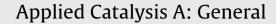
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# Hydroaminomethylation of eugenol with di-n-butylamine catalyzed by rhodium complexes: Bringing light on the promoting effect of Brönsted acids

a promoter, the linear product was obtained in up to 93% yield.

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#### ARTICLE INFO

## ABSTRACT

Article history: Received 3 July 2012 Received in revised form 15 August 2012 Accepted 17 August 2012 Available online 31 August 2012

Keywords: Hydroaminomethylation Acid promotion Tandem catalysis Renewable feedstock

## 1. Introduction

The hydroaminomethylation of olefins (HAM) is a three-step reaction consisting of the hydroformylation of an olefin, the condensation of the formed aldehyde with an added primary or secondary amine, and the catalytic hydrogenation of the resulting imine/enamine to yield the corresponding amine. The last two steps are closely related as the amine condensation is reversible and the hydrogenation step withdraws the imine/enamine from the equilibrium, driving the reaction to completion. This tandem transformation [1] is exemplified in Scheme 1 for the HAM of eugenol (1) with di-n-butylamine.

Although known for a long time [2], only recently has HAM gained importance in the synthesis of more complex molecules [3], such as pharmaceuticals and other biologically active substances [4–9]. The use of special ligands such as diphosphines [10], diphosphites [7], xanthene-based dipyrrolylphosphines [11], and tetradentated phosphorus ligands [12] has allowed good selectivity control associated with high activity. The development of biphasic systems, in which the catalyst is dissolved in water [13], ionic liquids [14], or multiphase thermophilic systems [15], has allowed for the easier catalyst recycling, which favors industrial applications. The advances in this synthetically efficient process have been recently reviewed [16].

Our group is involved in the preparation of useful or potentially useful chemicals employing transition metal complex catalyzed reactions applied to natural products that can be obtained in kiloton scale through sustainable methods [17–20]. We have recently reported the HAM of various monoterpenes to obtain amines, which have potential bioactivity [21]. Herein we report the HAM of eugenol (1) with di-n-butylamine (Scheme 1) to obtain three new amines. Despite the potential bioactivity of the products, to the best of our knowledge, it is the first time that HAM of arylpropenes of

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The hydroaminomethylation of eugenol with di-n-butylamine was performed employing a bis[(1,5-

ciclooctadiene)( $\mu$ -methoxy)rhodium(I)] as pre-catalyst. In the absence of phosphines, the catalyst was

efficient in the process, but the regioselectivity for amines was poor. For phosphine-promoted catalyst,

the chemoselectivity at the hydroformylation step improved, but the hydrogenation of enamine inter-

mediates was hampered. The regioselectivity within the class of amines was surprisingly high (>96%) for the linear product. The addition of triflic acid (10-20 mol%) improved significantly the efficiency of

HAM. Employing the 2,2'-bis((diphenylphosphino)methyl)-1,1'-binaphthyl as ancillary and triflic acid as

#### 2. Experimental

### 2.1. General procedure

natural sources is described.

Eugenol, di-n-butylamine, triphenylphosphine, sulfuric acid, para-toluenesulfonic acid, and trifluoromethanesulfonic acid were purchased from Aldrich. 2,2'-bis((Diphenylphosphino)methyl)-1,1'-binaphthyl (NAPHOS) was kindly donated by Prof. B. Hanson (Virginiatech-USA). Toluene was refluxed over sodium/ benzophenone for six hours and distilled under argon. [Rh(cod)( $\mu$ -OMe)]<sub>2</sub> was synthesized according to literature procedure [22].

### 2.2. Catalytic runs

The pre-catalyst  $[Rh(cod)(\mu-OMe)]_2$   $(5.0 \times 10^{-3} \text{ mmol})$ , the phosphorus ancillary (if any) and a PTFE-covered magnetic stirring bar were placed in a stainless steel bomb, which was closed and purged with three cycles of vacuum and argon. In a Schlenk tube, a solution was prepared by adding toluene (30 mL), eugenol (10 mmol), di-n-butylamine (10 mmol) and then the acid (if any). The solution was transferred under inert atmosphere to the bomb,

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