

論文内容の要旨

論文題目 **First-Row Transition Metal-Catalyzed Cross-Coupling Reactions for Selective Monofunctionalization**

(第一遷移金属触媒によるクロスカップリング反応を用いた選択的官能基化反応の開発)

氏名 中村 優希

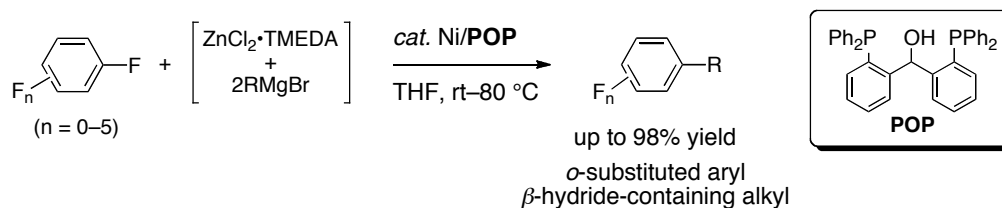
The present thesis describes two different strategies to accomplish selective monofunctionalization in cross-coupling reactions using first-row transition metal catalysts: (1) ligand-control to achieve nickel-catalyzed selective monofunctionalization of polyfluoroarenes with aryl- and alkylzinc reagents, and (2) oxidant-control to attain iron-catalyzed selective oxidative monoarylation of primary amines with organozinc reagents.

Chapter 1 describes the challenge of controlling the catalytic system to achieve product selectivity while maintaining high reactivity for the development of transition metal-catalyzed cross-coupling reactions. In order to achieve selective monofunctionalization when using starting materials that contain more than one reactive site, fine-tuning of the electronic and steric properties of the catalytic system becomes crucial. Two catalytic systems were designed based on these key factors to develop new methodologies of selective monofunctionalization reactions.

In Chapter 2, a combination of nickel and a newly designed hydroxybisphosphine **POP** ligand was found to be capable of activating an inert C–F bond of polyfluoroarenes followed by cross-coupling with diorganozinc reagents to selectively give monofunctionalized products (Scheme 1). Moreover, the coupling reaction using a variety of diorganozinc reagents, including sterically demanding and β -hydrogen-possessing alkylzinc reagents were found to undergo the coupling reactions.

The selectivity stemmed from the use of the **POP** ligand, where the hydroxyphosphine unit accelerated C–F bond activation in a push-pull mechanism through the bimetallic cooperation, and the bulky bisphosphine unit sterically expelled the product, preventing the activation of a second C–F bond.

Scheme 1. Nickel-catalyzed C–F monofunctionalization



Chapter 3 describes the development of iron-catalyzed oxidative reaction of a primary amine with an organozinc reagent, in which two nucleophiles are coupled together (Scheme 2). The reaction showed tolerance of halide, and produced various unsymmetric secondary aromatic amines selectively. The results of the stoichiometric reactions suggest that the crucial iron intermediate species contains more than one aryl and amide ligands, and upon heating and oxidation by 1,2-dichloroisobutane (DCIB) gives a mixture of aryl amine and diaryl products. This catalytic system selectively produces the corresponding secondary aryl amine over the tertiary aryl amine, in which the product selectivity is considered to originate from the coordination of the secondary amine product to intermediate iron species to provide sterical hinderance around the reactive metal center.

Scheme 2. Iron-catalyzed oxidative C–N coupling

