



# Quinones synthesis via hydrogen peroxide oxidation of dihydroxy arenes catalyzed by homogeneous and macroporous-polymer-supported ruthenium catalysts



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## ABSTRACT

Ruthenium(II)/dimethyl phenyloxazoline (Ru(II)/*dm*-Pheox) complex **2a** and its macroporous-polymeric-catalyst **4** were found to be very rapid and efficient catalysts in the hydrogen peroxide oxidation of 1,2- and 1,4-dihydroxy arenes. Most of the quinone products were delivered in 99% yield. The polymeric-catalyst **4** could be reused at least five times.

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## 1. Introduction

Quinones are useful compounds not only as synthetic intermediates<sup>1</sup> such as dienophiles in the chemical transformations, but also as biological active compounds.<sup>2</sup> For example, they have a potential value in cancer chemotherapy<sup>3</sup> as well as their antitumor, antibacterial, and antiprotozoan activities.<sup>4</sup> 2-Methyl-1,4-naphthoquinone (vitamin K<sub>3</sub>) and its derivatives are also used as blood coagulating agents<sup>5</sup> and as a supplement in animal feed<sup>6</sup> and currently attracting much attention because of its interesting pharmacological activities.<sup>7</sup> In addition, trimethyl-*p*-benzoquinone is a key compound in the vitamin E synthesis. Quinones are usually prepared by direct oxidations of hydroquinone, catechol, naphthols, and their derivatives.<sup>8</sup> Although a wide variety of oxidants were used for oxidation of dihydroxy arenes,<sup>9</sup> molecular oxygen and hydrogen peroxide are the best oxidants from the environmental and economical point of view as clean and cheap oxidants. There are several reported catalytic systems that have been developed for quinones synthesis using molecular oxygen and hydrogen peroxide as an oxidant. Among these catalytic systems are copper salts/O<sub>2</sub>,<sup>10</sup> ruthenium salts/H<sub>2</sub>O<sub>2</sub>,<sup>11</sup> Schiff base cobalt

complexes/O<sub>2</sub>, copper sulfate–alumina/O<sub>2</sub>,<sup>12</sup> and heteropoly and isopoly compounds/H<sub>2</sub>O<sub>2</sub><sup>13</sup> or O<sub>2</sub>.<sup>14</sup> The main drawback with the previous catalytic systems is the use of homogeneous catalysts that leads to two major problems, one is the catalyst separation and the second is the contamination of the quinone products by the transition metal traces. From this regard, using polymer-supported catalysts for quinone synthesis in the presence of hydrogen peroxide is an interesting research subject owing to the well-known advantages of the heterogeneous catalysts over the homogeneous catalysts such as the efficient recovery of the often-expensive catalysts, and potentially reuse of these catalysts. In addition, when using heterogeneous catalyst, there is no contamination of the reaction product by the metal traces. Especially, polymer-supported ruthenium complex was found to be effective as catalyst for the decomposition of H<sub>2</sub>O<sub>2</sub> along with good ability for recycling several times without loss of activity.<sup>15</sup> Notably, the insoluble cross-linked polymers are used widely as they are inert, non-toxic, thermally stable, and easy to be recycled.<sup>16</sup> Despite the tremendous efforts devoted to quinones synthesis using polymer-supported catalysts, kinetic studies<sup>17</sup> or limited substrate scope<sup>4a,18</sup> have so far been achieved. Recently, polymer-incarcerated platinum catalyst was found to be very efficient catalyst for aerobic oxidation of hydroquinone derivatives.<sup>19</sup> In this case, treatment of the recovered catalyst with base is essential for preventing the gradual decline in reusability. Although one catechol derivative was presented, Park

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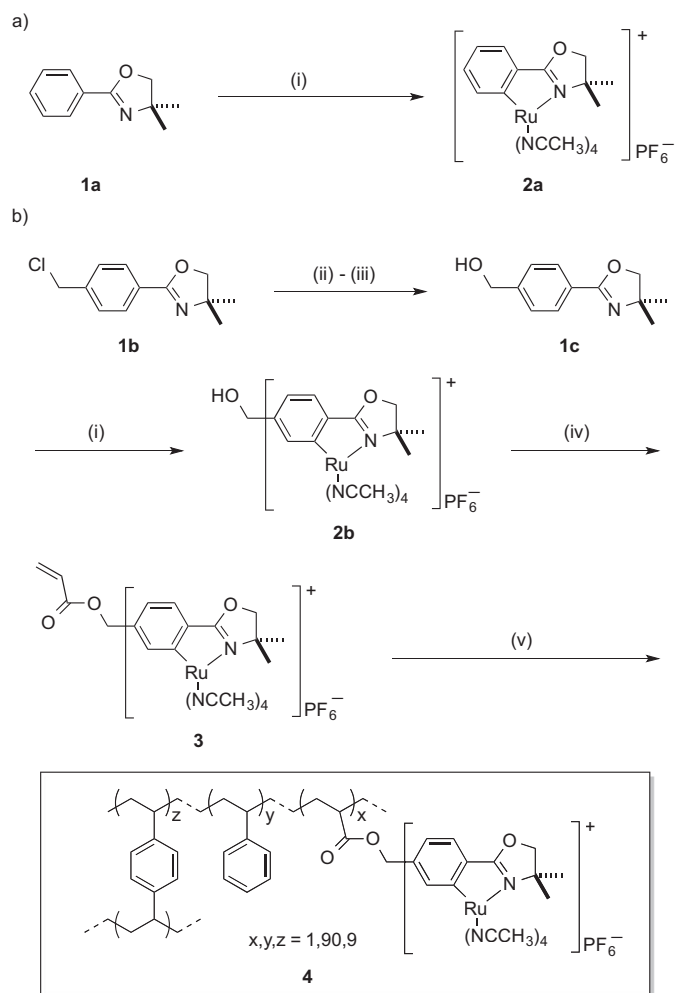
et al.<sup>20</sup> developed a highly efficient and recyclable copper catalyst (Cu/AlO(OH)) for the aerobic oxidation of a wide range of hydroquinones. Our recent study on quinones synthesis showed that Ru<sup>II</sup> and Ir<sup>I</sup> are efficient homogeneous catalysts for hydrogen peroxide oxidation of phenols and methoxyarenes.<sup>21</sup> As a complementary study for this interesting research area, we focused on the hydrogen peroxide oxidation of dihydroxy arenes by using macroporous-polymer-supported catalysts. To the best of our knowledge, there is no report with a wide substrate scope for oxidation of dihydroxy arenes using polymer-supported Ru<sup>II</sup>-catalyst and hydrogen peroxide as an oxidant.

## 2. Results and discussion

Very recently, we explored a novel strategy for the synthesis of macroporous-polymer-supported Ru<sup>II</sup>-catalyst.<sup>22a</sup> We found that the catalyst on cross-linked support with pores of molecular dimension has shown significant increase in its selectivity and reactivity due to high concentration of the active sites within the small pores. Inspired by our previous work, we successfully immobilized the catalyst **2a**<sup>22b</sup> onto a macroporous cross-linked polymeric-support to afford **4**. The catalysts **2a** and **4** promoted the hydrogen peroxide oxidation of a broad class of dihydroxy arenes to furnish the quinone products in excellent yields (99% in most of the cases). The polymeric-catalyst **4** could be reused at least five times without loss in reactivity. The Ru(II)/*dm*-Pheox catalyst **2a** could be easily synthesized in high yield as described on the previous report (Scheme 1a).<sup>22b</sup> Initially, we evaluated the catalytic activity of **2a** in hydrogen peroxide oxidation of 1,4-dihydroxy naphthalene using various solvents as shown in Table 1. Pleasingly, naphthoquinone products were obtained in quantitative yields with most of the used solvents. And THF was found to be the best solvent (Table 1, entry 4). It is noteworthy that the quinone products resulted in a pure form after extraction with diethyl ether or dichloromethane and there is no necessity for further column purification compared with the previous studies.

Next, by using THF as a solvent, we optimized the reaction conditions as shown in Table 2. We found that different loadings of catalyst **2a** quantitatively oxidized 1,4-dihydroxy naphthalene (Table 2, entries 1–5). A high TON was achieved with 0.01 mol % of **2a** (Table 2, entry 5) while a high TOF was obtained with 0.25 mol % of **2a** (Table 2, entry 3). When we replaced hydrogen peroxide by molecular oxygen as an oxidant, the naphthoquinone product was isolated in 25% yield in 1 day (Table 2, entry 7). The blank test showed that only 6% of the naphthoquinone product was obtained in 5 days (Table 2, entry 8). Since catalyst **2a** was found to be very efficient in quinone synthesis, we decided to immobilize it onto polymeric-support and evaluate its catalytic activity in hydrogen peroxide oxidation of various dihydroxy arenes. The steps to functionalize the homogeneous Ru-catalyst **2a** to be ready for the polymerization step started by the reaction between 4-(chloromethyl)benzoyl chloride and 2-amino-2-methyl-1-propanol to furnish the ligand **1b** in 86% yield. The Ru-catalyst **2b** was synthesized from **1b** in two steps in excellent yield (92%) as shown in Scheme 1b.

The monomeric Ru(II)/*dm*-Pheox complex **3** was readily prepared from **2b** in 70% yield as a new monomeric complex that was easily cross-link polymerized with styrene and 1,4-divinylbenzene (DVB) in the presence of 2,2'-azobisisobutyronitrile (AIBN) as an initiator. The reaction was carried out in the presence of water to afford the macroporous-polymer-supported Ru(II)/*dm*-Pheox (**4**) in quantitative yield, as shown in Scheme 1b and Fig. 1. The exact amount of the Ru(II)/*dm*-Pheox complex loaded onto the polymeric network was determined by elemental analysis of the nitrogen content. Encouraged by the excellent results from the homogeneous catalyst **2a**, we optimized the reaction



**Scheme 1.** Synthesis of catalysts **2a** and **4**. Reagents and conditions: (i) [RuCl<sub>2</sub>(benzene)]<sub>2</sub> (0.5 equiv), KPF<sub>6</sub> (4.0 equiv), 1 N NaOH (1.0 equiv), CH<sub>3</sub>CN, 80 °C, 24 h; (ii) AcONa·3H<sub>2</sub>O (5.0 equiv), NaI (5.0 equiv), CH<sub>3</sub>CN, reflux, 24 h; (iii) MeOH/H<sub>2</sub>O (5:1 v/v), 2.5 N NaOH (6.0 equiv), 3 h, 0 °C → rt; (iv) acrylic acid (3.0 equiv), DCC (3.0 equiv), DMAP (2.0 equiv), CH<sub>3</sub>CN, 0 °C → rt, 3 h; (v) styrene, DVB, AIBN (2.0 equiv), CH<sub>2</sub>Cl<sub>2</sub>, H<sub>2</sub>O, 60 °C, 24 h.

conditions with the polymeric-heterogeneous-catalyst **4**.<sup>23</sup> Under the optimized reaction conditions, we studied the hydrogen peroxide oxidation of various hydroquinone and catechol derivatives along with dihydroxy naphthalene by using **2a** or **4** as the catalyst (Table 3).

**Table 1**  
Solvent screening<sup>a</sup>

Entry	Solvent	Time	Yield <sup>b</sup> (%)
1	Toluene	21.5 h	37
2	Acetone	8 min	99
3	CH <sub>2</sub> Cl <sub>2</sub>	12.5 h	36
4	THF	5 min	99
5	1,4-Dioxane	7 min	99
6	DMF	10 min	99
7	CH <sub>3</sub> OH	8 min	99
8	Et <sub>2</sub> O	10 min	97

<sup>a</sup> Reactions were performed by using 0.34 mmol of 1,4-dihydroxy naphthalene in 1.0 mL of solvent with 0.0034 mmol of **2a** and 0.44 mmol of H<sub>2</sub>O<sub>2</sub>.

<sup>b</sup> Isolated yield.

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