

## ABSTRACT

This dissertation entitled "*Dehydrogenative C-C and C-P bond formation: Direct Access Towards Polyarylquinones, Axially Chiral Bi-aryls Phosphorylated (Hetero)-Arenes*" comprises five chapters that imply the concept of cross dehydrogenative coupling to synthesize C-C and C-P bonds. In the first two chapters using the CDC concept, direct phosphorylation has been described. The third chapter utilizes the concept of Pd-relay catalysis to synthesize diversely complex polyarylquinones. In the final part, an enantioselective version of CDC has been described using the concept of transient directing group and atropisomerism.

**Chapter 1:** Consist of a brief description of various C-H activation mechanism, different types of oxidative coupling reactions employed in C–C bond formation with the main emphasis on the dehydrogenative coupling of aromatic compounds is presented. In the second part of introduction the importance of chirality as well as different types of chirality is described with the main emphasis on axial chirality.

**Chapter 2:** Despite significant advancements in azoles phosphorylation, earlier protocols mainly focus on (benzo)thiazoles or (benz) oxazole moieties. So still, there is a lacuna in imidazole and benzimidazole phosphorylation along with the usage of the economical metal catalyst. In this context, Cu is an excellent choice due to its low expenses, ease of handling, and low toxicity. Its low reactivity makes C-H bond activation limited; as a result, Cu in C-P bond formation is rare. Herein, Cu-catalysed C-P bond formation by hetero cross dehydrogenative coupling reaction is reported. To the best of our knowledge, our protocol is the first strategy for achieving dehydrogenative C–P bond construction on various azoles like benzothiazoles, oxazoles, benzoxazoles, imidazoles, benzimidazoles, and indoles using Cu-catalyst.

**Chapter 3:** The ubiquitous nature of benzofulvene (BF) and their unique impact along with widespread application on organic molecules have elicited extensive attention in the areas of medicinal, material, polymer, organometallic, and porphyrin chemistry. Due to their fascinating aromaticity, the construction of benzofulvene core demands enormous attention in the scientific community. However, to the best of our knowledge, direct functionalization through CDC has not been realized so far on benzofulvene derivatives. To overcome this burden, a direct silver mediated dehydrogenative cross-coupling of C-H and P(O)-H to synthesize phosphorylated benzofulvenes is described here. A vast library of benzofulvenes can be efficiently phosphorylated under this protocol in good to moderate yields. Further mechanistic investigation implies the radical pathway for this reaction. The synthetic power of this methodology was further demonstrated by transferring the phosphorylated product into different value-added compounds.

**Chapter 4:** Polyarylquinones have tremendous applications in optoelectronics, photocatalysis, bioimaging, and pharmaceutically relevant materials. However, their synthesis is often challenging and plagued with various bottleneck steps. Here, we demonstrate a relayed addition of fulvene moieties onto quinones. The developed ligand-assisted Pd-catalysed dehydrogenative [2+2+2] cycloaddition reaction enables facile access to a new class of polyarylquinones. The key to the high regioselectivity achieved is the precisely controlled addition of the two fulvene units to the quinone conferred by the Pd catalyst. The work also establishes the broad substrate scope of the reaction and delves into the mechanism of the dehydrogenative coupling reaction. Moreover, single-crystal X-ray diffraction reveals

interesting packing motifs, suggesting these materials' suitability in optoelectronics. As a practical utilization of the reaction, various synthesized polyarylquinones with structural diversity were screened for redox properties and exhibited better antioxidant or chemotherapeutic properties.

**Chapter 5:** In this part, utilizing imines as the transient directing groups for bi-aryl aldehydes to gain axially chiral bi-aryls containing benzofulvenes using palladium catalysis has been developed. Thus, intermolecular oxidative C-H activation involving two C(sp<sup>2</sup>)-H bonds provides feasible access to axially chiral benzofulvene with excellent enantioselectivities and good to moderate yields.