INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title:
Development of Glycosyl ortho-[1-(p-MeOPhenyl) Vinyl]Benzoates (PMPVB) as Reactive Glycosyl Donors and Studies Toward the Synthesis of L-Sugars, non-ulosonic acids via Perlin Aldehydes

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SHORT ABSTRACT

Carbohydrates are one of the essential classes of biomolecules playing crucial roles in agriculture and medicinal chemistry. The high density of stereochemical information and relative rigidity of carbohydrates provide a wonderful stage upon which a number of substitutions can be done to make biologically active target molecules. Carbohydrate scaffolds in bioactive molecules exhibit different roles in physiological events such as cell development, immune system, bacterial and viral infection, etc. The tremendous medicinal potential of glycomolecules has been evoked by worldwide chemists to synthesize these bioactive molecules.

The contents of the thesis entitled "***Development of Glycosyl ortho-[1-(p-MeOPhenyl) Vinyl]Benzoates (PMPVB) as Reactive Glycosyl Donors and Studies Toward the Synthesis of L-Sugars, non-ulosonic acids via Perlin Aldehydes*****"** have been divided into six chapters based on the experimental works, and results during the complete course of my research period. **Chapter I** of the thesis is entitled the literature review of *n*-Pentenyl glycosides (NPG's) and Perlin aldehyde. **Chapter IIA** deals with glycosyl *ortho*-[1-(*p*-MeOPhenyl)vinyl]benzoates (PMPVB) as easily accessible, stable, and reactive glycosyl donors for *O*-, *S*- and *C*-glycosylation reactions under Brønsted acid catalysis. **Chapter IIB** describes catalytic stereoselective synthesis of 2-deoxy *α*-glycosides using glycosyl *ortho*-[1-(*p*-MeOPhenyl)vinyl]benzoates (PMPVB) as glycosyl donors. In **Chapter III**, we disclosed regio and stereoselective *C*-glycosylation of indoles using *ortho*-[1-(*p*-MeO-Phenyl)vinyl]benzoates (PMPVB) as glycosyl donors under Brønsted acid catalysis. **Chapter IV** focuses on three-step

synthesis of protected L-altrose from D-galactose-derived Perlin aldehyde. **Chapter V** contains the synthesis of Aryl-Polyols from Perlin aldehyde.

Chapter I describes the literature survey of the importance of carbohydrates towards natural products, different types of *n*-pentenyl glycosyl (NPGs) donor-based glycosylation towards *C-O*, *C-S*, *C-C*, *C-N*, linkages, synthesis of *δ*-hydroxy *α,β*-unsaturated aldehyde (generally called Perlin aldehyde), and synthesis of different types of L-sugars.

Chapter IIA describes the synthesis and reactivity of Fraser-Reid type alkene donors (PMPVB) donors, that can be catalytically activated under Brønsted acidic conditions (30 mol % Tf_2NH) as well as NIS/TMSOTf conditions. All types of glycosylation (*O*-, *S*-, *C*-) are occurring in just 5 min at 0 °C, proving the high reactivity of the PMPVB donors. Comparative studies under both Brønsted acidic conditions ($HNTf_2$) and NIS/TMSOTf conditions with the PVB donor indicate the PMPVB donors are superior in reactivity compared to PVB donors.

Chapter IIB describes 2-deoxy *ortho*-[1-(*p*- MeOPhenyl)Vinyl]Benzoates (PMPVB) donors, Fraser-Reid type alkene donors as benchtop stable and reactive glycosyl donors for a protecting group independent stereoselective synthesis of 2-deoxy-*α*-glycosides under simple Brønsted acid catalysis which can be activated by using standard NIS/TMSOTf condition also. It was observed that the 2-deoxy PMPVB donors are reacting well with 1.2 equiv. of glycosyl acceptor in the presence of 30 mol % of triflic acid (TfOH) at 0 °C in DCM medium and provided *α*-selective *O*-glycosides with good to excellent yields.

Chapter III describes a practically useful synthetic protocol for the regio and stereoselective synthesis of indolyl glycosyl derivatives from the stable yet PMPVB glycosides. The transformation can be achieved utilizing the simple Brønsted acid (Tf_2NH, 30 mol %) catalysis and does not require any metal catalysts or other expensive reagents.

Chapter IV describes a very practical, short, three-step synthesis of protected L-altrose from Perlin aldehydes that are easily accessible from the commercially available galactal via the stereo-inversion of the Perlin aldehyde derived triflate followed by the dihydroxylation.

Chapter V describes the synthetic procedure for the synthesis of *β*-hydroxy-*γ,δ*-unsaturated aryl ketones and conjugated *α,β,γ,δ* diene aryl ketones (*E*, *E*) easily. The regiospecific 1,2-addition of silyl enol ethers to saturated and unsaturated Perlin aldehydes has been achieved via the Mukaiyama aldol condition.