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Title: Novel Cascade Approaches for the Synthesis of Carbo- and Heterocycles

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Abstract:

The polycyclic acetals are recognized as an essential part of substructures widely present in natural products and pharmaceutically relevant molecules. They are often utilized as a key building block for the synthesis of complex targets. On the other hand, arene and heteroarene- fused cyclopentanes consisting of indole, thiophene, benzothiophene, benzofuran, and furans are abundant in a diverse range of bioactive natural products and pharmaceutically active molecules. Numerous synthetic strategies have been developed to access polycyclic acetals and cyclopenta[b]annulated arenes and heteroarenes by utilizing metal catalyst. The commonly employed strategies include acid or palladium-catalyzed glycosylation, base-mediated 1,4- addition reaction of Achmatowicz rearrangement product. On the other hand metal-catalyzed Alder-ene reactions and palladium-catalyzed Tsuji-Trost reactions of 1,4-dienyl acetates have also been doucemented for their synthesis. However, the development of general, efficient methods starting from the readily accessible materials remains an emerging research area. This thesis mainly focused on the design and development of metal-catalyzed strategies to polycyclic acetals, cyclopentadienes, indenes, cyclopentane fused benzothiophene and indoles. In this regard, part A in which first section will highlight an efficient diversity oriented approach towards the synthesis of furopyrans and bicyclic bisacetals via base-mediated Michael addition followed by transacetalization through oxonium ion intermediate. Michael addition takes place under basic condition and glycosylation takes place under acidic conditions are well explored on the Achmatowicz rearrangement product. Towards this, the second section will discuss the synthesis of oxygen and sulfur containing heterocycles via acid-catalyzed Michael addition followed by transacetalization. The synthetic utility of this strategy was further demonstrated to synthesize the core structure of alliuocide G 7. The third section will describe one-pot approach for the synthesis of benzofurans under mild Lewis acidic condition. The versatility of this methods established an unprecedented approach for the synthesis of medicinally important scaffolds such as pyran fusedbenzofurans and furocoumarins. Further, this method elaborated to the synthesis of 5,5-spiroketals in a short and efficient manner. In part B second section will describe an unprecedented Pd(II)promoted cyclization of 2,4-pentadienyl acetates to cyclopentadienes, indenes, and cyclopentenefused heteroarenes. The synthetic utility of this strategy was further demonstrated to formal total synthesis of paucifloral F.

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