Oral Defense Announcement
University of Missouri – St. Louis Graduate School

An oral examination in defense of the dissertation for the degree
Doctor of Philosophy in Chemistry with an emphasis in Organic Chemistry

Catherine Alex

Master of Science (Chemistry), University of Missouri-St. Louis, May 2018
Bachelor of Science-Master of Science, Indian Institute of Science Education and Research Pune (IISER-P), India, May 2016

Stereoregulated Mannosylation by Hydrogen-bond-mediated Aglycone Delivery

Date: July 15, 2021
Time: 10:00 a.m. to 12:00 p.m.
Place: Remote

Abstract
Carbohydrates are the essential biomolecules of life as they form the forefront of interactions with receptors, proteins, pathogens, or neighboring cells. On cell-surfaces, carbohydrates are mostly found as linear or branched glycoconjugates, and a majority of them are linked via either 1,2-cis or 1,2-trans $\alpha$-glycosidic linkages. There is no template-driven pathway for achieving the synthesis of glycans unlike other biomolecules like proteins and nucleic acids. The synthesis of 1,2-trans glycosides can be reliably achieved via the neighboring group assistance. The synthesis of 1,2-cis glycosides is difficult because, beyond weak anomeric effects, there are no forces helping in directing the stereoselectivity. The synthesis of $\beta$-mannosides is complicated further because even the anomeric effect is working against it. Current methods for $\beta$-mannosylation require specialized donors and super-low temperatures. Hydrogen-bond-mediated aglycone delivery (HAD) method introduced by our lab makes use of remote picoloyl groups that are capable of providing a strong stereodirecting effect. Among a variety of targets and substrates investigated, a highly stereoselective formation of $\beta$-mannosides can be achieved via the assistance of the remote 3- O-picoloyl group. This thesis is dedicated to the synthesis of novel glycosyl donors directed for achieving challenging $\beta$-mannosidic linkages present in the oligosaccharides containing D-mannosamine (ManNAc), D-mannuronic acid (ManA), and D-mannosamine uronic acid (ManNAcA). These residues are abundant in the microbial glycans, wherein they are connected via $\beta$-(1,2-cis) linkages and are deemed essential in the development of carbohydrate-based pharmaceuticals.

Defense of Dissertation Committee
Prof. Alexei V. Demchenko, Ph.D. (Chair)
Prof. Eike B. Bauer, Ph.D.
Prof. Bruce C. Hamper, Ph.D.
Prof. Keith J. Stine, Ph.D.