Overall Contribution and Remarks

- In this thesis entitled "**Direct Rh(III)–Catalyzed Site-selective Arylation, Macrocyclization of Quinoline Scaffolds and A New [4+1] Annulation to 2-Substituted Indane-1,3-diones**" described the development of new transition metal-catalyzed step-economical strategies for site-selective functionalizations and macrocyclization of quinoline based scaffolds. Besides, we have developed a new [4+1] annulation reaction. Under the newly developed protocols, different functional groups were introduced regio-selectively at the quinoline related scaffolds *via* metalation, metallocarbene formation, and subsequent migratory insertion.

- The journey was started by developing Rh(III)-catalyzed direct C8-arylation of quinoline *N*-Oxides using diazonaphthalen-2(1*H*)-ones under mild conditions. The method was extended with a wide scope and functional group tolerance. Related mechanistic studies were carried out to propose the plausible mechanism. In application, we were able to synthesize 8-azaBINOL in three straightforward pathway.

- Further, a Rh(III)-catalyzed C(sp^3)-H/ C(sp^2)-H arylation of 8-methyl/ formyl quinolines using quinone diazides was developed. The optimized method was operationally simple with large substrate scope. The method provided direct access to hetero-arylated phenol/naphthol scaffolds. We also applied this methodology for late-stage functionalizations of bioactive molecules.

- Next, the above developed protocol was extended to do a mild Rh(III)-catalyzed straightforward macrocyclization of 8-methylquinoline based scaffolds *via* migratory insertion. An intramolecular macrocyclization that features excellent functional-group compatibility has been illustrated by the successful synthesis of a library macrocyclic quinolines of different ring sizes and substitution patterns. The result significantly highlighted the synthetic interest of C-H functionalization

processes for the synthesis of new macrocyles incorporating heterocyclic scaffolds of potential interest in medicinal chemistry. All those developed protocols followed the redox-neutral pathway.

- Furthermore, the methodology for an improved synthesis of 3-cyanophthalides from phthalaldehydic acids was established by cyanation with $PhI(OAc)_2$–TMSCN in an organic medium. Easy isolation of the products, scalability and wide number of functional group tolerances with good to high yields made the procedure significant.

- In the final chapter, synthesis of novel 2-substituted indane-1,3-diones using [4+1]-Hauser annulation reaction with Morita-Baylis-Hillman adducts has been described. The annulation resulted an one-pot synthesis of indane-1,3-dione derivatives with completely new substitution pattern at C-2 with 46-73% yields. The method was simple, regioselective with a variety of functional group tolerance. A plausible reaction mechanism has also been proposed.

- Finally, it is expected that these analysis and investigations presented in this thesis will bring interest to the synthetic chemists in the field of annulations and transition-metal-catalyzed C–H bond functionalizations of electron deficient heteroarenes. The developed protocols will be helpful to synthesize various quinoline core containing pharmaceuticals and bioactive natural products.