Ph.D. Candidate

Genesis Infante

Graduate Academic Unit

Chemistry

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November 26, 2021

3:00 p.m.

Virtual Defence

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Examining Board:
Dr. James Tait (Chemistry)
Dr. Ghislain Deslongchamps (Chemistry)
Dr. Brynle Barrett (Physics)
Dr. Sara Eisler (Chemistry) Supervisor

External Examiner: Dr. Yuming Zhao
Department of Chemistry
Memorial University

The Oral Examination will be chaired by:
Dr. Patricia Evans, Associate Dean of Graduate Studies

BIOGRAPHY

Universities attended (with dates & degrees obtained):

2014 – present Ph.D. candidate, University of New Brunswick
2014 BSc, University of New Brunswick

Publications:

Infante, G.; Eisler, S. "Accessing Pyrrolones and Pyridinones: Controlling 5-exo and 6-endo Ring Closures in Heterocyclic Alkynylamides" *Can. J. Chem*. 2016, in press.

Infante, G.; Eisler, S. “Computational Analysis of the Competing 5-exo and 6-endo-dig Cyclizations in Heterocyclic Alkynylamides” *Chem. Eur. J*. in preparation

Infante, G.; Eisler, S. “Accessing fused azepino- and quinolin-isoindolinones via sequential anionic intramolecular cyclizations.” *Chem. Eur. J*. in preparation

Selected Presentations:

American Chemical Society National Meeting and Expo – San Diego, CA Poster: “Sequential Anionic Intramolecular Cyclization of Bis-Alkynylarene Amides toward Polycyclic Isoindolo-isoquinolines and –benzazepines” Aug 25-29, 2019

102nd Canadian Chemistry Conference and Exhibition – Quebec, QC Oral: “Regioselectivity Studies of Anionic 5-exo/6-endo-dig Cyclizations to Pyrrolone and Pyridinone Building Blocks” June 3-9, 2019

Gordon Research Conference (GRC) – West Dover, VT Poster: Computational Studies of Anionic Cyclizations of Heterocyclic Alkynylamides -Analysis of Structural and Stereoelectronic Effects on Regioselectivity July 21-27, 2018

Science Atlantic – CIC Chemistry Conference – Halifax, NS Oral: “Regioselectivity Studies of Anionic 5-exo/6-endo-dig Cyclization toward Pyrrolone and Pyridinone” – 2nd Place, Organic Presentation June 7-9, 2018

100th Canadian Chemistry Conference and Exhibition – Toronto, ON Poster: “Computational and Experimental Analysis of Anionic 5-exo/6-endo-dig Cyclization Toward Pyrrolone and Pyridinone Products” May 28-June 1, 2017

99th Canadian Chemistry Conference and Exhibition – Halifax, NS Oral: “Synthesis of Heterocyclic Pyridinones and Pyrrolones” June 5-9, 2016

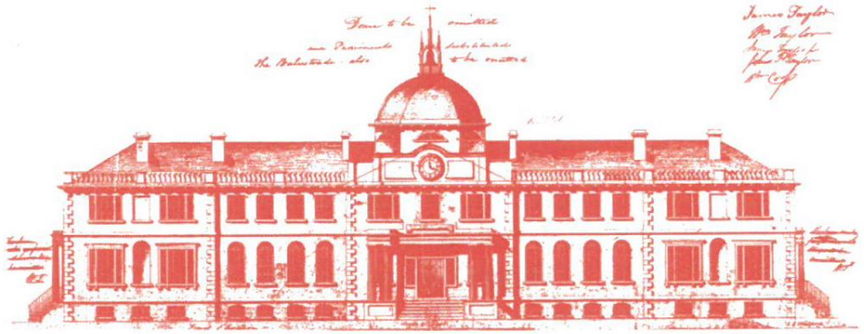
98th Canadian Chemistry Conference and Exhibition – Ottawa, ON Poster: “Extended π-Conjugated Isoindolinone Synthesis” June 13-17, 2015

Controlling Regioselectivity of Cyclization in Heterocyclic Alkynylamides

Abstract

Competitive 5-exo/6-endo anionic intramolecular cyclization reactions in heterocyclic alkynylamides were explored via experimental and computational analysis. The 5-exo-dig cyclization pathway is usually disfavoured in heterocyclic systems, and 6-endo products are often both the kinetic and thermodynamic products. However, it was discovered that it is possible to shift selectivity toward the 5-exo-dig pyrrolone products away from the less strained pyridinone products that are produced via the 6-endo-dig cyclization. Parameters such as identity of heteroatom, heteroatom positioning within the heterocycle, and functionality on the alkyne were investigated and in many cases were found to strongly influence product ratios.

A series of computational studies was performed to provide further insight into the 5-exo and 6-endo dig pathways in these heterocyclic systems. Theoretical predictions were found to reproduce experimental results, highlighting the predictive capabilities of the computations in determining preferred products. The established experimental and predictive computational protocols were then applied to more complex bis-alkynylamides. The subsequent competing tandem cyclization pathways, 5-exo/6-exo-dig and 5-exo/7-endo-dig, were predicted and controlled using established experimental and theoretical concepts from earlier studies.



Home of the School of Graduate Studies, Sir Howard Douglas Hall was designed by J.E. Woolford in 1825 and is the oldest university building in Canada still in use.

The University of New Brunswick recognizes that the university sits on traditional Wolastoqey territory. The river that runs right by our university – the St. John River – is also known as Wolastoq, along which live the Wolastoqiyik -- the people of the beautiful and bountiful river.

UNIVERSITY OF NEW BRUNSWICK

SCHOOL OF GRADUATE STUDIES

ORAL EXAMINATION

Genesis Infante

IN PARTIAL FULFILMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY