heterocyclic aldehydes, potassium alkyltrifluoroborates as well as a few α,β -unsaturated aldehydes. An X-ray crystal structure of a benzaldehyde *ortho* C–H iridation intermediate was also successfully obtained.

Introduction

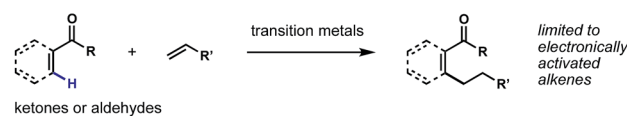
Aldehydes are among the most versatile functional groups in organic synthesis. However, their high reactivity and weak coordinating ability have rendered them recalcitrant directing groups in C–H functionalization reactions.¹ In recent years, significant progress has been made to leverage this commonplace functional group as the directing element to promote the metalation and subsequent functionalizations of proximal C–H bonds.² Nevertheless, missing from this repertoire is a general platform for the direct *ortho* C–H alkylations³ of (hetero) aromatic aldehydes. While related methods have been reported on the *ortho* C–H alkylations of aromatic ketones and aldehydes,⁴ β C–H alkylations of α,β -unsaturated ketones and aldehydes,⁵ as well as α C–H alkylations of aliphatic ketones,⁶ the coupling reagents were largely restricted to electronically activated alkenes in most cases, such as acrylates, styrenes and vinyl silanes.⁷ To further expand the utility of such transformations in synthesis, it would be ideal to develop aldehyde-directed C(sp²)–H alkylation reactions using versatile alkylating reagents.†

Our laboratory recently described a family of reactions to hydroxylate, methylate and fluorinate the *ortho* C–H bonds of benzaldehydes featuring Pd catalysis and the directivity of a structural element that arises in the course of the reaction through a reversible condensation.⁸ The ‘transient directing group (TDG)’ in these reactions is a putative Schiff base that is integral to catalyst binding and the subsequent palladation of

a flanking arene C–H bond; this later chemical event initiates the process that replaces the *ortho* hydrogen with a new substituent group.⁹ Pioneered by the Yu group,¹⁰ this appealing concept for expanding the potential of group-directed C–H functionalizations in organic synthesis is amenable to a wide variety of aldehydes, ketones and amines.¹¹ Our continued focus on C–H functionalizations mediated by TDGs prompted us to develop a new catalytic method for achieving direct *ortho* C–H alkylations of aromatic aldehydes. Unfortunately, in the evolution of this chemistry, we were unable to extend our successful, Pd-catalyzed *ortho* C–H methylation process to higher homologs (*e.g.* ethyl, propyl, *etc.*) due to the occurrence of undesired β -hydride eliminations (Scheme 1).^{8b}

We reasoned that it might be possible to suppress β -hydride elimination if the coordination sites on the transition metal

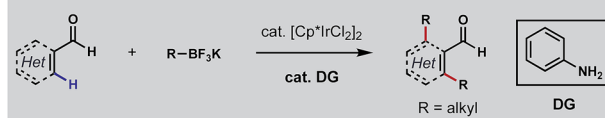
Pioneering studies (ref 4,5)



Our previous work



This work

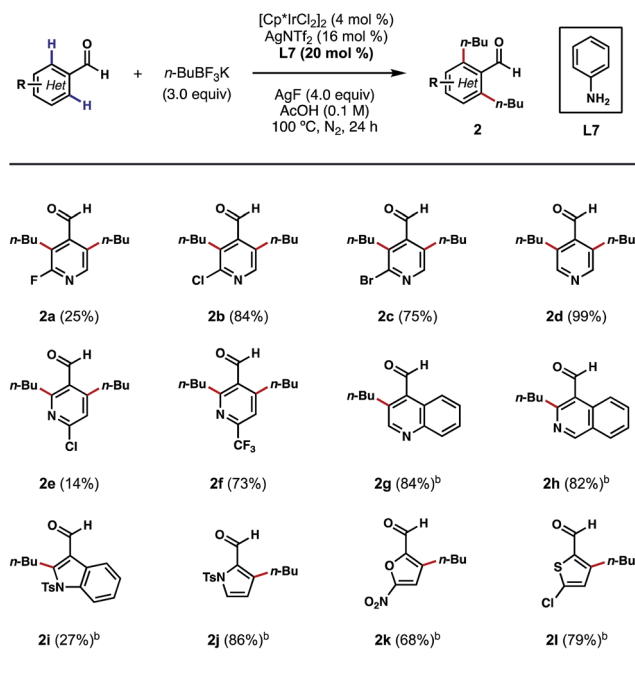


Scheme 1 Ir(III)-catalyzed, site-selective alkylations of (hetero) aromatic and α,β -unsaturated aldehydes using aniline as the catalytic ligand.

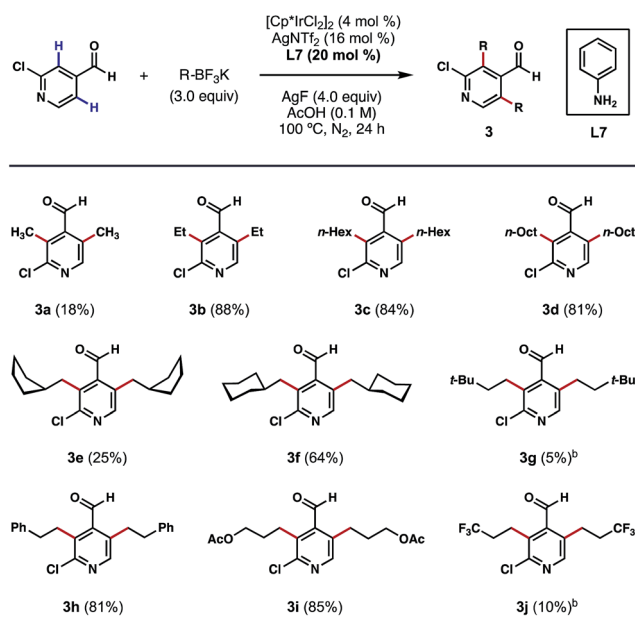
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† Electronic supplementary information (ESI) available: Experimental procedures, spectral data, and crystallographic data (CIF). CCDC 1861852. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8sc03606c





Scheme 3 Scope of heterocyclic aldehydes. ^aThe reactions were performed on a 0.3 mmol scale, and yields are reported as isolated yields. ^b*n*-BuBF₃K (2 equiv.) and AgF (3 equiv.) were used.



Scheme 4 Scope of potassium alkyltrifluoroborates. ^aThe reactions were performed on a 0.3 mmol scale, and yields are reported as isolated yields. ^bDCE (0.1 M) was used as the reaction solvent and the reaction temperature was 80 °C.

cases. Quinoline- and isoquinoline-carboxaldehydes were also amenable to this process, providing the *ortho* C–H alkylation products in greater than 80% yields (Scheme 3, **2g** and **2h**). Other five-membered heterocycles, such as indole, pyrrole,

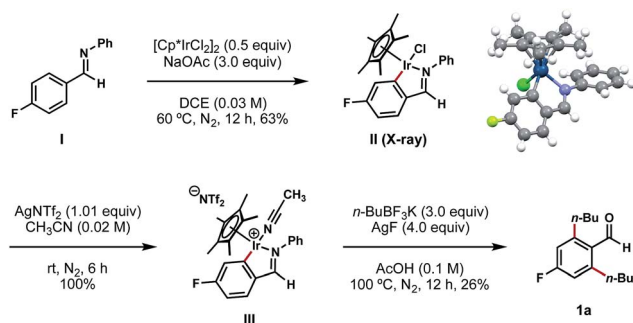
furan and thiophene were also viable substrates (Scheme 3, **2i–2l**). Interestingly, alkylation only occurred at the 2' position of the indole nucleus, a result that contrasts with the previous Pd-catalyzed *ortho* C–H arylation reaction (Scheme 3, **2i**).^{10d}

Having shown that direct *ortho* alkylations of diverse (hetero) aromatic aldehydes are possible, we evaluated the couplings of structurally diverse potassium alkyltrifluoroborates with 2-chloroisonicotinaldehyde. While the attempted *ortho* bis-methylations were disappointing (Scheme 4, **3a**), to the best of our knowledge, this is the first example of directly transforming the *ortho* C–H bonds of a heterocyclic aldehyde into methyl groups, a challenging process that is unattainable using our previous Pd-catalyzed C–H methylation protocol.^{8b} Gratifyingly, good reactivity was restored with other alkylation processes, such as ethylation, *n*-hexylation and *n*-octylation (Scheme 4, **3b–3d**). The reaction can also affix branched alicyclic groups (*e.g.* cyclopentylmethyl and cyclohexylmethyl) to the pyridine nucleus (Scheme 4, **3e** and **3f**). Chains terminating in *tert*-butyl groups may also be introduced, albeit in a low yield (Scheme 4, **3g**). We were also pleased to find that chains terminating in phenyl, acetoxy, and trifluoromethyl groups may also be introduced *via* this alkylation process (Scheme 4, **3h–3j**). While reaction efficiency was not completely satisfactory in certain cases, these examples demonstrate the generality of this method in introducing structurally diverse alkyl groups to the *ortho* position of a heterocyclic aldehyde regardless of their lengths, bulkiness and the functionalities that they contain. For certain potassium alkyltrifluoroborates that are labile at high temperatures or under acidic conditions, dichloroethane (DCE) was used as the reaction solvent and a lowered reaction temperature was employed (Scheme 4, **3g** and **3j**). In its current state of development, this method does not permit the use of secondary potassium alkyltrifluoroborates.

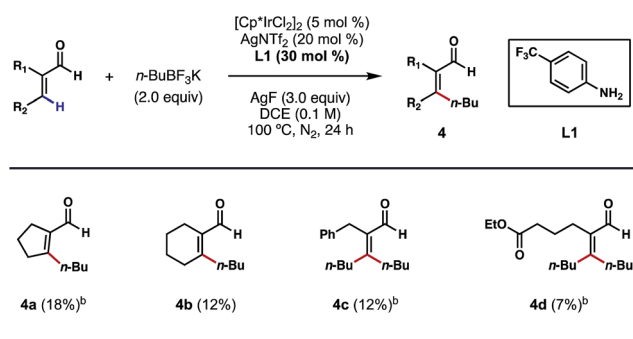
To gain mechanistic insights into this process, aldimine **I** (synthesized by a condensation reaction between 4-fluorobenzaldehyde and aniline; see ESI† for details) was exposed to a stoichiometric amount of [Cp*IrCl₂]₂ and an excess of NaOAc in DCE at 60 °C (Scheme 5).^{11d} In the wake of this reaction, we isolated a stable C–H iridacycle **II**; the structure of this complex was confirmed by X-ray crystallography (Scheme 5). This outcome provides a direct crystallographic evidence for an Ir(III) C–H insertion mechanistic pathway in this reaction instead of a simple conjugative addition of the Ir(III) catalyst to the electron-deficient arene. Further elaboration of complex **II** with AgNTf₂ in acetonitrile results in the formation of cationic Ir complex **III** in a quantitative yield.^{11d} To our delight, this air-stable cationic Ir species proved to be a competent intermediate in the bis-alkylation process and underwent conversion to compound **1a** upon treatment with *n*-BuBF₃K and AgF at 100 °C (Scheme 5).

Motivated by the above studies, we next explored the possibility of alkylating vinylic C–H bonds in α,β -unsaturated aldehydes; this would be a unique and desirable transformation in synthesis. In comparison to the plethora of research on arene C–H functionalizations, activation of non-aromatic, vinylic C–H bonds using transition metals poses a steeper challenge and is still underdeveloped. While a number of C(sp²)–C(sp³) bond





Scheme 5 Isolation and X-ray characterization of iridacycle II and its subsequent transformations. ^aAll yields are reported as isolated yields.



Scheme 6 Preliminary studies on the β C–H alkylations of α,β -unsaturated aldehydes. ^aThe reactions were performed on a 0.3 mmol scale, and yields are reported as isolated yields. ^bCrotonic acid (30 mol%) was an additive.

forming reactions were achieved primarily through C–H additions to carbonyls, imines and related, polarized π bonds,¹⁴ the direct coupling of vinylic C–H bonds with versatile alkyl boron reagents remains an unsolved problem in cross-coupling chemistry. With 4-trifluoromethylaniline (**L1**) as a key catalytic ligand and under the conditions shown in Scheme 6, a number of cyclic and acyclic α,β -unsaturated aldehydes were successfully alkylated at the β position (**4a–4d**). The exact role of crotonic acid is unclear at present, although it was found to be critical to reactivity in most cases. Surprisingly, both vinylic C–H bonds of acrolein substrates, either *cis* or *trans* to the formyl group, are alkylated under the conditions shown (Scheme 6, **4c** and **4d**); despite its modest efficiencies, this interesting and potentially important reaction type clearly merits further development.

Conclusions

In summary, a convenient method was developed for the *ortho* C(sp²)–H alkylations of (hetero)aromatic aldehydes as well as β C–H alkylation of α,β -unsaturated aldehydes using potassium alkyltrifluoroborates as versatile alkylating reagents. The key to these transformations was the use of [Cp*IrCl₂]₂ as a pre-catalyst, which, in combination with aniline as the catalytic ligand, promotes the desired C(sp³)–C(sp²) reductive

elimination without β -hydride elimination. This method offers an attractive, new approach to the late stage C(sp²)–H alkylations of aldehyde-containing substrates.

Conflicts of interest

There are no conflicts to declare.

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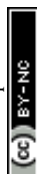
Notes and references

† General experimental procedure for the *ortho* C–H alkylations of (hetero) aromatic aldehydes: a 20 mL oven-dried scintillation vial equipped with a cross-shaped stir bar was charged with an aromatic aldehyde (0.30 mmol), [Cp*IrCl₂]₂ (9.6 mg, 0.012 mmol), AgF (0.152 g, 1.20 mmol) and *n*-BuBF₃K (0.147 g, 0.9 mmol). The vial was transferred to a glovebox filled with N₂, wherein AgNTf₂ (18.6 mg, 0.048 mmol) and aniline (5.6 μ L, 0.060 mmol) were added. The vial was capped tightly with a PTFE-lined green cap and taken out of the glovebox. Degassed AcOH (3 mL) was added through a syringe, and the vial was heated in a pie-block at 100 °C under vigorous stirring for 24 h. After cooling to r.t., the reaction mixture was filtered through a pad of Celite® and washed with EtOAc (15 mL). The filtrate was then concentrated *in vacuo* and the resulting residue was purified by flash silica gel column chromatography.

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