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Heterogeneous Fe-N-C Cocatalyst for Hydroquinone Oxidation Enables Aerobic Oxidation of Primary Alcohols to Aldehydes

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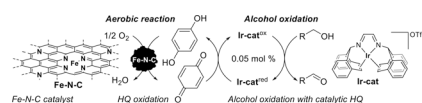
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Abstract

Benzoquinone (BQ) is commonly used as a cocatalyst in multi-component catalyst systems for aerobic oxidation of organic molecules. Such methods often proceed by a redox cascade in which a secondary catalyst supports aerobic oxidation of hydroquinone (HQ) to BQ. The present study shows that a commercially available non-precious metal heterogeneous catalyst, PAJ-Fe-N-C, is much more efficient than established homogeneous catalysts for aerobic oxidation of HQ to BQ, and this improved reactivity is crucial to support aerobic oxidation of primary alcohols to aldehydes with the homogeneous iridium catalyst, [Ir(trop₂DAD)]OTf (trop₂DAD = *N,N*-bis(5-*H*-dibenzo[*a,d*]cycloheptene-5-yl)-1,4-diazabuta-1,3-diene). The combination of this heterogeneous/homogeneous catalyst system operates with Ir catalyst loadings as low as 0.05 mol % and turnover frequencies $\geq 350 \text{ h}^{-1}$.

Graphical Abstract



A commercially available heterogeneous Fe-N-C catalyst supports efficient aerobic oxidation of hydroquinone to benzoquinone, outperforming homogeneous molecular cobalt and iron cocatalysts that have been used to support redox cascades. This Fe-N-C/benzoquinone cocatalyst system supports the highly efficient oxidation of primary alcohols to aldehydes with 0.05 mol % of a homogeneous Ir catalyst in organic solvent.

Keywords

Aerobic; alcohol oxidation; benzoquinone; catalysis; aldehydes

Homogeneous transition-metal complexes and benzoquinone (BQ) are highly effective cocatalysts for aerobic oxidation of organic molecules,^[1–5] and they are featured in Pd-catalyzed oxidation of alkenes^[6,7] and allylic C–H oxidation^[8–12] and in Pd-, Ru-, and

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Fe-catalyzed dehydrogenation of alcohols and saturated C–C bonds.^[13–16] These catalyst systems often feature a third component that supports hydroquinone (HQ) oxidation by O₂, providing the basis for a biomimetic redox cascade similar to that shown in Figure 1A.^[1] (Pseudo)macrocyclic Co or Fe complexes, such as Co(salen), Co(salophen), and Fe(Pc) (Pc = phthalocyanine) are amongst the most commonly used cocatalysts (Cat₁) for *in situ* hydroquinone oxidation.^[1,4,17] The Grützmacher laboratory has developed homogeneous Ir catalysts for selective oxidation of primary alcohols to aldehydes (Figure 1B)^[18–20] that exhibit excellent activity; however, the requirement for (super)stoichiometric benzoquinone as the oxidant limits the atom economy and complicates product isolation. Attempts to use electrochemical catalyst regeneration^[21] or Co(salophen)/BQ co-catalysts with O₂ as the stoichiometric oxidant^[20] have not led to effective performance. We postulated that more efficient aerobic oxidation of HQ could overcome these limitations and considered whether such reactivity could be accessed with heterogeneous “Fe-N-C” catalysts (Figure 1C).^[22–24] First-row transition metals incorporated into nitrogen-doped carbon materials (M-N-Cs) have been extensively studied as electrocatalysts for the oxygen reduction reaction (ORR) in fuel cells.^[25–29] and one of these catalysts is now commercially available through Pajarito Powder (herein, “PAJ-Fe-N-C”).^[30] Single-atom catalysts of this type have been the focus of growing interest for aerobic oxidation of organic molecules.^[22–24] Here, we show that PAJ-Fe-N-C is a very active catalyst for aerobic oxidation of HQ, providing the basis for efficient Ir-catalyzed alcohol oxidation with O₂ as the stoichiometric oxidant.

Recent studies in the Stahl lab have investigated aerobic oxidation of HQ derivatives with M-N-C catalysts (M = Co or Fe) in aqueous solution,^[31–35] and PAJ-Fe-N-C was independently shown to be much more active than other M-N-C catalysts for aerobic oxidation reactions in organic solvent (oxidative dehydrogenation of hydrazones to diazo compounds).^[36] Together, these results raised the prospect that PAJ-Fe-N-C might be a good cocatalyst for HQ oxidation in organic solvent and thereby contribute to more effective aerobic oxidation reactions.

We elected to investigate this possibility with [Ir(trop₂DAD)]OTf [**Ir-2**; trop₂DAD = *N,N*-bis(5-*H*-dibenzo[*a,d*]cycloheptene-5-yl)-1,4-diazabuta-1,3-diene),^[19] a catalyst that shows higher activity than the cyclohexyldiamine derivative, **Ir-1** (Figure 1B).^[18,20] Initial tests investigated oxidation of benzyl alcohol, using catalytic BQ (10 mol %) with Co(salophen) and **Ir-2** under 1 atm of O₂. Similar to previous efforts with 1-octanol as the substrate,^[20] the reaction showed poor results; less than 20% benzaldehyde was observed after 30 min and only slight improvement was observed at longer reaction times (Figure 2A). Analysis of the BQ speciation during the reaction revealed that BQ is completely reduced to HQ by the first time point and never recovers (Figure 2B). Similar observations were made when the same reaction was repeated with Co(salen) and Fe(Pc) as the cocatalyst, rather than Co(salophen) (see Figure S1 in the Supporting Information). The ineffectiveness of these reactions implicates one or more problems in the proposed catalytic redox cascade, shown in Figure 2C. For example, inefficient reoxidation of HQ could result in decomposition of an unstable reduced form of the Ir catalyst.

The results in Figure 2 prompted us to probe independently the aerobic oxidation of HQ with a series of different homogeneous and heterogeneous catalysts^[17] at the same 100:1

BQ:catalyst molar ratio used in the alcohol oxidation reaction. The molecular catalysts, Co(salen), Co(salophen) and Fe(Pc) show only modest performance, with none of them promoting full conversion of HQ to BQ and all showing a plateau in reactivity (Figure 3A). Heterogeneous Pt catalysts developed by Kobayashi and coworkers have been used to promote aerobic oxidation of HQ derivatives,^[37] but commercially available Pt/C and Pd/C catalysts are even less effective than molecular catalysts under the present reaction conditions (Figure 3B). In contrast, PAJ-Fe-N-C affords complete conversion of HQ to BQ within 20 min. This reactivity is further enhanced in the presence of catalytic NaO^tBu (0.1 mol %), which is present in the alcohol oxidation conditions. Under these conditions, only 0.1 mol % PAJ-Fe-N-C is needed to achieve >95% conversion of HQ to BQ within 20 min (see additional optimization data in Figures S7, S8 and Table S1 in the Supporting Information). In addition, we have evaluated several previously reported Fe-N-C materials, including Fe-Phen-C,^[38,39] Fe-Pc-C,^[40] and Fe-PANI-C,^[41] which were synthesized according to the literature procedures (Phen = 1,10-phenanthroline; Pc = phthalocyanine; PANI = polyaniline, see Figures S2–S6 and Section 3 of the Supporting Information for characterization data). These materials exhibited lower catalytic activity compared to PAJ-Fe-N-C (see Figure S9 in the Supporting Information).

These observations motivated efforts to explore PAJ-Fe-N-C as a cocatalyst in **Ir-2**-catalyzed alcohol oxidation (Figure 4A). An initial test of benzyl alcohol oxidation under conditions similar to those in Figure 2, but with 0.1 mol % PAJ-Fe-N-C rather than Co(salophen) as the cocatalyst, led to full conversion to benzaldehyde within 1 h. Therefore, subsequent efforts focused on optimizing the catalyst system further (i.e., reducing the loadings of PAJ-Fe-N-C, **Ir-2**, and BQ), while still accessing full conversion to benzaldehyde within 5 h. Representative data, illustrated in Figure 4B, led to a final catalyst composition of 0.05 mol % **Ir-2**, 0.03 mol % PAJ-Fe-N-C, 10 mol % BQ, and 0.1 mol % NaO^tBu (see section 6 of the Supporting Information for additional optimization data, Figures S12–S15, Tables S2–S3). Analysis of other BQ derivatives showed that the best results are obtained with the unsubstituted BQ (Figure 4B.iv).

BQ is toxic^[42] and readily sublimes, even at room temperature,^[43] and these features present significant hazards and complications when handling BQ on large scale. HQ does not present similar issues, so a final optimization effort focused on replacing BQ with HQ as the cocatalyst (Figure 5).^[44] The full reaction mixture without the **Ir-2** catalyst (i.e., with the alcohol, catalytic PAJ-Fe-N-C, and HQ) was stirred under O₂ and led to complete BQ formation within minutes. The **Ir-2** catalyst was then added to initiate alcohol oxidation, and full conversion to the aldehyde was achieved in less than 5 h, matching the performance observed when BQ was used as the cocatalyst (cf. Figure 5 and Figure S16 in the Supporting Information).

The modified conditions, with HQ as the cocatalyst and 0.05 mol % of **Ir-2** and 0.03 mol % PAJ-Fe-N-C, were then used to examine reactions with a collection of other substrates (Figure 6). Good-to-excellent reactivity was observed across an array of primary alcohols, including benzyl alcohols with electronically donating, neutral, and withdrawing substituents, affording products in >90% isolated yield. The selectivity for primary alcohol reactivity is evident with substrate **1d**, which contains both a primary and secondary alcohol.

Aldehyde **2d** is obtained in 89% isolated yield. NMR analysis of the crude product mixtures shows 96% yield of **2d** with 4% yield of the ketone-aldehyde double oxidation product. Furfuryl alcohol shows good reactivity, affording the aldehyde in 90% yield, but the reaction of 2-(hydroxymethyl)pyridine, **1f**, is unsuccessful under these conditions. Aliphatic primary alcohols show good reactivity, evident with 3-phenylpropanol and 1-octanol, which afford aldehydes **2g** and **2h** in excellent yield (95% and 92%, respectively). Oleyl alcohol is a readily available seed oil and the aldehyde **2i** is obtained in excellent yield (91%) with 20 mol % HQ loading (see Table S4 in the Supporting Information for further reaction optimization). The *cis* alkene is unaffected by the reaction. Fatty aldehydes of this type are natural components of insect pheromones and citrus essential oils, and routes to these compounds are of interest for crop protection^[45] and as fragrances.^[46,47] Cyclopropylmethanol affords aldehyde **2j** in 96% yield. Aliphatic aldehydes are much more susceptible to overoxidation to the carboxylic acid, relative to benzylic alcohols; however, most substrates formed the aldehyde selectively. Among the substrates tested, only 4-(2-hydroxyethyl)-2,2-dimethyl-1,3-dioxolane, led to a mixture of aldehyde and acid (60% **2k** and 28% of the corresponding carboxylic acid). Collectively, these results establish important benchmarks for the aerobic oxidation of primary alcohols. While other catalyst systems, such as (bpy)Cu/TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidine *N*-oxyl) appear to have better tolerance of heterocycles such as pyridine,^[48] **Ir-2** exhibits a unique combination of high catalytic turnovers and rate and aldehyde selectivity with aliphatic alcohols. The turnover numbers (TONs) approaching 2000 and turnover frequencies (TOF) of $\geq 350 \text{ h}^{-1}$ are much higher than those observed with (bpy)Cu/TEMPO, for which TON/TOF values of approximately 20/20 h^{-1} are typical.

The results outlined herein highlight the importance of efficient catalytic aerobic oxidation of HQ on the outcome of redox cascades that use BQ as a cocatalyst. Use of the commercially available PAJ-Fe-N-C catalyst supports replacement of benzoquinone with O₂ as the stoichiometric oxidant and enables efficient Ir-catalyzed alcohol oxidation at room temperature. This work shows that the non-precious-metal PAJ-Fe-N-C heterogeneous catalyst offers significant advantages over the previously used homogeneous cocatalysts, such as Co(salophen) or Fe(Pc), in addition to precious-metal heterogeneous cocatalysts. This work provides a foundation for exploration of other applications of PAJ-Fe-N-C or related M-N-C cocatalysts that leverage the synergistic benefits of homogeneous and heterogeneous cocatalysis to support more sustainable synthetic methods.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

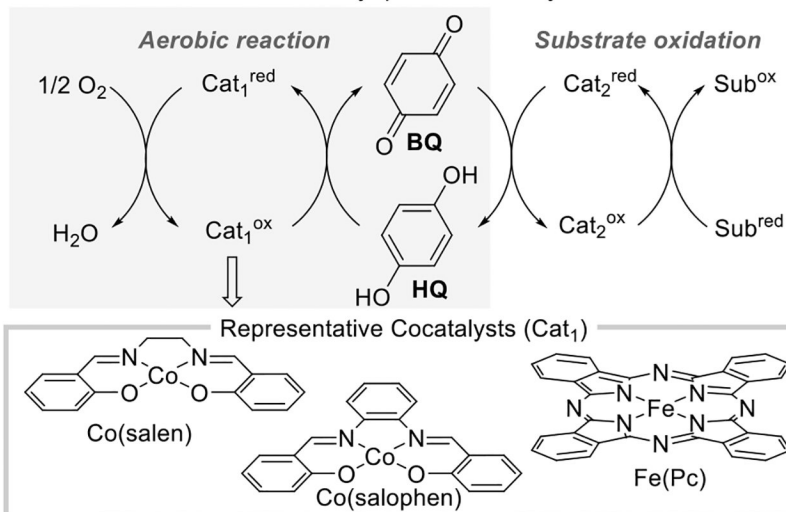
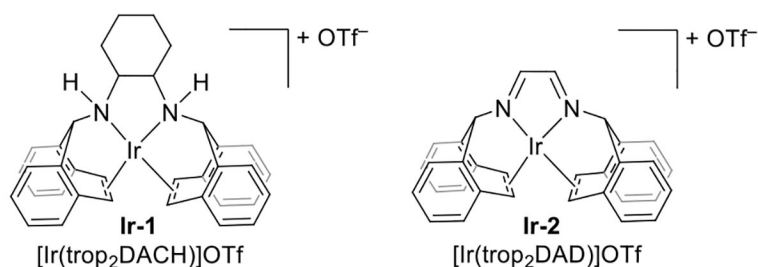
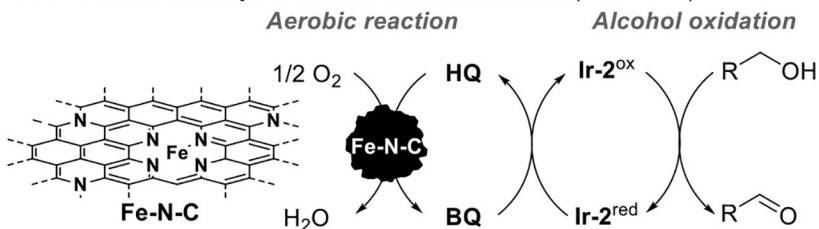
Acknowledgements

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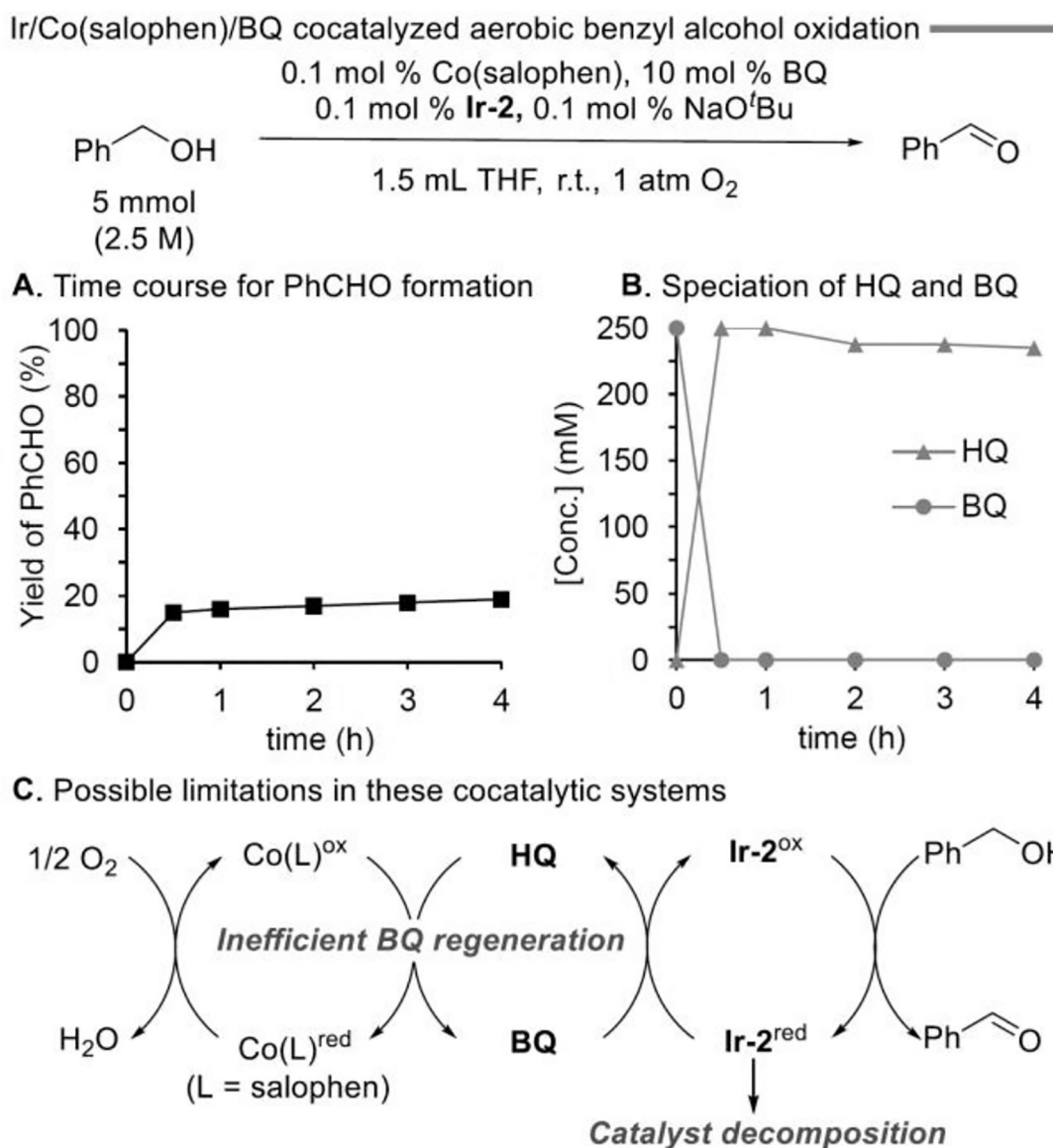
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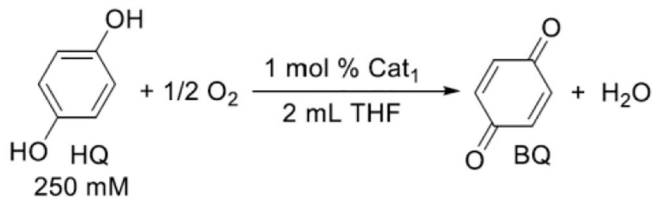
A. Aerobic oxidations mediated by quinone cocatalyst**B. Ir-catalysts used in alcohol oxidation with stoichiometric BQ****C. Fe-N-C/HQ cocatalyzed aerobic alcohol oxidation (*this work*)****Figure 1.**

A) Aerobic benzoquinone (BQ) regeneration in catalytic redox cascades in the oxidation of organic molecules. B) Iridium-catalysts that support efficient alcohol oxidation with stoichiometric BQ. C) Application of heterogeneous Fe-N-C cocatalysts to support aerobic BQ reoxidation and Ir-catalyzed alcohol oxidation.

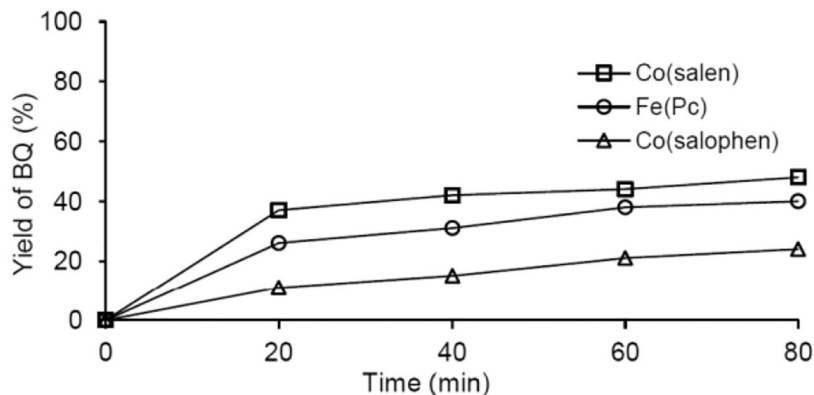
**Figure 2.**

Iridium-catalyzed aerobic oxidation of benzyl alcohol using catalytic BQ and Co(salophen) cocatalyst. A) Time course data for benzaldehyde (PhCHO) formation. B) Speciation of HQ and BQ during the reaction. C) Possible limitations in these multicatalytic systems.

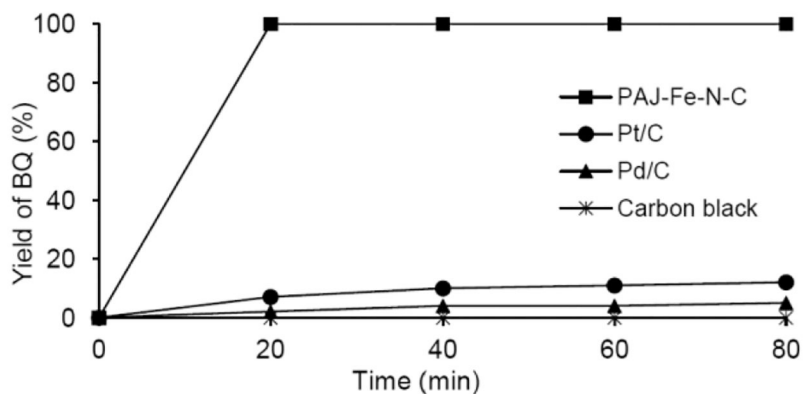
Aerobic oxidation of hydroquinone



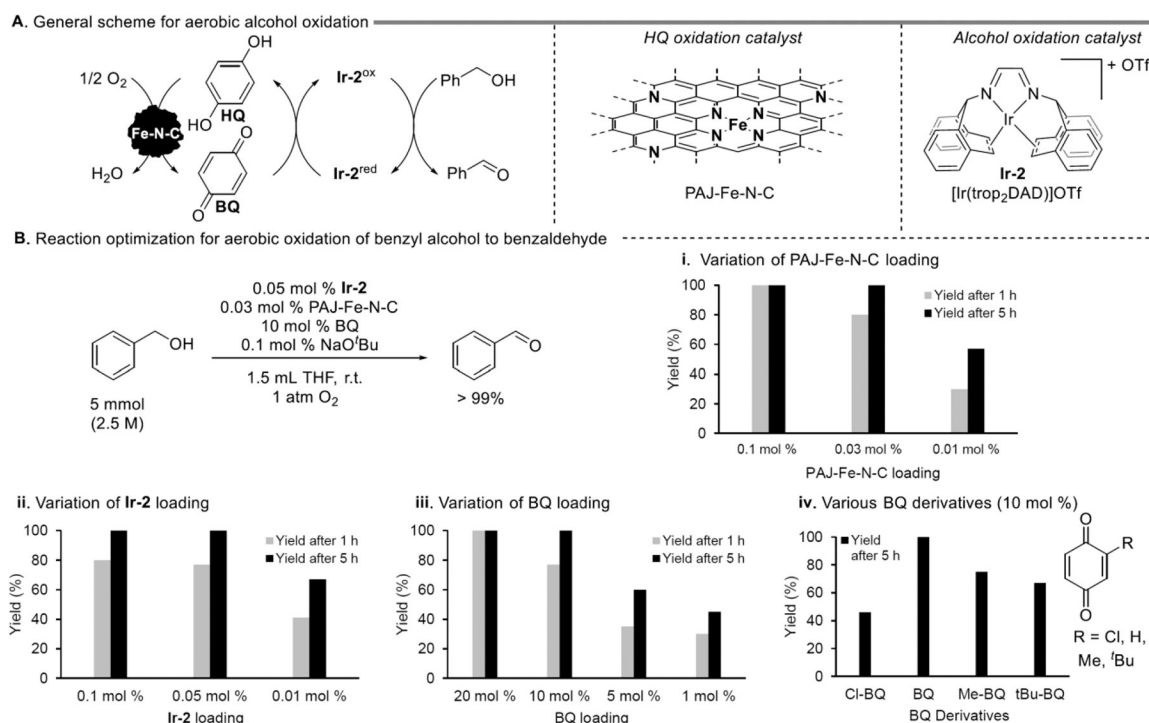
A. 1 mol % molecular catalyst



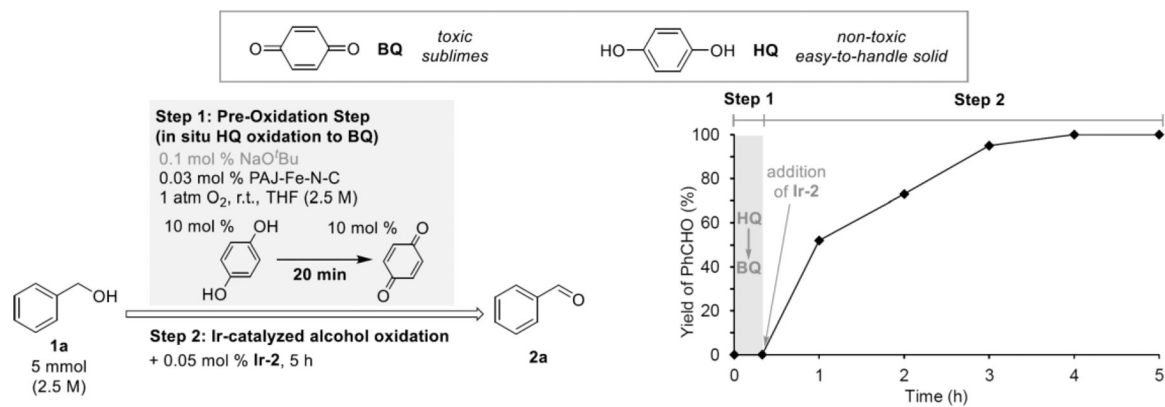
B. 1 mol % (based on metal content) heterogeneous catalyst

**Figure 3.**

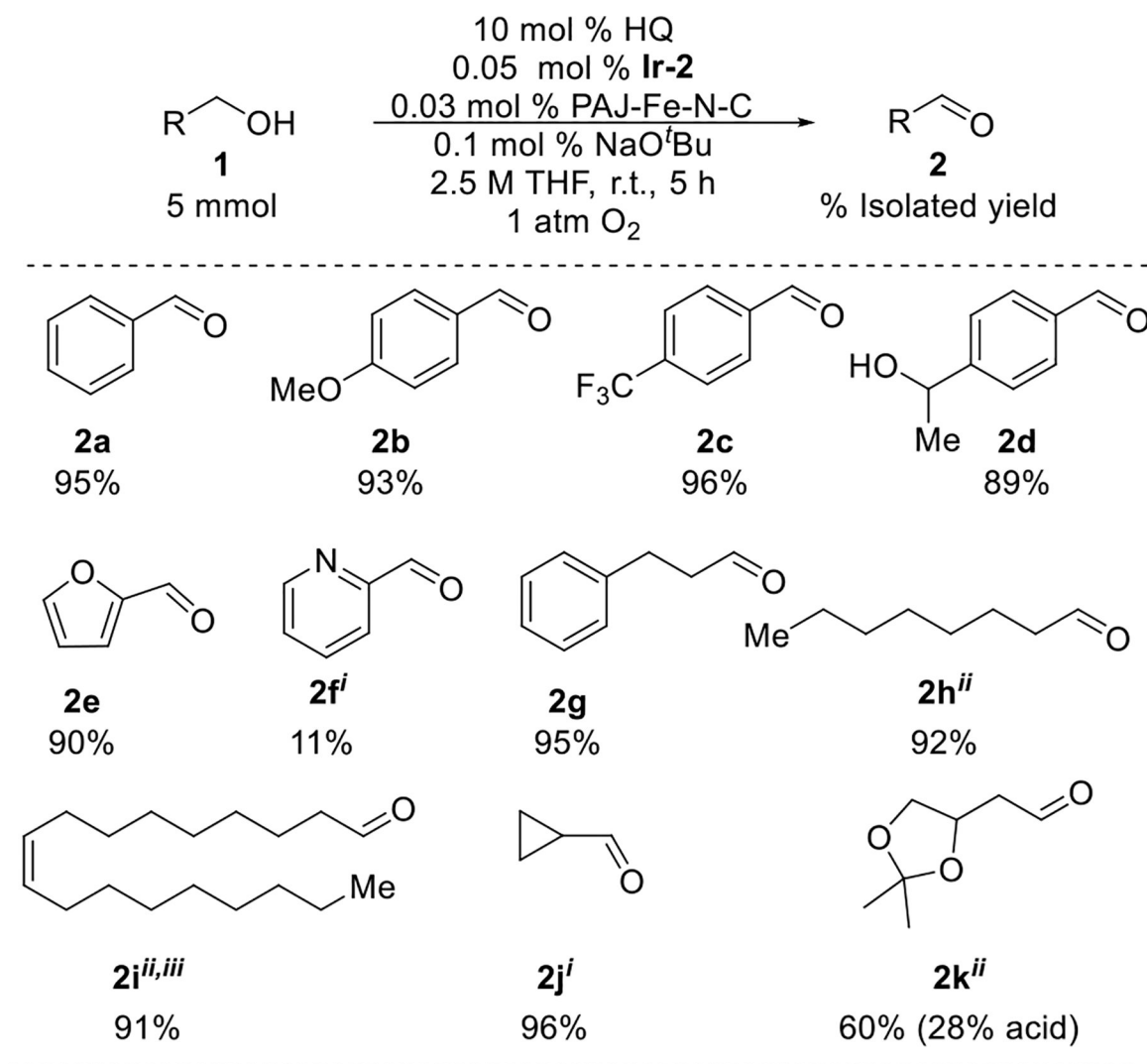
Aerobic hydroquinone oxidation. Reaction conditions: 0.5 mmol HQ in 2 mL THF under 1 atm O₂. A) HQ oxidation with 1 mol % molecular catalyst (Co(salen), Co(salophen) and Fe(Pc)). B) HQ oxidation with 1 mol % heterogeneous catalyst based on metal content (PAJ-Fe-N-C, Pt/C, Pd/C, or carbon black).

**Figure 4.**

PAJ-Fe-N-C/quinone-cocatalyzed aerobic alcohol oxidation using [Ir(trop₂DAD)]OTf (**Ir-2**) as a homogeneous catalyst. A) General scheme for aerobic alcohol oxidation. B) Reaction optimizations for aerobic oxidation of benzyl alcohol to benzaldehyde. Reaction conditions: 5 mmol benzyl alcohol in 1.5 mL THF (2.5 M), 0.1 mol % NaO^tBu under 1 atm O₂, varying loadings of BQ, **Ir-2** and PAJ-Fe-N-C. (i) Variation of PAJ-Fe-N-C loading, PAJ-Fe-N-C (0.1–0.01 mol %) with 10 mol % BQ and 0.1 mol % **Ir-2**; (ii) Variation of **Ir-2** loading (0.01–0.1 mol %) with 10 mol % BQ, 0.03 mol % PAJ-Fe-N-C; (iii) Variation of BQ loading (1–20 mol %) with 0.03 mol % PAJ-Fe-N-C, 0.05 mol % **Ir-2**; (iv) Various BQ derivatives (10 mol %) with 0.03 mol % PAJ-Fe-N-C and 0.05 mol % **Ir-2**.

**Figure 5.**

Time-course data for aerobic oxidation of **1a**, involving in situ oxidation of the **HQ** cocatalyst to **BQ**. All reaction components except **Ir-2** are present in the **Step 1** reaction mixture, and the alcohol oxidation is initiated by addition of 0.05 mol % **Ir-2** (**Step 2**).

**Figure 6.**

Substrate scope for aerobic alcohol oxidation using cocatalytic **Ir-2**, hydroquinone (HQ), and PAJ-Fe-N-C. Reaction conditions: 5 mmol alcohol, 10 mol % HQ, 0.05 mol % **Ir-2**, 0.03 mol % PAJ-Fe-N-C, 0.1 mol % NaO^tBu in 1.5 mL THF under 1 atm O₂ for 5 h at room temperature. Isolated yield was reported. ⁱNMR yield; ⁱⁱ0.1 mol % **Ir-2**, ⁱⁱⁱ20 mol % HQ.