UREAP APPLICATION FORM

THOMPSON RIVERS UNIVERSITY
Office of Research and Graduate Studies

First Name: Emily

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Student ID: T00609571 Start Date of Project: 15/11/2022 (DD/MMM/YYYY)

Please complete all sections of this application form.

1. FACULTY MENTORS INFORMATION

1.1 Who is your Primary Faculty Mentor? Dr. Dipesh Prema

1.2 Who is your Secondary Faculty Mentor? Dr. Kingsley Donkor

NOTE: Your Primary and Secondary Faculty Mentors must each complete a Faculty Mentor Support Form. Forms can be found under the attachments tab within your TRU Romeo UREAP application and on the TRU UREAP webpage under information and Forms for Faculty Mentors..

2. PROJECT DESCRIPTION

2.1 Provide an abstract of your proposed research: (maximum 1500 characters)

Amines are a versatile group of organic compounds that have a wide range of applications in multiple industries, including pharmaceuticals and agriculture. Various methods are utilized in the synthesis of amines, however, catalytic hydroamination is favored due to its high atom economy. Within large-scale industries, hydroamination reactions are commonly catalyzed by rare transition metals – options that are expensive, toxic and have a low abundance. This project focuses on the development of a catalyst utilizing inexpensive and readily available first-row transition metals, such as iron. Bulky imino-phosphine ligands will firstly be synthesized via a schiff base condensation of a specific amine and aldehyde. Although the aldehyde will predominantly be 2-(diphenylphosphino)benzaldehyde, the included aniline will vary between 4-triylaniline or 2,4,6 trimethylaniline. The synthesized imino-phosphine ligands will then be coordinated to a first-row transition metal – focusing on iron. The resulting catalysts will be tested in a hydroamination reaction to determine their efficacy. Each synthesized compound will undergo a detailed characterization via 1H and 13C, nuclear magnetic resonance, NMR, spectroscopy. Due to the significance of nitrogen-based compounds, and the global movement toward sustainability, the development of a hydroamination catalyst that is comprised of an abundant, in-expensive and non-toxic materials is of great interest to chemists and industries worldwide.

2.2 Provide a brief literature review for your proposed research: (maximum 3500 characters)

Nitrogen containing compounds are building blocks in inorganic chemistry and represent a vital component to countless industries, with applications ranging from simple dyes to cleaning products [1]. On account of the increased global demand for amine-based products, these commodity chemicals are projected to grow annually by 8.3 %, a staggering statistic indicating their significance [1]. A direct result of their rising market value is the need for inexpensive and efficient synthetic methods, and there is

none better suited than the hydroamination process. Hydroamination is a chemical reaction that involves the direct addition of an N-H bond, often an alkyl amine, to an unsaturated C-C bond, being alkenes or alkynes, which allows the formation of amines, such as enamines and imines [2].

Hydroamination Reaction

The hydroamination reaction is a very attractive route to nitrogen containing compounds due to its simplicity and proposed 100 % atom efficiency [1-5]. Of the available functional groups able to participate within this reaction, alkynes have achieved the most success due to its increased spontaneity compared to alkenes [2, 5] Although, current research has focused on the use of non-activated alkenes within hydroamination reactions due to their ability to directly produce stable amines [4]. This process remains challenging as alkenes have significantly high reaction barriers and increased electron density between the carbon bonds [1, 3, 6]. As a result, an effort to develop effective catalysts has been the focus of much hydroamination research in recent years [3, 7].

Hydroamination Catalysis

Catalytic approaches to hydroamination reactions have been reported in the recent decades to further increase its efficiency for industrial applications. These catalysts commonly involve precious metals, with studies including elements such as mercury, thallium [2], rhodium [9], palladium, and zirconium [10] as well as rare-earth metals such as organolanthanides [7]. Despite the favorable properties of these catalyst's, such as efficiency, stability, and selectivity, precious metals and rare-earth metals are non-abundant, expensive, as well as hazardous to the environment due to their associated toxicity [6]. Computational chemistry has indicated that in the hydroamination of alkenes, Group 10 transition metals are more suitable as catalysts, specifically nickel complexes [11].

Conclusion

The development of efficient hydroamination reactions targeting alkenes is an essential endeavour due to its wide applicability. Additionally, while it is common place to utilize precious metals and rare-earth metals as catalysts in hydroamination reactions, these complexes are unsustainable and the need for economically and environmentally conscious catalysts is ever present.

2.3 What is the hypothesis or research question for your proposed research? Include any specific objectives: (maximum 500 characters)

This research aims to develop an efficient synthesis for a catalyst to be used in a hydroamination reaction utilizing a first-row transition metal and an iminophosphine ligand. Objectives include synthesizing and characterizing an iminophosphine ligand with the use of multiple anilines, such as 4-tritylaniline or 2,4,6 trimethylaniline, as well as facilitating a complexation reaction with a first-row transition metal, such as iron.

2.4 Provide a description of the research methodology/methodologies and analysis that you intend to employ in completing this research: (maximum 1500 characters)

This research will include qualitative and quantitative components in order to develop an efficient synthesis. Laboratory techniques such as reflux, filtration and rotary evaporation will be employed for the synthesis of the iminophosphine ligand and coordination of this ligand to a metal centre. Structure elucidation for each synthesized and coordinated compound will be achieved by utilizing the Bruker Avance 500 MHz NMR spectrometer focusing on 1H and 13C analysis. In characterizing these compounds, the success or need for adjustment of each reaction will be determined.

2.5 Provide a description of how your research will significantly impact your field of study:

(maximum 1500 characters)

Amines are a crucial component to countless industries and allow us to drink purified water and receive relief with medications. The development of an efficient synthesis to produce these compounds is of great interest to not only chemists, but to that of the global economy and environmental welfare. Additionally, successful use of first-row transition metals in catalysis will impact the perspective towards all chemical processes in the present and future due to its increased sustainability. This is especially important as currently there is an international movement towards greener and more environmentally friendly processes.

2.6 Describe your plans to disseminate your research findings: (maximum 500 characters)

At the completion of this research project, I will present a poster and oral presentation at the Thompson Rivers University Undergraduate Research Conference this upcoming spring. Additionally, I plan to submit an abstract so as to attend a conference this coming summer, such as the Western Canadian Undergraduate Chemistry Conference.

2.7 List the references that you have citied throughout your research proposal observing the appropriate citation style for your discipline: (maximum 3500 characters)

1.Streiff, S.; Jérôme, F. Chem. Soc. Rev., 2021, 50, 1512-1521.

2.Pohlki, F.; Doye, S. Chem. Soc. Rev., 2003, 32, 104-114.

3.Müller, T.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. Chem. Rev. 2008, 108, 3795-3892.

4.Ackermann, L.; Bergman, R. G.; Loy, R. N. J. Am. Chem. Soc. 2003, 125, 11956-11963.

5.Yim, J. C.; Schager, L. L. EurJOC. 2014, 31, 6825-6840.

6.Ludwig, J. R.; Schindler, C. S. Chem. 2017, 2, 313-316.

7.Hong, S.; Marks, T. J. Acc. Chem. Res. 2004, 37, 673-686.

8.Ohmiya, H.; Moriya, T.; Sawamura, M. Org. Lett. 2009, 11, 2145-2147.

9.Utsunomiya, M.; Kuwano, R.; Kawatura, M.; Hartwig. J. F. J. Am. Chem. Soc. 2003, 123, 5608-5609.

10.Müller, T. E.; Beller, M. Chem. Rev. 1998, 98, 675-704.

11.Senn, H. M.; Blöchl, P. E.; Togni, A. J. Am. Chem. Soc. 2000, 122, 4009-4107.

3. PROJECT TIMELINE WITH BENCHMARKS

3.1 Provide a timeline for your project that includes key benchmarks: (maximum 1000 characters)

January

•Begin synthesis of an iminophosphine ligand using aniline. Develop ability for rotary evaporation, filtration, and reflux

•Characterize synthesized ligands using the Bruker Avance 500 MHz NMR spectrometer

February

•Synthesize iminophophsine ligand using a more difficult and expensive aniline, such as 4-tritylaniline and 2,4,6-trimethylaniline

•Characterize this ligand using the NMR spectrometer

•Begin reactions focusing on coordinating the iminophosphine ligands to a metal centre, namely iron

March

•Continue optimizing coordination reactions between select iminophosphine ligands and iron

•Characterize the resulting compound with the NMR spectrometer to determine success

•Test the previously synthesized catalysts with alkenes, such as cyclohexene, and anilines

•Prepare a poster and presentation for the TRU Undergraduate Research Conference

April

•Prepare abstract to submit to an upcoming conference, ideally the Western Canadian Undergraduate Chemistry Conference

NOTE: Please refer to the UREAP Help Guide for a project timeline example. Students must demonstrate a willingness to engage in 12 weeks or equivalent of sustained research per the Terms of Reference.

4. OPERATING GRANT BUDGET PROPOSAL

4.1 The UREAP award offers up to $1000 toward direct research expenses. These expenses must be preapproved by the UREAP committee in the adjudication phase. Use the provided template under the

Attachments tab in the TRU Romeo UREAP application to complete your budget proposal.
Copy amount from the TOTAL AMOUNT line of the budget here. Total Amount: $ 956.20

4.2 Additional budget information: (maximum 500 characters)

If I am not successful in receiving the additional operating grant, the supplies, and extra funds that I will require will be supplied by my supervisor, Dr. Dipesh Prema's, grants.

5. CONTRIBUTION TO ACADEMIC/PROFESSIONAL GOALS

5.1 Describe how this project will contribute to your academic and/or professional goals:

(maximum 1000 characters)

The development of sustainable catalysis is a rising movement within the sciences due to increased awareness of our environment. My involvement in this research process will allow me to have hands-on experience of the method development included with synthesizing a novel catalyst, which will provide me with experience that I can apply throughout the sciences, such as chemistry, biochemistry, and biology. Through the courses I have taken at TRU, such as advanced level inorganic chemistry and organic chemistry, I will be able to utilize my background knowledge so as to support and drive this research to success. Additionally, participating within this research will provide me with an opportunity to develop my ability to work in a professional laboratory, and cooperate with supervisors and fellow research students. This experience, and the skills I will develop by participating, will aid in my future endevours for either graduate school within the chemistry discipline, or medical school.

NOTE: Include your role in conceiving of the project, your role in the implementation of the project, and your overall academic objectives – explaining how this project will help to advance those objectives.