



# Room temperature aerobic oxidation of alcohols using $\text{CuBr}_2$ with TEMPO and a tetradentate polymer based pyridyl-imine ligand

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## ABSTRACT

A series of tetradentate pyridyl-imine terminated Schiff-base ligands has been investigated for their ability in the catalytic oxidation of alcohols when combined with copper bromide ( $\text{CuBr}_2$ ) and 2,2,6,6-tetramethylpiperidyl-1-oxy (TEMPO). Analogous bidentate ligands showed poorer catalytic activity and the ratio of Cu:ligand was of crucial importance in maintaining high yields. The polydimethylsiloxane (PDMS) derived pyridyl-imine terminated ligand combined with copper(II) ions affords an effective and selective catalyst for aerobic oxidations of primary and secondary alcohols under aqueous conditions. Preliminary mechanistic studies suggest that bimetallic complexes may be playing a role in the catalytic transformation.

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## 1. Introduction

The selective oxidation of primary and secondary alcohols to their corresponding aldehydes and ketones is an important functional group transformation in organic synthesis [1–3]. Traditionally, this is accomplished by addition of stoichiometric amounts of inorganic oxidants (e.g.  $\text{KMnO}_4$ ,  $\text{CrO}_3$ ,  $\text{SeO}_2$ , and  $\text{Br}_2$ ), which often generate environmentally hazardous or toxic by-products [4]. There is a growing trend to develop safer and more environmentally friendly chemistry. From this perspective, it is not surprising that aerobic oxidation of alcohols using inexpensive and non-toxic air or  $\text{O}_2$  as the sole terminal oxidant has continued to gain much interest in recent years [5–7]. The high atom efficiency of the reaction and non-toxic by-products make aerobic alcohol oxidations a promising and attractive synthetic method.

Many highly efficient catalysts for the aerobic oxidation of alcohols have been developed recently using palladium [8–11], platinum [12], ruthenium [13] and rhodium complexes [14–17]. In the interest of sustainability, there has been significant development in the use of more abundant and cheaper transition metals such as iron [18,19] and copper as active catalysts. Following the first reported aerobic oxidation of activated primary alcohols by Semmelhack et al. [20] in 1984, inexpensive and abundant copper has attracted much attention in the field of

alcohol oxidations. Markó et al. have done pioneering work in this field and developed three generations of  $\text{CuCl}$ –phenanthroline catalytic systems, associated with di-*tert*-butyl hydrazine-1,2-dicarboxylate (DBADH<sub>2</sub>) and strong base, for aerobic oxidation of alcohols [21–25]. Also, there has been significant interest in using the free radical TEMPO (2,2,6,6-tetramethyl-piperidyl-1-oxy) or analogues as efficient co-catalysts in the aerobic oxidation of alcohols [26–33]. Sheldon and Reedijk et al. have reported the efficient use of copper–bipyridine and copper–pyrazole/TEMPO systems in oxidation reactions under air [34–37]. Subbaryant et al. have reported a TEMPO/Copper–salen system that could efficiently oxidize a wide range of benzylic and heterocyclic alcohols (e.g. 2-furylmethanol) under an oxygen atmosphere [38]. Repo et al. recently reported a highly efficient catalytic system based on TEMPO/Copper diimine (10 bar oxygen) and 2-*N*-arylpyrrololecarbaldimino (1 atm oxygen) systems for alcohol oxidation [39,40]. In recent studies, Koskinen et al. and Stahl et al. have described improved bipyridine–Cu–TEMPO catalytic systems for the effective oxidation of alcohols [41,42]. In both of these studies, trifluoromethanesulfonate copper salts were found to afford greater activity compared with copper halides, and use of *N*-methyl-imidazole as the base was advantageous. Furthermore, detailed kinetic studies performed by Koskinen and Kumpulainen indicate that bimetallic copper species play a crucial role in these transformations [41].

We have previously prepared siloxane-derived ligands containing phosphorus donor atoms and used these ligands in C–C coupling reactions [43,44]. More recently, others have prepared pyridine

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