

# Switchable activity of a Ru catalyst bearing an annulated mesoionic carbene ligand for oxidation of primary amines

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## Abstract

The catalytic activity of a Ru complex **1**, bearing a fused  $\pi$ -conjugated imidazo [1,2-*a*] [1,8]naphthyridine-based mesoionic carbene (MIC) ligand, is examined for the oxidation of primary amines. Complex **1** affords nitrile or imine depending on the nature of the terminal oxidants and solvents used in the reactions. Primary amines are converted to nitriles using NaIO<sub>4</sub> in EtOAc/H<sub>2</sub>O mixture, whereas imines are obtained under O<sub>2</sub> balloon pressure in toluene. A variety of nitriles and imines are accessed with high yields and selectivity. A set of control experiments, reaction profiles, and kinetic studies are undertaken to disclose the mechanistic details for nitrile and imine formation. The catalytic reactions illustrate a subtle dependency on the choice of oxidants and solvents in the oxidation of primary amines.

## KEYWORDS

catalysis, mesoionic carbene, oxidation, primary amine

## 1 | INTRODUCTION

Direct oxidation of primary amines is an important transformation in organic chemistry, which affords a variety of valuable products, such as, nitriles, imines, amides, azo compounds, and amine-oxides.<sup>[1]</sup> Nitriles and imines are particularly useful intermediates to access a range of pharmaceuticals, biologically active compounds, heterocycles, and industrially important compounds.<sup>[2]</sup> Transition metal-catalyzed selective synthesis of nitriles and imines via oxidative dehydrogenation of amines has been developed in the past decades<sup>[3]</sup>; however, most of these methods suffer from poor selectivity. The formation of nitrile proceeds via two sequential oxidative dehydrogenations of primary amines, whereas dehydrogenation followed by transamination gives imine (Scheme 1).

James's group reported the aerobic oxidation of amines to nitriles using a Ru(II)-porphyrin catalyst.<sup>[4]</sup> Taketoshi's group demonstrated oxidative dehydrogenation of

aromatic primary amines upon treatment with a Ru catalyst with an equimolar amount of K<sub>2</sub>CO<sub>3</sub> in the presence of O<sub>2</sub> to give the corresponding nitriles.<sup>[5]</sup> Selective formation of nitriles in the presence of a (4,4'-*t*Bu<sub>2</sub>bpy)CuI/ABNO (ABNO = 9-azabicyclo[3.3.1]nonan-3-one-*N*-oxyl) catalytic system has been reported by Kim and Stahl.<sup>[6]</sup> Biondini's group reported the oxidation of primary amines into nitriles using a Ni catalyst with potassium persulfate as oxidant in aqueous micelles medium.<sup>[7]</sup> In parallel, methodologies for selective synthesis of imines from amines have also been developed.<sup>[8]</sup> Huang's and Hu and Kerton's groups independently reported the formation of homo-coupled imines using CuI/TEMPO and CuBr<sub>2</sub>/TEMPO catalytic systems, respectively.<sup>[9]</sup> Bäckvall reported a Ru catalyst in combination with an electron-rich quinone and [Co(salen)] complex, which selectively oxidizes secondary amines to imines in air.<sup>[10]</sup> Further, Hazra's group reported the aerobic oxidation of amines to imines with a Co complex of *N,N'*-bis