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Green and mild laccase-catalyzed aerobic oxidative coupling of benzenediol derivatives with various sodium benzenesulfinates

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Abstract

The oxidative coupling reaction between hydroquinone or catechols and various sodium benzenesulfinates was investigated using the laccase from *Trametes versicolor*, in the presence of O_2 in a phosphate buffer solution at room temperature to afford sulfonyl benzenediols in 75-95% yield.

Keywords: Laccase enzyme, catechol, sodium benzenesulfinates, O_2, phosphate buffer solution, oxidative coupling, sulfonyl benzenediols

Introduction

The laccase (benzenediol: oxygen oxidoreductase, EC 1.10.3.2), is a well-known multicopper catalyst for the oxidative coupling reaction of diverse compounds to form various C-C, C-N or C-O bonds.[1-4]

Laccases are interesting eco-friendly enzymes since they use air and produce water as the only by-product. Additionally, they work under mild conditions and have been used in industry,[5-7] as well as for a range of organic transformations.[8-10] Different laccases have been studied which exhibit a wide temperature and pH range (usually pH 4-6),[11-13] and are stable in various organic solvents.[14,15] The relevant mechanism has been comprehensively discussed in the literature.[16,17]

Laccases are also used as catalysts for the synthesis of dyes, cosmetics and pharmaceutically active compounds.[18-22] For example, Wellington and co-workers reported a direct laccase-mediated synthesis of compounds with anticancer activity,[23,24] while Beifuss and co-workers used laccases for various oxidation reactions to yield carpanones and benzopyrans, as well as for sesamol trimerisation.[25,26]

Sulfones are ubiquitous in medicinal chemistry,[27] and agrochemicals targets.[28] Diaryl sulfones are also important synthons, and are broadly applied in organic chemistry because of their industrial applications.[29] Aryl sulfones are useful building blocks which are found in many drugs, such as the antibacterial Dapsone,[30] Laropiprant,[31] a prostaglandin D_2 antagonist, or the COX-2 inhibitor Vioxx.[32] Recently, diaryl sulfones have been shown to inhibit HIV-1 reverse transcriptase, as well as possess antitumor and antifungal activities.[33]

Although the preparation of sulfonyl benzenediol derivatives *via* the oxidative coupling reaction between benzenediols and sodium sulfinate using potassium ferricyanide as an oxidant[34] and electrochemical methods have been reported,[35-37] these methods suffer from some problems in that potassium ferricyanide is a toxic oxidant, and there are some disadvantages with organic electrochemical processing.[38]