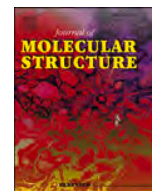




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Chan–Evans–Lam coupling for the synthesis of N–aryl derivatives catalyzed by copper(I) chloride and sterically varied imidazolium salts at mild reaction conditions

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ABSTRACT

First-row transition–metal–catalyzed organic transformations have received colossal interest in the modern synthetic organic chemistry due to their step– and atom–economic approaches. As a consequence, direct arylation of azoles through C–H or N–H activations acquired a broad spectrum of applications for accessing valuable small organic molecules that are of pharmaceutical interest. In this connection, sterically varied coumarin–functionalized imidazolium salts bearing bromide (5–7) and hexafluorophosphate anions (8–10) have been prepared and used as NHC precursors. The salts have been characterized by both, spectroscopic and analytical techniques. A hexafluorophosphate salt 9 was also studied for its structure using the single-crystal XRD technique. The salts that indeed, generate carbene that trap Cu(I) to form Cu(I)–NHC complexes *in situ* for the Chan–Evans–Lam C–N coupling of 1H–azoles/anilines and phenyl/thiopheneboronic acids, resulting in the formation of N–aryl derivatives in moderate to excellent yields. The structure–activity relationship studies revealed that the steric bulk around the metal center would help increase the catalytic Chan–Evans–Lam C–N coupling potential of the catalysts.

1. Introduction

Transition–metal–catalyzed C–H and N–H functionalizations in a wide range of organic transformations that result in the formation of valued specialty chemicals of pharmaceutical interests gained significant attention over the past two decades [1]. Among others, Pd catalyzed cross-coupling reactions are at the forefront to access catalytically challenging conversions [2], however, cost effectiveness is a major advantage of using late first-row transition metal–based catalysts. Amongst, Cu is an abundant metal, used extensively in several catalytic reactions such as Ullman, Chan, Evans, and Lam cross-coupling reactions [3]. The work of later three is collectively known as Chan–Evans–Lam coupling, which is a nucleophile– nucleophile approach; similar to that of Pd–catalyzed Suzuki cross-coupling reaction. The Chan–Evans–Lam coupling proceeds through different Cu

species in oxidation states either +1, +2 or +3, and hence it follows different mechanisms to form the desired products. Advantageously, the Cu–catalyzed Chan–Evans–Lam cross-coupling reactions yielded a variety of target molecules with promising functional group tolerance at mild reaction conditions in an atom economic way. More specifically, numerous N–heterocycles have been arylated with a range of substituted phenylboronic acids to yield targeted products in high conversions [4]. The well accepted mechanism is the one electron redox process with change in the coordination number of Cu atom, and hence a stabilizing ligand around the metal in different oxidation state plays a significant role in achieving high conversion.

In this aspect, N–heterocyclic carbenes (NHCs), highly regarded as strong σ –donors and poor π –acceptors that make metal–carbene carbon bond more robust, which in deed, avoids oxidative decomposition and enables extended catalyst stability during catalytic process [5]. Aply

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