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

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Master of Science (Chemistry), University of Southern Illinois Edwardsville, May 2018
Bachelor of Science (Biological Sciences), University of Southern Illinois Edwardsville, May 2015

New Methods for Stereoselective Glycosylation in Application to Significant Biomedical Targets

Date: November 20th, 2023
Time: 10:00 a.m. to 12:00 p.m.
Place: Benton 517

Abstract
Glycosyl halides have been utilized for glycosylation reactions since the early studies by Arthur Michael, nearing the end of the 19th century. Koenigs and Knorr then utilized silver salts to activate glycosyl bromides and chlorides to create synthetic glycosides. Many efforts to improve the outcome of reactions with glycosyl halides have emerged. The key emphasis has traditionally been placed on reaction rates, product yields, and stereocontrol. Recently, our lab reported that silver(I) oxide-mediated Koenigs-Knorr glycosylation reaction can be dramatically accelerated in the presence of catalytic acid additives. Methods to improve glycosylation was explored using mannosyl and glucosyl bromides. However, all previous reactions lacked stereocontrol in application to the synthesis of 1,2-cis glycosides, which remains a notable challenge in synthetic carbohydrate chemistry, as discussed in Chapter 1.

Presented herein is a thorough investigation of stereocontrolled 1,2-cis galactosylation under cooperatively catalyzed Koenigs-Knorr reaction conditions in application to galactosyl bromides (Chapter 2). Activation with different silver salts and catalytic acid additives were used to improve stereoselectivity of reactions with galactosyl donors containing common protecting groups to assist in stereocontrol. These methods have led to an exploration of galactosylation using galactosyl chlorides (Chapter 3). This study has shown that stereoselective glycosylation can be achieved using cooperative catalyst system comprising a silver salt and bismuth(III) triflate additive, or even in the presence of bismuth(III) triflate alone. Synthesis of significant biomedical targets was also explored using galactosyl halides and the previously studied activation methods. Presented will be a synthesis of differentially sulfated keratan sulfate repeating units (Chapter 4).

Defense of Dissertation Committee
Prof. Alexei V. Demchenko, Ph.D. (Chair)
Prof. Keith J. Stine, Ph.D.
Prof. Eike Bauer, Ph.D.
Prof. Michael Nichols, Ph.D.
Prof. Cristina De Meo, Ph.D.