April 9, 2022

20th Raymond N. Castle Student Research Conference

#usfchemistry

University of South Florida
Department of Chemistry

20th Raymond N. Castle Student Research Conference

Saturday, April 9th, 2022

Department of Chemistry, University of South Florida

Table of Contents

Agenda

Breakfast and Registration *(ISA 7th Floor)*	08:00am - 09:00am
Oral Session A *(ISA 3048)*	09:10am - 11:20am
Oral Session B *(ISA 3050)*	09:10am - 11:20am
Oral Session C *(ISA 2023)*	09:10am - 11:20am
Lunch *(ISA 7th Floor, Chipotle)*	11:30am - 01:30pm
Poster Session *(ISA 7th Floor)*	12:15pm - 01:45pm
Oral Session D *(ISA 1051)*	02:00pm - 04:10pm
Oral Session E *(ISA 1061)*	02:00pm - 04:10pm
Castle Introduction *(ISA 1061, Edward Turos, Ph.D.)*	04:20pm - 04:40pm
Plenary Presentation *(ISA 1061, Hans Renata, Ph.D.)*	04:40pm - 05:40pm
Award Ceremony *(ISA 1061)*	05:45pm - 06:00pm

Remembering Raymond N. Castle

Raymond N. Castle was born on June 24, 1916 in Boise, Idaho where he attended Boise High School and Boise Junior College. A 1938 graduate in Pharmacy from the University of Idaho, Southern Branch in Pocatello, he completed the M.A. degree in Chemistry at the University of Colorado at Boulder in 1941. Shortly thereafter, he became a Chemistry instructor at the University of Idaho and then in 1943, returned to the University of Colorado in Boulder for a Ph.D. in Chemistry with a minor in Microbiology. After two years as a research chemist at the Battelle Memorial Institute in Columbus, Ohio, Dr. Castle accepted a position at the University of New Mexico as an Assistant Professor of Chemistry. He served as Chairman of the Chemistry Department from 1963 until 1970 before moving to Brigham Young University as Professor of Chemistry.

In 1981, Dr. Castle joined the faculty at University of South Florida as a Distinguished Research Professor. He and his wife, Ada, were a vibrant part of the Chemistry Department and for many years sponsored the Castle Lecture Series, which brought in numerous prominent scientists for lectures at USF .

A prolific researcher, Dr. Castle was an internationally recognized father figure in heterocyclic chemistry, both for his research and his involvement in meetings, symposia, and editorial boards. In 1964, he founded the Journal of Heterocyclic Chemistry and served as its editor. He also edited the Lectures in Heterocyclic Chemistry series, a publication of plenary lectures given at the International Congresses of Heterocyclic Chemistry and was the American advisory editor for the English translation of the Russian Journal of Heterocyclic Compounds. He lectured at hundreds of institutions worldwide. He was General Chairman of the First International Congress of Heterocyclic Chemistry held in Albuquerque (1967), Secretary of the Second International Congress held in Montpellier, France (1969), and Vice-President of subsequent Congresses held in Sendai, Japan, Salt Lake City, Utah, Ljubljana, Yugoslavia, and Tehran, Iran. Dr. Castle was also Chairman and Committee Member for the American Chemical Society. In addition, he was cofounder of the International Society of Heterocyclic Chemistry, which he served as Chairman of the Executive Committee, and President (1973-1975). Professor Castle received numerous awards and honors, including the prestigious International Award in Heterocyclic Chemistry (1983) for outstanding contributions to the field of heterocyclic chemistry, presented in Tokyo, Japan. Dr. Castle was listed in the first edition of Who's Who in Science and in Who's Who in the World.

The Chemistry Department remains deeply indebted to Professor Castle for his many outstanding contributions to the Department, and to science overall. He would have been a strong supporter of this student symposium, and thus, it is fitting that we dedicate this and future symposia to his memory.

Special Thanks

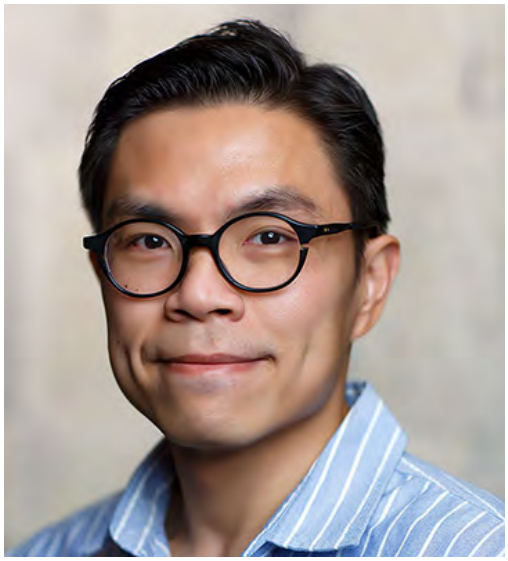
Dr. Dean F. Martin is Distinguished University Professor Emeritus and Director of the Institute for Environmental Studies at the University of South Florida, where he has been a member of the faculty since 1964. Dr. Martin received his B.A., with Honors, from Grinnell College (1955), where he met his future wife Barbara while both were chemistry majors. They were married in 1956 while both attending Pennsylvania State University as graduate students and in 1958 Dr. Martin received his Ph.D. and Mrs. Martin her Master's degree. In 1958-59, he was a National Science Foundation Post-Doctoral Fellow at University College, London after which he returned to the States and accepted a faculty position at the University of Illinois, Urbana-Champaign, as Instructor and Assistant Professor of Inorganic Chemistry (1959-1964). He received (1969-1974) a Career Development Award from the Division of General Medical Sciences, NIH, to study the chemistry and chemical environment of algal toxins. In 1970-71, he was a Visiting Professor of Physiology and Pharmacology at Duke University Medical Center.

Dr. Martin and his wife share research interests concerned with coordination chemistry in natural water systems, including problems of red tide and aquatic weeds. Currently, they are investigating the removal of metals and organic compounds from water by means of supported chelating agents. Dean Martin is the author or co-author of over 300 publications, including four books. He was the recipient of the 1975 Florida Award and the 1987 Civic Service Award of the Florida Section, ACS; in 1978, he received the F. J. Zimmermann Award in Environmental Science from the Central Wisconsin Section, sponsored by Zimpro Inc.; and in 1983, he was elected Fellow of the American Association for the Advancement of Science. Dean and Barbara Martin were the co- recipients of the 1994 Medalist Award of the Florida Academy of Sciences, its highest award. Dean Martin has been active in the Florida Section of the American Chemical Society (Chairman, 1986), and he has held several positions in the Aquatic Plant Management Society (President, 1986-87). Both of the Martins have received the Alumni Award of Grinnell College.

The Martins have endowed six chemistry funds, including the George Bursa Award, given annually to a deserving graduate student within the Chemistry Department who has demonstrated notable professional dedication and consideration for others, as well as a Graduate Student Travel Award. Together the Martins have edited Florida Scientist since January 1984 and are now Editors Emeriti. Dr. Martin initiated and continues to edit the departmental newsletter and has written a departmental history to coincide with the 40th Anniversary of the founding of the department.

The Martins have six children; Diane, Bruce, John, Paul, Brian, and Eric, and seven grandchildren.

Plenary Speaker, Hans Renata Ph.D.



Professor Hans Renata is an associate professor at Scripps Florida. Prior to his independent career, he trained with Prof. Phil Baran in natural product total synthesis and Prof. France Arnold in enzyme engineering and its application in biocatalysis. Research in the Renata lab is focused on the development of new biocatalysts for C—H oxidation and their applications in the chemoenzymatic synthesis of bioactive natural products.

A central theme in this direction is the design of chemoenzymatic strategies towards unusual peptides and highly oxidized terpenes that features unusual but powerful disconnections by taking advantage of the unique selectivity profile of natural and engineered enzymes. Additionally, his lab is also interested in adapting their chemoenzymatic approaches in the generation of useful compound analogs and chemical probes to study disease-relevant processes. In this area, his lab has been exploring the pharmacology, structure-activity relationships and cellular target specificity of two highly modified peptide natural products, GE81112 B1 and cepafungin I.

For his research contributions, Professor Renata has been recognized with several awards, including the NIH Maximizing Investigators' Research Award, the NSF CAREER award, the Sloan Fellowship and the Chemical and Engineering News Talented 12 award.

Plenary Presentation

Combining Synthetic Chemistry and Biology for Streamlining Access to Complex Molecules

By virtue of their unrivaled selectivity profiles, enzymes possess remarkable potential to address unsolved challenges in chemical synthesis. The realization of this potential, however, has only recently gained traction. Recent advances in enzyme engineering and genome mining have provided a powerful platform for identifying and optimizing enzymatic transformations for synthetic applications and allowed us to begin formulating novel synthetic strategies and disconnections. This talk will describe our recent efforts in developing a new design language in chemical synthesis that centers on the incorporation of biocatalytic approaches in contemporary synthetic logic. Case studies will focus on the use of this platform in the chemoenzymatic syntheses of complex natural products and also highlight how this platform could serve as a starting point to enable further biological and medicinal chemistry discoveries.

Oral Session Breakdowns

Oral Session A (ISA 3048)

Barbara Chiu	*09:10am - 09:30am*
Jessica Young	*09:35am - 09:55am*
Ashton Taylor	*10:00am - 10:20am*
Intermission	*10:20am - 10:35am*
Nathan Grimes	*10:35am - 10:55am*
Steven Soini	*11:00am - 11:20am*

Oral Session B (ISA 3050)

Cole Gibson	*09:10am - 09:30am*
Alexander Mariscal	*09:35am - 09:55am*
Gina Pantano	*10:00am - 10:20am*
Intermission	*10:20am - 10:35am*
Ankai Wang	*10:35am - 10:55am*
Herrmann Antoine	*11:00am - 11:20am*

Oral Session C (ISA 2023)

Intermission	*09:10am - 09:35am*
Harriet Thompson	*09:35am - 09:55am*
Yafeng Wang	*10:00am - 10:20am*
Intermission	*10:20am - 10:55am*
Benjamin Smith	*11:00am - 11:20am*

Oral Session D (ISA 1051)

Sean Bradley	*02:00pm - 02:20pm*
Krishna Yadavalli	*02:25pm - 02:45pm*
Ruixuan Gao	*02:50pm - 03:10pm*
Intermission	*03:10pm - 03:25pm*
Mohammad Nazmus Sakib	*03:25pm - 03:45pm*
Joshua Welsch	*03:50pm - 04:10pm*

Oral Session E (ISA 1061)

Rose Pittman	*02:00pm - 02:20pm*
Matthew Saunders	*02:25pm - 02:45pm*
Julian Melendez	*02:50pm - 03:10pm*
Intermission	*03:10pm - 03:25pm*
Paul Orndorff	*03:25pm - 03:45pm*
Nicole A. Miller	*03:50pm - 04:10pm*

Oral Presentation Abstracts (Morning Session A)

Utilizing the MAtCH Model to Analyze Student Problem-Solving

Within the field of chemistry education, problem-solving has been recognized as an important skill lacking in many undergraduate students. Due to the overuse of algorithmic questions in exams, students have difficulty approaching conceptual problems that require them to apply previous knowledge to novel situations. The MAtCH model (methods, analogies, theory, context, and how) was recently developed to outline components of expert explanations of their research. This model was applied to transcripts of undergraduate students solving three open-ended problems in a think-aloud protocol to gain a deeper understanding of where they lack proficiency, as well as suggested implementations for chemistry classrooms. This presentation will discuss the revisions needed to adapt the model definitions and further investigate the elements of promoted and impeded student problem-solving found from the coding.

Presented by: Barbara Chiu *(Undergraduate, Chemistry Education)*

An evaluation of online Peer-Led Team Learning to promote student success

This presentation seeks to examine the effectiveness of peer-led team learning (PLTL) pedagogy when it is implemented in an entirely online environment. Previous evaluations of PLTL demonstrated effectiveness of this pedagogy when used with in-person teaching, but an online environment is expected to pose unique challenges to students, and therefore, past work may not generalize to online environments. In a General Chemistry II (GCII) course where sections were taught using either an Online-Didactic pedagogy or an Online-PLTL pedagogy, an evaluation on students GCII test scores and pass rates was performed. Test scores tended to be higher for Online-PLTL students than Online-didactic students. As well, Online-PLTL students had a higher likelihood of earning a passing grade in the course which corresponded to a lower proportion of students withdrawing from the course. The results indicate that PLTL was an effective instructional technique at the research setting.

Presented by: Jessica Young *(Graduate, Chemistry Education)*

Acoustic Disruption and Neutralization of Lipid Vesicles for Mass Spectrometery Analysis

Analyzing lipid assemblies, including liposomes and extracellular vesicles (EVs), is challenging due to their size, diverse composition, and tendency to aggregate. The use of mass spectrometry (MS) allows for broad analysis of lipid classes. However, current sample preparation methods, including the use of detergents, may not account for the variability of these lipid assemblies. Meanwhile, such vesicles form with simply a lipid bilayer membrane and play important roles in drug discovery and delivery. We investigate the effects of high frequency surface acoustic waves (SAW) to lyse and fragment lipid assemblies to facilitate direct MS analysis using by corona discharge (CD). DOPC derived liposomes served as the model lipid assembly for our investigation. SAW chips were

commercially sourced from Deurion and were also used as the nebulization source. Various higher frequency SAW chips were fabricated in-house at frequencies ranging from 16-98 MHz.

Presented by: Ashton Taylor *(Graduate, Analytical Chemistry)*

Vapor Modifier Control to Enhance FAIMS Analysis with Mass Spectrometry

In Field asymmetric ion mobility spectrometry (FAIMS) the incorporation of vapor phase modifiers into the carrier gas creates a platform where a variety of chemical interactions can be exploited to increase the separation between compounds. Previously, we have demonstrated improvements in the analysis of fentanyl and related compounds through the addition of a water vapor modifier showing strong promise for forensic applications. The identification of chemical chirality of complex organic compounds, such as amino acids, via FAIMS-MS has been shown to be possible by incorporating a chiral complexing agent (BBS) that differentially binds to different enantiomeric forms. Addition of a chiral vapor phase modifier enhances the separative capabilities leveraged with FAIMS through a chirally preferential clustering-declustering solvation effect. As an improvement to bubbler systems, an HPLC pump, an ultrasonic nebulizer, and a volatile organic compound (VOC) sensor are used.

Presented by: Nathan Grimes *(Graduate, Analytical Chemistry)*

Mineralized lignocellulose biocomposites for remediation of environmental pollutants

Dangerous levels of contaminants found in groundwater such as arsenic (As) present a significant threat to developing parts of the world. Nanocrystalline iron oxides such as ferrihydrite (Fh) and magnetite (Mt) have been studied for removal of these compounds due to their high surface areas and binding interactions with environmentally relevant pollutants. Mineralized filters comprised of lignocellulose matrices and nanocrystalline iron oxides provide a low-cost, technology for the rapid removal and immobilization of heavy metals such as As. In this study, water samples of known As concentrations were passed through mineralized filters and examined using Microwave Plasma Atomic Emission Spectroscopy (MP-AES) to quantify removal of As. Filters were analyzed via Scanning Electron Microscopy Energy Dispersive X-ray Spectroscopy (SEM-EDS) to determine retention of the mineral phase and quantification of adsorbed As. Removal of As was found to be approximately 50-80% from water samples.

Presented by: Steven Soini *(Graduate, Inorganic Chemistry)*

Oral Presentation Abstracts **(Morning Session B)**

Spin dynamics simulations of topological magnetic nanoparticles

Magnetic nanoparticles have the potential for a variety of applications in medicine, energy, and computing. However, the intersection of nanoparticles and topological magnetic materials is relatively unexplored; typical studies of nanoparticles focus on the small-size, superparamagnetic

regime, while studies of topological magnetic materials often focus on bulk-like scales. We use spin dynamics simulations to investigate the crossover from superparamagnetic to single domain topological magnetic states in model nanoparticles. We simulate a cubic nanoparticle with sizes varying from 1 to 60 nm using the LLG equation dependent on external field sweeps at finite temperatures. The dependence of the topological charge and other properties on the nearest-neighbor Heisenberg exchange, nearest-neighbor surface DMI, and external field is explored. The appearance of novel textures and the penetration of these textures into the bulk indicate highly-nontrivial topological properties of the nanoparticle system. Our work presents some of the first results for an entirely new regime of magnetic nanoparticles and could seed novel fields of magnetization studies.

Presented by: Cole Gibson *(Undergraduate, Physical Chemistry)*

Ethane/Ethylene Separation in NKMOF-8-Me and NKMOF-8-Br: Support for Grand Canonical Monte Carlo Simulation to Explore Metal-Organic Frameworks

The separation of hydrocarbon mixtures is traditionally done by cryogenic distillation, which is costly and requires significant energy investment. It has been demonstrated that metal-organic frameworks (MOFs) are able to carry out such separations via competitive physisorption of gases. Two MOFs synthesized at Nankai University, NKMOF-8-Me and NKMOF-8-Br [Geng, S.; et al. J. Am. Chem. Soc. 2021, 143, 8654-8660.], were designed for ethylene purification from C2H6/C2H4 mixtures. It has been demonstrated through experimental measurements that both MOFs exhibit selectivity for ethane over ethylene. Grand canonical Monte Carlo (GCMC) simulations reproduced isotherms and isosteric heat of adsorption (Qst) values that are in reasonable agreement with the corresponding experimental data for a range of temperatures and pressures for both MOFs. The simulations were performed with and without the inclusion of polarization, and by altering the repulsion/dispersion parameters and partial charges.

Presented by: Alexander Mariscal *(Undergraduate, Physical Chemistry)*

Electronic Transport in Chiral Quantum Materials

Topological quantum materials have unusual magnetic and electrical properties due to the interaction between electrons involving their spin, orbit, charge, and the materials' symmetries. Their electronic states can be topologically protected by the dimensionality and global symmetries of the material, which allows us to control these unique macroscopic properties from the atomic scale, a significant advantage for next-generation technologies. We want to explore the effects breaking inversion symmetry with the crystal structure has on the electronic structure and transport of 3D topological semimetals. We will accomplish this by utilizing the Landauer-Bttiker formalism and wave function approach to calculate the transport with a Python package called KWANT. By changing the strength of spin-orbit coupling, spin-orbit interaction, and crystal symmetry, we expect to see an increase in the transport signature of these materials.

Presented by: Gina Pantano *(Graduate, Physical Chemistry)*

Innovated B/N Frustrated Lewis Pairs for CO reduction: a DFT study

Challenges in global energy shortage have promoted studies in finding alternative and sustainable energy resources, for example, utilization and reduction of CO molecule. Herein, by employing computational simulations, we have developed and investigated an innovated intramolecular metal-free frustrated Lewis pairs (FLPs) as a catalyst for the CO reduction reactions. By applying nitrogen heterocycles and organoboron structure, the FLP catalyst is able to hydrogenate CO directly from dihydrogen and produce methanol as final product. The mechanism and reaction path of the CO reduction reaction have been investigated using density functional theory. The simulation data indicate that the proposed catalyst may greatly reduce the activation energy barrier and hold promise in developing metal-free catalyst for the CO reduction reactions.

Presented by: Ankai Wang *(Graduate, Physical Chemistry)*

Topological magnetic textures in cubic nanoparticles

Magnetic topological spin textures are promising for fundamental physics, next-generation devices, and dense data storage. There is a unique coupling between the electronic and the magnetic structure, which can be efficiently manipulated by electromagnetic external fields, such as laser light. We study the magnetic structures from the trivial ferromagnetic state to the highly sought-after topological spin texture, i.e., skyrmions. We take an innovative approach by tackling finite-size cubic nanoparticles where we minimize the Gibbs free energy due to the competitions of the Heisenberg exchange, Dzyaloshinskii-Moriya Interaction (DMI) applied only at the surfaces of the nanoparticles, and various other magnetic interactions. We show that the spin field has a non-trivial topology with bounded regions of high topological charge which can be associated with skyrmions. Our analytical results are compared with that of spin-dynamic simulations.

Presented by: Herrmann Antoine *(Graduate, Physical Chemistry)*

Oral Presentation Abstracts **(Morning Session C)**

New 1-(3-(2-Amino-2-oxoethoxy) phenyl) piperidine-3-carboxamide Derivatives as Small-Molecule Inhibitors for the -Catenin/BCL9 ProteinProtein Interaction

A series of 1-(3-(2-amino-2-oxoethoxy)phenyl)piperidine-3-carboxamide derivatives was reported as new small molecule -catenin/B-cell lymphoma 9 (BCL9) proteinprotein interaction (PPI) inhibitors. Compounds 1821 were found to disrupt the -catenin/BCL9 PPI with IC50s of 0.852.7 M in competitive inhibition assays. The disruption effects of 21 on the -catenin/BCL9 PPI in cellular context were demonstrated by pulldown inhibition experiments using SW480 cell lysates. A series of cell-based studies revealed that 21 dose-dependently suppressed transactivation of Wnt/-catenin signaling, downregulated expression of Wnt target genes, and inhibited growth of cancer cells with hyperactive -catenin signaling. 21 was also more potent than previously reported analogue ZW4864

in suppressing transcription and expression of Wnt target genes and Wnt-dependent cancer cell survival. All in all, 21 represents a promising starting point for further optimization of -catenin/BCL9 PPI inhibitors.

Presented by: Harriet Thompson *(Undergraduate, Biochemistry)*

Selpercatinib Protac derivatives with different linkers act as RET degraders

Selpercatinib(LOXO-292) is a 2020 FDA approved highly potent drug for rearranged during transfection (RET) altered thyroid cancers and non-small-cell lung cancers(NSCLC). However, resistances were found RET G810C/S mutations at solvent front region and RETY806C/N mutation the hinge region. With these two mutations, resistance is developed and selpercatinib can't show good potent efficacy. Here, based on the patent WO 2018/071447 Al, we choose several potent structures that are different from Selpercatinib at the solvent exposed area and test them against wild type RET cell and mutated RET cell. From the cell results, these structures do not show good potency towards both wild type RET cells and mutated RET cells. Alternatively, now we are trying to develop selpercatinib based protac derivatives. The hydrophobic binding part of Selpercatinib and different E3 ligases are joined by several kinds of linkers. From western blotting results, two compounds can degrade P-RET and RET protein as low as 50nM. However, these two compounds can't kill cells after 3 or 5 days even if much higher concentration is used.

Presented by: Yafeng Wang *(Graduate, Organic Chemistry)*

Antibiotic Activity Driven Natural Product Discovery from Mangrove Endophytic Fungi

With the emergence of multi-drug resistant bacteria, natural product researchers are using more advanced techniques to discover novel drugs. Following prior success of fungal secondary metabolites as antibacterial agents, the expression of silent biosynthetic gene clusters (BGCs) may provide such innovation. Mangrove endophytic fungi were cultured in the presence of the DNA modifiers HDACi or DMNTi and subsequently screened for bioactivity against the ESKAPE pathogens. Using the global natural product social molecular networking (GNPS) software of LC-MS/MS fragmentation patterns resulted in the dereplication of several known compounds, as well as identified three new derivatives which were isolated and characterized using 1D and 2D nuclear magnetic resonance (NMR) spectroscopy and electrospray ionization mass spectrometry ESIMS). The lead compound bears structural similarity to a known compound with increased activity against Enterococcus faecium and Staphylococcus aureus pathogens.

Presented by: Benjamin Smith *(Graduate, Organic Chemistry)*

Oral Presentation Abstracts (Afternoon Session D)

Efforts toward the enantioselective total syntheses of various marine natural products

Today, we are seeing tremendous issues with the presence of multi-drug resistant bacterial infections and still do not have a reliable way to treat many of these infections. Darwinolide is a natural product isolated from Dendrilla membranosa, a cactus-sponge native to Antarctica and was found to have a high bioactivity in degrading Methicillin-Resistant Staphylococcus aureus (MRSA) biofilms. A structurally similar natural product, membranolide, is a synthetic target of ours so we can further explore the bioactivity of this similar diterpene natural product. Relatedly, we are pursuing the enantioselective total syntheses of the oxeatamides, which are a class of natural products isolated from Darwinella oxeata.

Presented by: Sean Bradley *(Graduate, Organic Chemistry)*

Diastereoselective phospha-Michael addition of aryl phosphinates catalyzed by a phase transfer agent

We are engaged in the development of a catalytic diastereoselective approach to the construction of organophosphinate compounds that are valued in the inhibitor design of metalloproteinase implicated in tumor metastasis mechanisms. Our strategy involves the phospha-Michael addition of aryl phosphinates to -disubstituted vinyl ketones under the action of crown ethers as phase transfer catalysts (PTCs). Reaction conditions using phosphinate nucleophile containing a non-racemic menthyl substituent led to enantiopure chiral phosphinate adducts with the generation of an -quaternary stereocenter in high diastereoselectivities. A closed transition state model is proposed to explain the stereoselectivity in these addition reactions with the observed selectivity rationalized as preferential attack of phosphinate on vinylketones in the S-cis conformation. This methodology entails the use of phase transfer chemistry under uniquely mildly basic conditions.

Presented by: Krishna Yadavalli *(Graduate, Organic Chemistry)*

Development of lipidated polycarbonates with broad-spectrum antimicrobial activity

Antimicrobial resistance is being considered a global challenge owing to the lack of discovery of effective antibiotic agents. By harnessing the characteristics of the antimicrobial peptides, a range of polycarbonates bearing primary amine groups and hydrophobic groups were synthesized by ring-opening polymerization. The hydrophobic/hydrophilic group ratios were adjusted and the lengths of the alkyl group at the end of the polymers were modified to achieve the best combination which exhibited the highest antimicrobial susceptibility and optimal selectivity. The mechanism was studied by performing membrane depolarization test and observing under microscope.

Presented by: Ruixuan Gao *(Graduate, Biochemistry)*

Potential New Synthetic Ketogenic Molecules: Ester Derivatives

Ketone bodies are produced in our liver during prolong fasting and carbohydrate restricted diet, in a process called ketosis. Ketosis has already been proven as effective tool for medical uses as it showed influences on treating epilepsy, type 2 diabetes and weight loss. Ketone bodies are produced by metabolism of molecules called Long chain triglycerides (LCTs) which we gain from dietary fat. However, medium and shorter chain triglycerides made from fatty acids are more ketogenic. Herein, we aimed at synthesis of short and medium chain ester derivatives of potential new ketogenic molecules for further exploration.

Presented by: Mohammad Nazmus Sakib *(Graduate, Organic Chemistry)*

Tuaimenals B-H: Novel meroterpenes from an Irish deep-sea soft coral of the genus Drifa with cytotoxicity against HPV-positive cervical cancer

Cervical cancer, despite being nearly entirely preventable through human papillomavirus (HPV) vaccination and regular screening, remains the fourth most common cancer affecting women worldwide with over half a million new cases and 311,000 deaths reported in 2018. However, the possibility of new anticancer therapies could serve to save the lives of those women already affected by this disease. Herein, we report the isolation, characterization, and biological activities against the CaSki HPV-positive cervical cancer cell line of tuiamenals B-H (1-7), novel meroterpenes from an Irish deep-sea coral of the genus Drifa. The structure elucidation of these secondary metabolites bearing a highly substituted chromene core was achieved using a combination of 1D and 2D nuclear magnetic resonance (NMR) spectroscopy and electron impact (2) and electrospray ionization (1, 3-7) mass spectrometry.

Presented by: Joshua Welsch *(Graduate, Organic Chemistry)*

Oral Presentation Abstracts **(Afternoon Session E)**

Identification of Potential SARS-CoV-2 Inhibitors Using Flexible Docking-Based Drug Repurposing of Antivirals

This work aims to screen antiviral compounds as potential inhibitors of the SARS-CoV-2 virus using a fully flexible docking method. Antiviral compounds that are either FDA approved or in the experimental phase were selected as candidates. Three proteins critical to viral function were selected as targets of the study: Mpro, PLpro, and TMPRSS2. Docking was conducted using a novel CHARMM-based flexible docking method, which allowed for flexibility of both the protein and the ligand, providing a more thorough search of conformational space. The enhanced flexibility of this method, combined with its ability to sample an explicitly solvated complex, provides a more thorough insight into how the antivirals may interact with these protein targets in a biological

context. Based on favorable Glide scores of the docked protein-ligand poses, the results reveal that a portion of the original antiviral compounds are potentially viable as inhibitors of the virus.

Presented by: Rose Pittman *(Graduate, Physical Chemistry)*

A high dimensional parameter search method to determine force field mixing terms in molecular simulations

Molecular simulations depend on parameter sets for molecules that are developed independently of one another for use with water models. These parameters are often assumed to be transferrable; however, in many recent works this has been shown to work poorly for cases, especially when ions are involved. We have developed a method, using the ParOpt software from our group, to optimize Lennard-Jones cross-terms between cations and small-molecule representatives of lipids to ensure accurate reproduction of gas-phase geometries and energies from ab initial calculations. This method is a generic method that can be applied to mix any two independently developed MM force-fields.

Presented by: Matthew Saunders *(Graduate, Physical Chemistry)*

Inclusion of high-field target data in AMOEBAs calibration improves predictions of protein-ion interactions

The reliability of molecular mechanics simulations to predict ion binding to proteins depends on their accuracy in describing protein-water, ion-water and ion-protein interactions. Protein and ion force fields are typically constructed independently of each other, and in simulations consisting of both proteins and ions, protein-ion interaction energies are estimated using some predefined set of force field mixing rules. This, however, does not guarantee the reliability of predicted ion-protein interactions and in fact yield large errors. Here we use the polarizable AMOEBA force field to demonstrate that errors in ion-protein interactions can be reduced systematically by incorporating high electric field target data during calibration of protein parameters. Recalibration of descriptors for peptide backbones and side chains consisting of carbonyls, hydroxyls and carboxylates reduces the error from 8.7 to 5.3 kcal/mol and 9.6 to 6.3 kcal/mol for interactions with Na^+ and K^+.

Presented by: Julian Melendez *(Graduate, Biochemistry)*

Sequence effects of uracil damaged DNA

Uracil is a common type of lesion in DNA that arises from either spontaneous deamination of cytosine or errors in the replication process. DNA containing uracil is excised from the genome in the base excision repair (BER) process by uracil DNA-glycosylase (UDG). It is hypothesized that UDG activity is dependent on the intrinsic deformability of the base steps neighboring the uracil. A diverse set of uracil-damaged DNA sequences have been studied using molecular dynamics (MD) simulations, and global and local properties have been investigated to examine the role of sequence in repair.

Presented by: Paul Orndorff *(Graduate, Physical Chemistry)*

Optimizing Protocols for Computing NMR Chemical Shifts for Saccharide-like Species

Cellulose is a readily abundant polymer in nature that is being investigated as an alternative fuel source. Computational methods can aid experimentalists by providing chemical shifts related to cellulosic biomass. As a prelude to future work, we conduct an investigative benchmark with a set of small carbohydrate analogs to identify which quantum-mechanical/molecular-mechanical (QM/MM) methods are the most accurate and the least computationally expensive when computing carbon-13 (13C) NMR chemical shifts. We find that 13C root mean square error converges when a QM solvent sphere of 4 or more about a solute is used, showing a selection of method/basis set pairings that yield errors less than 3.0 parts per million. We also show that computational time can be greatly reduced while retaining and, in some cases, improving accuracy by employing a mixed basis set approach, wherein the QM region is partitioned into large basis set (inner) and small basis set (outer) regions.

Presented by: Nicole A Miller *(Graduate, Physical Chemistry)*

Poster Presentation Abstracts (Midday Session)

Electrochemical Detection of Cd(II) Ions in Environmental Samples Using Nanoelectrodes

Heavy metal contamination is a rising global concern and bioaccumulation of toxic metals in the food chain leaves human beings highly vulnerable to exposure; thus, it is crucial to develop an exemplary metal sensor. This study focuses on developing a portable, low-cost, and robust sensor capable of providing accurate information on metal speciation. We use ion transfer between two immiscible electrolyte solutions (ITIES) to detect Cd(II) in environmental samples. Our electrode is borosilicate glass with an inner radius of 300 nm. We calibrate our nano-sensor in various matrices to show its capability to withstand the complicated matrices without fouling. Furthermore, we show our sensor can accurately detect Cd(II) levels in a water sample collected from Indian River Lagoon, Melbourne, FL; thus, demonstrating its power as an environmental monitoring tool. To the best of our knowledge, this is the first time a nano-sensor for the detection of Cd(II) based on ITIES is being reported.

Presented by: Muzammil Ahmed *(Graduate, Analytical Chemistry)*

Computational Support for Predicting Molecular Interactions in the Electrospinning of Nanofibers: A Review

Drug design has advanced into the use of nanofibers, which can be used in the fabrication of any treatment design. The electrospinning technique allows for a core and layered drug design, of a nanofiber, and this method provides a more specific drug release than other methods of nanofiber creation. Computational predictions of the polymer layering process of electrospinning has been touched upon, but no method is utilized for modeling the predicted electrospun nanofiber product with and without specific drug inclusions.

Presented by: Brandi Cook *(Graduate, Analytical Chemistry)*

Extracting Glycerol Dialkyl Glycerol Tetraether From Sediments

Glycerol dialkyl glycerol tetraether (GDGT) are membrane lipids that have been synthesized in archaea. GDGT can contain up to eight cyclopentane rings in its structure. There are different variations of GDGT depending on the position of the cyclopentane rings which is affected by temperature. The distribution of the six different variations of GDGT will be used to calculate the tetra ether index which is a temperature proxy that can be used to reconstruct past sea surface temperature. Extraction of GDGT is important since the TEX86 value is calculated using the distribution of the GDGT variants. The different parameters that are being tested is the amount of sediments used in each sample, the origin location of the sediments, and automatic vs. manual extraction. After extraction, the samples will be filtered to prevent any contaminations from

passing through to the HPLC-MS which will be used to collect the data. With the data, the ideal parameters for extraction will be discovered.

Presented by: Carlos Hernandez *(Undergraduate, Analytical Chemistry)*

Orbitrap mass spectrometry for the determination of stable isotopes in amino acids.

The fractionation of carbon and nitrogen isotope enrichment in biological tissues, including fossil skeletons, potentially records information on the trophic level of an organism, dietary sources, and important primary producers. Because heavier nitrogen isotopes bioaccumulate in consumer tissues and skeletal organics relative to diet, the isotope ratio nitrogen in fossil skeletons opens a window into the diets of ancient organisms and a means of answering big questions about the evolution of ecosystems in deep time. Organic compounds in soft tissues begin to decay shortly after the organisms death but may be preserved in trace amounts within the intra- and inter-crystalline matrix of skeletal minerals. Current methods of determining isotope enrichment require upwards of 20ug of nitrogen or carbon for sample analysis, becoming ineffective for prehistoric analysis. The proposed alternative method employs an Orbitrap mass spectrometer for its high resolution and low limits of detection.

Presented by: Alexandra S Keidel *(Graduate, Analytical Chemistry)*

Liposome Characterization and Use as a Standard for Exosome Analysis

Exosomes are extracellular vesicles with lipid bilayers that range from 40-160 nm in size. They are released by eukaryotic cells to carry cargo including proteins, DNA, and RNA to other cells in the body. Exosomes have been studied since the 1980s, where they were first believed to be linked to the metastasis of various cancers. As a result, liposomes, which are synthetic extracellular vesicles, may be used to mimic exosomes in terms of composition, size, and cargo that they carry and make robust internal standards for exosome analysis via mass spectrometry. Additionally, their versatility has made them a lucrative choice in fields including drug discovery, as they have been used as a delivery vehicle for a wide range of drugs. Encouraged by the tunability of liposomes, we have synthesized vesicles in a range of sizes (50-200 nm) as well as included components in the lipid bilayers that mimic those found in exosomes. Particle sizing methods including dynamic light scattering (DLS) as well as tunable resistive pulse sensing (TRPS) were used to validate the sizes of the liposomes synthesized.

Presented by: Sandra Khalife *(Graduate, Analytical Chemistry)*

Electrodeposition of dopamine onto carbon-fiber microelectrodes to enhance Cu2+ detection with fast-scan cyclic voltammetry

Neurological disorders affect millions of people despite the wide variety of medications developed to slow down progression. The lack of efficient drugs available highlights the need for a deeper understanding of the etiology of these diseases and the effect of environmental factors, such as heavy metals. Traditional methods of metal ion detection are in vitro analysis, thus eliminating real-time measurements and therefore lack insight into the relationship between heavy metals and these diseases. In this study, we fabricated a carbon-fiber microelectrode electrodeposited with

dopamine to enhance the detection of Cu^{2+}. We characterized our sensor with dopamine and Cu^{2+} with fast-scan cyclic voltammetry and optimized electrodeposition time through comparison and chose the best one. We performed all experiments in a buffer solution that mimics artificial CSF, showcasing the ability of our sensors for the in vivo detection of Cu^{2+} with high sensitivity and excellent biocompatibility.

Presented by: Noel Manring *(Graduate, Analytical Chemistry)*

Comparison of Two Extraction Methods of GDGTs from Sediment Cores from Areas of High and Low Lipid Concentration

In this study we investigated extraction methods for qualitative analysis of glycerol diakyl glycerol tetraethers (GDGTs). These GDGTs are specific membrane lipids that exist in thermophilic archaea and these archaea biosynthesize the lipids. They are a biomarker for archaea and are essential to studies in paleogeochemistry. For the GDGTs in the archaea to be useful in these studies they must be effectively extracted from sediment cores. For this reason, the extraction methods of GDGTs must be compared to use the GDGTs as quantitative biomarkers. The samples used were from Antarctic and Gulf of Mexico sediments to observe the extraction effectiveness at high and low lipid concentration. The sediments were also observed at higher and lower quantities to see if this caused an effect on the results. The data was analyzed using an HPLC-MS to locate which GDGTs were found and their yield. The results revealed that the manual extraction method (SONIC) produced a higher yield.

Presented by: Delaney Sellers *(Undergraduate, Analytical Chemistry)*

Lipid Identification Using MALDI-MSI for Drosophila melanogaster

To produce inclusive and widespread metabolite profiles with the spatial information in the model organisms, Matrix-Assisted Laser Desorption/Ionization Mass spectrometric Imaging (MALDI-MSI) can be used. A tool within the MALDI-MSI technology, allows a generation of in situ profiles of the entire model organism. In cases where solvent extraction protocols cannot be adhered to, specifically in instances where the identification of biomolecules are unstable within the extraction conditions, MSI can be used as an alternative approach. Within this particular research that we have conducted, we utilized MALDI-MSI for the fruit fly to spatially profile different classes of lipids in Drosophila melanogaster in positive ionization mode using 2,5-Dihydroxybenzoic acid as the matrix. MSMS fragmentation was conducted directly on the tissue for selected lipid species for lipid identification.

Presented by: Harsheen Marwah *(Undergraduate, Biochemistry)*

Immunosuppressants and nanotechnology: innovations in nanoformulations and drug delivery systems

Immunosuppressants are a class of medications that are often used for treatment of autoimmune diseases, immune-mediated diseases, and preventing organ rejection after allograft transplantations.

Nanomedicine is a rapidly developing subject that is improving the administration of immunosuppressants in clinical patients through innovations of distinct drug delivery systems and nanoformulations. Although relatively new, nanomedicine has been invaluable towards the research and development towards improving efficacy and safety of therapeutical compounds. Nanoparticles have been used as carrier molecules for immunosuppressants as a form of transporting payload with site-specific targeting and less adverse effects. This review will focus on the different aspects of drug delivery systems involving different types of available immunosuppressants, how they are incorporated in nanoscale drug delivery systems, and how they can be potentially and how they can be potentially improved in the future.

Presented by: Kevin Nuno *(Graduate, Biochemistry)*

Spectroscopic and Thermodynamic Characterication of CthEgtB

EgtB is a nonheme iron sulfoxide synthase that is involved in the biosynthesis of ergothioneine, which is a natural product that plays a role in infection response and antioxidant mediation. EgtB initiates the key step of C-S bond formation between its Cys and a His derivative substrates. Among the sulfoxide synthases that initiate an oxidative C-S bond, EgtB from Chloracidobacterium thermophilum (Cth) stands out because it adopts a D2 tetrameric quaternary structure as compared to all other EgtBs, which are monomeric. Motivated by this structural divergence, we analyzed the unfolding pathways of CthEgtB as a function of temperature, pH, and denaturant. The secondary structure and thermodynamic parameters of CthEgtB unfolding were evaluated using circular dichroism. It was found that CthEgtB follows unfolding pathways that are highly sensitive and dependent on initial conditions. The knowledge in this study have elucidated structural properties required for CthEgtB oligomerization.

Presented by: Kassidy Rodriguez *(Graduate, Biochemistry)*

Synthesis and Optical Properties of Double Halide Perovskites based on Chiral Linkers

Halide perovskites have a unique, defining structure that has many fascinating properties and significant potential towards real world applications. Despite this, traditional lead-based perovskites are often difficult to use due to their instability and toxicity. By the formation of double perovskites, we can eliminate the need for lead, while producing a greener material with equally exquisite optoelectronic features. The addition of chiral linkers allows for further control of the structural and optical traits of the corresponding materials, without the need for toxic elements. We present here the synthesis of new families of double perovskite crystals using chiral organic linkers by a wet-chemical synthesis method, based on silver or copper and antimony or bismuth. Preliminary data indicates the successful formation of new crystal phases, while the determination of the optical properties render them suitable candidates for optoelectronic and spintronic devices.

Presented by: Alissa Anderson *(Undergraduate, Inorganic Chemistry)*

Fabrication of twisted Graphene bilayers and Moire pattern electrical effects

Exploring the manufacturing and transportation of pristine, large area mono-layer graphene films, and the stacking of said films into bilayer graphene homostructures. Stacked layers of graphene

are explored at a variety of "twist" angles between the two layers, which exhibit curious electrical/ quantum mechanical properties such as room-temperature superconductivity.

Presented by: Marcus Harvison *(Undergraduate, Inorganic Chemistry)*

Creation and Analysis of Novel Lead and Lead-Free Pervoskites

Perovskites are a class of inorganic materials most useful in the fields of solar cell technology and flexible electronics, due to their ability to conduct electricity well while maintaining it under applied forces. Though commonly formulated using lead, recent experiments search for lead-free alternatives to more positively impact the environment. Newly discovered linkers are used in this experiment along with lead and lead-free metal combinations to form perovskite crystals which are then analyzed with powder x-ray diffraction (PXRD), single crystal x-ray diffraction (SXD) and then with various photochemical and thermal analysis tools to determine the properties of the perovskites and their possibility for application.

Presented by: Leah Lepore *(Undergraduate, Inorganic Chemistry)*

Evaluation and Identification of Antifungal Activity of Mangrove Endophyte against Candida Sp.

The wide range of adverse effects that Candida Sp. can demonstrate in humans and the ever-growing multi-drug resistance profiles of the certain strains can result in life-threatening infections that remain uninhibited due to the limited clinical treatment available. Mangrove endophytes have shown significant promise in the development of new treatments because they can synthesize bioactive secondary metabolites. Secondary metabolites are especially interesting to scientists because these compounds typically demonstrate biologically active properties that can be used in antibiotics and antifungal treatments. With the limited antifungal treatments and the growing resistance of C. albicans and C. auris, the production of new secondary metabolites. The objectives of this paper are to isolate a bioactive compound through bioassay-guided fractionation as well as conduct DNA sequencing to determine the identity of fungal compound HF14-16C-2A-HDAC to assist in the development of new treatments.

Presented by: Jessica Bay *(Undergraduate, Organic Chemistry)*

Anti-plasmodial activity of Gardenia imperialis

Malaria is a widespread disease by female anopheles mosquito. There are 5 parasite species that cause malaria in humans with P. falciparum and P. vivax posing the greatest threat. In 2020, nearly half of the worlds population was at risk of malaria. Previous malaria research has resulted in combating the deadly disease using various drug discovery techniques. Natural products have played crucial roles in the fight against malaria from the discovery of artemisinin, quinine, and lapachol. Gardenia imperialis is a small plant found in Tropical Africa. Fungus living on the plant generate secondary metabolites known to have anti-plasmodial activity against PfDd2 species of Plasmodium and has antileishmanial potency. As part of this research project, fungal extracts were

concurrently subjected to bioassay and nuclear magnetic resonance (NMR) spectroscopy guided approaches to aid in the search for compounds with anti-plasmodial activity.

Presented by: Sylvester Osei Bobbie *(Graduate, Organic Chemistry)*

Isolation and identification of fungal Natural Products against multi-drug resistant pathogenic Candida spp.

Newly optimized high-throughput growth-inhibition assays for seven strains of Candida spp. bring forth several promising leads for antimicrobial drug discovery. Candida albicans, and newly emerging related pathogen Candida auris, are multidrug resistant fungal species that cause life-threatening infections. A fungal library of 10,000 extracts collected from mangroves across Florida and Mexico was subject to an optimized growth-inhibition assay to determine promising fungal species against either or both Candida species. Further analysis of extracts and subsequent fractions was performed via NMR, mass-spectrometry, and the Global Natural Products Social Molecular Network (GNPS) which allows for fast dereplication and targeted isolation of novel bioactive secondary small molecules.

Presented by: Sarah Grace Dietrick *(Graduate, Organic Chemistry)*

Synthesis of Activated Barium

Organometallic reagents are among the most powerful tools for C-C bond formation in the arena of organic synthesis. In light of the development of new or improved synthetic methodologies for C-C bond formation, reactions that involve the development of new organometallic reagents are of great interest. In our laboratories, novel organobarium reagents have been prepared. Barium metal in its reactive form has been prepared by a similar protocol for reactive calcium reagents. Following Riekes method for calcium, the corresponding anhydrous metal halide is reduced by lithium naphthalenide or biphenylide at room temperature. Also, we have applied these methods toward the preparation of various structurally diverse complex molecules as well as the preparation of a biochemically important aldehyde, 3,4-Dihydroxyphenylacetaldehyde (DOPAL). Thus, our initial results toward the preparation of DOPAL will be presented.

Presented by: Michael Gorman *(Undergraduate, Organic Chemistry)*

One-Bead-Two-Compound Macrocyclic γ-AApeptide Screening Library against PTGER2

Identification of molecular ligands that recognize peptides or proteins is significant, but poses a fundamental challenge in chemical biology and biomedical sciences. Development of cyclic peptidomimetic library is scarce and thus discovery of cyclic peptidomimetic ligands for protein targets is rare. Herein we report the One-Bead-Two-Compound (OBTC) combinatorial library based on a novel class of the macrocyclic peptidomimetics γ-AApeptides. In order to develop the library, we utilized the coding peptide tags synthesized with Dde-protected γ-amino acids, which were proved to be orthogonal to solid phase synthesis of γ-AApeptides. Employing the thioether linkage, the

desired macrocyclic γ-AApeptides were found to be effective for ligand identification. This new approach of macrocyclic peptidomimetic library may lead to a novel platform which provides unique source of ligands for biomacromolecular surface recognition and function modulation.

Presented by: Meng Gu *(Graduate, Organic Chemistry)*

Efficient Synthesis of Cyclopropylacetylene, a Crucial Synthetic Intermediate for Efavirenz Using a Mild Chlorinating Reagent (Ph_3PCl_2)

Cyclopropylacetylene (CA) is a key intermediate in the synthesis for the HIV reverse transcriptase inhibitor Efavirenz, an antiviral drug used to treat HIV. CA is an expensive raw material, difficult to obtain, employed in the preparation of medicaments to combat AIDS. The efficient process for the preparation of CA is described, in which cyclopropyl methyl ketone is chlorinated with PCl5. The resulting 1,1-dichloro-1-cyclopropylethane is isolated and then dehydrochlorinated with potassium tert-butoxide in toluene to form CA. However, the chlorination protocol has been found to take place with appreciable cyclopropyl ring opening. A mild chlorinating reagent is predicted to reduce ring-opening side products. For this, a one-pot synthesis was employed using dichlorotriphenylphosphorane—Ph_3PCl_2—as the mild chlorinating agent. This route resulted in 1,1-dichloro-1-cyclopropylethane, and after further treatment with a strong base, CA was produced. Additional synthetic routes will also be presented.

Presented by: Emily Hutchinson *(Undergraduate, Organic Chemistry)*

Synthesis and optimization of resveratrol-natural product inspired [3.2.1] bridged bicyclic compounds as potent neuroprotective agents

Synthesis and optimization of resveratrol-natural product inspired [3.2.1] bridged bicyclic compounds as potent neuroprotective agents We have previously established a synthesis route towards all-carbon [3.2.1] bridged bicyclic that we have termed "resveramorphs" or "RVMs" since their structures were inspired by a resveratrol natural product known as vitisinol D. These novel compounds were found to protect synaptic transmission against oxidative stress in Drosophila melanogaster studies. However, our six-step synthesis route is currently limited by a low yielding reductive aldol step, which was pioneered in our group. In this presentation, our attempts to optimize this bottleneck step will be presented along with mechanistic insights gained thus far.

Presented by: Elyse Jutte *(Graduate, Organic Chemistry)*

Covalent tethering post-modification of isoG assembly for Cs+ ionophore

A series of deoxy isoG analogs were synthesized and applied for Cs+ coordination. Deoxy isoG derivative with modification on ribose (tert-Butyldimethylsilyl ether) was applied to assemble with Cs cation. Critical solvents ($CDCl^3$ and CD3CN) and anions (BPh^{4-}, $BARF^-$, and PF^{6-}) effects were revealed, leading to the controllable formation of various stable isoG pentaplex, including singly charged decamer, doubly charged decamer, and 15-mer, etc. The X-ray crystal structure of $[isoG20Cs3]^{3+}(BARF^-)^3$ was successfully obtained, which is the first example of multiple-layer deoxy isoG binding with Cs^+ cation. Furthermore, the covalent post-modification of a hydrogen-bonded

assembly was discussed. Olefin metathesis and thiol-yne were used to cross-link isoG subunits to form cyclic pentamer or polymer. The resulting iaoG folds could be applied as a Cs^+ ionophore.

Presented by: Mengjia Liu *(Undergraduate, Organic Chemistry)*

Synthesis of Peptidomimetics as Potential Anticancer Agents and Biomedical Applications

Numerous physiological and pathological stimuli induce programmed cell death (apoptosis), and the Bcl-2 family of oncoproteins plays a central role in this regulation. Proteins such as Bcl-2 are known to inhibit apoptosis, and uncontrolled cell survival due to Bcl-2 overexpression has been proven to make a significant contribution to tumor formation. With this in mind, we have directed our attention toward the synthesis of a variety of non-peptide inhibitors of oncoproteins Bcl-2. Recently, we have disclosed efficient protocols leading to the synthesis of carbazate and dithiocarbazate peptidomimetics, respectively. This study is now being extended to the synthesis of other de novo analogs. Utilizing our aforementioned protocols, various scaffoldings are being employed for the development of novel artificial biomolecules, which may result in biological behaviors regarding the disruption of protein-protein interactions and may serve as potential therapeutics in clinical chemotherapy.

Presented by: Robert Logue *(Undergraduate, Organic Chemistry)*

Onset of Hyperconjugation in the Transition State of Carbonyl Addition by Deactivation of Periplanar Vicinal Bonds

The previously observed preferential syn delivery of hydride anion in the reduction of the carbonyl group of 5-chloro- and 5-fluoroadamantan-2-one are inverted if the identities of all hydrogen and fluorine atoms are reversed. A similar and somewhat smaller alteration is observed.

Presented by: Kyle Manuel *(Undergraduate, Organic Chemistry)*

Unprecedented endo cyclizations involving carbon additions on unactivated carbon-carbon triple bonds catalyzed by potassium tert-butoxide

We report endo-dig exclusive intramolecular cyclitive additions of unactivated propargyl alkynes via a carbon nucleophile, catalyzed by potassium tert-butoxide at or below room temperature. Cyclization leads to products such as dihydro-furans and dihydro-pyrans provided there is a C-O bond at the propargyl position. Numerous substrate classes bearing a modestly acidic C-H bond undergo cyclization including those without carbonyl-based electron withdrawing groups traditionally found in the Conia-ene reaction. We present evidence that the endo-dig mode of attack involves vinyl anion formation and that this anion is stabilized by hyperconjugation with an adjacent C-O pi*-orbital. The generality of this transformation will also be discussed along with the mechanistic insights such studies have enabled.

Presented by: Kristina Nugent *(Graduate, Organic Chemistry)*

The identification of new Suberitenones from the Antarctic sponge Suberites sp.

Natural products have been used as medicine to treat humans since ancient times due to their therapeutic properties. The secondary metabolites derived from terrestrial and marine sources have the potential to be novel, bioactive compounds, which can potentially be used as new drug candidates. I have recently worked on the Antarctic sponge Suberites sp. to identify new chemical compounds. During my research, I extracted, isolated, and purified a new Suberitenone from the Suberites sponge collected in Antarctica in 2018 with the goal to find new, bioactive metabolites. Running 1H NMR, 13C NMR, HSQC, HMBC, COSY, and NOSEY, I was able to identify the purified compound and compare it to libraries. The chemical compound has not previously been reported in literature and the final step is to test for bioactivity. The compound has been tested for bioactivity against ESKAPE, Malaria, Candida, and J774 cells, but no activity has been confirmed yet.

Presented by: Stine H Olsen *(Graduate, Organic Chemistry)*

Identification of Novel Antibacterial Agents From Fungal Extracts

Bacterial resistance to antibiotic drugs is an ever-increasing threat. ESKAPE pathogens (Enterococcus faecium, Staphylococcus aureus, Klebsiella pneumoniae, Acinetobacter species, Pseudomonas aeruginosa, Enterobacter species) cause a significant amount of antibiotic bacterial infections worldwide, and thus, the study of new antibiotic agents that can be of use against these bacteria is of upmost necessity. Having millions of years of experience against microbes, Fungi are well equipped to battle bacteria. They produce a wide array antibacterial agents that have been used in modern medicine ever since the 1930s with the discovery of penicillin from Alexander Flemmings studies. Emulating this, the study of several fungal species from honeymoon Island was conducted using ESKAPE Assays, HPLC, LC-MS QTOF as well as 1-D and 2-D NMR to find new potential antimicrobial Agents.

Presented by: Ezequiel Cruz Rosa *(Graduate, Organic Chemistry)*

Studies of New Synthetic Ketogenic Molecules

Ketosis is a metabolic state where the liver produces small molecules called ketone bodies during prolonged fasting and carbohydrate restriction. Most of the cells in our body can use ketone bodies as a source of energy. More importantly, ketosis has already been proven an effective treatment for epilepsy and type 2 diabetes, and is being studied for some neurological disorders as well. Although, a good amount of research has been done on the effects of the ketogenic diet, the synthesis of novel compounds that might contain ketogenic activity has thus far been neglected. Herein, our endeavor is to synthesis potential new ketogenic compounds for further exploration. Some of these are described in this presentation.

Presented by: Mohammad Nazmus Sakib *(Graduate, Organic Chemistry)*

Extraction, Fractionation, and Metabolomic Analysis of Endophytic Fungal Sample EG12-41E-2

Healthcare facilities are haunted by a myriad of virulent and drug-resistant bacterial strains. In 2019, the Word Health Organization released a report revealing that such diseases are responsible for 700,000 annual deaths around the world. Among these bacteria can be found the infamous ESKAPE pathogens: Enterococcus faecium, Staphylococcus aureus, Klebsiella pneumoniae, Acinetobacter baumannii, Pseudomonas aeruginosa, and Enterobacter spp. Here, we attempt to inhibit the growths of the ESKAPE pathogens by utilizing the secondary metabolites found within the endophytic fungal sample EG12-41E-2. Liquid chromatography was used to fractionate the fungal sample. The resulting fractions were evaluated using NMR, QTOF-LC/MS, and bioassays. The results of the assays revealed which fractions were bioactive. These fractions were further deconstructed using HPLC to isolate the bioactive molecules. Attempts were made to elucidate the isolated compounds in hopes of discovering novel metabolites.

Presented by: Samuel Sarratt *(Undergraduate, Organic Chemistry)*

Confirming Stereochemistry of Sch725674 Using X-Ray Crystallography

Natural products chemistry offers an area for novel biologically active molecules in hopes for use in the pharmaceutical/medicinal industry. The fungal sample Ive been working on, named TAP14-279b-5b, was collected from Tapachula Chiapas, Mexico in 2014. It has activity against the ESKAPE pathogens, but through isolation and purification techniques, I can determine which compound is responsible for this. So far, I have purified one compound - Sch725674, isolated from various fungi - which crystallized out of my MPLC fraction F. Running 1H NMR, 13C NMR, and HSQC along with using SMART NMR, we confirmed the structure of the compound. After completing some literature search, this compound has bioactivity against Saccharomyces cerevisiae and Candida albicans. Using x-ray crystallography, I was able to run a 1H NMR to confirm that the stereochemistry of the four carbinol protons is (4R, 5S, 7R, 13R), which which has not been previously reported.

Presented by: Stephanie Paola Suarez *(Graduate, Organic Chemistry)*

Design and Synthesis of Stable Four-Coordinated Benzotriazole-Borane with Tunable Fluorescence Emission

A new class of stable four-coordinated benzotriazole-borane compounds was developed via gold-catalyzed alkyne hydroboration. The application of polymeric (BH2CN)n reagent gave the formation of cyano-amine-boranes (CAB) complexes with less basic N-heterocyclic amines and anilines. Various new CABs were investigated in catalytic hydroboration to synthesize N-B cycles. The 1,2,3-benzotriazoles were identified as the only feasible N-source, giving the four coordinated borane N-B cycles (BTAB) in excellent yields (up to 90%) with good functional group tolerability. This new class of polycyclic N-B compounds showed excellent stability toward acid, base, high temperature, and photo-irradiation. The facile synthesis, excellent stability, strong and tunable fluorescence emission make BTAB interesting new fluorescent probes for future chemical and biological applications.

Presented by: Qi Tang *(Graduate, Organic Chemistry)*

Synthesis of Thiazole Derivatives with Hantzsch Condensation

By performing a Hantzsch condensation reaction on thiocyanates of acetophenone or propiophenone with several aniline derivatives, a library of N-Substituted 2-aminothiazole compounds have been synthesized. Improved synthesis of these compounds is a focus in medicinal chemistry due to unique biological activities exhibited by these molecules, including use as antimicrobial agents, anti-cancer or anti-tumor agents, and potential activity in combating neurodegenerative diseases. The library of aminothiazoles synthesized in this work is also being evaluated to prevent neural cell death and stop the progression of Alzheimer's disease.

Presented by: John Tatum *(Undergraduate, Organic Chemistry)*

One-pot reductive acylation and silylation of various benzoquinones, naphthoquinones and anthraquinones

The reversible reduction of quinone compounds to their hydroquinones is commonly seen in nature and is associated with the built-in triggering mechanisms of various potent antibiotics such as mitomycin C and daunomycin. Regulating this process can be challenging due to the relative ease of oxidation of the reduced hydroquinones, often yielding other unwanted products. The use of oxygen-protecting groups as a means of trapping the hydroquinone reduction products, is a strategy our lab is studying. Our goal is to execute the one-pot reductive acylation or silylation of photo-sensitive biologically active quinones to their hydroquinone forms. We aim to use this strategy to access otherwise unstable hydroquinones and study their enzymatic cleavage properties and capabilities to serve as pre-reduced, O-protected prodrugs.

Presented by: Katrinah Tirado *(Graduate, Organic Chemistry)*

Facile Synthesis of Hetero Polyaromatic Hydrocarbons (PAH) via Styryl Diels-Alder Reaction with Conjugated Diynes

The styryl dehydro-Diels—Alder reaction with conjugated diyne is reported. While typical alkyne-styrene condensation required elevated temperature ($>$ 160 C), the application of conjugated diyne allowed effective transformation under milder condition (80 C). Thermal stable triazole-gold catalyst further improved the reaction performance (up to 90% yield), giving the desired alkynyl-naphthalene in one step with molecular oxygen as the oxidant. Sequential alkyne activation gave various polyaromatic hydrocarbons (PAHs) in excellent overall yields, highlighting the efficiency of this new strategy for the preparation of PAHs with good functional group tolerability and structural diversity.

Presented by: Jingwen Wei *(Graduate, Organic Chemistry)*

Mass spectrometry-guided isolation of polyketide macrolides from the Antarctic tunicate Synoicum adareanum

Defenseless against predation and subject to competitive ecosystems, marine invertebrates rely on an evolutionary mechanism to promote survival: secondary metabolites, also known as natural products (NPs). NPs act as species-specific chemical defenses. Bioactive by design, many NPs derived

from marine invertebrates display cytotoxic and antimicrobial properties. NPs of particular interest are a class of macrolides known as palmerolides, found in Synoicum adareanum. This project aimed at the isolation of palmerolides from S. adareanum for downstream bioassays. Fractionation was achieved via a progression of separations: column chromatography followed by HPLC (high pressure liquid chromatography). Analysis of each fraction used quadrupole time-of-flight mass spectrometry (QTOF MS) to identify palmerolide-like fragmentation. The hits underwent further HPLC to achieve pure isolates. Structural verification of the palmerolide isolates was performed using via 1H NMR and mass spectrum data.

Presented by: Jennifer Williams *(Undergraduate, Organic Chemistry)*

Benzotriazole as a novel directing group to facilitate C-H functionalizations

C-H bond functionalization has been a long-standing problem, for its selectivity and reactivity. For the last two decades, directing group strategies have stands out, showing its power in precise and high-yielding functionalizations on C-H bonds. C-H bond functionalization catalyzed by palladium could go through Pd(0)-Pd(II) cycle and Pd(II)-Pd(IV) cycle, while the Pd(II)-Pd(IV) cycle is compatible for both C-C and C-X formations. Herein we report a new series of benzotriazole directing groups, with three coordination site to interact with the metal atom, which can accelerate C-H Bond functionalization through Pd(II)-Pd(IV) catalytic cycle, achieving C-C and C-X bond formation reaction.

Presented by: Chengkai Xu *(Graduate, Organic Chemistry)*

Synthesis and development of biodegradable antimicrobial guanylated polycarbonate polymers

The increasing resistance of antibiotics become a major concern in public health. Substantial interest has been devoted to the development of biodegradable antimicrobial polymers as a solution for combating antibiotic resistance. Herein, we report the design and synthesis of biodegradable antimicrobial random guanylated polycarbonate copolymers initiated by carbon chain that containing guanidium derived monomers and hydrophobic monomers. With different equivalence of monomers and different length of carbon chain, a series of antimicrobial polymers were synthesized. The antimicrobial activities against both Gram-negative and Gram-positive bacteria of these polymers are reported, as well as the hemolytic activity. The time kill assay show these polymers have low tendency to derivate the resistance. Other bacterial studies were also involved for drug-resistance determination, that suggest these polymers antimicrobial via membrane disruptions.

Presented by: Menglin Xue *(Graduate, Organic Chemistry)*

Diastereoselective phospha-Michael addition of aryl phosphinates catalyzed by a phase transfer agent

We are engaged in the development of a catalytic diastereoselective approach to the construction of organophosphinate compounds that are valued in the inhibitor design of metallo proteinases. Our strategy involves the phospha-Michael addition of aryl phosphinates to -disubstituted vinyl ketones under the action of phase transfer catalysts (PTCs). Reaction conditions using crown ethers as

PTCs led to high diastereoselectivities in most cases and when the phosphinates nucleophile contains a non-racemic menthyl substituent, additions led to enantiopure phosphinate adducts. A closed transition state model is proposed to explain the stereoselectivity in these addition reactions with the observed selectivity rationalized as preferential attack of phosphinate on vinyl ketones in the S-cis conformation.

Presented by: Krishna Yadavalli *(Graduate, Organic Chemistry)*

Investigating the effects of linker substitution on H2 adsorption between two isostructural Metal-organic Frameworks (MOFs)

The effects of linker substitution on the H2 adsorption mechanism between two isostructural metalorganic frameworks (MOFs), MOF-505 and NOTT-101, were investigated using grand canonical Monte Carlo simulations. Three potential energy functions of increasing complexity for the H2 were used for the simulations. Simulations of H2 adsorption in both MOFs resulted in isotherms that are in reasonable agreement with the experimental values at 77 K and various pressures. The preferred sites of adsorption for both MOFs at low pressures were found to be located near the Cu(II) ions of the copper paddlewheels, which is consistent with experimental expectations. The distinct linkers for the MOFs contributed to the quantitative differences in the calculated MOF partial charges, predicted H2 adsorption isotherms, and calculated isosteric heats of adsorption (Qst) for simulated models. Notably, it was observed through simulation that MOF-505 exhibit higher low-pressure H2 uptake than NOTT-101.

Presented by: Louis Herrera *(Undergraduate, Physical Chemistry)*

Judges

Faculty

Laura Anderson, Ph.D.
Bill Baker, Ph.D.
Kirpal Bisht, Ph.D.
Marie Bourgeois, Ph.D.
Sherrisse Bryant, Ph.D.
Jianfeng Cai, Ph.D.
Marlius Castillo, Ph.D.
Daniel Cruz-Ramírez de Arellano, Ph.D.
Theresa Evans-Nguyen, Ph.D.
Kimberly Fields, Ph.D.
Wayne Guida, Ph.D.
William Hungerford, Ph.D.
Scott Lewis, Ph.D.
Wenqi Liu, Ph.D.
Abdul Malik, Ph.D.
Andrii Monastyrskyi, Ph.D.
Tony Pham, Ph.D.
Hans Renata, Ph.D.
Xiaodong Shi, Ph.D.
Ioannis Spanopoulos, Ph.D.
Christie Tang, Ph.D.
Ed Turos, Ph.D.
Arjan van der Vaart, Ph.D.
Sameer Varma, Ph.D.
H. Lee Woodcock, Ph.D.

Graduate

Nathaniel Johnson

Organizing Committee

Sponsor(s)
Tampa Bay ACS
Chemistry Council of Graduate Students

Cover Art/Design
Julian Melendez

Staff and Faculty Support
Ryan Jahn
Joshue Martinez
Roberto Avergonzado
Kaitlyn Kroner
Paige Romero
Karissa Budnack
Joy E. Harris, Ph.D.
Kimberly Fields, Ph.D.
Scott Lewis, Ph.D.

Committee Members
Julia Dematteo
Briley Humphrey
Donna Trask
Sihao Li
Odesha Taylor
Nicole Boose
Paul Orndorff
Ayesha Farheen
Xue Zhao
Shelby Kell
Stephanie Suarez
Angelie Matar

Committee Chairs
Brandon Yik
Nicole A. Miller
Dianna Kim
Guy W. Dayhoff II

Support Office
Office of High Impact Practices and Undergraduate Research