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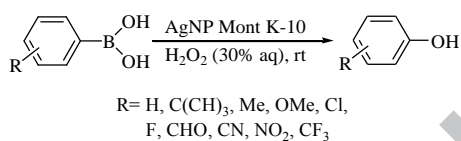
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### Catalysis by mont K-10 supported silver nanoparticles: a rapid and green protocol for the efficient *ipso*-hydroxylation of arylboronic acids

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## Catalysis by mont K-10 supported silver nanoparticles: a rapid and green protocol for the efficient *ipso*-hydroxylation of arylboronic acids

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### ABSTRACT

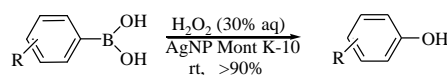
A mild and efficient methodology has been developed for the *ipso*-hydroxylation of arylboronic acids using montmorillonite K-10 supported silver nanoparticles (AgNPs) as catalyst and aqueous H<sub>2</sub>O<sub>2</sub> as oxidant. The reactions were performed at room temperature within short reaction time under solvent- and base-free conditions. This catalyst shows good reusability.

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Phenols and their derivatives are naturally occurring molecules which play significant role in the synthesis of pharmaceuticals, agrochemicals and polymers.<sup>1</sup> Existing protocol for preparing phenolic compounds involves nucleophilic substitution of activated aryl halides,<sup>2</sup> and copper-catalyzed transformation of diazoarene and benzene.<sup>3</sup> Recent research efforts have established arylboronic acids as an alternative precursor for the synthesis of phenols. Arylboronic acids are considered as most versatile organometallic species and find wide application in different organic transformations because of the greater stability and structural diversity.<sup>4</sup> Accordingly a number of remarkable results have been reported on the *ipso*-hydroxylation of arylboronic acids using CuSO<sub>4</sub>-phenanthroline,<sup>5</sup> [Ru(bpy)<sub>3</sub>Cl<sub>2</sub>].6H<sub>2</sub>O,<sup>6</sup> clay-entrapped Cu(OH)<sub>x</sub>.<sup>7</sup> Additionally different metal-free catalytic systems such as H<sub>2</sub>O<sub>2</sub>-poly(N-vinylpyrrolidone),<sup>8</sup> NH<sub>2</sub>OH,<sup>9</sup> potassium peroxydisulphate,<sup>10</sup> Amberlite IR-120 resin,<sup>11</sup> I<sub>2</sub>,<sup>12</sup> Al<sub>2</sub>O<sub>3</sub>,<sup>13</sup> Boric acid<sup>14</sup> and aqueous H<sub>2</sub>O<sub>2</sub><sup>15</sup> have been successfully applied for the synthesis of phenols from arylboronic acids. The concepts of green chemistry focus on the design, manufacture, and the use of chemicals and chemical processes with no pollution potential and are economically and environmentally practicable. In this respect the development of heterogeneous catalyst is particularly suitable due to better separation and recycling advantages over homogeneous systems. Moreover use of nano particle as alternative catalyst in different organic transformation is an emerging area of research.<sup>16</sup> Thus the development of heterogeneous catalytic systems based on solid supported-metal nanoparticles for *ipso*-substitution of arylboronic acids with improved yield and simple reaction protocol still remains a major challenge.

In this communication we wish to report a highly efficient protocol for *ipso*-hydroxylation of arylboronic acids using inexpensive and air-stable mont K-10 clay supported AgNPs as catalyst and aqueous hydrogen peroxide as oxidant at room temperature under solvent-, ligand-, and base-free conditions. To the best of our knowledge, this is the first example of oxidative *ipso*-hydroxylation of arylboronic acids using mont K-10 supported AgNPs synthesized by green route.

Initially we have synthesized AgNPs following a green synthetic route using AgNO<sub>3</sub> as metal precursor and leaf extract of *Phlogacanthus thyriformis*, as reducing agent<sup>17,19</sup> and subsequently immobilized in mont K-10 support.<sup>18,19</sup> We observed that arylboronic acid reacts with aqueous H<sub>2</sub>O<sub>2</sub> in the presence of mont-K 10 supported AgNPs to give the corresponding phenols in good to excellent yields (Scheme 1).



**Scheme 1.** *ipso*-Hydroxylation of arylboronic acid to phenol using aqueous H<sub>2</sub>O<sub>2</sub> as oxidant and Ag-Mont K-10 as catalyst

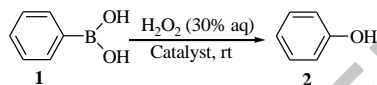
To examine the effectiveness of mont-K 10 supported AgNPs as catalyst in the hydroxylation reaction, phenylboronic acid (**1**, 1mmol) was chosen as a model substrate and the reactions were carried out at room temperature.<sup>20</sup> The results are summarized in Table 1. Initially, we carried out the hydroxylation reaction using 30% aqueous H<sub>2</sub>O<sub>2</sub> at room temperature for 1 h and we have obtained only trace amount of phenol **2** (Table 1, entry 1). Since, most of the reagents and substrate are insoluble in water, we carried out the reaction in presence of acetonitrile and ethanol.

However no improvement in yield was observed (Table 1, entries 2 and 3). Interestingly, the yield of **2** was enhanced to 88% within 25 minute on introducing AgNP Mont K-10 (5 mg, 0.052 mol% of AgNP) as catalyst (Table 1, entry 4). Encouraged by the good results, we started to screen the effect of various solvents (2 mL) on the reaction using 5 mg of catalysts. The reaction was found to proceed in both protic and aprotic solvents, although variations in yields were observed (Table 1, entries 4-7). However, best result was obtained when no solvent was used (Table 1, entry 8). To optimize the minimum amount of catalyst required for the hydroxylation reaction, we performed several test reactions under controlled condition using different amount of AgNP mont K-10 (Table 1, entries 11, 12) and found that 5 mg of catalyst is sufficient for the smooth oxidation of 1 mmol of the substrate (Table 1, entry 8). Use of high or low catalyst loading doesn't improve the yield of the product. During the course of our study, we found that 0.5 mL of hydrogen peroxide was sufficient for the effective conversion. However, the reaction did not proceed in the absence of H<sub>2</sub>O<sub>2</sub> (Table 1, entry 13). Moreover AgNP mont K-10 is found as better catalyst compare to simple mont K-10 in terms of lower catalyst loading and lower oxidant loading (Table 1, entry 14).

With the standard reaction in hand, we evaluated the scope and limitation of the protocols based on variety of electronically diverse arylboronic acids and the results are summarized in Table 2. We observed that the reaction went smoothly with a variety of substituents on the aromatic substrate. Arylboronic acid with electron donating and withdrawing

**Table 1**

Optimization of reaction condition for AgNP Mont K-10 mediated *ipso*-hydroxylation<sup>a</sup>



Entry	Oxidant	Solvent	AgNP Mont K-10 Catalyst (mg)	Time (min)	Yield (%) <sup>b</sup>
1	H <sub>2</sub> O <sub>2</sub>	-	-	60	5
2	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> CN	-	60	8
3	H <sub>2</sub> O <sub>2</sub>	EtOH	-	60	7
4	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> CN	5	25	88
5	H <sub>2</sub> O <sub>2</sub>	MeOH	5	45	80
6	H <sub>2</sub> O <sub>2</sub>	THF	5	30	75
7	H <sub>2</sub> O <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	5	35	78
8	H <sub>2</sub> O <sub>2</sub>	-	5	15	92
9	H <sub>2</sub> O <sub>2</sub>	-	5	60	80 <sup>c, d</sup>
10	H <sub>2</sub> O <sub>2</sub>	-	5	60	65 <sup>c, e</sup>
11	H <sub>2</sub> O <sub>2</sub>	-	3	35	80
12	H <sub>2</sub> O <sub>2</sub>	-	10	30	82
13	-	CH <sub>3</sub> CN	5	24h	Trace
14 <sup>f, g</sup>	H <sub>2</sub> O <sub>2</sub>	-	5	60	20 <sup>f, g</sup>

<sup>a</sup>Reaction conditions: phenylboronic acid (1mmol), H<sub>2</sub>O<sub>2</sub> (30% aq, 0.5 mL); room temperature, air

<sup>b</sup>Isolated yields

<sup>c</sup>The reaction did not reach completion

<sup>d</sup>0.4mL H<sub>2</sub>O<sub>2</sub>

<sup>e</sup>0.3 mL H<sub>2</sub>O<sub>2</sub>

<sup>f</sup>0.5 mL H<sub>2</sub>O<sub>2</sub> and Mont K-10 (5 mg) was used

<sup>g</sup>The reaction did not reach to completion

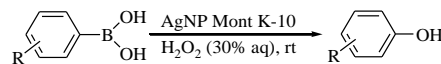
substituents such as OMe, Me, *t*-butyl, F, Cl, NO<sub>2</sub>, CHO showed the *ipso*-hydroxylation reaction in good yields (85-95%). Meta substituted arylboronic acid also gives the product in excellent yield under the current reaction conditions (Table 2, entries 10-12).

To study Ag leaching, the oxidation reaction of phenyl boronic acid was started in the usual way. After completion of the reaction, the reaction mixture was subjected to centrifugation, followed by dilution (with water, 5 mL) and filtration. The leached silver in the filtrate was analyzed by ICP-AES, and was determined to be below the detection level (<0.020 ppm).

Reusability of a catalyst makes it even more attractive due to ecological and industrial relevance. AgNP mont K-10, being a

**Table 2**

AgNP mont K-10 catalyzed synthesis of phenol<sup>a</sup>



Entry	R	Time (min)	Yield (%) <sup>b, c</sup>
1	H	15	92
2	4-C(CH <sub>3</sub> ) <sub>3</sub>	20	95
3	4-Me	25	93
4	4-OMe	15	90
5	4-Cl	15	89
6	4-F	20	85
7	4-CHO	25	91
8	4-CN	30	87
9	4-NO <sub>2</sub>	35	85
10	3-CF <sub>3</sub>	20	88
11	3-Me	25	90
12	3-OMe	20	91

<sup>a</sup>Reaction condition: ArB(OH)<sub>2</sub> (1 mmol), AgNP Mont K-10 (5 mg), H<sub>2</sub>O<sub>2</sub> (30% aq, 0.5 mL); room temperature.

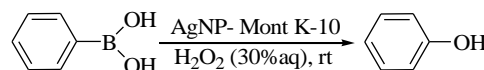
<sup>b</sup>Yields of isolated products.

<sup>c</sup>All compounds were characterized by <sup>1</sup>H NMR, GC-MS and FT-IR.

solid heterogeneous catalyst, could be easily recovered by simple filtration and recycled. The recyclability of the catalyst was investigated (Table 3) for the hydroxylation of phenylboronic acid under the same reaction conditions. Effectiveness of the catalyst was studied upto seven consecutive cycles without significant loss in activity. The slight decreasing trend of the product formation was due to physical loss of the mont K-10 supported AgNPs during separation and purification. To examine the reusability of the catalyst, the reaction was carried out with phenylboronic acid (8 mmol) using mont K-10 supported AgNPs (40 mg) and H<sub>2</sub>O<sub>2</sub> (30% aqueous, 4 mL). We were able to isolate 92% of phenol in the first catalytic cycle. After completion of the first reaction, the catalyst was recovered by centrifugation and then washed for several times with ethanol followed by distilled water (3×5 mL) and dried at 110<sup>0</sup> C for 2 h in an oven. The residual amount of the catalyst was found to be 35 mg. It was then subjected to another run of hydroxylation reaction by adjusting the amount of phenylboronic acid and H<sub>2</sub>O<sub>2</sub>. The same procedure was followed for each consecutive cycle.

**Table 3**

Reusability of the AgNP- Mont K-10 catalyst in the synthesis of phenola



Entry	Run	Yield <sup>a</sup> (%)
1	1 <sup>st</sup>	92
2	2 <sup>nd</sup>	92
3	3 <sup>rd</sup>	90
4	4 <sup>th</sup>	90
5	5 <sup>th</sup>	88
6	6 <sup>th</sup>	85
7	7 <sup>th</sup>	85

<sup>a</sup>Yields of isolated products.

In conclusion, we have developed a simple, efficient and reusable methodology for the *ipso*-hydroxylation of arylboronic acids and their derivatives to phenols using aqueous hydrogen

peroxide as oxidant and Mont K-10 supported AgNPs as catalyst. Due to mild reaction conditions our method has the advantage of broad functional group compatibility for both electron-rich and electron poor substituents. In addition to this, ligand, base and solvent-free condition as well as short reaction time make this methodology quite attractive with promise of future applications.

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- Synthesis of silver nanoparticles: 2 ml of the leaf extract (*Phlogacanthus thyrsoformis*) was added to 20 ml of 0.01 M AgNO<sub>3</sub> solution and kept for 2-3 minutes at room temperature before stirring for 4 hours. The color of the reaction mixture was found to change from colorless to a transparent yellow and finally to a dark brown solution, attributing the reduction of Ag<sup>+</sup> to Ag<sup>0</sup>. The resulting solution was centrifuged and the nanoparticles were collected for characterization (see the supporting information).
- Preparation of montmorillonite clay supported AgNP catalyst: The formed AgNPs were suspended in 30 ml of distilled water and ultrasonicated for about 15 minutes. To the silver nano suspension 500 mg of mont K-10 clay was added, and then stirred for 24 hours at room temperature. The formed precipitate was filtered and collected over a round dish. Then it was heated at 110 °C for 3 h under oven followed by calcinations at 400 °C for 4 hour in a silica crucible in furnace, and then stored under moisture-free condition and characterized (see the supporting information). ICP-AES analysis indicated loading of 0.225 mg of AgNP in per 20 mg of Montmorillonite.
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- General procedure for the hydroxylation of arylboronic acid*: A 50 mL round bottom flask was charged with arylboronic acid (1 mmol), 30% aqueous H<sub>2</sub>O<sub>2</sub> (0.5 mL) and 5 mg of Ag-mont K-10 without using any solvent system and the reaction mixture was stirred at room

temperature under aerobic condition. The progress of the reaction was monitored by TLC. After the completion of the reaction, the solid was separated by filtration, extracted with diethyl ether. The combined organic layers were dried over by anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated in a rotary evaporator under reduced pressure. The crude was purified by column chromatography on silica gel (hexane: ethyl acetate, 9:1) to afford the desired product. The purity of the compound was confirmed by <sup>1</sup>H NMR, GC-MS and FT-IR.