

Seton Hall University

## eRepository @ Seton Hall

---

Petersheim Academic Exposition

Petersheim Academic Exposition

---

4-21-2020

## Book of Abstracts

Seton Hall University

Follow this and additional works at: <https://scholarship.shu.edu/petersheim-exposition>

---



## **ROSE MERCADANTE SEMINAR SERIES**

**Department of Chemistry and Biochemistry**

**25<sup>th</sup> Departmental Symposium**

*in conjunction with*

**The Petersheim Academic Exposition**

**Book of Abstracts**

**Online Poster Symposium**

**April 21-22 2020**

## **Foreword**

Over 25 years ago, Dr. Matthew Petersheim had the idea that the Academic excellence of the University should have a time each year when it was celebrated. He believed that a focus on research and scholarship and a celebration of academic excellence was the least that could be done to reward those pursuing this central goal of Seton Hall University. The result of this idea was the Academic Exposition. After his untimely death in 1998, the Exposition was named in his honor. Each year, the Academic Exposition continues to reinforce Dr. Petersheim's vision.

The Department of Chemistry and Biochemistry has held a Research Symposium each year of the Petersheim Academic Exhibition. Dr. Petersheim was our colleague and Chair of the Department, so his vision of a celebration of research and scholarship is one that we share.

This year, the Academic Exposition has faced unique challenges. The epidemic due to COVID-19 has resulted in unforeseen changes in teaching, scholarship and research. The Department of Chemistry and Biochemistry has risen to meet these challenges, and keeping true to the vision of the Petersheim Academic Exposition, we have moved our Research Symposium to an online format. In this book, you will find Abstracts of all of the posters presented online, organized by research mentor. The online poster session can be found at the Chemistry Biochemistry Graduate Student Blackboard site, as a collection of Wikis, also organized by research Mentor.

Hazard Zet Forward!

Dr. James E. Hanson  
Director of Graduate Studies  
Department of Chemistry and Biochemistry  
Seton Hall University

## Table of Contents

### **Keynote Address**

Dr. Jane Wissinger, University of Minnesota	4
---	---

### **Antonacci**

Kiara Franklin & Gianna Cole	5
Anne Pino & Andrew D'Amato	6

### **Badillo**

Mannesah Georges et al	7
Darwin Glynn, Michael Freddy et al	8
Jason Saway et al	9
Alexandr Trifonov et al	10

### **Buonopane**

Lizeth Chicas et al	11
Giovanna Dabbagh et al	12
Chloe Demesmin et al	13
Sarah R. Kenney et al	14
Jessica Roman et al	15
XiuXlu Sammis-McCoy & Nicholas DeFilippo	16

### **Fadeev**

Henry Grau	17
------------	----

### **Gorun**

Mary Okorie, Adam Kmeck & Ayunni Yussof	18
Marius Pelmus et al	19

### **Hanson**

Daniel Goldman	20
Usha Kalra	21
Taylor McKeever & Usha Kalra	22
Miguel Medico, Ayunni Yussof & Dr. Tin-Chun Chu (Biology)	23
Edrice Sediq & Brandon Pineda	24

### **Kazakevich**

Dinah Lee	25
Timothy Nowak & Alexey Makarov	26

### **Kelty**

Jeffrey Raab & Dr. Gary Martin	27
--------------------------------	----

**Laviska**

William Kohmann	28
William Midolo	29
Kyle Otto	30
Anthony Rodriguez	31
Andi-Kaye Walters	32

**Marzabadi**

Anne Pino	33
-----------	----

**Murphy**

Rebecca Gilchrist & Allyson Dixon	34
Alexa Skalski & Allyson Dixon	35
Nataly Suarez & Florian Balan	36

**Sabatino**

Sunil Shah et al	37
------------------	----

**Snow**

Nicole Charles	38
Hetal Rana	39
Shipra Patel	40
Sean McCann	41

**Wiedman**

Elizabeth Boyer et al	42
Makayla Manfredi et al	43
Abigail Richter & Marinelle Geda	44

## Keynote Address

### Green Chemistry Curriculum: Paying it Forward for a Sustainable Future

Jane E. Wissinger

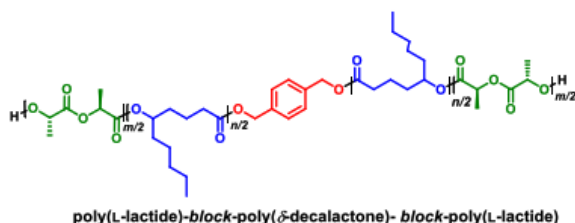
University of Minnesota, Department of Chemistry

Chemistry, as a central science, has an essential role to play in addressing the grand challenges of sustainability that face our world today. Therefore, chemistry educators have the responsibility of training students to have the skills needed to understand these problems and address them through a lens of people, planet, and profit. Green chemistry principles provide the tools needed to achieve these goals through pollution prevention and “benign by design” strategies of innovations.

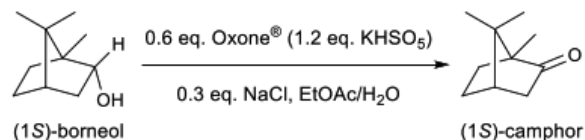
This presentation will share how incorporation of green chemistry experiments into the University of Minnesota organic chemistry laboratory curriculum over fifteen years ago has snowballed in unexpected and advantageous directions. Immediately, undergraduate and graduate students associated with the laboratory course were inspired by green chemistry’s modern and creative approach to minimize environmental impact, reduce waste, and improve safety of chemical syntheses. This catalyzed research efforts to develop new green curriculum materials spearheaded by these students who could then see their efforts excite new classes of students in green chemistry practices. Several projects involved collaborations with faculty in the department providing the added benefit of connecting course work to active research programs. Of special emphasis was the development of polymer experiments, based on recent innovations from the NSF-funded Center for Sustainable Polymers, illustrating environmentally-friendly syntheses of plastics made from renewable feedstocks and design for degradation.

Green chemistry initiatives have since expanded within the department through a popular senior level green chemistry course, new experiments incorporated in additional laboratory courses, safety programs, ACS student chapter activities, and outreach efforts. Proudly, we have a growing network of graduates who are now college professors and high school chemistry teachers incorporating green and sustainable chemistry into their own classrooms; often feeding back into our programs. Surveys indicate that students of all disciplines value learning about green chemistry and appreciate the importance it will play in a sustainable future.

#### New Polymers from Renewable Resources



#### Greener Oxidation of Natural Products



**Title**

Chitosan in Cosmetic Chemistry

**Authors**

Kiara Franklin, Gianna Cole, Dr. Cosimo Antonacci, Dr. James Hanson

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

The experiment observed the synthesis of two environmentally sustainable materials, chitosan and vanillin to create the compound, ChiVan. Chitosan is a very common compound in the cosmeceutical industry, especially in formulations. Chitosan is derived from crustacean shells making it an inexpensive, safe, and natural resource for cosmetic products as an emulsifying agent, a vehicle for controlled delivery, and as an antioxidant. While chitosan has many useful properties, the smell from the crustacean derivative is not a pleasant smell for consumers. By adding vanillin, the chitosan can be used for its cosmetic properties while also being enjoyable to the consumer. In this research, the application of chitosan and vanillin imines were utilized based on their known synthesis with one another. To start, chitosan was dissolved with 0.2M acetic acid and the solution was stirred for 2 hours. Different amounts of vanillin were added to the chitosan mixture, starting at 0.1 g and increasing by 0.1 g until 0.7 g of vanillin were added. Before being added to the chitosan solution, the vanillin was dissolved in ethanol. The vanillin and chitosan mixture stirred for another hour to create a homogeneous mixture. The different amounts of vanillin allowed for the masking of the smell of the crustacean shell. The different variations of ChiVan can then be added to formulations for cosmetic products without the disadvantage of the crustacean smell. We report here the progress toward developing these Chi-Van conjugates for cosmetic applications.

**References:**

1. Ilic, I., Meurer, M., Chaleawlerthumpon, S., Antonietti, M., Liedel, C. RSC Adv., 2019, 9, 4591.

**Title**

Successful methods of promoting and teaching chemistry to children ages 3-12

**Authors**

Anne Francine A. Pino, Andrew D' Amato Jr., **Dr. Cosimo Antonacci**, Dr. Cecelia Marzabadi, Dr. Joseph Badillo

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

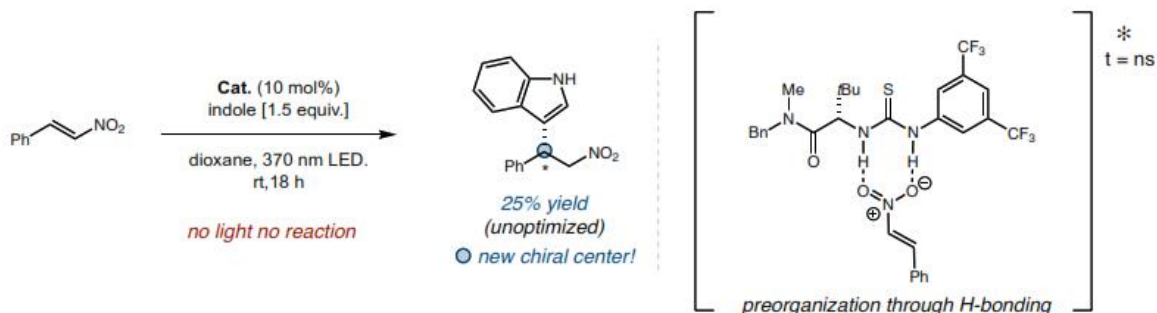
As STEM careers are becoming more popular, STEM education is as important as ever. This research was to propose viable and functional methods of teaching chemistry to young children through interactive demos. Investigation of effective ways to capture children's attention, retain their engagement, and effectively teach chemistry and science related topics in a timely manner was conducted. The study was to investigate under several booths at the ACS ChemEXPO 2019 the best method to engage and teach children. Major findings include that personability, repetition, and an interactive activity led to children learning about chemistry while also finding the activity enjoyable. The finding concluded that effective and successful engagement of children to STEM fields require personal engagement, active participation, and positive encouragement from those presenting the information.



## Asymmetric Conjugate Additions using Chiral Thiourea Photoacids

Mannesah Georges, Alexander Bulsiewicz, Alejandro Cubillos, and Joseph Badillo\*

Seton Hall University, Department of Chemistry and Biochemistry, 400 South Orange Ave, South Orange, New Jersey 07079



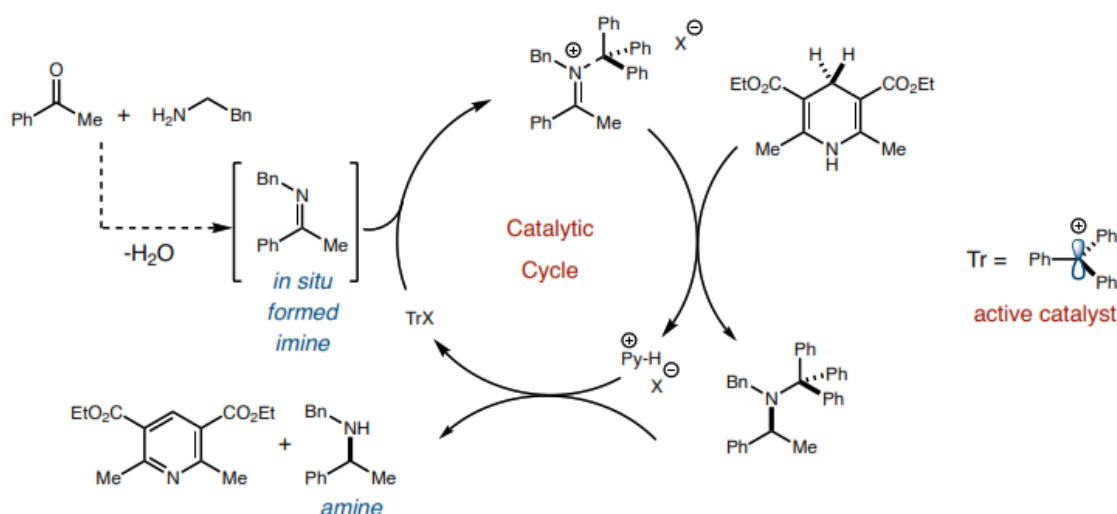
A photoacid is a molecule that is a weak acid in its ground state and becomes more acidic upon absorption of light. This project outlines the untapped potential for chiral photoacids as catalysts for use in the conjugate addition of indoles to  $\alpha,\beta$ -unsaturated carbonyls and nitro olefins. Preliminary results demonstrate that using catalytic photoacid facilitates the conjugate addition of indole with *trans*- $\beta$ -nitrostyrene in up to 25% yield. This presentation describes our efforts to optimize this reaction by investigating a variety of reaction parameters such as concentration, catalyst, solvent, and light source.

## Carbocation Catalyzed Transfer Hydrogenation of Imines

Darwin Glynn, Michael Freddy, Caitlyn Ortega, Joey Wu, and Joseph Badillo\*

Seton Hall University, Department of Chemistry and Biochemistry, 400 South Orange Ave, South Orange, New Jersey 07079

This presentation will discuss the development of carbocation catalyzed conditions to form imine compounds *in situ* from the corresponding ketones and amines. Upon its formation, the imine then undergoes carbocation catalyzed transfer hydrogenation, from Hantzsch ester, to form the corresponding amines (Figure 1). Using 20 mol% trityl tetrafluoroborate as the carbocation catalyst, in DCE as the solvent, we have shown that we can access a wide range of amines in up to >95% yield. The amines are then purified by column chromatography and characterized using NMR spectroscopy. Specifically, this presentation will discuss both the substrate and catalyst scope for these transformations, as well as challenges with product isolation. The development of chiral carbocation catalysts will also be discussed.



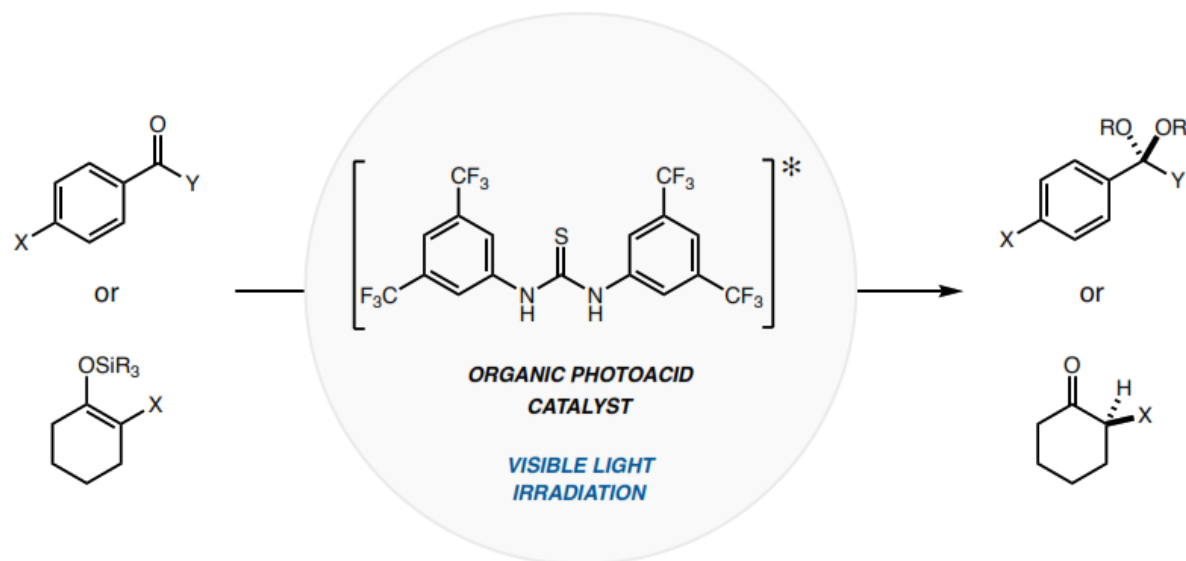
**Figure 1:** Reaction mechanism for the carbocation catalyzed transfer hydrogenation of imines.

## Thiourea Photoacid Catalysis: Acetalization of Carbonyls and Excited State Proton

### Transfer with Enol Silanes

Jason Saway, Kathryn McCoy, Abigail Pierre, and Joseph Badillo\*

*Seton Hall University, Department of Chemistry and Biochemistry, 400 South Orange Ave, South Orange, New Jersey 07079*



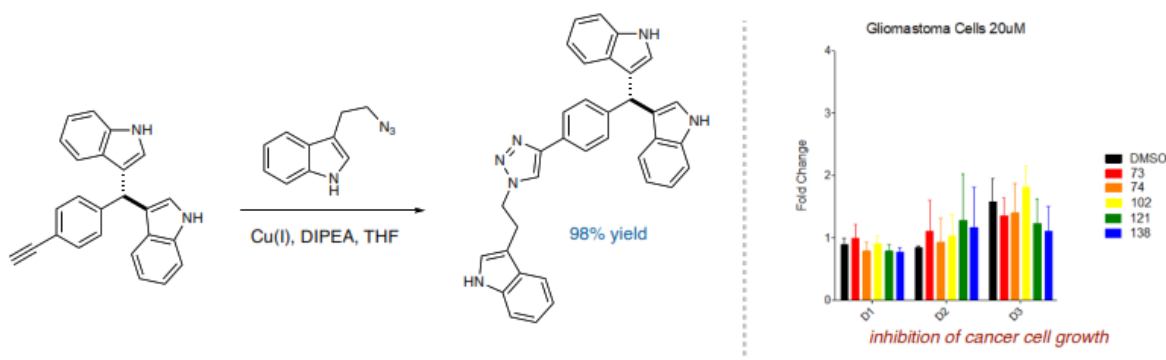
Photoacid-catalyzed synthesis strategies have recently gained interest in the synthetic organic community due to the use of visible light as a mild way to activate organic processes. Photoacid catalysts can reduce reaction times and more importantly eliminate the need for harsh reagents and the production of toxic waste products. We have observed that visible light-activated thioureas facilitate product formation in a variety of reactions. Here we show that Schreiner's thiourea catalyzes the formation of C–O bonds. Using 10 mol% photoacid catalyst enables the photoinduced acetalization of aldehydes with a range of alcohols. The acetals produced are important for the multistep synthesis of complex natural products and other biologically relevant products. In addition, preliminary results using thioureas as excited state proton transfer (ESPT) catalysts for the protonation of enol silanes is discussed.

## Synthesis of Triazole Containing Triarylmethanes and 3,3'-Diaryloxindoles

Alexandr Trifonov, Jason Saway, Jennifer Orth, Milan Patel, Mackenzie McCann<sup>‡</sup>, Karina Helou<sup>‡</sup>, Isabella Somera<sup>‡</sup>, Cosimo Antonacci\*, Suzanne Gantar<sup>‡\*</sup>, and Joseph Badillo\*

*Seton Hall University, Department of Chemistry and Biochemistry, 400 South Orange Ave, South Orange, New Jersey 07079*

*<sup>‡</sup>Seton Hall University, Department of Biology, 400 South Orange Ave, South Orange, New Jersey 07079*



Triarylmethane compounds derived from various aldehydes and indoles have been studied for their potential to treat a variety of cancers. Some of the compounds studied have exhibited selectively for cancer cells vs. normal ones. Recently, our laboratory developed a photoacid catalyzed strategy for the synthesis of triarylmethanes and 3,3'-diaryloxindoles. This presentation will discuss the synthesis and optimization of a variety of triazole containing triarylmethanes and 3,3'-diaryloxindoles using copper-catalyzed azide-alkyne cycloaddition (CuAAC) chemistry in order to evaluate their anti-cancer properties. These triazole modified compounds have the potential for divergent selectivity relative to their parent compounds, due to their unique structure. In addition, work to increase the solubility of these molecules in aqueous media to study their DNA-binding properties in collaboration with Prof. Cosimo Antonocci will be discussed. Preliminary biological studies in collaboration with the Gantar Lab in the Department of Biology for a variety of triarylmethanes synthesized in our laboratory will also be presented.



## Evaluation of amino acid function groups effects on conjugated diene formation

Lizeth V. Chicas\*, Varoon P. Dave, Viral S. Shah, Rev. Gerald J. Buonopane, Ph.D.  
Department of Chemistry and Biochemistry  
Seton Hall University, South Orange, NJ 07079

Studying protein-lipid interactions and oxidation reactions are essential for the study of biological and metabolic damage to proteins and the development of various diseases (Estévez, 2011). Many food systems affect overall health in a negative manner since food proteins are susceptible to oxidative reactions, affecting the nutritional quality and shelf-life of food (Xiong, 2000). Lipids also oxidize due to high temperature, light, enzymes, metals, natural sensitizers, and oxygen during food processing and storage (Jackson & Penumetcha, 2019). To retard or inhibit lipid and protein oxidation, antioxidants are incorporated in food systems to preserve food quality. The oxidation of both the fatty acid methyl linoleate and proline, acting as the antioxidant, and their interaction reactions were assessed in this study. Four samples were prepared with equivalent mmoles of methyl linoleate (ML) and proline: ML and 1-tert-butoxycarbonyl-L-proline (ML-Boc-P), ML and methyl ester proline (ML-ME-P), and ML and N-Z-L-proline ester (ML-NZL-P) and five individual samples were prepared as a control group. The samples were weighed, transferred in 10 mL glass vials, and mixed. All glass vials were incubated in an oven at 37°C for Day 1 to Day 5. Samples were pulled out at respective time points, cooled to room temperature, samples were diluted via iso-octane solvent, and sample solutions were centrifuged before analysis. The conjugate dienes were determined using UV/Vis spectroscopy at 230 nm. The concentration of conjugated dienes (mmole/mol ML) was calculated using Beer's Law. In general, the results showed that conjugate diene formed with respect to increased incubation times in individual methyl linoleate and mixed samples. Conjugate dienes did not form in Day 1 in any of the samples. Most conjugate diene formed in ML-P and the lowest in ML-ME-P samples.

**Title**

Antioxidant Activities of Essential Oils and Synthetic Antioxidants in Model Food Systems Using the  $\beta$ -Carotene Bleaching Method

**Authors**

Giovanna Dabbagh\*, Mariez Aziz, Viral Shah, and Rev. Gerald J. Buonopane, Ph.D.

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

Food stability depends on lipid and protein macromolecules and their ability to avoid oxidation. The accumulation of reactive oxygen species (ROS) results in lipid and protein breakdown, which reduces the quality of fresh and processed foods. To maintain food quality and prolong shelf life, the fat and amino acid sources can be protected by the addition of antioxidants, which hinder the rate of oxidation. With the concerns that commercial synthetic food additives may not be the safest option for human consumption, natural antioxidants have been considered as safer preservatives. The food industry can adopt better means for food preservation if results show that essential oils are effective. In this study, the synthetic antioxidants, butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA), were compared with natural antioxidants, or essential oils (EOs), clove and thyme, in emulsions containing the polyunsaturated fatty acid linoleic acid. Antioxidant analysis of these model food systems was carried out using the  $\beta$ -carotene bleaching method, which quantifies fatty acid oxidation through the interaction of  $\beta$ -carotene with free radicals. Samples were prepared with different concentrations of the antioxidants and the absorbances were measured at 470 nm using a MetaSpec UV/Vis Spectrophotometer. Samples containing clove EO and BHA demonstrated high antioxidant activity. The manipulation of additional independent variables, such as the temperature of incubation and the types of fatty acids, will be completed in a future study.

**Title**

Assessing Antioxidant Activity of Essential Oils of Clove (*S. aromaticum*), Sweet Basil (*O. basilicum*), and Thyme (*T. vulgaris*) Using the TBARS Assay

**Authors**

Chloe F. Demesmin\*; Chisomo L. Gomonda; Ashley N. Robert; Viral Shah; and Rev. Gerald J. Buonopane.

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

Due to growing widespread interest in using natural preservatives in food, this research aimed to assess the antioxidant abilities of clove (*S. aromaticum*), sweet basil (*O. basilicum*), and thyme (*T. vulgaris*) essential oils, as possible natural antioxidants in lipid food systems. The antioxidant effect of various essential oils was tested using the Thiobarbituric Acid Reactive Substances (TBARS) Assay to measure malondialdehyde (MDA) concentration through UV-Vis spectroscopy. The control food system sample contained linolenic acid that was mixed with tween 20 as an emulsifier, and a phosphate buffer of pH 7.2. Then, the remaining samples were treated with either clove essential oil (C) at 0.01% (w/v), sweet basil essential oil (SB) at 0.01%(w/v) or thyme essential oil (T) at 0.01% (w/v). Each solution was made in duplicate. The emulsions were kept in a room temperature environment for 8 days and then tested on days 4 and 8. The UV-Vis absorbance was measured at 532 nm for essential oil sample solutions, and compared with an MDA standard curve to determine the concentration of MDA present in the samples. After the 8 day period, thyme oil was shown to have 10.57 ppm of MDA present in the solution, exhibiting the highest antioxidant activity of all three essential oils.

**Title**

Analyzing Sweet Basil Genome After Cold Plasma Treatment Boosts Growth

**Authors**

Sarah R. Kenney\*, William P. Davis, Fr. Gerry Buonopane, Dr Jose Lopez and Dr. Mary J Berger

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

This study examined potential genetic alterations to Sweet Basil (*Ocimum basilicum Genovese*) due to cold atmospheric plasma jet treatment, as well as general changes in seed germination and seedling growth. The cold fusion plasma is a combination of helium and atmospheric air-jet application using the power parameters of 5ml/sec He and electrical power of 27.6kHz at 10-11kV. The treatments were for seeds, roots, stems, and leaves, for 30 and 60 seconds, the seeds treated once overall and the other plant parts once a week. It was observed that treated plants showed a quicker germination rate, in addition to a significant difference in growth markers than control. The plasma-treated and controlled plant's DNA was isolated, prepared, and examined by gel from the DNA. The gel electrophoresis was prepared using agarose gel for the wells and run in TAE buffer. One of the processes was the preparation of cleaning the proteins that surround the DNA molecule. Once cleaned, DNA was used to run an electrophoresis examination of treated plants' and control DNA. Our findings were negative for any changes in the treated DNA compared to the control. These results indicated that the treatment of seeds with cold plasma promotes growth and a larger yield of the plant; and does not mutate the genome.



**Title**

"Effects of Proline in the formation of Hydroperoxides in Lipid Oxidation"

**Authors**

Advisors: Rev. Gerald Buonopane Ph.D. and Viral Shah

Jessica Roman, Amber Chaudhary, Amarilis Rodriguez

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

Lipid oxidation over food storage is a serious challenge for the food chemist because it is an explosive reaction and difficult to control. This can result in the loss of acceptable sensory qualities of a large amount of food. The rate of oxidation is dependent on the degree of unsaturation which increases with more double bonded fatty acids. Lipid oxidation has been measured through markers of free radicals such as conjugated dienes and hydroperoxides. The resulting hydroperoxides tend to be some of the most harmful intermediates of lipid oxidation that can even lead to physiological distress, i.e., diseases. This experiment focused on using the amino acid proline to potentially lower the amount of hydroperoxides that are produced. Although proline is a non-essential amino acid, it is necessary for the proper function of joints and tendons, because it is a part of collagen.<sup>1</sup> Proline has also been shown to have antioxidant properties. This experiment tested mixtures of different proline derivatives, as well as regular proline, on the potential oxidation of the unsaturated fatty acid, methyl linoleate. The different proline versions used were N-Tert-Butoxy-carbonyl-D- Proline, L- Proline Methyl Ester, and N-Z-L-Proline Methyl Ester. A UV/Vis Spectrophotometer was used to analyze the different mixtures of proline and methyl linoleate over a storage time of five days. Mixtures of the two were taken out of the oven at different intervals and analyzed via spectrophotometry. It would be expected that with the presence of proline (versus control samples with lipid and no proline) the potential formation of lipid hydroperoxides will decrease.

**References:**

1. Proline. <https://aminoacidsguide.com/Pro.html>

## Determination of the Antioxidant Activity of Ginger Root Essential Oil Using the DPPH Method

Nicholas DeFilippo, XiuXiu Sammis-McCoy, and Rev. Gerald J. Buonopane\*  
Seton Hall University, Department of Biochemistry and Chemistry, South Orange, NJ

This study continues our laboratory's assessment of the antioxidant activity of essential oils. Essential oils are volatile compounds, which are extracted from aromatic plants using techniques like steam distillation. Many essential oils are known to have antioxidant properties. Antioxidant efficacy found in essential oils retards or inhibits the deleterious effects that arise from lipid oxidation. Free radicals that form in the explosive oxidation reaction are very unstable and reactive, causing in food products the production of a variety of off-flavor and off-aroma compounds. Because other researchers have found that ginger root essential oil has antioxidant properties, we chose it as the focus of our study. Ginger root was studied at different concentrations [0.1g/mL 0.2 g/mL 0.3 g/mL 0.4 g/mL 0.5 g/mL] mixed with methanol. Antioxidant analysis employing the stable free radical DPPH (2,2-diphenyl-1-picrylhydrazyl) was used to determine possible antioxidant protection from ginger root essential oil. Absorbance of the sample solutions was measured using a UV/Vis spectrophotometer at a wavelength of 518 nm. Results of the study showed that there was a higher amount of antioxidant activity particularly at higher concentrations of ginger root oil.

**Title**

Surface Chemistry and Surface Properties of Energetic Nitrocellulose

**Authors**

Henry Grau

Advisor: alexander Fadeev

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

This research describes an investigation into the wettability of nitrocellulose (NC), most importantly to nitroglycerin (NG), which are key components of formulations used to propel military ammunition. NG demonstrates complete wetting of NC and, overtime, NG sweats on the NC surface and leaks out. The leaking out of NG from the solid matrix is a known cause of fires and explosions resulting from storage. The origin of this research is inspired by the need to engineer a solution to leakage problems of energetic plasticizer in NC based propellant. While searching for a viable material for a specific application, we journeyed into the very specific details

We describe approaches for producing a ‘tunable’ NC surface that is derived from a two-step process using the reaction of 3-(triethoxysilyl-propyl) isocyanate followed by reactions with alkyl-, fluoroalkyl-, or phenyl-silane, producing NC surfaces ranging in lyophobicity. Each functional group allows various degrees of reduced wettability of NC with NG. SEM analysis of modified NC materials suggests bulk properties of NC were not affected by silane. XPS provided evidence of chemically modified fibers. Increased lyophobicity of modified NC demonstrate increased thermal stability and equivalent energetic properties compared to bare NC. NC was characterized by dynamic contact angles using water, hexadecane, and NG as probe fluids. Wettability of modified NC demonstrated significant variations in surface energy in accordance with the nature of surface functionalities. we discuss the macro and microscopic methods of measuring contact angles. The contact angles of the modified NC changed over a wide range demonstrating surfaces with “tunable” wetting. NC grafted with fluoroalkyl-groups showed the most NG-repelling properties ( $\theta_{Adv}/\theta_{Rec} \sim 90^\circ/50^\circ$ ). Estimation of contact angles on nitrocellulose treated fibers allowed insight of the surface properties showing an increase in surface curvature and reduced capillary effect.

**Title**

**Anchorable Fluorinated Phthalocyanines for Photodynamic Inactivation and Detection**

**Authors**

Mary Chioma Okorie; Ayuni Yussof; and Adam Kmeck

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

Phthalocyanines (Pcs) are a class of photosensitizers that can generate singlet oxygen ( $^1\text{O}_2$ ), which decays to form reactive oxygen species (ROS), including hydroxyl ( $\text{HO}\cdot$ ) and superoxide radical ( $\text{O}_2^{\cdot-}$ ) using visible light. These radicals target non-specific C-H bonds. Microorganisms thus cannot develop resistance to ROS attack. Organic photosensitizer self-destruction is a hurdle to practical applications such as catalysis and photodynamic therapy, but the hurdle can be resolved via Pc fluorination.<sup>1</sup> A functionalized fluoro Pc,  $\text{F}_{48}\text{H}_7(\text{COOH})\text{PcZn}$  was purified through column chromatography and characterized by UV-Vis, HRMS and  $^{19}\text{F}$ NMR spectroscopies. Preliminary experiments reveal its antibacterial activity in DMF/  $\text{H}_2\text{O}$  solutions<sup>2</sup>. The coupling of the Pc with branched poly-lysines has been attempted and is currently in progress. The aim of this coupling is to enhance the water solubility of the photosensitizer.

**References**

1. Patel, P.; Patel, H.H.; Borland, E.; Gorun, S.M.; Sabatino, D., Chem. Commun. **2014**, 50, 6309-6311.
2. A. Yussof, unpublished results

**Acknowledgments:**

The Center of Functional Materials at Seton Hall University is gratefully acknowledged for financial support.

## **Synthesis, X-ray Structures, Photo-Physics and Singlet Oxygen Production of Fluorinated Phthalocyanines**

Marius Pelmus, Christopher Colomier, Hemant H. Patel, Olivia C. Xiao, Ralph Foglia, Marta Suazo, Sergiu M. Gorun\*

Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079

\*Correspondence should be addressed to: [sergiu.gorun@shu.edu](mailto:sergiu.gorun@shu.edu)

Fluorination is a common technique for enhancing the chemical inertness and thermal stability of organic molecules. This technique was applied in the production of robust phthalocyanines, catalytic and/or photocatalytic materials designed to function in harsh oxidative environments. As phthalonitriles are common phthalocyanine precursors, their fluorination is the preferred path for fluorine introduction in the phthalocyanine macrocycle. The susceptibility of fluorinated phthalonitriles to aromatic nucleophilic substitutions leads to functionalization options, the amino derivatives being the focus of this report. Amino fluorinated phthalocyanines comprise an electron donor  $\rightarrow$  acceptor substituents combination, which lowers the phthalocyanine efficiency for singlet oxygen photo production likely due the amino nitrogen lone-pair conjugation with the electron-deficient aromatic ring. Competitive conjugation of the lone-pair with a carbonyl group introduced via acylation weakens the donor effect of the amino group and thus enhances the catalytic efficiency of the phthalocyanines. By applying this strategy amino fluorinated phthalonitriles and phthalocyanines were converted to acetyl, bis-acetyl, succinyl, perfluoro-butyryl derivatives. Spectroscopic data and X-ray single-crystal determinations confirmed the synthesis results while providing atomic-level structural information for 4 acylated phthalonitriles and 6 acetylated phthalocyanines.



<b>Title</b>	Polyol conjugates of glutaric anhydride: precursors for clavulanate bioconjugates
<b>Authors</b>	Daniel M. Goldman and Dr. James E. Hanson

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

## Abstract

Potassium Clavulanate is an established antibiotic adjuvant of the semi synthetic penicillin Amoxicillin used in the treatment of gram negative bacteria. Commonly used in adults and children to treat infections of the urinary tract, respiratory tract, ear, sinuses, and skin. Common side effects of Amoxicillin Clavulanate are nausea, vomiting, headache, diarrhea, gas and stomach pain. The purpose of this research is to develop biopolymer conjugates of potassium clavulanate as suicide inhibitors that exhibit improved enzyme inhibition activity of the beta lactamase enzyme. A library of six polyhydroxy substrates consisting of phloroglucinol, myo-inositol, dipentaerythritol, xylitol, methyl alpha-D-glucopyranoside and glycerine were chosen to be esterified with glutaric anhydride and then coupled to potassium clavulanate. The initial reaction conditions for each individual substrate were 80 °C for sixteen hours with stoichiometric amounts of pyridine and glutaric anhydride. Characterization was done by  $^1\text{H}$  and  $^{13}\text{C}$  NMR. The bioconjugates will be evaluated by a *beta lactamase assay* protocol based on the hydrolysis of the substrate nitrocefin to evaluate inhibition activity.

**Title**

Quaternary Pyridinium Salts: Synthesis and Applications

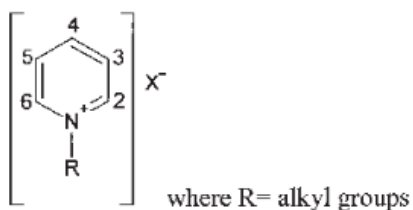
**Authors**

Usha Kalra and Dr. James E. Hanson

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

Quaternary pyridinium salts are compounds of high interest and can be found in many natural and bioactive compounds. Pyridinium salts show wide applications such as acylating agents and phase transfer catalysts, dyes, surfactants, cosmetics, pharmaceuticals, polymerization, catalysis, sensors and electrolytes. Apart from this, they also possess germicidal properties, and thus can be used in various other biological activities such as drug delivery and gene therapy and DNA binding. Our ultimate goal is to synthesize water soluble cationic porphyrin by using quaternary pyridinium salts. The most common method for the synthesis of pyridinium salt is a  $S_N2$  type reaction of pyridine with alkyl halides. The preparation of such pyridinium (N pyridyl benzaldehyde) moiety with triethylene glycol chain is described. Additionally, column chromatography is used to purify, and NMR technique is used to characterize the product. This research represents universal method for preparation and identification of quaternary pyridinium.

**References:**

- 1) Subbiah Sowmiah, José M. S. S. Esperança, Luís P. N. Rebelo and Carlos A. M. Afonso. Pyridinium salts: from synthesis to reactivity and applications. *Org. Chem. Front.*, 2018, 5, 453
- 2) Paraag Madaan, Vinod A. Tyagi. Quaternary pyridinium salts: A review. *J. Oleo Sci.* 57, (4) 197-215 (2008)

**Title**

Syntheses and Applications of Cationic Phthalocyanines

**Authors**

Taylor McKeever, Usha Kalra, Dr. James E. Hanson

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

Cationic phthalocyanines have exhibited significant functions in science, particularly as intercalating agents that fit within the double helix structure of deoxyribonucleic acid. Their application as intercalating agents is not their limit as they have many other applications such as in cancer treatment. The two syntheses of interest, methyl-3,4-dicyanopyridium iodide (MDCP-I) and 4,5-dicyano-1,3-dimethyl-3-H-pyrrol-1-ium (DiCNMH-pi), have been studied countlessly using different analyses. These analyses include Nuclear Magnetic Resonance, Infrared Radiation, and UV-VIS spectroscopy. Synthesis of cationic phthalocyanines is a process that is thorough and takes much scrutiny in the reactants used, experimental conditions, and contrasting procedural references. Each synthesis whether successful or incomplete has led to researchers performing adjustments in procedures in order to produce that best version of each product (MCD-I and DiCNMH-pi). Observations made during research presented potential in testing applications of cationic phthalocyanines. However, the most significant interest of this study is accurately determining success of using the product of both syntheses as intercalating agents and possibly in other applications of science.



**Title**

**Formulation and Evaluation of Antibiotic microspheres against Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus***

**Authors**

Miguel Medico <sup>a</sup>, Ayuni Yussof <sup>b</sup>, Dr. Tin-Chun Chu <sup>b</sup>, Dr. James E Hanson <sup>a,\*</sup>

*a) Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

*b) Department of Biological Sciences, Seton Hall University, South Orange NJ 07079*

**Abstract**

Plant-derived flavonoids are a large group of naturally occurring phenylchromones found in fruits, vegetables, tea, and wine. Flavonoids have shown to have a wide range of biological activities, including antiallergic, antibacterial, anti-inflammatory, antimutagenic, antioxidant, antiproliferative, antithrombotic, antiviral, and hepatoprotective effects. A certain flavonol glycoside has antiplatelet, antiviral, antihypertensive properties, as well as strengthen the capillaries of blood vessels. These properties are potentially beneficial in preventing diseases and protecting the stability of the genome. Erythromycin (ERY) is a bacteriostatic macrolide antibiotic. ERY is effective against skin and the upper respiratory tract infections caused by Gram-positive bacteria. Poly (DL-lactide-co-glycolide) (PLGA) has been approved for several biomedical applications in humans and is widely used for drug delivery. PLGA has been successful as a biodegradable polymer because it undergoes hydrolysis in the body to produce the original monomers, lactic acid and glycolic acid, which are metabolized in the Krebs cycle to produce carbon dioxide and water. In this investigation, the antibacterial and biological properties of flavonoid-PLGA and erythromycin-PLGA microparticles were studied. Two types of bacterial strains, *Staphylococcus aureus* and *Escherichia Coli* were chosen to evaluate the antibacterial activity of microparticles formed by solvent evaporation technique.

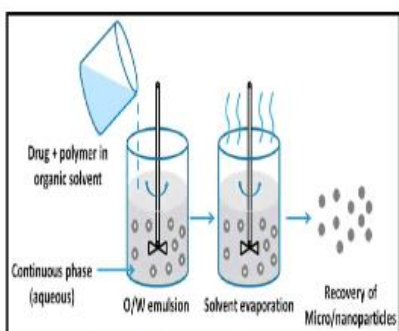
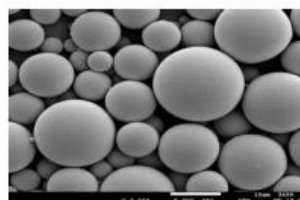


Figure 1: Solvent evaporation technique.



**Title**

Photoactive Polymer Composites

**Authors**

Edrice Sediq, Brandon Pineda, and Dr. James Hanson

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

Our research focused on the analysis of perfluorinated phthalocyanine photosensitizers ( $F_{64}PcZn$ ) coated onto titanium dioxide ( $TiO_2$ ) and embedded in a polysiloxane support to prepare a photosensitive surface. The photosensitivity of these surfaces was analyzed through the incorporation of varying dyes methyl orange being of interest. Over a three hour period of irradiation in front of visible light through a broad band light projector the methyl orange dye produces singlet oxygen  $^1O_2$  resulting in decomposition in aqueous solutions contacting the polymer surface. Further study is being performed to determine a proper polymer-solvent system through the sampling of polymers varying in fluorination and solubility in desired solvents. Upon preliminary analysis a 10% polysulfone in cyclohexanone solution produces a film which yields desired results with an aim for further testing in the means of contact angle determination. Future progress with the aforementioned surfaces involves analysis of a more "natural" photosensitizer.

<b>Title</b>	Surface Characterization of Blended Silica and C18 Adsorbents and Mixed-Mode Adsorbents by Low Temperature Nitrogen Adsorption
<b>Authors</b>	<u>Dinah Lee</u> , Yuri V. Kazakevich

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

## Abstract

Mixed-mode chromatography is becoming increasingly popular in pharmaceutical and biopharmaceutical applications due to its unique selectivity and retention of a variety of compounds [1]. Adsorbents with surface bonded ligands of different nature are used in mixed-mode chromatography. Solutes interact with those ligands through more than one interaction mode or mechanism. It is because of these complex interactions, however, that it is difficult to predict chromatographic behavior of analytes on mixed-mode columns. Characterization of different mixed-mode columns on the basis of surface energy characteristics has not been explored.

We selected formalistic normalization and indexation approach for characterization of these adsorbents. The most universal energetic characterization for highly different surfaces arguably could be C-constant of BET equation. According to Gregg and Sing [2] C-constant represent the exponent of the excessive energy of nitrogen-surface interaction over its condensation energy at 77 K. The mixtures of silica and C18-modified silica (Luna 5  $\mu$ m Silica - Phenomenex), and C18 (Luna 5  $\mu$ m C18 – Phenomenex), in the proportions where their surface area was incremented by 10% for each indexation point was chosen as index scale. C-constant of these mixtures were measured using Micromeritics nitrogen adsorption system.

A variety of commercially available mixed mode columns were unpacked and the materials were analyzed by LTNA. Adsorption isotherms, surface area, and BET constants were obtained for all the blended materials in various ratios and the mixed-mode materials. A linear relationship between the BET C-constant and the blend ratio of silica has been observed. The results from the commercial mixed mode packing material showed similar surface energy characteristics to single mode C18 materials. This data suggests that the BET C-constant maybe a viable parameter that can be used to characterize mixed-mode columns on the basis of surface energy. Chromatographic characterization will be performed by studying the retention behaviors of model analytes to illustrate the hydrophobic and hydrophilic properties of the blended stationary phases.

Utilizing this surface energy scale in conjunction with the study of retention behaviors on mixed-mode material could lead to improvements in the understanding of method development on mixed-mode columns, allow the comparison of commercialized mixed-mode columns, and even predict retention behavior of an analyte in mixed-mode columns.

## **Measuring Longitudinal Temperature Gradients under Ultra High-Performance Liquid Chromatography Conditions**

Timothy Nowak, Alexey Makarov, and Yuri Kazakevich  
Department of Chemistry and Biochemistry  
Seton Hall University

The usage of sub-2-micron particles in liquid chromatography is very popular in liquid chromatography since faster and more efficient chromatographic separations can be achieved in comparison to traditional (3 $\mu$ m, 5 $\mu$ m) particle size stationary phases. However, the reduction of the particle size leads to a significant increase in backpressure. In addition, heat is generated when the mobile phase passes through a column of finely packed particles. As the heat dissipates through the column, non-uniform temperature gradients can occur both along (longitudinal gradients) and across (radial gradients) the column. However, the environment surrounding the stationary phase bed influences the gradient temperature dissipation. In this study, we measure the longitudinal temperature gradients, while assessing its impact on the chromatographic behavior for several analytes.



**Title**

Impact of Perfluorination on Homonuclear One-bond  $^{13}\text{C}$ - $^{13}\text{C}$  Coupling Constants

**Authors**

Jeffrey Raab, Gary Martin, Stephen P. Kelty

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

The  $^1J_{\text{CC}}$  in benzene is 57Hz and the size of the coupling constant can be varied by adding substituents to the ring.<sup>1</sup> Depending on the substituent, the coupling constant can be raised significantly, which can be of great advantage; larger coupling constants correspond to shorter delays leading to smaller losses due to relaxation processes, giving correlations that are, in turn, easier they are to detect. Minimizing sensitivity losses is critically important in experiments that have intrinsically low sensitivity under the best circumstances. In 4-amino 3, 5, 6-trifluoro-phthalonitrile, some of the  $^1J_{\text{CC}}$  were observed to be in the range of 80 Hz using the INADEQUATE<sup>2,3,4</sup> pulse sequence confirming the substantial increase in the magnitude of the coupling constants as a consequence of perfluorination. This large increase in coupling constants may also be exploited in other NMR experiments affording better means of characterizing perfluorinated compounds.

## References:

- 1) Weigert F. J.; Roberts J. D. *J. Am. Chem. Soc.* **1972**, 94, 6021-6025.
- 2) Bax A., Freeman R, Kempell S. P *J. Am. Chem. Soc.* **1980**, 102, 14, 4849-4851.
- 3) Buddrus J.; Bauer H. *Angew Chem., Int. Ed.* **1987**, 26, 625-642.
- 4) Buddrus J.; Lambert J. *Magn Res. Chem.* **2002**, 40, 3-23.

<b>Title</b>	Greener synthesis of polyaromatic ligands based on a 1,2-diimine motif
<b>Authors</b>	William Kohman and David A. Laviska

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

## **Abstract**

The development of new materials for use in fluorescent and phosphorescent organic light emitting devices (OLEDs and PHOLEDs) continues to inspire interest in novel organometallic complexes that might have potentially unique photophysical properties. Our group has been working on applying the tenets of Green Chemistry to existing literature protocols for various coupling reactions in order to reduce additives and by-products while yielding bi- and polyaromatic molecules for use as ligands in transition metal complexes. Utilizing a high-yielding variation of a Schiff base condensation reaction, we are attempting to synthesize a family of ligands based on a 1,2-diimine motif. Starting with benzil (a 1,2-diketone) and two equivalents of aniline, we have synthesized 1,2-tetraphenylethane-1,2-diimine, though yields have not been reproducible and we are still in the process of optimizing the synthetic scheme, including microwave heating parameters. A range of additional reactants have been chosen that will yield a family of ligands based on the 1,2-diimine motif, and these molecules will be used in building cationic and neutral complexes of iridium and other later transition metals.

**Title**

Modifying the classic “benzoin condensation” reaction in order to synthesize a family of 1,2-diketones for use as building blocks in the synthesis of quinoxalines and related molecules

**Authors**

William Midolo and David A. Laviska

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

Our group has been working on applying the tenets of Green Chemistry to existing literature protocols for several coupling reactions in an effort to synthesize bi- and polyaromatic molecules for use as ligands in transition metal complexes. One particularly desirable class of compounds includes substituted quinoxalines; these molecules have been shown to be useful as ligands in complexes with remarkable photophysical properties. Quinoxalines are heterocyclic aromatic compounds that can be synthesized from 1,2-diketones such as benzil and aromatic diamines such as 1,2-phenylenediamine. Other related target molecules include substituted benzoquinoxalines and pyrazines, and members of our research group are currently optimizing syntheses of these species using established protocols and commercially available starting materials. Since emissive tunability (both steric and electronic) of the ultimate metal complexes relies on ligand substituents, we would like to synthesize a broader range of starting reactants than those that are currently available from commercial suppliers. To that end, results from preliminary attempts to broaden the scope of the classic “benzoin condensation” reaction to build new 1,2-diketones from a range of substituted aldehydes will be presented.

<b>Title</b>	Designing a comprehensive sequence of experiments around a single renewable molecule: Using furfural as a platform for teaching synthetic organic chemistry
<b>Authors</b>	Kyle Otto and David A. Laviska

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

## **Abstract**

Over the past year, several members of our research group have focused on curricular development in support of a new Green Chemistry Initiative. Specifically, we have worked on piloting and/or modifying green(er) experimental protocols taken from the literature for implementation in our organic chemistry teaching laboratories. One well-known protocol involves substituting the renewable aldehyde furfural for benzaldehyde in the classic benzoin condensation; we now include a modified version of this green(er) “furoin condensation” in our teaching sequence. Since aldehydes are versatile molecules and renewable reagents are highly desirable, we decided to explore other reactions using furfural as a starting point. Based on promising preliminary results with a couple of syntheses (aldol condensation, pinacol coupling), we realized that the scope of reactions could be expanded to encompass experiments that illustrate most of the concepts taught throughout second-semester organic chemistry. In thinking about helping students make connections between different classes of reactions, we also realized that a common starting material (or derivative) could serve to underline the relationships between broad reaction classes (oxidation/reduction, acid/base catalysis, etc.). Therefore, we are currently in the process of developing a comprehensive lab sequence designed entirely around furfural. Preliminary results and our future plans will be presented.



**Title**

Greener protocols for synthesizing substituted quinoxalines for use as cyclometallating ligands in transition metal complexes

**Authors**

Anthony Rodriguez and David A. Laviska

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

Quinoxalines are heterocyclic aromatic compounds (also known as benzopyrazines) and represent an important structural motif; quinoxaline derivatives are used as components of commercial dyes and are found in an array of pharmaceutical compounds. They are also of keen interest to our group due to their potential for acting as mono-, di-, and even tridentate ligands in transition metal complexes. In order to explore the physical and chemical properties of these ligands, we have synthesized a series of substituted quinoxalines using a newly-developed protocol that is significantly greener than literature precedents. Details of the methods will be presented, including the use of microwave heating which drastically reduces the reaction times, gives good-to-excellent yields, and high product purity. After synthesizing and fully characterizing 2,3-diphenyl-, 2,3-difuranyl-, and 2,3-dipyridylquinoxalines, we broadened the scope of the reaction to include a diverse array of substituents, focusing on fluorinated analogs. With a family of ligands in hand, we have begun synthesizing and characterizing novel hetero- and homoleptic metal complexes (also employing greener methods); preliminary results of these studies will be presented.

**Title**

Synthesis and characterization of a family of benzoquinoxalines for use as ligands in transition metal complexes

**Authors**

Andi-Kaye Walters and David A. Laviska

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

New materials for use in state-of-the-art organic light emitting devices (OLEDs) are being vigorously researched, and organometallic complexes of iridium and other late transition metals hold great potential due to their highly desirable photophysical properties. While the choice of transition metal is a critical determinant of emissive properties, it is the surrounding ligand system that affords the ability to fine tune to desired wavelengths, and therefore colors, of light production. Polyaromatic heterocycles such as quinoxalines have been extensively studied when used as bidentate ligands in tris-ligated (homo- or heteroleptic), octahedral metal complexes. Our group has developed an improved, greener synthesis of these molecules and other related systems such as benzoquinoxalines – a slightly larger molecule with five aromatic moieties. As a family of ligands, the benzoquinoxalines have been significantly less studied, but represent an extension of conjugation that may lead to interesting emissive properties. To date, we have successfully synthesized a family of seven benzoquinoxalines and started utilizing them as ligands in complexes of iridium. Details of the synthesis and characterization of the ligands and metal complexes will be presented.

**Title**

Synthesis of carbohydrate analogs as potential CNS therapeutic agents

**Authors**

Anne Francine A. Pino, Dr. Cecelia Marzabadi

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

Disorders of the Central Nervous System (CNS) are alarmingly increasing as the human population is gradually aging. With this concern, CNS disorders affect people of all race, gender, and ages. Diseases such as epilepsy, addiction, bipolar disorder, and Parkinson's are causes for major concern and research to treat and possibly prevent these diseases. Carbohydrates are one of the most abundant natural chemical compounds. They are known for their availability as well as their versatility when it comes to applications and synthesis. We propose to synthesize carbohydrate derivatives via glycals, to surpass the blood brain barrier in hopes of treating CNS disorders. We will be building positive results from previously synthesized compounds. Our research consists of preparing modified carbohydrates that bear more robust 4,6-acetal derivatives. Derivatives synthesized will be tested in receptor and animal models for CNS disease.

**Title**

Synthesis of Bridging Ligands via Microwave Reactions for use in Photodynamic Therapy

**Authors**

Rebecca S. Gilchrist\*, Allyson N. Dixon and Dr. Wyatt R. Murphy

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

Chemotherapy makes up a large part of the regimen doctors and other health care professionals use in order to treat cancer. Most patients who undergo chemotherapy are treated with platinum-based drugs. Despite their widespread usage, platinum-based drug therapy has presented several major drawbacks. These include drug resistance, a limited spectrum of action, and severe side effects in the patient.

Our research group has decided to investigate the use of alternative transition metals, such as iridium, to be used as central ions within a bimetallic antitumor organometallic compound. In order to do so, known and novel bridging ligands were synthesized using microwave conditions. These include the 2,3-di-(2'-pyridyl)quinoxaline derivatives. Ir(III) complexes display rich photophysical properties and high quantum yields overall. Iridium cyclometalated complexes are known for their stability. However, ligand-bridged bimetallic Ir(III) complexes are relatively unexplored, unlike Ru(II) and Re(I).

Microwave synthetic conditions were used in order to minimize reaction times. A minimization in reaction time allows for faster screening of the reaction conditions, which leads to an increase in the over productivity of the research. Use of the microwave reactor also allowed our research group to maintain a green chemistry approach to ligand synthesis, as multistep reactions could be carried out in a single reaction flask, avoiding wasteful reaction-isolation-purification-reaction cycles. The greener synthesis of products from these laboratory experiments aims to minimize the amount of waste generated, lower the quantity and therefore the cost of materials, and utilize safer, nontoxic reagents.

**Title** Microwave synthesis and electrochemical characterization of novel heteroleptic Ir(III) cyclometallated complexes with C<sup>N</sup> ligands and N<sup>N</sup> cuproine derivatives

**Authors** Alexa Skalski, Allyson Dixon, Wyatt R. Murphy Jr.

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

## **Abstract**

Organic Light Emitting Diodes (OLEDs) and Light Emitting Electrochemical Cells (LECs) are of increasing interest due to their ability to serve as displays and alternative light sources. A library of heteroleptic iridium complexes were synthesized using modified and newly developed microwave reactor techniques. These synthetic methods are greener, utilizing more benign solvents, less energy, higher yields and minimal use of chromatographic separations. Various C<sup>N</sup>-cyclometalating ligands, and N<sup>N</sup>-donative ligands were utilized in the complex ion structures. Cuproines are 2,2'-bipyridine and 1,10-phenanthroline derivatives with substituents that induce steric crowding around the metal ion. Photophysical and electrochemical data of the complexes offer insight to the difference in excited states of complexes when ligands are changed. These data will include absorption and emission spectra, radiative quantum yields and excited state lifetimes.



**Title**

Preparation of OLED Phosphors via Green Chemistry Methods

**Authors**

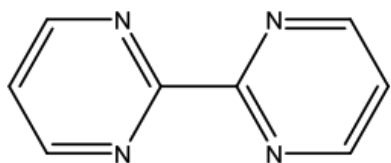
Nataly Areosa Suarez, Florian Balan, Dr. Wyatt Murphy

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

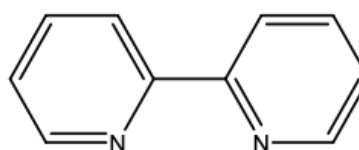
**Abstract**

Since the original discovery of this unique bifunctional interaction, a rich chemistry of homo- and heteroleptic complexes of Ir(III) with cyclometallating ligands such as 2-phenylpyridine involving simultaneous metal-nitrogen and metal carbon bonds has advanced. These reactions require reflux times of 18 to 24 hours, which impedes rapid progress. A developing area of chemistry involves the use of commercial microwave chemical reactors to conduct the reactions in significantly shorter periods while minimizing environmental damage. The Department of Chemistry and Biochemistry is also incorporating green chemistry principles into the curriculum. In accordance with this goal, an evaluation of microwave reactors from several manufacturers was made by the Murphy research group, along with developing new microwave-based reaction conditions. From this, the group explored their first step, which involved reproducing the Monos procedure with 2-phenylpyridine (ppy) to learn how to use the microwave reactor. As the conditions are now known, the skills required to perform microwave synthesis are more efficient.

Now, the two specific ring ligands shown below are being explored:



2,2'-bipyrimidine



2,2'-bipyridine

Thus,  $[\text{Ir}(\text{ppy})_2(2,2'\text{-bipyrimidine})](\text{PF}_6)$  and  $[\text{Ir}(\text{ppy})_2(2,2'\text{-bipyridine})](\text{PF}_6)$  were prepared via microwave techniques based on the knowledge and experience gained from the previous laboratory experiments. As for future plans, each complex developed will be characterized by elemental analysis, NMR spectroscopy, and electronic spectroscopy. In both cases, the possibility of either  $\text{N}^{\wedge}\text{N}$  or  $\text{C}^{\wedge}\text{N}$  bonding is possible. NMR spectroscopy will be crucial in determining which mode of coordination will occur.

**Title**

**Self-assembly of higher-order siRNAs and their Bioconjugates for Silencing the Glucose Regulated Chaperones in Cancer**

**Authors**

Sunil S. Shah<sup>1</sup>, Gina L. Antuono<sup>1</sup>, Vanessa E. Colmenares<sup>1</sup>, Adah E. Beck<sup>1</sup>, Jorge A. Ramos<sup>2</sup>, Uri Samuni PhD<sup>2</sup>, Jenny Zilberberg, PhD<sup>3</sup> and David Sabatino, PhD<sup>1\*</sup>

1. Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079
2. Department of Chemistry and Biochemistry, Queens College, CUNY Flushing NY 11367 & PhD Programs in Chemistry and Biochemistry, The Graduate Center, CUNY New York NY 10016
3. Center for Discovery and Innovation, Hackensack University Medical Center, Nutley NJ 07110

**Abstract**

The Glucose-regulated proteins (GRPs), are a class of chaperone proteins of the endoplasmic reticulum that serve as key sensors for misfolded proteins and trigger the unfolded protein response (UPR) under physiological and pathological stress conditions. Moreover, GRPs have been found to be over-expressed and cell surface localized in a wide range of cancer types, where they regulate cancer initiation, proliferation, adhesion and invasion which contributes to metastatic spread and resistance. Thus, the GRPs have been classified as clinically relevant biological markers in cancer detection and treatment. Short-interfering RNA (siRNA) are among the most commonly used gene therapeutics due to their ability to silence oncogenic mRNA expression and potentially inducing cancer cell death through the RNA interference (RNAi) pathway. Towards this goal, our research program has pioneered a versatile solid phase synthesis strategy for the generation of linear, branch and hyper-branch RNA templates that have been used to self-assemble high-order siRNA nanostructures and for the incorporation of biological probes (ex. fluorophores, metals and fatty acids) for potentiating cancer detection and treatment. Furthermore, cell penetrating and targeting peptides (CPPs and CTPs) are currently being developed for optimizing siRNA delivery applications. Taken together, these new siRNA constructs represent the next generation of more efficient siRNAs for screening important oncogene targets for cancer gene therapy applications.

Reference:

Cultrara CN, Shah S, Kozuch SD, Patel MR, Sabatino D. Solid phase synthesis and self-assembly of higher-order siRNAs and their bioconjugates. *Chem Biol Drug Des.* 2019; 93(6):999-1010.

## **FINITE DIFFERENCE STUDIES OF PEAK SHAPES AND SIMULATION MODELS OF HPLC AND GC PEAKS IN CHROMATOGRAPHY: A COMPARATIVE STUDY**

Nicole Charles

Mentor: Dr. Nicholas Snow

Department of Chemistry and Biochemistry (Seton Hall University)

Chromatography simulation models present various capabilities, such as modeling the effects of pressure programming, column dimensional changes, serially coupled columns, and peak broadening. Optimization of these models aims at improving the process performance based on the current modelling and providing general guideline or trends for the separation systems. A novel VBA simulation software has been developed in-house to run in Microsoft Excel and to generate a numerical representation of the chromatographic peak shape. This software uses four dimensionless input parameters to generate a numerical representation of each peak and computes its characteristics such as  $t_R$ ,  $\sigma^2$ ,  $k'$ , and the USP peak tailing factor. Statistical moment analysis is employed to compute the retention time and variance of each peak along with tailing factor.

The aim of this study is to demonstrate how this new program compares with other HPLC and GC simulations programs in particular EZGC, DryLab and other programs currently available online. In this work, chromatography data will be acquired for compounds such as caffeine and phenol that have previously shown to exhibit tailing peaks within the right conditions. Results obtained will be then compared with outputs from the readily available Restek EZGC simulation software as well as others, in the hope to better understand linear elution strength model. We also plan to compare the separation performance through our simulation and optimization in order to better understand why a given operational mode perform better or worse than other readily available chromatography programs. In this manner, the proposed methodology could provide complete insights into some principle mechanisms of separation techniques.



## Using Thermodynamics to Evaluate Stationary Phase polarity in Gas Chromatography.

Hetal Rana and Nicholas H. Snow

Department of Chemistry and Biochemistry

Gas chromatography is a separation method in which the components of a sample partition between a stationary phase and a mobile phase (carrier gas). The stationary phase is usually a polymer coated or chemically bound to a solid support or the column wall and its function is to separate different components, based on their relative vapor pressure and their intermolecular interactions with the stationary phase. If the sample polarity is similar to the stationary phase polarity, then the retention time increases because the intermolecular interactions are stronger and if the polarities are different then its retention time decreases.

Generally, the polarity of a stationary phases is calculated by determining phase constants using five probes namely: Benzene, 1-butanol, 2-pentanone, 1-nitropropane, and pyridine. These are termed McReynolds Constants. The Kovats retention index of each probe on the stationary phase of interest is determined and then compared to the retention indices on squalane to determine the McReynolds constant for that probe. The five McReynolds constants can summed to obtain polarity values and calculate an overall polarity number. This method has some limitations, including the use of squalane, which is not readily available, as the standard stationary phase. In the present work, Van't Hoff plots are used to determine the thermodynamic quantities:  $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta(\Delta G^\circ)$  for the McReynolds test probes and alkanes on polar and non-polar columns. Considering ZB-1 as reference other stationary phase are evaluated using thermodynamic retention indexes. This value provides a more general means for comparing stationary phase polarity and using thermodynamics to estimate whether a given stationary phase will be selective for a proposed separation.

**Title**

Polyol-induced Extraction of Glucocorticoids from water

**Authors**

Shipra Patel, Dr Nicholas H Snow

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

Polyol-induced Extraction is used for the extraction and analysis of glucocorticoids. Polyol-induced extraction is an extraction technique developed and patented by Drs. John Sowa, Wyatt Murphy, and Mithilesh Deshpande at Seton Hall University, as a technique for extracting water from mixtures with polar organic liquids or the reverse. In Polyol-induced extraction, a solvent mixture of acetonitrile and water can be separated by adding a polyol mass separating agent such as glycerol, sorbitol, erythritol, xylitol etc. The focus of this work is to demonstrate polyol-induced extraction as an effective extraction technique in trace analysis of drugs. In this work Glycerol is used as a mass separating agent in the extraction of glucocorticoids from water into polar organic solvents. Seven different glucocorticoids were extracted by polyol-induced extraction and analyzed by Gas chromatography. Percent recovery and partition coefficients were determined for each glucocorticoid. The glucocorticoids studied included beclomethasone, cortisone acetate, prednisone, hydrocortisone, prednisolone, dexamethasone, and methyl prednisolone. Extraction was performed at 0°C, in 1:1 ACN/Water mixture using 20% Glycerol. All seven glucocorticoids were extracted with percent recovery ranging from 93.8 to 97.1%.

**Title**

Re-examination of Gas Hold-up Time in Gas Chromatography

**Authors**

Sean McCann & Nicholas Snow

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

In gas chromatography, the gas hold-up time ( $t_m$ ) is the time required for an unretained compound to elute from the column. It is a function of several physical parameters: carrier gas viscosity ( $\eta$ ), the column dimensions ( $L$  and  $r$ ), the inlet and outlet pressures ( $P_i$ ,  $P_o$ ) and their ratio ( $P$ ). Over the temperature range in GC, the exponential relationship between gas viscosity and temperature approximates as linear (at constant pressure), so if the retention time of a substance increases linearly with temperature, then the substance is unretained, and can be used for gas hold-up time measurement. This relationship has been utilized within this research to present other compounds to deduce gas hold-up time. Other compounds are needed since the commonly used ones: methane and butane, cannot be injected without removing the attached autosampler present on almost all gas chromatographs. Thus, research was done into the effectiveness of other compounds, as well as an overall presentation of different methods for gas hold-up time acquisition throughout the literature in order to re-examine it for a clearer picture. Multiple compounds on multiple columns were found to be suitable for  $t_m$  measurement, and the analysis of the literature allowed the new data to be shown in a broader scope.

### **Microwave Peptide Synthesis for Frenatin 2.3**

Elizabeth Boyer\*, Makayla Manfredi, Axel Martinez, and Dr. Gregory Wiedman  
Department of Chemistry and Biochemistry, Seton Hall University, South Orange, NJ 07079

Frenatin 2.3, a peptide with the amino acid sequence GLVGTTLLGHIGKAILG, may serve as an emulsifier to remove oil contamination from water. This experiment focuses on synthesis by microwave as a method to improve the efficiency of creating Frenatin 2.3 as compared to solid-phase peptide synthesis by hand. The processes of solid-phase peptide synthesis, microwave peptide synthesis, and a combination of both were used throughout this experiment. It was hypothesized that an increase in total yield and crude purity, but a decrease in the time of synthesis were expected when Frenatin 2.3 was synthesized by microwave rather than solid-phase synthesis by hand. Through the process of microwave synthesis, the deprotection process was approximately 1.5 minutes. Oxyma and Diisopropylcarbodiimide were used to couple the peptide in 4 minutes. In contrast, in solid-phase peptide synthesis by hand deprotection took 20 minutes and coupling one hour. Each amino acid only required coupling once by microwave, unlike solid-phase peptide synthesis. By hand, some amino acid needed to be coupled two to three times because coupling was not complete after one round. 73 hours were required for complete Frenatin 2.3 synthesis by hand. In contrast, Frenatin 2.3 synthesis was complete in 1.5 hours in the microwave synthesizer. These results suggest that the heat from the microwave allowed the coupling process to be accelerated and synthesis was able to occur more efficiently. Due to time constraints, the yields of the peptides done by each process were unable to be analyzed. As a result, the crude purity of each peptide was also unable to be analyzed. Future experiments will focus on analysis and purity of Frenatin 2.3 peptides via both methods.

## **Microwave Peptide Synthesis and Solid Phase Peptide Synthesis for Frenatin 2.3**

Makayla Manfredi\*, Elizabeth Boyer, Axel Martinez, and Gregory Wiedman

Department of Chemistry and Biochemistry, Seton Hall University, South Orange, NJ 07079

The peptide Frenatin 2.3 has been hypothesized to be used as an emulsifier to remove oil contamination from water. As there is an increase in demand to synthesize peptides this has caused an influx of research to decide the best methodology to determine the yield, crude purity, and total length of time. The basic methods being tested are solid-phase peptide synthesis, microwave peptide synthesis, and a combination of both to see which process generated the most efficient product. In the synthesization of Frenatin 2.3, it was hypothesized by using microwave irradiation the quality and purity of the peptide would increase while the time to synthesize would decrease. The total time for solid phase peptide synthesis was about 73 hours whereas the microwave peptide synthesizer took about 88 minutes to create the peptide chain. In the microwave synthesizer, the coupling system included Oxyma and Diisopropylcarbodiimide where the solid-phase peptide synthesis included Dimethylformamide, Dichloromethane, and Methanol chemicals. Using the microwave synthesizer, the cycle for deprotection was 1.5 minutes and coupling was 4 minutes; in solid-phase synthesis deprotection was 20 minutes and coupling was 1 hour. For the analytical component such as HCPC and mass spec tests, the results are pending and will be completed as a future project. In conclusion, only part of the hypothesis was able to be concluded, the total amount of time was drastically reduced between the two main methodologies. Although the peptide created in the microwave synthesizer was only a test of 2X amino acids instead of 5X, it was determined that this method was more efficient.



**Title**

Aptamers towards West Nile virus spike protein blocking drugs

**Authors**

Abigail Richter\*, Marinelle Geda, Dr. Gregory Wiedman

*Department of Chemistry and Biochemistry, Seton Hall University, South Orange NJ 07079*

**Abstract**

The purpose of this research is to use SELEX to sequence an aptamer that binds with high efficiency to a spike protein found on the West Nile virus.

The West Nile Virus (WNV) operates through a spike protein to inject its genetic material into cells to replicate, and by determining an aptamer that blocks the spike protein, the virus would not be able to replicate. The spike protein was built on Rink Amide resin using Solid Phase Peptide Synthesis, and the peptide was then used to label carboxyl magnetic beads. Using PNP, the extent of labeling was checked and determined to be 92.81  $\mu\text{mol}$ . The N-40 DNA library was used as the initial DNA pool for SELEX, incubated with the magnetic beads, and washed to remove DNA that did not show affinity towards the peptide. The DNA left was then eluted and reamplified using PCR, an absorbance at 260 nm was taken, and if a high peak was present, the next round of SELEX was performed. A total of 5 rounds of SELEX were able to be performed, and a peak was present in the final round.

The DNA was becoming more selective, so the SELEX process for WNV can be continued at a later time.



**Dr. Matthew Petersheim**  
**1953-1998**