ABSTRACT

The thesis entitled "**Cp*Co(III)-Catalyzed Ketone Directed Annulative π-Extension: Route to Access Polycyclic Aromatic Hydrocarbons (PAHs)**" has been divided into four chapters.

Keywords: *fused arenes, bay-region selective apex, contorted nanographenes, alkyne benzannulation, Scholl reaction, Cp*Co(III)-catalysis, peri-annulation, benzo[e]pyrenes, pyrenes, carbazole-embedded tetracene.*

Chapter 1 explores the "bottom-up" approach of the APEX reaction, a step-economic π-extension to access polycyclic aromatic hydrocarbons (PAHs) with a defined shape, edge structure, atomic precision and degree of π-extension. PAHs are heavily utilized in materials science due to their extended π-conjugation, effective π–π interactions, narrow HOMO-LUMO bandgaps, lower redox potentials, superior chemical stability, and high mechanical strength.

Chapter 2 pronounces the synthesis of fused arenes such as benzo[*e*]pyrenes, benzotetraphenes, and pyrenes using Cp*Co(III)-catalyzed APEX reaction at the (masked) bay region of arene-derived ketones and internal alkynes. Furthermore, 1,1'-bipyrenes, pyrene-dione motifs, and dibenzo-tetracene moieties are also accessed. Comprehensive DFT analyses support the suggested mechanism, identifying the nucleophilic attack on the ketone as the rds.

Chapter 3 focuses on producing contorted nanographenes employing a one-pot Cp*Co(III)-catalyzed *peri*-annulation and alkyne benzannulation cascade with arene-derived ketone and 1,3-dialkyne. Critical steps in the reaction include *peri*-C–H activation, alkyne migratory insertion, nucleophilic attack, dehydration, aromatization, and 5-*exo*-dig/6-*endo*-dig cyclization. Detailed DFT studies confirm the mechanistic pathway and help to elucidate the formation of the major nanographenes.

Chapter 4 explores the construction of cruciform carbazole-embedded tetracene motifs initiating from 1*H*-indole-2-carboxaldehyde via a step-wise APEX protocol employing Wittig olefination, benzannulation, and Scholl reaction. The chapter also covers DFT modeling of these moieties to analyze their conformation, energy levels, and distribution of frontier orbitals.