Pd/Ir Dual Catalyzed synthesis of Diaryl Ketones from Aromatic Aldehydes and Arylboroates

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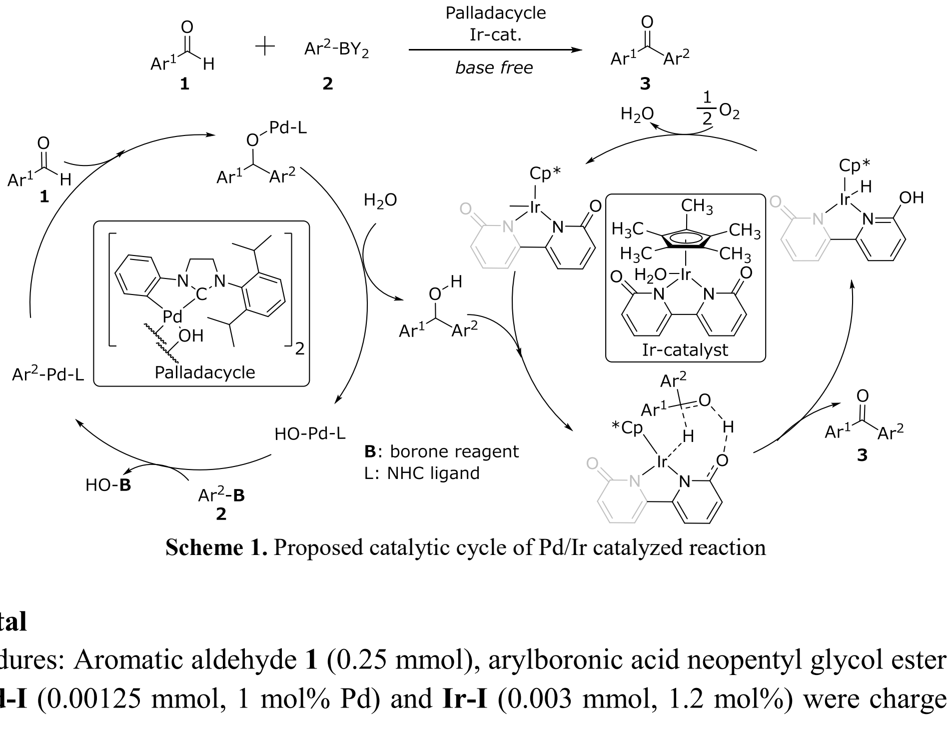
Abstract: Pd and Ir dual catalyzed one-pot synthesis of diarylketones from aromatic aldehydes and arylboronates was developed. In this catalytic synthesis, the 1,2-addition first occurred by NHC-coordinated palladacycle catalyt and then the oxidation of secondary alcohols was proceeded by iridium catalyst under O_2 atmosphere.

Keywords: Pd/Ir dual catalysis, diarylketone, nucleophilic addition, oxidation.

1. Introduction

Diarylketones are important structures found in natural products, flavors, pharmaceuticals, and organic materials, thus various synthetic methods have been developed. The oxidation of secondary alcohols is the classical synthesis of diarylketones but has been generally required the use of an excessive oxidants such as MnO_2, Cr reagents, Dess-Martin reagents and more. Therefore, the transition metal catalyzed oxidation of secondary alcohols have been attracted attention from the viewpoint of green chemistry in recent years.[1] In a past decade, transition metal catalyzed one-pot syntheses of diarylketones from aromatic aldehydes and arylboron compounds were developed, but these reaction needed excess amount of oxidants such as aryl halide or dialkylketones.[2] On the other hand, we previously reported N-heterocyclic carbene (NHC) coordinated palladacycle complexes catalyzed 1,2-addition of arylboron reagents to various carbonyl compounds.[3] Herein, we demonstrated the one-pot synthesis of diarylketones from ardehyde and arylboronates by continuously actting our Pd-catalyzed 1,2-addition and Ir catalyzed dehydrogenative oxidation (Scheme 1).



Scheme 1. Proposed catalytic cycle of Pd/Ir catalyzed reaction

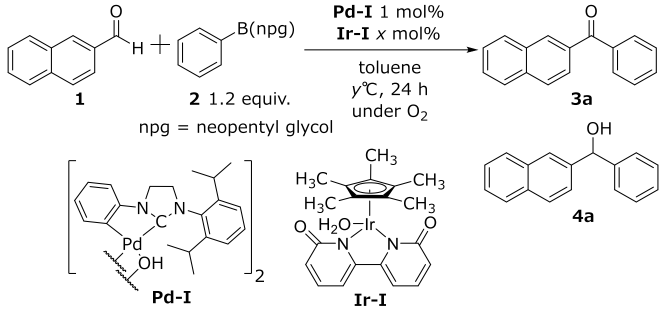
2. Experimental

General Procedures: Aromatic aldehyde **1** (0.25 mmol), arylboronic acid neopentyl glycol ester **2** (0.3 mmol, 1.2 equiv.), **Pd-I** (0.00125 mmol, 1 mol% Pd) and **Ir-I** (0.003 mmol, 1.2 mol%) were charged in a 10 mL test tube. The inside of the test tube was exposed with oxygen flow for 30 seconds, then toluene (0.5 mL) were added in the test tube. The test tube was sealed with Teflon liner screw cap and was placed into an oil bath preheated at 120 °C. After the reaction mixture was stirred for 24 hours and cooled to room temperature. The corresponding product was obtained after column chromatography (hexane/ethyl acetate: 7/1 to 5/1).

3. Results and discussion

The scope of the equivalent of **Ir-I** and reaction temperature for Pd/Ir catalyzed synthesis of 2-naphthylphenylketones using 2-naphthaldehyde **1** and phenylboronic acid neopentyl glycolate 2 (Table 1). Although the use amount of **Ir-I** catalyst hardly affected the yield of **3**, the rise in the reaction temperature remarkably improved the yields (entries 1−5).

Table 1. Examination of amount of **Ir-I** and reaction temperature



Entry	x mol% of Ir	Temperature	yield[a]
1	2 mol%	100℃	64%
2	4 mol%	100℃	54%
3	1 mol%	100℃	64%(33%)[b]
4	1 mol%	120℃	90%(4%)[b]
5	1.2 mol%	120℃	97%

a) Isolated yields of ketone **3a**

b) Isolated yields of Alcohol **4a** in parentheses.

The scope and limitations of aryl boronates was examined using the optimum conditions (**Figure 1**). Weaker electron donating or withdrawing groups such as phenyl, tert-butyl, chloro and methoxycarbonyl groups substituted arylboronates were converted to the corresponding alcohols in excellent yields (**3b** and **3d**−**3g**). On the other hand, strong electron donating or withdrawing groups such as methoxy and nitro group substituted arylboronates showed lower reactivity (**3b** and **3h**).

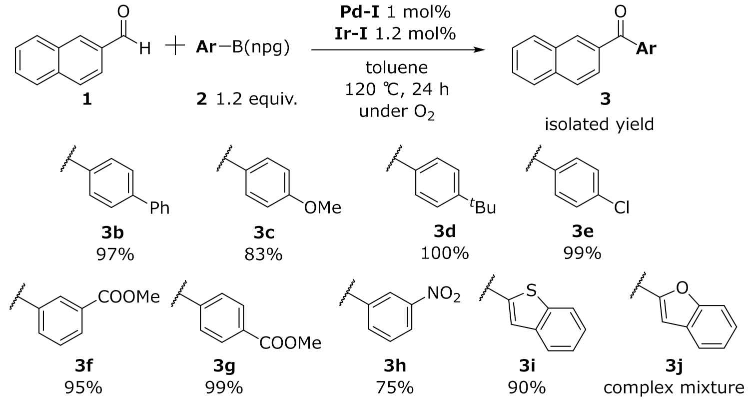


Figure 1. Substrate scope of srylboronates.

4. Conclusions

We have developed Pd/Ir catalyzed synthesis of diarylketones via Pd-catalyzed 1,2-addtion of arylboronates to aldehydes and Ir-catalyzed dehydrogentive oxidation used arylaldehydes and arylboronates. This method has important features as dual catalysts and free of bases.

References

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