

# Pd–Au–Y as Efficient Catalyst for C–C Coupling Reactions, Benzylic C–H Bond Activation, and Oxidation of Ethanol for Synthesis of Cinnamaldehydes

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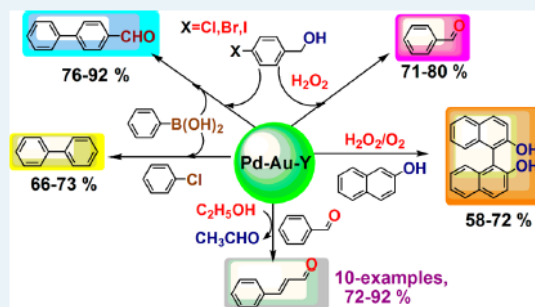
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## Supporting Information

**ABSTRACT:** Pd–Au nanoalloy supported on zeolite-Y (Pd–Au–Y) matrix was found to be an effective catalyst for C–Cl bond activation and oxidative coupling of 2-naphthol, leading to the formation of various biaryl products and 1,1'-bi-2-naphthol, BINOL. The same catalyst was also highly efficient for selective oxidation of benzylic alcohols to benzaldehydes. Cinnamaldehydes were obtained directly from benzaldehydes by aldol condensation with acetaldehyde generated in situ by partial oxidation of ethanol in the presence of Pd–Au–Y catalyst at 120 °C under basic condition. The biaryl products were also obtained directly from benzylic alcohols in a one-pot system by reacting with phenylboronic acid. The formation of biaryls from benzylic alcohols was believed to occur via one-pot benzylic C–H and C–Cl bond activation. A high % yield of biaryls, BINOL, aldehydes, and cinnamaldehydes was obtained by performing different reactions using the single Pd–Au–Y catalyst. The strong interaction of chloro-benzylic alcohol was predominantly located at active gold species. X-ray photoelectron and diffuse reflectance spectroscopic studies revealed the strong interaction between Pd and Au particles. Electrochemical studies provided proper evidence for the individual role of the nanoparticles (NPs) in one-pot synthesis of biaryls from benzylic alcohols.

**KEYWORDS:** Pd–Au NPs, zeolite-Y, biaryls, aldehydes, BINOL, cinnamaldehydes



## 1. INTRODUCTION

C–Cl bond activation, oxidative coupling of 2-naphthols, selective oxidation of alcohols, and aldol-type condensation reaction leading to the formation of C–C coupled product, aldehyde, and cinnamaldehyde are considered to be some of the important classes of organic reactions.<sup>1–14</sup> Out of the different forms of Suzuki–Miyaura cross-coupling (SMCC) reactions, the formation of biaryls by C–Cl bond activation is highly appreciable due to the low cost of chloro-derivatives compounds.<sup>7,8,15–19</sup> Pd-based catalysts either in the homogeneous or in the heterogeneous form are best known for SMCC reaction.<sup>5,8,20–22</sup> However, it has been found that the C–Cl bond activation process with single Pd metal is less effective.<sup>5,7,8</sup> Recent studies suggested that alloying of Pd with other metals like Ni, Au, Co, etc., led to successful activation of the C–Cl bond in the SMCC reaction.<sup>5,7,8,23</sup> We also found that Pd–NiO nanocatalyst supported on the zeolite-Y matrix was an effective heterogeneous catalyst for C–

Cl bond activation in SMCC reaction.<sup>7</sup> As the reports on C–Cl bond activation for biaryl product formation are limited, finding a highly active and reusable heterogeneous catalyst for C–Cl bond activation would be highly beneficial.

Apart from the coupling of aryl chlorides, the oxidative coupling of 2-naphthol to 1,1'-bi-2-naphthol commonly known as BINOL is considered to be an important oxidative coupling reaction due to the high applicability of BINOL in pharmaceutical products and also as chiral auxiliary.<sup>9–11,24</sup> The oxidative coupling of 2-naphthol is rather a difficult process as the yield is often very poor. Fe(III)-Schiff base catalysts are better known for such catalytic conversion.<sup>10,11,24</sup> Most of the catalytic oxidations of 2-naphthol to BINOL are performed using air or molecular oxygen (O<sub>2</sub>).<sup>9–11,24</sup> O<sub>2</sub> as

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