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Doctoral dissertation: Cross-coupling reactions C(sp²)-C(sp³) using 3-d transition metals catalysts

ABSTRACT

Transition-metal-catalyzed cross-couplings have become a central method for the construction of C–C bonds in organic synthesis. The powerful cross-coupling processes are routinely implemented on an industrial scale for the production of pharmaceuticals, crop protection agents and complex functional materials. Nevertheless, until recently, industrially relevant examples of cross-coupling reactions have been largely limited to noble metals, mainly palladium. Recently, much interest has been devoted to 3d-transition metals. The high natural abundance, low cost and in many instances more sustainable profile, mean that these catalysts are well-poised for use in catalytic transformations. Simultaneously, the engagement of C–O electrophiles provides a powerful alternative to aryl halides in cross-coupling reactions. In particular, aryl tosylates are an attractive class of C–O electrophiles for cross-coupling due to ease of synthesis, low price, high stability and the possibility for orthogonal employment of prevalent phenols.

The aim of the doctoral thesis was to develop effective cross-coupling reactions $C(sp^2)$ - $C(sp^3)$ aryl tosylates with challenging alkyl Grignard reagents possessing β -hydrogens using 3d-transition metals catalysts: iron, nickel and cobalt. The reaction is catalyzed by well-defined nickel complex (Ni(dppe)Cl₂), and iron and cobalt catalytic systems generated *in situ* (Fe(acac)₃/NMP and CoF₃/IPr·HCl). Each of them presents in turn: the process of optimizing the reaction conditions, the scope of used electrophilic and nucleophilic compounds, preliminary mechanistic studies and examples of the potential application of the developed methods in the preparation of industrially important organic molecules.