



Cyclometalated Ir(III) complexes-catalyzed aerobic hydroxylation of arylboronic acids induced by visible-light



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ABSTRACT

The cyclometalated Ir(III) complexes-catalyzed aerobic hydroxylation of arylboronic acids under visible-light has been successfully developed. This catalytic system has a broad substrate scope, affording a series of phenols smoothly with the highest isolated yield up to 95%. Moreover, this protocol is capable to synthesize several useful phenols containing bulky moieties, which are potential candidates or intermediates used as pharmaceuticals and functional materials. The Ir(III)-catalyzed hydroxylation of arylboronic acids could be applied in a one-pot synthesis of several important phenol derivatives, including 1,1'-methylene-bis(2-naphthol), 2,3-dihydro-1*H*-naphtho[2,1-*e*][1,3]oxazine and a bioactive compound **LUF5771**.

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1. Introduction

Phenols frequently occur in numerous biologically active compounds and have been widely used as versatile synthetic intermediates.¹ Generally, phenols are prepared by substitution of aryl halides. These methods, however, need the use of catalysts with attendant ligands under harsh reaction conditions.² Later, investigation showed that commercially available arylboronic acids could be converted into phenols by strong oxidizing agents (e.g. H₂O₂, oxone), while the amount of oxidants and reaction time needed to be controlled carefully to avoid over-oxidation.³ As a new and reliable method emerged in organic synthesis in the past decade, the visible-light photocatalysis has attracted lots of interests.⁴ In 2012, the first visible-light photocatalyzed conversion of arylboronic acids to phenols was reported by Xiao and co-workers using Ru(bpy)₃²⁺ as the photocatalyst and molecular O₂ as the oxidant.⁵ Subsequently, several photocatalysts have been used for the preparation of simple aryl phenols from arylboronic acids by visible-light irradiation, including dyes,⁶ C₆₀-bodipy,⁷ α-Fe₂O₃⁸ and MOFs.⁹ The cyclometalated Ir(III) complexes also demonstrated tremendous potentials as powerful catalysts in organic synthesis.¹⁰ The major advantages of Ir-based photocatalysts are

the ease of tuning the complex to achieve desired redox potentials through modification of the cyclometalating ligands, and relatively long excited states lifetimes for the efficient electron transfer processes.¹¹ However, to the best of our knowledge, Ir(III)-catalyzed hydroxylation of arylboronic acids has not been established yet.

The phenols containing bulky moieties are more widely used as the building blocks in pharmaceuticals and organic synthesis relative to simple molecular structures. Consequently, lots of efforts have been made in the preparation of these compounds. For example, 3,5-diphenylphenol is an important intermediate for preparation of the human luteinizing hormone receptor antagonist (**LUF5771**), which has been implicated in fertility and ovarian cancer.¹² So far, 3,5-diphenylphenol was synthesized from 3,5-dibromophenol via the palladium-catalyzed Suzuki-Miyaura reaction or from 3,5-diphenylcyclohexenone via the palladium- or copper-mediated aerobic dehydrogenation as well as through Robinson annulation of α,β-unsaturated ketones with α-fluoro-β-ketoesters (Fig. 1).¹³ In addition, the phenols with triphenylamine or carbazole moieties are building blocks for the construction of electrochemical devices and pharmaceuticals,¹⁴ which are usually obtained by using the standard deprotection of methoxyphenyl group with BBr₃.¹⁵ However, as far as we know, arylboronic acids as the sole starting materials for the direct synthesis of these phenols have not been reported, and the photosynthetic method for the preparation of phenols containing bulky moieties remains unexplored. Therefore, the development of an efficient and convenient

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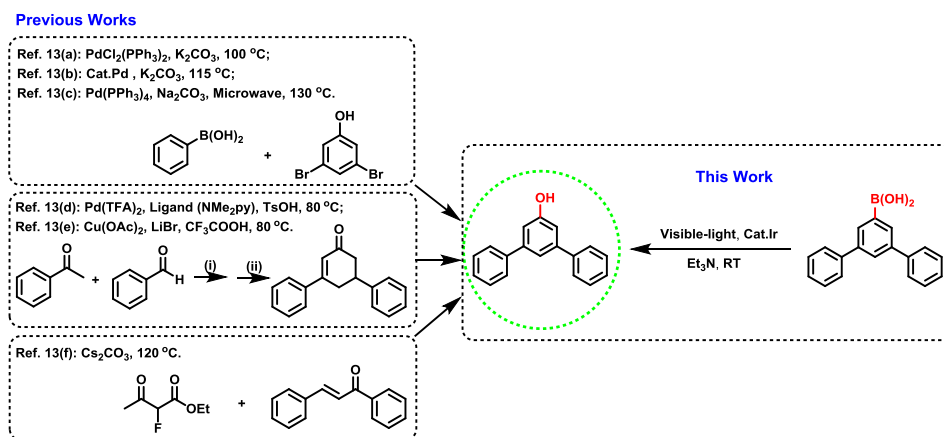


Fig. 1. Various synthetic approaches to 3,5-diphenylphenol.

methodology for the direct synthesis of these important phenols from arylboronic acids by the visible-light photoredox catalysis is greatly desired.

By chemically manipulating the [Ir(ppy)₂(phen)]PF₆ with an ester group on the phenyl ring of 2-phenylpyridine (ppy), three ester-substituted bis-cyclometalated Ir(III) complexes with long luminescent lifetimes and excellent photostability have been developed by our group recently¹⁶ (**C1–C3**, Fig. 2). The aforementioned desired properties of these ester-substituted Ir(III) complexes have the potential and motivation as photocatalysts for organic synthesis. Herein, we report the synthesis of phenols from arylboronic acids using these Ir(III) complexes as the photocatalysts under visible-light irradiation for the first time. Various substituted arylboronic acids underwent this transformation smoothly and provided the corresponding phenols in good to excellent yields. Moreover, this method is capable to synthesize phenols containing bulky moieties. Interestingly, several important phenol derivatives, including 1,1'-methylene-bis(2-naphthol), 2,3-dihydro-1*H*-naphtho[2,1-*e*][1,3]oxazine and a bioactive compound **LUF5771**, can be prepared efficiently via the photocatalysis-involved one-pot synthesis.

2. Results and discussion

2.1. Optimization of reaction conditions

Initially, the hydroxylation of 4-methoxyphenylboronic acid (0.5 mmol) in the presence of photocatalysts (2.0 mol%) and (*i*-Pr)₂NEt (2.0 equiv) in DMF (4 mL) under air by visible-light irradiation at room temperature was chosen as a model reaction for the optimization of reaction parameters. The results are collected in Table 1. As expected, using [Ir(ppy)₂(phen)]PF₆ as photocatalyst, the corresponding product was obtained in a 64% yield within 6 h (Table 1, entry 1). Encouraged by the result, a series of control

Table 1

Optimization of reaction parameters for the hydroxylation of 4-methoxyphenylboronic acid.^a

Entry	Photocatalyst	Yield ^b (%)
1	[Ir(ppy) ₂ (phen)]PF ₆	64
2	[Ir(ppy) ₂ (phen)]PF ₆ (no light)	nr
3	[Ir(ppy) ₂ (phen)]PF ₆ (oxygen-free)	nr
4	no photocatalyst	trace
5	[Ir(ppy) ₂ (phen)]PF ₆ (no amine)	trace
6	C1	78
7	C2	80
8	C3	76

^a Reaction conditions: 4-methoxyphenylboronic acid (0.5 mmol), DMF (4 mL), (*i*-Pr)₂NEt (1.0 mmol), photocatalyst (2.0 mol%), in air, 6 h.

^b GC yield, internal standard method.

experiments were performed to investigate the influences of different reaction parameters on the reaction. The results (entries 2–5, Table 1) reveal that visible-light, air, photocatalyst and amine are all essential for the successful transformation.

The results in Table 1 show that the ester-substituted Ir(III) complexes (**C1–C3**), demonstrated higher catalytic activity compared with that of the parent complex [Ir(ppy)₂(phen)]PF₆ under the same conditions, resulting in 76–80% yields of the product (Table 1, entries 6–8). **C2** with the longest lifetime ($\tau = 2.83 \mu\text{s}$, see the Supporting Information, Table S1) is the best photocatalyst, providing the highest yield of 80%. The reason for this might be that Ir(III) complexes with longer excited state lifetimes are favorable for this transformation.¹⁷ A survey of solvents and amines showed that DMF and Et₃N are ideal for this process (see the Supporting Information, Table S2 and Table S3, for details). With the optimized conditions in hand, the scope of substrates was explored for this protocol and the results are summarized in Table 2.

2.2. Scope and limitations of substrates

This catalytic system demonstrated excellent compatibility with a wide range of functional groups, e.g., cyano, aldehyde, carboxyl, ester, acylamino, nitro, etc. The conversion efficiency was affected by electronic effects of the substrates. It was clear that arylboronic acids bearing electron-withdrawing groups (Table 2, **2a–2f**) showed higher reactivity than those bearing electron-donating groups (**2g**, **2i**). For example, 4-formylphenylboronic acid afforded the product **2b** in a 94% yield after 5 h, while 4-methoxyphenylboronic acid gave the corresponding product **2g** in an 80% yield after 9 h. In

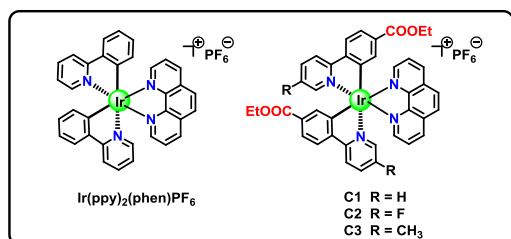


Fig. 2. Chemical structures of the photocatalysts for this study.

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