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SHORT COMMUNICATION

D-Glucosamine as an efficient and green additive for palladium-catalyzed Heck reaction

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The Heck coupling of haloarenes with various alkenes was successfully performed in the presence of 0.5 mole % $Pd(OAc)_2$ and 1.0 mole % D-glucosamine as an additive with K_2CO_3 as the optimal base in a mixture of H_2O/iPrOH ($\varphi_r = 2:1$) as the reaction solvent at 80 °C after 6 h. D-Glucosamine was found to be an inexpensive, air-stable, easy to available, and efficient additive in palladium-catalyzed Heck reactions of aryl iodides (67–95 % conversion) and bromides (38–72 % conversion).

Keywords: D-glucosamine, $Pd(OAc)_2$, Heck reaction, aqueous medium

Palladium-catalyzed arylation of olefins, the Heck reaction, as one of the most versatile methods for C—C bond formation is an extremely useful and general technique in the preparation of biologically active functionalized olefins which are important intermediates or products in drug discovery, pharmaceuticals, and agricultural compounds (Heck, 1987; Wolfson & Dlugy, 2007; Bräse & Meijere, 1998; Bagherzadeh et al., 2012).

Driven by environmental and economic concerns, numerous efforts have been devoted to the development of the Heck reaction under benign conditions, e.g. with water as the solvent (Li & Chan, 1997; Cornils & Herrmann, 1998; Grieco, 1998). Although there are some reports on the Heck reaction in mixed aqueous organic solvents in the presence of Pd-catalysts with water soluble phosphine ligands (Genet & Savignac, 1999; Iranpoor et al., 2010), however, most phosphine-based ligands are water and/or air-sensitive (Phan et al., 2006; Andersen & Keay, 2001; Martin & Buchwald, 2008). Therefore, it is highly desirable to design water soluble, efficient and phosphine-free ligands to avoid the use of expensive and water and/or air-sensitive phosphines in palladium catalyzed coupling reactions (Allam & Singh, 2011).

In recent years, carbohydrate derivatives have gained great attention because of their potential applications as advanced soft materials in syntheses, drug delivery, enzyme immobilization, etc. (Diéguez et al., 2007; Monopoli et al., 2010). Despite their obvious potential for ligand degradation, many carbohydrate decorated ligands seem to be relatively stable under aerobic reaction conditions (Bradshaw et al., 2011; Makhubela et al., 2011). The low costs but especially the high environmental friendly nature and water solubility of D-glucosamine (D-GlcN) as one of the most naturally abundant molecules (Thakur et al., 2011) has led us to explore its usefulness as an additive in palladium-catalyzed Heck reactions in an aqueous medium.

To develop a general catalyst for palladium-catalyzed Heck reactions, the application of $Pd(OAc)_2$/D-GlcN as an efficient system in the Heck coupling reaction of olefins with aryl halides is reported herein (Fig. 1).

Firstly, a model reaction involving iodobenzene and butyl acrylate was performed to optimize the reaction conditions. Various parameters including bases, solvents and palladium salts were investigated.

In the initial investigations, the effect of bases on the Heck reaction in *N*,*N*-dimethylformamide (DMF) as the solvent at 80 °C was examined. Various bases including KOH, K_2CO_3, Na_2CO_3, K_3PO_4, NaOAc, and

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