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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.

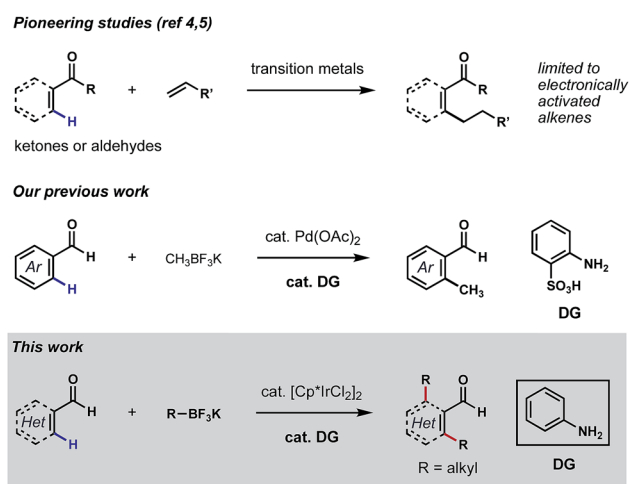
Introduction

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



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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Scheme 2 Scope of substituted benzaldehydes. ^aThe reactions were performed on a 0.3 mmol scale, and yields are reported as isolated yields. ^b $n\text{-BuBF}_3\text{K}$ (2 equiv.) and AgF (3 equiv.) were used.

were fully saturated during the $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^2)$ reductive elimination step. Inspired by the recent success of TDG-enabled *ortho* C–H amidation of benzaldehydes *via* Ir(III) catalysis,^{10d,11d,11e} we envisioned that the well-established $[\text{Cp}^*\text{IrCl}_2]_2$ pre-catalyst might be suitable for a successful C–H alkylation reaction,¹² as coordinative saturation is enforced by the Cp^* and the cyclometalated groups. The $\text{Cp}^*\text{Ir}(\text{TDG-Ar})(\text{alkyl})$ species could undergo selective $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^3)$ reductive elimination, followed by re-oxidation of Ir(I) to Ir(III) to complete the catalytic cycle. Herein, we describe the first examples of Ir(III)-catalyzed, mono- and bis-alkylations of the *ortho* C–H bonds of a range of substituted (hetero)aromatic aldehydes using potassium alkyltrifluoroborates as the source of the alkyl groups and aniline as the catalytic ligand (Scheme 1). The combination of reagents

allowing these transformations also permit β C–H alkylations of α,β -unsaturated aldehydes, albeit in low yields.

Results and discussion

We began our studies by treating 4-bromobenzaldehyde with an excess of $n\text{-BuBF}_3\text{K}$ in the presence of $[\text{Cp}^*\text{IrCl}_2]_2$, silver additives, anilines and oxidants in various solvents under an inert atmosphere at elevated temperatures. After an extensive screening and optimization effort, we were pleased to find that the desired *ortho* bis-alkylation reaction took place in a nearly quantitative yield after a 24 h reaction that employed 4 mol% of $[\text{Cp}^*\text{IrCl}_2]_2$ as the catalyst, 16 mol% of AgNTf_2 as the chloride scavenger, 20 mol% of aniline as the catalytic ligand, 3.0 equivalents of $n\text{-BuBF}_3\text{K}$ as the alkylating reagent, 4.0 equivalents of AgF as the oxidant and acetic acid (0.1 M) as the solvent at $100\text{ }^\circ\text{C}$ (see ESI† for a complete list of optimization experiments).

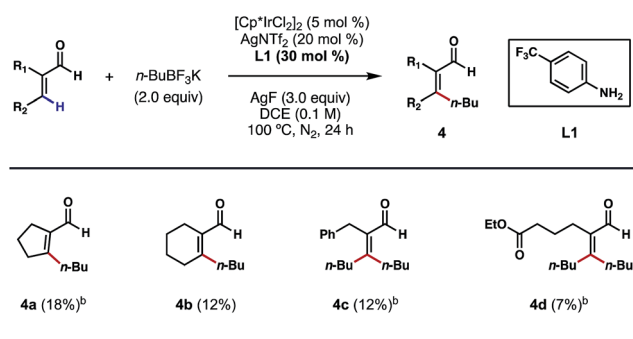
With an effective procedure in hand, we investigated the reactions of various substituted benzaldehydes to probe the scope of this C–H alkylation process. As depicted in Scheme 2, a number of electron-withdrawing groups, such as halogens, trifluoromethyl, ester and nitrile groups, were well tolerated at the *para* position, delivering the desired products mostly in excellent yields (**1a–1f**). Interestingly, with *meta*-trifluoromethyl and ester-substituted benzaldehydes as the substrates, the alkylation only took place at the less sterically crowded *ortho* position (Scheme 2, **1g**, **1h**, **1n** and **1o**). However, when smaller *meta*-substituents, such as halogens and methoxy groups were present, it was possible to introduce a second alkyl group even at the more crowded *ortho* position (Scheme 2, **1i–1m**, **1p** and **1q**). This result also stands contrast to our previous Pd-catalyzed *ortho* C–H methylation reaction,^{8b} which only afforded mono-methylated products with *meta*-substituents on the substrates. Mono-alkylation was also successful in the presence of an *ortho* substituent on the substrate, such as fluoro, methyl and methoxy groups. In most cases, the reactions proceeded without any erosions in performance (Scheme 2, **1r–1x**). The current limitations of this method are (1) *ortho*-chlorinated or brominated substrates were incompatible with this process; and (2) mono-alkylations can be challenging to achieve on sterically unbiased substrates even with 1 equivalent of the coupling reagent.

Encouraged by these outcomes, we next sought to apply this process to the *ortho*-alkylations of heterocyclic aldehydes. Traditionally, alkylations of N-heterocycles were realized through the venerable Friedel–Crafts and Minisci reactions.¹³ However, in these processes, alkylations typically occur at the most electron-rich and electron-poor sites of the heterocycles, respectively. We questioned if this electronic preference could be overridden by a TDG on the aldehyde component, so that the desired alkylation process would occur exclusively at the *ortho* positions of the substrates. Indeed, with nicotinaldehydes or isonicotinaldehydes as the substrates, the *ortho* C–H bis-alkylation process proceeded efficiently in most cases (Scheme 3, **2a–2f**). While the reaction yields tended to vary with different substitution patterns, the regioselectivity was unaffected in all





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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