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Iridium-catalyzed carbonyl group-directed oxidative coupling of arenes with alkenes



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ABSTRACT

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Introduction

The oxidative coupling of arenes with alkenes to form vinylarenes is an attractive alternative to the Mizoroki-Heck coupling reaction with the advantage that it is atom economic and does not require functionalized coupling partners.¹ After the initial discovery of the stoichiometric reaction between Pd(II)-olefin complexes and arenes,² a catalytic version involving Pd(OAc)₂ and an oxidant emerged.³ Chelation-assisted oxidative coupling of an arene with an alkene, via orthometallation followed by C=C bond insertion, to give an o-vinylarene is another example of such a catalyzed oxidative coupling, which has been demonstrated with various metal systems including palladium,⁴ rhodium,⁵ ruthenium,⁶ and cobalt.⁷ Although there are many studies on iridium catalyzed alkylation of arenes with alkenes,⁹ there are none for the oxidative coupling of an arene with an alkene; the closest is a direct oxidative coupling of furans with alkenes.⁸ We recently reported the hydroamination of alkynes with aromatic amines via activation of the alkyne C to bond with $[Cp^*IrCl_2]_2$ (1).¹⁰ For example, the reaction of **1** with alkyne and aniline leads to the formation of an orthometallated aminocarbene complex via alkyne hydroamination and subsequent ortho C-H bond activation.^{10a} It therefore occurred to us that it may be possible to achieve ortho C-H alkenylation of aniline derivatives with this system.

The C—H activation of acetanilide, **2a**, followed by oxidative coupling to methyl acrylate was found to proceed smoothly in the presence of **1** and additives to afford the mono- and di-alkeny-lated products **4a** and **5a** in 86 and 9% yields, respectively (Table 1, entry 1). An optimization study showed that other silver salts, such as, $AgBF_4$ and $AgSbF_6$, may be used as additive (entries 2 & 3), but the additive, oxidant (Cu(OAc)₂) and catalyst were all essential (entries 5–7), as is a slight excess of the acrylate (entry 12).

The iridium complex [Cp*IrCl₂]₂ is a good catalyst for the directed oxidative coupling of arenes with alke-

nes; a wide range of carbonyl functionalities (NHCOR, CONH₂ and COR) can be employed as the directing

Changing the oxidant from $Cu(OAc)_2$ to AgOAc increased the yield of **5** (entry 4), while lowering the catalyst loading to 3 mol% did not affect the yield significantly (entry 8). Use of coordinating solvents (acetonitrile or methanol) was detrimental (entries 9 & 10) and although the reaction proceeded at ambient temperature, it required a longer reaction time (entry 11).

A substrate scope study was carried out on a 0.2 mmol scale with 3 mol% catalyst loading (Table 2). Acetanilides with both electron-donating and electron-withdrawing *para* substituents were tolerated, affording good yields of the mono-alkenylated products (entries 2–6), along with ~10% yields of the di-alkenylated products (see SI). With *meta* substituted acetanilides, only mono-alkenylated products were obtained and olefination occurred selectively *para* to the functional group R, irrespective of whether it is electron-donating (R = Me) or electron-withdrawing (R = Cl, Br) (entries 7–9). The reaction did not proceed with unactivated alkenes (1-octene and *trans*-2-hexene).

This suggests that the stereochemistry of alkenylation in these cases is driven by steric factors. That halogen functional groups were tolerated, with no dehalogenation or Heck-coupling products



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Table 1

Optimization study for 1-catalyzed formation of 4a and 5a.



Entry	Deviation from standard conditions	Yield of 4 + 5 (%) ^a
1	None	86 + 9
2	AgSbF ₆ as additive	80 + 13
3	AgBF ₄ as additive	80 + 6
4	AgOAc as oxidant	49 + 34
5	No silver salt additive	15
6	No oxidant	10
7	No catalyst 1	-
8	3 mol% of 1	82 + 8
9	ACN as solvent	-
10	MeOH as solvent	-
11 ^b	Reaction temperature = 30 °C	23
12 ^b	1.0 equivalent of methyl acrylate	40 + 20

^a Isolated yields.

^b Incomplete reaction.

Table 2Substrate scope study of 1-catalyzed formation of 4a and 5a. Yields reported are isolated yields.



Entry	R	DG	Product (% yield)
1	Н	NHCOMe	4a (82)
2	4-Me	NHCOMe	4b (80)
3	4-OMe	NHCOMe	4c (81)
4	4-NO ₂	NHCOMe	4d (64)
5	4-Br	NHCOMe	4e (70)
6	4-Cl	NHCOMe	4f (66)
7	3-Br	NHCOMe	4g (75)
8	3-Cl	NHCOMe	4h (71)
9	3-Me	NHCOMe	4i (89)
14	2-Cl	NHCOMe	4n (67)
15	Н	COMe	6a (72)
16	4-Me	COMe	6b (73)
17	4-Cl	COMe	6c (79)
18	3-OMe	COMe	6d (71)
19	2-Cl	COMe	6e (61)
20	Н	CONH ₂	8a (64)
21	Н	CONH ₂	8b (73) ^a
	R NHCOMe 1.5 eq	1 (3 mol%) <u>AgPF₆ (20 mol%)</u> Cu(OAc) ₂ (2 eq) DCE, 80 °C, 24 h A	

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