IRIDIUM-CATALYZED ORTHO-AND META-SELECTIVE C-H BOND BORYLATION AND SILYLATION OF AROMATIC MOLECULES

ABSTRACT
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THESIS

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Ranjana Bisht
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Co-Supervisor
Dr. Buddhadeb Chattopadhyay
Assistant Professor
Centre of Biomedical Research (CBMR)
SGPGIMS Campus, Raebareli Road
Lucknow 226014, Uttar Pradesh, India

Supervisor
Dr. Gajanan Pandey
Professor
Department of Applied Chemistry
School for Physical Sciences
Babasaheb Bhimrao Ambedkar University
LUCKNOW-226 025

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Abstract

Iridium-catalyzed C-H activation/borylation has augmented appositeness and sophistication of transition metal-catalyzed direct C-H functionalization which was being availed for molecule synthesis over the past century. Unarguably, the advent of C-H borylation has tackled various unresolved problems prevalent in organic synthesis such as synthesis of 3,5-bromochlorophenol, which was multistep and laborious task. In contrast, Ir-catalyzed C-H borylation enabled its synthesis in just two steps. But the main governing factor for determination of product regioselectivity was sterics. With constant development in this protocol such as employment of directing groups strategy realizes the *ortho* C-H activation/borylation to proceed in a placid fashion, then further advancement occurred as the concept of traceless directing group was introduced. The flaws of early concepts paved the way for the influx of novel approach of amalgamation of transition metal catalysis with noncovalent interaction to achieve the goal of proximal and distal C-H activation/borylation.

The prominent features of this approach are mildness, versatility of C-B bonds, atom as well as step economic and environmentally benign which makes it more popular than the protocols which were practised for C-H functionalization before its inception.

The work compiled in this thesis, is divided into five chapters. First chapter summarizes the seminal events in Iridium-catalyzed *ortho* and *meta* C-H borylation and C-H silylation method. The two methodologies hold considerable promise in activating the inert C-H bonds of arenes, heteroarenes and aliphatic systems. The significant role played by organosilicon and organoboron compounds in a broad array of fields such as organic synthesis, pharmaceutics, polymer and ceramic industry amplifies the efficacy of these protocols.

Second chapter explains the decisive role of nature of ligand in determining the product regioselectivity. Usage of traceless directing group and hemilabile ligand leads to *ortho* functionalization, while employing electronically rich 3,4,7,8 tetramethylphenanthroline ligand facilitated noncovalent interaction (electrostatic and

B-N interaction) to accomplish remote '*meta*' functionalization of same benzaldehyde substrate.

The third chapter presents how by prudent designing of ligand on the catalyst (modification of Bpin by Beg) and employment of traceless directing group led to exquisite *ortho*-selectivity of aniline, its derivatives and heteroaromatics, releasing it from the shackles of all previous shortcomings.

The fourth chapter describes achievement of previously unmet challenge of accessing and activating 6,6'-position of Binol by maneuvering the sterics of catalyst-ligand assembly. In situ protection with HBpin followed by borylation with B_2pin_2 afforded regioselectively remote (6,6') diborylation. Corresponding diarylated products are formed through subsequent Suzuki cross-coupling.

Fifth chapter discusses the development of an efficient methodology for *ortho* C-H activation/silylation of aromatic, heteroaromatic benzaldehydes and phenylpyridines, in addition to this it elucidates the role played by silylating reagent in devising a distinct catalytic manifold from existing catalytic systems for *ortho* C-H silylation.

In the last, sixth chapter summary of all the work has been discussed.