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# C<sub>70</sub> Fullerene-Catalyzed Metal-Free Photocatalytic *ipso*-Hydroxylation of Aryl Boronic Acids: Synthesis of Phenols

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**Abstract.** A metal-free  $C_{70}$  fullerene-catalyzed method has been developed for the *ipso*-hydroxylation of aryl and heteroaryl boronic acids to corresponding phenols under photocatalytic conditions. The reaction proceeds under oxygen atmosphere and the mechanistic study revealed that  $C_{70}$  plays a critical role in the generation of reactive oxygen species in the presence of blue light. Reactions in the presence of <sup>18</sup>O-labelled water and oxygen confirmed the generation of reactive oxygen species from oxygen molecule.

Amine used as a reductant could be recovered in the form of imine. The current method is also applicable to the synthesis of aryl ethers in one-pot two-step process.

**Keywords:** C<sub>70</sub> fullerene; boronic acids; phenols; photocatalysis; metal-free

## Introduction

Phenol represents an important class of compounds that find applications in pharmaceuticals and polymers.<sup>[1]</sup> Phenols also constitute an integral part of natural products such as flavonoids, phenolic acids, coumarins and lignans and are biologically most active antioxidants, anti-cancerous, and antiallergic agents.<sup>[2]</sup> Adhering to the importance of phenols, a number of methods have been developed synthesis including non-oxidative for their electrophilic substitution,<sup>[3]</sup> hydroxylation of aryl halides using hydroxide salts,<sup>[4]</sup> ligand-assisted, water-mediated hydroxylation of aryl halides,<sup>[5]</sup> pyrolysis of sodium salt of benzene sulfonic acids, air oxidation of cumene, Dow process, <sup>[6]</sup> and hydrolysis of diazonium salts.<sup>[7]</sup> Although efficient, these traditional methods require harsh reaction conditions which limit their practical use in the organic synthesis. In addition, there is always a need for new methodologies with better efficiency, high selectivity, and least waste generation.

Recently, boronic acids have been explored as a viable substrate for the synthesis of phenols where oxidative hydroxylation of aryl boronic acids

furnished the corresponding phenols.<sup>[8]</sup> Leading examples include electromediated *ipso*hydroxylation,<sup>[9]</sup> flavin-catalyzed biomimetic hydroxylation,<sup>[10]</sup> UV-Vis-light-induced<sup>[11]</sup> and metal-catalyzed<sup>[12]</sup> synthesis of phenols from boronic acids (Scheme 1).



**Scheme 1.** Selected methods for the synthesis of ary alcohols from aryl halides and aryl boronic acids.

During the last decade, photocatalysis has emerged as a powerful tool for the organic synthesis due to mild reaction conditions, high selectivity, and simple reaction setup.<sup>[13]</sup> Currently, metal-based photocatalysts are being used extensively, and hydroxylation of aryl boronic acids to aryl alcohols using metal photocatalysts has also been achieved.<sup>[14]</sup> Beside these metal-catalysts, some metal organic framework (MOF),<sup>[15]</sup> porous organic framework (POF)<sup>[16]</sup> and organophotocatalyst<sup>[17]</sup> have also been used for the synthesis of aryl alcohols from aryl boronic acids/esters. Regardless of high efficiency, the low recyclability, longer reaction time, high cost and toxicity poses a limit on their use in large-scale synthesis. Consequently, there is a need for the development of a new strategy that can overcome all these limitations.

Fullerenes are well-known photosensitizer with very high quantum yields ( $\Phi \approx 1$ ) for the generation of reactive oxygen species.<sup>[18]</sup>  $C_{60}$  and  $C_{70}$  fullerenes are well known to produce reactive oxygen species in the presence of light<sup>[18,19]</sup> and find use in many oxidative processes including photodynamic therapy<sup>[20]</sup> in cancer treatment. However, there are limited reports on the use of fullerenes in organic synthesis which includes photooxygenation of olefins and dienes,<sup>[21a]</sup> oxidation of phenol to quinone<sup>[21b]</sup> and sulfides to sulfoxides.<sup>[22]</sup> In a recent report, the C<sub>70</sub> photocatalyzed oxidation of secondary benzylic amines to imines was also reported, where the reactions required very low catalyst loading and afforded high yields of products. Additionally, products and catalyst could be separated by a simple chromatography without workup.<sup>[23]</sup>

Combining the property of fullerenes to produce reactive oxygen species<sup>[23]</sup> and boronic acids to undergo oxidative hydroxylation in the presence of superoxide radical anion,<sup>[14]</sup> we envisioned fullerenes as an efficient photocatalyst for the conversion of aryl boronic acids to aryl alcohols. C<sub>60</sub> fullerene-based photocatalyst was reported to catalyze the hydroxylation of phenylboronic acid. This strategy involves the use of complex C<sub>60</sub> triad and tetrad photosensitizer, which require multistep synthesis, high catalyst loading and excessive amount of solvent.<sup>[24]</sup> Herein, we report the environmentally benign pristine C<sub>70</sub> fullerene<sup>[25]</sup> as a photocatalyst for aerobic oxidative hydroxylation of aryl boronic acids to corresponding phenols (Scheme 1).

## **Results and Discussion**

Reaction conditions were screened by the photoirradiation of phenylboronic acid in the presence of fullerenes  $C_{60}$  and  $C_{70}$  using white ( $\lambda = 400-800$  nm), blue ( $\lambda = 450-475$  nm) and green ( $\lambda = 510-530$  nm) lights in different solvents and *N*,*N*-diisopropylethylamine (DIPEA) as an electron donor. The best reaction conditions were obtained with  $C_{70}$  as a photocatalyst; blue LED as a light source in chloroform as solvent and DIPEA as an electron donor (Table 1, entry 1). Phenol was obtained in only 15% when  $C_{70}$  was replaced with  $C_{60}$ 

(entry 2). Low efficiency of  $C_{60}$  fullerene can be attributed to its very less absorption of light at this much low concentration.<sup>[26]</sup> Changing the light source to white/green LED, decreased the yield to 85%/49%, respectively (entries 3, 4). To confirm the role of each component, control experiments were carried out. In the absence of photocatalyst or light, no product was detected, thus explaining the photocatalytic nature of this transformation (entries 5, 6).

#### **Table 1.** Optimization study<sup>a</sup>

B(	OH) <sub>2</sub> C <sub>70</sub> Fullerene (0.05 mol%), DIPEA (2 eq.)		Н
1a	Blue LED (6W), O <sub>2</sub> , 12h, CHCl <sub>3</sub> (0.05 M)	2a	
			_ /
Entry	Variation from standard condition	2a yield	
1	None	>99 (97) <sup>[c]</sup>	
2	C <sub>60</sub> fullerene catalyst (0.05 mol%)	15	
3	White light instead of blue light	85	
4	Green light instead of blue light	49	
5	Without catalyst	n.d. <sup>[d]</sup>	
6	Without light	n.d.	
7	Under N <sub>2</sub>	trace	
8	Without DIPEA <sup>[e]</sup>	trace	
9	Air instead of O <sub>2</sub>	61	
10	Acetone instead of CHCl <sub>3</sub>	82	_
11	0.1 M CHCl <sub>3</sub>	54	
12	1 equiv. Of DIPEA	88	
13	0.025 mol% of C70	90	
14	9h instead of 12h	89	

<sup>*a*</sup>Reagents and conditions: **1a** (0.1 mmol),  $C_{70}$  fullerene (0.05 mol%), DIPEA (2 equiv.),  $O_2$  balloon, CHCl<sub>3</sub> (0.05 M), Blue LED light, 12 h. <sup>*b*</sup>Yield determined by NMR analysis of crude reaction mixture using 1,1,2,2-tetrachloroethane as internal standard. <sup>*c*</sup>Isolated yield in parenthesis. <sup>*d*</sup>n.d.: not detected, <sup>*e*</sup>DIPEA = diisopropylethylamine.

Only traces of product were detected when reaction was carried out either under nitrogen atmosphere or in the absence of amine donor (entries 7, 8). When the reaction was carried out under air, only 61% of product was obtained (entry 9). Chloroform was found to be the best solvent under optimized reaction conditions (entry 10).<sup>[23,26]</sup> Decreasing the amount of solvent, amine, catalyst or time proved detrimental to the reaction, providing reduced yield of the desired product (entries 11, 12, 13 & 14).

With the best-optimized reaction conditions in hand, substrate scope was explored with different aryl boronic acids (Table 2). Aryl boronic acids with electron withdrawing or donating substituent at *para*-position were successfully converted into corresponding alcohols with excellent yields (**2b-m**). Aryl boronic acid with 4-ethyl and 4-amyl substituent afforded corresponding phenols **2b** and **2c** in 88% and 94% isolated yield, respectively. Substituents

such as phenyl, methoxy, trimethylsilyl, acetoxy were also well tolerated providing the desired product in excellent yields (**2d-g**). Boronic acid with nitrile substituent at *ortho-*, *meta-* and *para-*position afforded corresponding phenols in 67-93% yield (**2r**, **2n**, and **2h**). Halogen substituted phenols **2l** and **2m** were synthesized in good to excellent yields. *Para*substituted acetyl and methyl ester boronic acid also reacted well under present reaction conditions (**2j**, **2k**).

#### **Table 2.** Scope with aryl boronic acids<sup>*a*</sup>



<sup>a</sup>Reagents and conditions: 1 (0.2 mmol),  $C_{70}$  fullerene (0.05 mol%), DIPEA (2 equiv.),  $O_2$  balloon, CHCl<sub>3</sub> (0.05 M), Blue LED light, 12h.

Phenols with a carboxylic acid substituent at metaand *para*-position were also synthesized in good to excellent yields, respectively (20 and 2i). 3,5dimethyl substituted phenol (2t) was obtained in 82% yield. In case of 3-acetamido phenylboronic acid, the low yield of the corresponding phenol was observed (2p). Phenylboronic acid with vinyl ether substituent at *ortho*-position provided 77% vield of corresponding phenol (2u). Further, polyaromatic boronic acids were studied under the developed reaction conditions. Polycyclic phenols such as  $\alpha$ -naphthol (2w), anthracene-2-ol (2x) and pyrene-1ol (2y) were obtained in 68%, 46% and 82% yields, respectively. In the case of 2-phenylvinylboronic acid, acetophenone was observed in 60% yield (2z).

Boronic acid derivative of vitamin E was successfully converted into corresponding phenol (**2aa**).

To expand the generality of the developed catalytic method, heterocyclic boronic acids were also explored for the synthesis of corresponding phenols. Heterocycles such as 3- and 8-quinoline boronic acid gave the corresponding hydroxy-quinoline in good yields (**4a-b**). Other heterocyclic boronic acids such as 6-indolyl (**3c**), 2,6-dimethoxy-3-pyridine (**3d**) and 2-methoxy-5-pyrimidine (**3e**) boronic acids were also converted to the corresponding phenols in 37-55% yields (**4c-e**).

#### **Table 3.** Scope with hetero-arylboronic acids.<sup>*a*</sup>



<sup>a</sup>Reagents and conditions: 3 (0.2 mmol),  $C_{70}$  fullerene (0.05 mol%), DIPEA (2 equiv.),  $O_2$  balloon, CHCl<sub>3</sub> (0.05 M), Blue LED light, 12h.

Further, 4-methoxyphenol was obtained in 63% yield, when potassium 4methoxyphenyltrifluoroborate was reacted under standard reaction conditions (Scheme 2).



Scheme 2. *ipso*-Hydroxylation of potassium 4-methoxyphenyltrifluoroborate using  $C_{70}$  catalyst.

To test the applicability of the developed photocatalytic approach for a preparative synthesis, a gram scale reaction for the hydroxylation of 4biphenylboronic acid was performed. However, in this case, the conversion was low and therefore, the reaction time was increased to 48h. But even after 48h only 62% yield of the desired product was observed due to less conversion. Use of two 6W blue LED bulbs provided 78% and 91% isolated yield of the desired product after 24h and 48h, respectively (Scheme 3).



#### Scheme 3. Scale-up reaction

A one-pot, two-step synthesis of ether from boronic acid was also attempted, and for our delight, 4-cyanoboronic acid was successfully converted to 4-

ÓMe

63% yield

allyloxybenzonitrile (5) in one-pot, two-step process (Scheme 4). In the first step phenol was prepared under standard reaction condition, and after evaporating the solvent, 4-cyanophenole was refluxed with 2 equiv. of allyl bromide in the presence of 2.5 equiv. of  $K_2CO_3$  in CH<sub>3</sub>CN for 12h.



**Scheme 4.** One pot, 2-step synthesis of ether from aryl boronic acid.

To get an insight into the reaction pathway of current metal-free photocatalytic *ipso*-hydroxylation, we carried out different control experiments. UV-visible absorption analysis of different components of the reaction showed that it is only  $C_{70}$  fullerene, which shows absorption in the visible region at 468 nm (Figure 1).



**Figure 1**. UV-Visible spectrum of different components used in the reaction.

Quantum yield of the catalyst in this system was found to be 0.94 ( $\approx$ 1). The crude reaction mixture analysis with LC-MS resulted in detection of diisopropylamine, thus confirms the involvement of amine donor in the course of the reaction.<sup>[26]</sup> Although acetaldehyde was not detected in LC-MS analysis of crude reaction mixture, diisopropylamine might be formed through hydrolysis of corresponding imine generated after proton abstraction from diisopropylethylamine radical cation by intermediate **B** (Scheme 8).<sup>[27]</sup>



Scheme 5. Mechanistic study.

Further to confirm the role of amine, 1,2,3,4tetrahydroisoquinoline was used instead of DIPEA (Scheme 5, equation i).

In this experiment, oxidation of benzylic amine to imine (6b) was observed along with the desired product. Imine (6b) was isolated in 75% yield, providing an alternate pathway for the synthesis of 3,4-dihydroisoquinolines. Also, we analyzed the crude reaction mixture with TOF-MALDI mass analyzer, but no amine C70 adduct was detected (Figure SI4), thus ruling out the direct interaction of with fullerene under current reaction amine conditions. Also, the fluorescence quenching experiments showed that the DIPEA was not functioning as a quencher of excited C<sub>70</sub> fullerene catalyst as the decrease in fluorescence intensity of  $C_{70}^*$  by DIPEA was negligible (Figure SI5). In the presence 2,2,6,6-tetramethylpiperidinooxy of (TEMPO) as a radical quencher, no product was observed, which confirms the radical mechanism of reaction. (Scheme 5, equation ii)

Photocatalyzed oxidative hydroxylation of boronic acids has been proposed to involve the superoxide radical anion ( $O_2$   $\dot{}$ ) as reactive oxygen species.<sup>[14]</sup> When the reaction was carried out in the presence of 1 equiv. of each DABCO and 1,4-benzoquinone product yield decreased to 34% and 26%, respectively. This reduction in the product yield confirms the presence of  ${}^1O_2$  and  $O_2$   $\dot{}$  as DABCO and 1,4-benzoquinone are known to quench these ROS respectively <sup>[28]</sup>(Scheme 6).



Figure 2. Progress of reaction with time.

Later, when we analyzed the progress of the reaction with time, it showed a linear relationship as the yield of the product increases linearly with time (Figure 2).

To predict the oxygen source in phenol, we carried out the reaction in the presence of <sup>18</sup>O–labelled water and oxygen (Scheme 7). The GC-MS analysis of crude reaction mixture showed no incorporation of labelled oxygen in phenol when the reaction is carried out in the presence of <sup>18</sup>O-labelled water. However, <sup>18</sup>O incorporation was found in the <sup>18</sup>O–labelled oxygen gas.<sup>[26]</sup> The result presence of of these reactions indicates the generation of reactive from oxygen molecule oxygen species by photoactivated C<sub>70</sub> fullerene catalyst.



Scheme 7. Labelled oxygen experiments.

Based on these preliminary studies and literature reports,<sup>[14a,17c,23]</sup> the probable mechanism was proposed (Scheme 8), involving photocatalytic oxidative hydroxylation of aryl (hetero-aryl) boronic acids to corresponding phenols. C70 fullerene-catalyst on irradiation with blue LED light comes to an excited state, where it has greater tendency to generate singlet oxygen <sup>1</sup>O<sub>2</sub> from triplet oxygen <sup>3</sup>O<sub>2</sub> via energy transfer process. Superoxide free radical  $(O_2 - )$ , thus generated from  ${}^1O_2$  through single electron transfer (SET) process from DIPEA, attacks the electron deficient boron centre to form intermediate B.



**Scheme 8.** Probable reaction pathway for the synthesis of aryl alcohols from aryl boronic acids.

After the abstraction of proton from amine free radical cation A generated in SET step, B leads to formation of intermediate C. Removal of hydroxyl anion from C followed by aryl migration generates intermediate D, which on hydrolysis provides the desired product.

### Conclusions

In conclusion, we have disclosed an efficient photocatalytic method for the synthesis of arylalcohols using nascent  $C_{70}$  fullerene as photocatalyst under mild conditions. This developed method is applicable for the synthesis of a variety of phenols as well as heterocycle phenols. The preliminary mechanistic study revealed the critical role of  $C_{70}$  fullerene in generating ROS in the presence of blue LED.

# **Experimental Section**

#### **General Methods**

**Reagent Information:** Unless otherwise stated, all reactions were carried out under oxygen atmosphere in screw cap reaction vials. All solvents were bought from. Sigma Aldrich in a sure-seal bottle and used as such. Chemicals were bought from Sigma Aldrich, Alfa-aesar and TCI and used as such. For column chromatography, silica gel (230-400 mesh) from Merck was used. A gradient elution using *n*-hexane and ethyl acetate was performed based on Merck aluminum TLC sheets (silica gel  $60F_{254}$ ) for the purification of products.

**Analytical Information:** The melting points were recorded on a Bronsted Electro Thermal 9100. All isolated compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, LC-MS. Also, all the compounds were further characterized by HRMS. Mass spectra were recorded on Water Q-ToF-Micro Micromass. Copies of <sup>1</sup>H, <sup>13</sup>C NMR can be found in the NMR supporting information.

Nuclear magnetic resonance spectra were recorded either on a Bruker-Avance 300 or 600 MHz instrument. All <sup>1</sup>H NMR experiments are reported in units, parts per million (ppm) and were measured relative to the signals for residual chloroform (7.26), acetone (2.05) and methanol (3.31) in the deuterated solvents. All <sup>13</sup>C NMR spectra were reported in ppm relative to deuterated chloroform (77.23), acetone (29.84) and methanol (49.00) and all were obtained with <sup>1</sup>H decoupling. Optimization studies were done by NMR and NMR yield were calculated by using tetrachloroethane as an internal standard.

General Procedure for Synthesis of aryl alcohols from corresponding boronic acids: To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar, 168  $\mu$ L of C<sub>70</sub> solution (1 mg/ 2 mL in toluene) (0.05 mol%) was added and dried over rotary evaporator. To this phenyl boronic acid (24.2 mg, 0.2 mmol) and chloroform (4 mL) were added followed by the addition of diisopropylamine (69.6  $\mu$ L, 2 equiv). The reaction vial was closed with screw cap, purged with oxygen and kept for vigorous stirring under blue LED light (strip or single bulb) at room temperature for 12 h. For experimental setup, see supporting information. After completion, reaction mixture was dried over rotary evaporator and purified by flash chromatography using silica gel (230-400 mesh size) as stationary phase and *n*-hexane: EtOAc as an eluent.

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# FULL PAPER

C<sub>70</sub> Fullerene-Catalyzed Metal-Free Photocatalytic *ipso*-Hydroxylation of Aryl Boronic Acids: Synthesis of Phenols

Adv. Synth. Catal. Year, Volume, Page – Page

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