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Title: Synthesis of useful organic molecules by C-C bond formation and C-H activation reactions

Abstract:

In this work, we have performed various C-C bond formation reactions using heterogeneous and homogeneous Pd-catalysts and under transition metal free condition. We have also explored the use of heterogeneous Pd-catalyst in C-H activation reaction of 2-arylbenzoxazinones.

We have demonstrated the use of heterogeneous magnetic palladium catalyst in C-C cross coupling reactions, such as oxidative Heck coupling and Tsuji-Trost allylic coupling reactions involving organosilanes as the aryl donors. Starch coated magnetic nanoparticles supported palladium catalyst was very easy to recover magnetically and was recycled efficiently in the subsequent batches. All the reactions were performed in air and thus necessity of air and moisture free reaction condition is avoided. The present protocols show wide substrate scope and good yields of the products.

Recently dithiocarbamates have become popular as valuable synthetic intermediates in the synthesis of various organosulfur compounds. We have used dithiocarbamates in the decarboxylative-decarbonylative C-C bond formation reaction to prepare thioamide compounds. Arylglyoxylic acids have been employed here in the decarboxylative-decarbonylative thioamidation reaction with the dithiocarbamate intermediates prepared *in situ* by the prompt reaction of amines and carbon disulfide. A series of thioamide compounds were synthesized involving different arylglyoxylic acids and various secondary amines, primary amine, aniline, amino acid derivative. The reaction is proposed to proceed *via* acyl radical intermediate in presence of persulfate oxidant and Pd(II)-catalyst.

Dithiocarbamate salts have also been explored in C-C thioamidation reaction of styrene in presence of ammonium persulfate and molecular oxygen. A series of thioamide compounds with different structural variations have been prepared in good yields. Various cyclic/acyclic secondary amines, aromatic amine, benzylamine and amino acid based thioamides have been prepared following the protocol. The protocol has further been applied on decarbonylative-thioamidation of benzaldehyde and toluene and decarboxylative-thioamidation of benzoic acid. The reaction mechanism has been proposed by isolation of reaction intermediate and GC-MS analysis of the reaction mixture. Post-synthetic potential of synthesized thioamide has been checked by C-C cross-coupling reaction *via* C-N bond cleavage.

We have developed a C-H activation protocol of 2-arylbenzoxazinones in aqueous medium under open aerial atmosphere at close to room temperature (40°C) using magnetic Pd-catalyst. 2-Arylbenzoxazinones react with phenylglyoxylic acids *via* decarboxylative C-H acylation followed by cyclization reaction to produce the isoindolinone compounds. The reaction can be arrested at the intermediate step to obtain the *ortho*-acylated derivatives at a certain lower temperature. The heterogeneous Pd-catalyst is easy to separate magnetically and shows good recyclability.

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