GOLDWATER SCHOLARSHIP

CHEMISTRY
GOLDWATER RECIPIENT:

2021-2022 APPLICATION

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PROFILE INFORMATION

PERSONAL DETAILS

First Name	John
Last Name	Smith

CAREER/PROFESSIONAL ASPIRATIONS

What is the highest degree you plan to obtain?	Ph.D.
In 1-2 sentences, describe your career goals and professional aspirations. It will be used in publications if you are selected as a scholar	Ph.D. in Chemistry. Aspire to lead research efforts that will benefit society, such as bioinorganic medicinal chemistry.

What are your career goals and aspirtations? Indicate which area(s) of mathematics, science, or engineering, you are considering pursuing and specify how your current academic program and your overall educational plans will assist you in achieving your career goals and professional aspirations

After completing my undergraduate degree, I plan to enroll in a chemistry Ph.D. program with an emphasis on inorganic chemistry. I am interested in advancing fields that benefit society, and strive to be a lead researcher at the cross-section of inorganic and medicinal chemistry. In the next year, I plan to supplement my ongoing inorganic research with more biochemical experiences, to help refine the graduate programs I will apply to. During my undergraduate studies, I've worked extensively in the Saouma lab, investigating organometallic complexes for CO2 reduction. When I initially joined in February 2020, I was unable to physically be in lab due to the pandemic. However, I kept in contact with the principal investigator (PI), Prof. Saouma, and she used the spring and summer of 2020 to remotely teach me the fundamentals of lab techniques (e.g. cyclic voltammetry, and 1H-NMR & IR spectroscopies) and to discuss projects. It was challenging to learn. My organic chemistry coursework would be later in the fall and I had only taken 2 semesters of in-person general chemistry labs. However, learning the background and procedures enabled me to write a proposal for my university's undergraduate research opportunity program (UROP), which the Office of Undergraduate Research (OUR) selected for funding. I began research fall 2020 which allowed me to practice organic techniques in lab, like column chromatography, in parallel with my class lectures. Conducting research in the Saouma lab has also taught me how to think critically and problem solve. In one of my projects, the literature procedure reported a 1H-NMR spectrum that had too many peaks for the number of symmetric hydrogens on the desired compound. With the help of my PI, I determined that it was an impurity and I figured out what adjustments needed to be made to purify the compound. I have also learned how difficult, yet rewarding, it is to consolidate research into a presentation. For example, this past summer I gave an oral presentation to my Research Experiences for Undergraduates Program (REU) cohort and then a poster presentation at the OUR summer symposium, where I presented with other STEM-focused undergraduates to a general audience. This has improved my presentation skills and given me the confidence share my research on the national stage at the spring 2022 ACS national meeting (San Diego). Notably, this conference will allow me to explore bioinorganic chemistry; I have always been interested in how bio and inorganic chemistry are intertwined. In addition, I have applied to biochemical summer research programs to nurture these research skills since I only have experience in inorganic research. Attending this conference and participating in these programs both hone my presentation skills as well as solidify the topics I want to focus on for my Ph.D. Overall, I look forward to a career where I can utilize inorganic chemistry to benefit humanity and my future career in research.

Describe an activity or experience that has been important in helping shape or reinforce your desire to pursue a research career in STEM.

In my senior year of high school, I developed and executed two scientific inquiries for the International Baccalaureate (IB) program. The minimum requirement for the program was to spend 10 hours, but I spent 20 hours on each experiment. They weren't revolutionary — one was a literature review on heavy metal contamination in plants and the other an experiment with different salt bridges in galvanic cells — but I loved the process. I would talk to my teachers every day after school and ask why my results had changed, or how I could adapt my experiment to show more definitive results. I questioned why salt bridges with different ion charges affected or didn’t affect the rate of deposition of copper on the electrode. I spent hours reading literature and cross analyzing the different papers to compare the effects of heavy metal poisoning in plants. My curiosity piqued when I read that some heavy metals, in small amounts, actually improves some plants’ metabolic pathways. Even after I finished my lab reports, I still had unanswered questions. Through these projects, I realized my passion for research; I had a passion for asking questions and a pressing desire for answers.

In what way did COVID-19 or other hardships over the past couple years affect your research career plans and did those events alter your ability to pursue those plans? If you have had to make changes, in what way(s) did you adapt to the situation? If COVID-19 did not influence your plans, simply state there was no impact.

When I joined the Saouma lab in February 2020, the plan was be conduct synthetic experiments in lab. However, due to the pandemic, the university decided to shutdown access to research labs that only reopened in May for postdocs and graduate students. I was one of four undergrads in the Saouma lab affected by this decision. As my project is synthesis-based, this delayed my plans. I did not let this deter me and I stayed in contact with the PI, the only one out of four undergrads. My PI virtually taught me different analytical techniques and I also studied what other researchers had concluded, which allowed me to deepen my understanding of the Mn compounds I was to work with. While it was not what we had originally planned, this time proved invaluable in strengthening my foundation knowledge of my project, and writing skills (as I wrote a UROP proposal for funding). In the fall 2020 when the labs were less restricted, I was the only undergrad that started to work. While the university allowed for some experimental work, we had to follow social distancing protocols. Thus, while I could be physically in lab, my mentor mostly guided me virtually. It was difficult to learn how to use equipment without a demonstration, however, with detailed guidance from my mentor's and senior lab members, I quickly learned how to operate in the lab independently. Thanks to this, in January 2021 when the other undergraduates started, I could help mentor them.

Optional Question: Goldwater Scholars will be representative of the diverse economic, ethnic and occupational backgrounds of families in the United States. Describe any social and/or economic impacts you have encountered that influenced your education - either positively or negatively - and how you have dealt with them.

My parents are first-generation immigrants from China. My father came as a post-doctoral researcher and my mother with a high school education. Education was highly valued in our household. Ultimately, my mother earned a master's; tuition costs left us with little for living expenses but they were persistent. It's from watching them that I developed my work ethic and dedication to education — I used to fold napkins for a restaurant when I was seven for pocket money to buy books because I had read through all the children's books at the library. When I graduated high school, my parents could not help with college expenses. My mother had started a business, and my father was a professor 11/12 months in China. That left me responsible to provide for my education. In order to pay for tuition and housing, I've worked 2-3 part-time jobs since my freshman year at the university. I found i) funding for my research, employment as ii) an eye recovery technician, and iii) employment as a waitress. Some days I would wake up at 5 AM to study before classes, conduct research after classes, run to my job as a waitress, then scurry to my job as an eye bank technician, and finally return home at midnight. I persevered through the long days and sleepless nights (quite literally) and learned how to prioritize and manage my time. Through these difficulties, I've reflected on how committed I am to my education; I'm resolved to go beyond my undergraduate studies and obtain a doctorate degree.

RESEARCH PROJECTS AND SKILLS

RESEARCH PROJECT #1

Synthesis and Analysis of Mn Catalysts for Electrochemical Reductions of CO_2

Dates	08/2020-04/2021
Average Hrs/Wk	15 (academic year); 10 (summer)
Name of Project Mentor	Caroline Saouma
Position and Affliation of Project Mentor	Associate Professor of Chemistry University of Utah
Where the research was performed	University of Utah
Do you have paper/publications/presentations related to this project?	No

Description of research, including your involvement in AND contribution to the project

This research project investigates the impact of changing L in $LMn(CO)_3Br$ species (L is a chelating nitrogen ligand), on the electrocatalytic interconversion of CO_2 and formic acid (FA). Léval et al. showed the catalysts were effective at decomposing FA to CO_2 and H_2 with base addition. Dr. Bhattacharya, determined that a similar $(bpy)Mn(CO)_3Br$ was viable for electrocatalytic reduction of CO_2 to FA. My project focuses on testing these Mn species as electrocatalysts for both CO_2 reduction to FA and FA oxidation to CO_2, allowing for a single mechanistic picture to emerge. I synthesized the $LMn(CO)_3Br$ complexes and will test their electrocatalytic capabilities via cyclic voltammetry (CV) and bulk electrolysis in the future (2022-2023 academic year). This work was supported by funding from the Undergraduate Research Opportunities Program at the University of Utah (fall 2020 and a spring 2021 renewal), allowing me to be the sole researcher on this project.

Research Skills: Briefly describe any research skill(s) you developed while working on this project that will be important going forward in your research

This was my first chemistry lab experience; I learned lab routines such as column chromatography, TLC, and 1H-NMR analysis. The complexes are air-, moisture- and light-sensitive so I learned Schlenk techniques and glovebox procedures. These skills were foundational for my next project.

RESEARCH PROJECT #2

Conversion of CO_2 to CO Using Mn Electrocatalysts

Dates	04/2021-ongoing
Average Hrs/Wk	15 (academic year); 40 (summer)
Name of Project Mentor	Caroline Saouma
Position and Affliation of Project Mentor	Associate Professor of Chemistry University of Utah
Where the research was performed	University of Utah
Do you have paper/publications/presentations related to this project?	**Poster; Presenter** Wang, A., & Saouma, C. T. "Conversion of CO2 to CO Using Mn Electrocatalysts" OUR 2021 Summer Symposium, online, August 5, 2021.

Description of research, including your involvement in AND contribution to the project

This project focuses on the characterization of proposed intermediates of (bpy)Mn(CO)3X catalyzed reduction of CO2 to CO (catalyst: X=Br; intermediates: X=CO(OMe), CO(OH), CO) . I am synthesizing these intermediate species, which will then be used to study their electrochemical properties by CV. I will be comparing the electrochemical behavior of (bpy)MnCO(OH) to [(bpy)Mn(CO)4]+ to see at what potentials CO production occurs and gain mechanistic insight. By doing this, we will gain a better understanding of how to favor a protonation-first pathway, where addition of a proton will generate [(bpy)Mn(CO)4]+ which can be reduced to release gaseous CO. This will overall contribute towards an understanding of how to generate CO with less energy input. This work was supported by the Research Education for Undergraduates (REU) Program (summer 2021) and by an NSF grant #1945646 (fall 2021-present), allowing me to be the sole researcher on this project.

Research Skills: Briefly describe any research skill(s) you developed while working on this project that will be important going forward in your research

I refined my CV and 1H-NMR collection techniques and analysis. I have become more comfortable using Schlenk lines and gloveboxes to ensure light-, air-, and moisture-free conditions. I've developed new analytical techniques such as IR spectroscopy, and doing reactions with toxic gases like CO.

RESEARCH PROJECT #3

Relocation of Lab

Dates	08/2021-12/2021
Average Hrs/Wk	10 (academic year)
Name of Project Mentor	Caroline Saouma
Position and Affliation of Project Mentor	Associate Professor of Chemistry University of Utah
Where the research was performed	University of Utah
Do you have paper/publications/presentations related to this project?	No

Description of research, including your involvement in AND contribution to the project

This project focused more on the logistical aspects of research. I learned and aided in chemical disposal and clean up, as well as how to transport (air-, light-, and water-sensitive) chemicals. I aided in the equipment disassembly, including gloveboxes and IR instruments. After the relocation, I aided in the reassembly of equipment, including gas cylinders, gloveboxes, IRs, and high vacuum Schlenk lines. This was funded the University of Utah Chemistry department.

Research Skills: Briefly describe any research skill(s) you developed while working on this project that will be important going forward in your research

I've learned how to repair the listed equipment, some of which use sensitive parts or toxic chemicals (i.e. mercury monometers for a Schlenk line). I've also learned how to troubleshoot equipment malfunctions and interface with equipment technicians.

MENTOR RECOGNITION

LETTER WRITER INFORMATION

OTHER ACTIVITIES/ ACCOMPLISHMENTS

Activity/ Accomplishment	Hospital Volunteer
Organization/Scope of Activity	University of Utah/Community
Role/ Involvement	I help patients find where they need to be in the new hospital layout and help direct visitors to the resources they need. I also help to screen COVID in visitors and staff and ensure safety protocols are met.
Position/Length of Involvement	Member/Academic Year

Activity/ Accomplishment	Eye Recovery Technician
Organization/Scope of Activity	Utah Lions Eye Bank/Other
Role/ Involvement	As an employee of the Utah Lions Eye Bank, an extension of the John A. Moran Eye Center and a nonprofit organization that facilitates the gift of sight worldwide, I am highly trained in the surgical recovery of eyes for transplantation and research.
Position/Length of Involvement	Technician/More than one academic Year

Activity/ Accomplishment	Restaurant Server
Organization/Scope of Activity	Other
Role/ Involvement	By having positive communication with guests and collaborating with several servers to provide quick and impressive service, I improve customer experiences. As the second-most-senior staff member, I am in charge of training new employees.
Position/Length of Involvement	Senior Staff Member/More than one academic Year

Activity/ Accomplishment	Teacher's/Learning Assistant
Organization/Scope of Activity	University of Utah/College/University
Role/ Involvement	Worked in conjunction with the professor and teaching staff to develop study plans for students. In Spring 2020, I was a Teacher's Assistant for General Chemistry. In Fall 2020, I was a Learning Assistant for mathematics.
Position/Length of Involvement	Teacher's/Learning Assistant (TA/LA)/Academic Year

RECOGNITIONS

Recognition/Type	REU Fellowship/National
Year	2021
Description	Awardees are chosen from a competitive national and local applicant pools. Selection is based on an excellent personal statement and academic records.

Recognition/Type	UROP/College/University
Year	2021
Description	Applicants prepare an application that includes a detailed research proposal. Stipend awarded by College of Science faculty to conducted proposed research. Granted twice for Fall 2020 and Spring 2021.

Recognition/Type	Mark Thomas Rozelle Award/National
Year	2021
Description	Awarded to students excelling in Organic Chemistry courses.

Recognition/Type	Breckenridge Honors Scholarship/College/University
Year	2021
Description	Awarded to top scoring student in Honors General Chemistry courses.

Recognition/Type	Utah Flagship Scholarship/College/University
Year	2019
Description	Merit-based selection of incoming university first-years.

CURRENT COLLEGE/UNIVERSITY

GPA	3.89
Graduation Year	Spring 2023

COURSEWORK

RESEARCH ESSAY

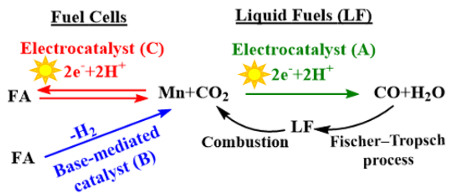

Fig. 1. Summary of the interconversion of CO_2, CO, and FA (Mn= catalyst). Overview of research I conducted: **(A, green):** summer 2021 and **(C, red):** fall 2020 – spring 2021. **(B, blue):** FA oxidation explored by Léval et al.

Electrocatalytic Studies of CO_2 Reduction Using Mn Complexes

UN Secretary-General Guterres put it best at the 2021 COP26 U.N Climate Summit: "*Our addiction to fossil fuels is pushing humanity to the brink. We face a stark choice: Either we stop it — or it stops us* (1)." One method to address this crisis is to recycle atmospheric CO_2 to liquid fuels; the first step of which is to electrocatalytically convert CO_2 to CO. By using solar energy to provide the electrons for the reduction of CO_2, this method becomes a net-zero CO_2 emission energy source (Fig. 1, A), allowing for use of existing infrastructure. Alternatively, CO_2 can be reduced to formic acid (FA), which is pertinent to advancing fuel cells, whereby FA is oxidized to CO_2 (Fig. 1, B, C). Expensive Ru and Re complexes facilitate these reductions, however, more research is needed to develop catalysts that make use of earth-abundant and inexpensive metals. *My work entails exploring Mn complexes for the electrocatalytic interconversion of CO_2 and CO or FA.*

Recently, the dehydrogenation of formic acid to CO_2 and H_2 was explored by Léval et al. (2). They found that $LMn(CO)_3Br$ species, where L is a chelating N-N ligand, are viable for this reaction (Fig. 2, left); the identity of L (Fig. 2, red boxes) greatly impacts both the rate of FA dehydrogenation and yields of CO_2 & H_2 (2). This interested me because a former graduate student in the Saouma group, Dr. Bhattacharya, showed that the related $(bpy)Mn(CO)_3Br$ species (Fig. 2, red box) can electrocatalytically reduce CO_2 to FA (5). Given that this species is viable for FA dehydrogenation (2), albeit at a lower performance, I wanted to see if: **a)** the ligands would have an effect on electrocatalytic CO_2 reduction (Fig. 2, blue, clockwise), and **b)** if these complexes can be used as electrocatalysts for FA oxidation (Fig. 2, blue, counterclockwise). Electrochemical FA oxidation is rare (6) and if these Mn complexes can electrochemically reduce CO_2 and oxidize FA with low energy input, it would be an ideal electrocatalyst for fuel cell purposes (Fig. 1, C). For this project, I focused on four Mn complexes (Fig. 2, red boxes). My work involves synthesizing ligands A and C (as the other two ligands are commercially available), metalation with Mn, and electrocatalytically testing these different Mn complexes to gain insight into the feasibility & mechanism of the electrocatalytic interconversion of CO_2 and FA.

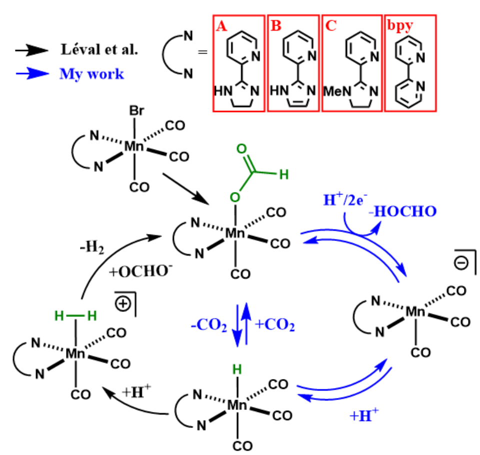

Fig. 2. (black): Mechanistic scheme for the thermal dehydrogenation of FA to CO_2 and H_2 (2). **(blue):** Proposed electrocatalytic formate oxidation and CO_2 reduction (focus of my project).

When I began my research, there were strict social distancing guidelines. I learned how to use equipment from schematics, through remote discussions with my PI, and by learning at a distance from other lab members. This taught me to be more observant of my research methods and to think critically of both my own technique and the literature I was relying on for syntheses. For example, the literature NMR spectrum of

A$Mn(CO)_3Br$ (Fig. 2) reported ten unique resonances (2). However, the structure of the desired product indicates that there should be only seven unique hydrogens (nine total). After following the literature preparation, I obtained the same ten resonances along with a few additional resonances. After a discussion with my PI, I determined that the literature could have inadvertently reported impurities in their spectrum. As such, I had to figure out how to purify this (and other Mn) products. This was not a trivial task as these compounds are light/moisture/air-sensitive and required me to work in the dark in a glovebox. I succeeded, and my ^1H NMR spectrum of the crystallized AMn(CO)3Br material showed the expected seven resonances (nine total).

Once I synthesized these Mn complexes, I ran initial cyclic voltammograms (CVs) in spring 2021 which, unexpectedly, showed a complicated electrochemical image (Fig. 3). There were not distinct reversible redox peaks. After discussing with my PI, we decided I would focus on $(bpy)Mn(CO)_3X$, which is electrochemically more straightforward to interpret (Fig. 3, blue; X = Na^+). I will return to the other Mn complexes once I am more comfortable collecting and interpreting electrochemical data. If successful, this will result in a first author publication with my PI (no other authors).

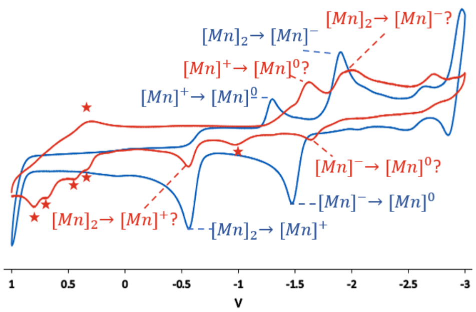

Fig. 3. CVs of A$Mn(CO)_3Br$ **(red)** and $[Na]^+[(bpy)Mn(CO)_3]^-$ **(blue)** in MeCN with Fc/Fc^+ reference. $[Mn]^0$ is the neutral $LMn(CO)_3$ species which quickly dimerizes to $[Mn]_2$. $[Mn]^+$ and $[Mn]^-$ correspond to Mn(I) and Mn(-1) species, respectively. (?) indicate redox events that mirror those in $[(bpy)Mn(CO)_3]^-$ and (★) correspond to unknown redox events.

I have been studying the $(bpy)Mn(CO)_3Br$ system since summer 2021, following up on work initiated by Dr. Bhattacharya (Fig. 4). This catalyst is well-known for CO_2 to CO conversion under less acidic conditions, following the reduction-first mechanism shown in Fig. 4 (5). Carter et al. (3) showed theoretically that the protonation-first mechanism may be thermodynamically more feasible under certain conditions. This is desirable, as it would allow for catalysis to occur at a lower over-potential (less energy input). To gain insight into this mechanism, my research focuses on synthesizing and characterizing some of the proposed intermediates of the catalytic cycles shown in Fig. 4: $(bpy)Mn(CO)_3COOH$ and $[(bpy)Mn(CO)_4]^+$. I also want to prepare and characterize $(bpy)Mn(CO)_3COOMe$ (Fig. 5, pink, Me) to serve as a synthetic analogue to the more reactive $(bpy)Mn(CO)_3COOH$.

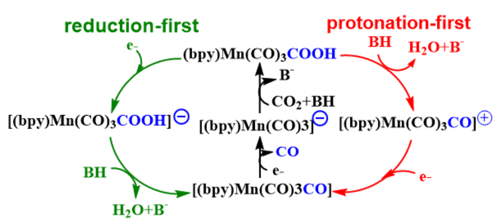

Fig. 4. Proposed mechanism for reduction of CO_2 to CO by $(bpy)Mn(CO)_3Br$. **(green):** Reduction-first mechanism occurs at more negative potentials (observed in most studies). **(red):** A more desirable protonation-first mechanism which occurs at less negative potentials. Itis challenging to access because little is known about the pK_a of the hydroxy carbonyl ligand (which I plan to estimate as part of the characterization).

Dr. Bhattacharya prepared $(bpy)Mn(CO)_3COOX$ (X = H, Me) by addition of hydroxide or methoxide to $[(bpy)Mn(CO)_4]^+$, though she noted reproducibility issues which I corroborated (Fig. 5). I determined that the starting material, $[(bpy)Mn(CO)_4]^+$, initially thought to be a stable species, was actually $[(bpy)Mn(CO)_3(MeCN)]^+$. I suspect that the irreproducibility is due to the inadvertent use of $[(bpy)Mn(CO)_3(MeCN)]^+$, which gives intractable mixtures of product, instead of $[(bpy)Mn(CO)_4]^+$, which gives clean reactions.

My first task was to synthesize pure $[(bpy)Mn(CO)_4]^+$, which I initially attempted following the established 2-step procedure (Fig. 5, red). I found that using fluorinated salts such as $AgBF_4$ or $TlPF_6$ in the first step produces $[(bpy)Mn(CO)_3(MeCN)]^+$ along with an impurity, which I believe is a Mn-F complex, given that it's diagnostic NMR resonances only appear when using a fluorinated counter-anion. Switching to non-fluorinated salts such as $NaBPh_4$ and AgOTf in MeCN affords the desired intermediate $[(bpy)Mn(CO)_3(MeCN)]^+$ cleanly. However, addition of CO (step 2) only yields partial conversion to $[(bpy)Mn(CO)_4]^+$, even when run in dichloromethane, under elevated pressures of CO, and allowing the reaction to run for different lengths of time (as ascertained by IR spectroscopy). I believe this is due to the electron-deficient Mn preferentially coordinating MeCN over CO.

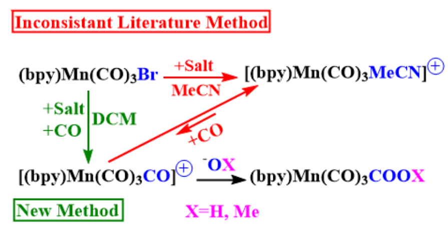

Fig. 5 Syntheses of: **a)** $[(bpy)Mn(CO)_4]^+$ following the literature (red) & new (green) method, and **b)** $(bpy)Mn(CO)_3COOX$ (X = H, Me). DCM = dichloromethane.

Hence, I had to develop a new synthetic route. I found that bromide extraction from $(bpy)Mn(CO)_3Br$ must be done in a non-coordinating solvent and in the presence of an atmosphere of CO to give the desired $[(bpy)Mn(CO)_4]^+$ quantitatively (Fig. 5, green). Once I found the correct combination of solvent (DCM) and salt ($AgBF_4$), I prepared pure samples of $[(bpy)Mn(CO)_4]^+$, which I believe Dr. Bhattacharya may not have reproducibly done. I am now in position to prepare the desired complexes in high yield and pure form. I will fully characterize the species, which includes getting solid-state structures.

I also explored how to synthesize $LMn(CO)_3Br$ precursors more easily. I found that certain time and labor-intensive aspects of the procedure could be eliminated. For example, the compounds are not so sensitive that strict Schlenk technique and inert atmosphere workup is necessary. This allows me to more readily make the precursors in pure form on a large scale, and has allowed me to guide two more junior undergrads on the syntheses of related Mn compounds (for a different project).

At present, I am working to complete the characterizations and electrochemical studies of these Mn intermediates. Once completed, this project initiated by Dr. Bhattacharya and continued by me, will be formalized into a publication. By finding a synthetic route that gives access to the proposed intermediates, I will be able to conduct electrocatalytic testing and preforming additional characterizations. This will provide a better understanding of the mechanistic landscape of this catalyst.

1. https://www.un.org/press/en/2021/sgsm20997.doc.htm. (accessed Nov 16, **2021**).
2. Léval, A., Agapova, A., Steinlechner, C., Alberico, E., Junge, H., & Beller, M. *Curr. Green Chem*. **2020**, *22*, 913.
3. Riplinger, C., & Carter, E. A. *ACS Catal*. **2015**. *5*, 900.
4. Bhattacharya, M. (2020). *Role Of Amines In The Capture And Conversion Of Carbon Dioxide To Carbon Monoxide And Formate Using Homogeneous And Heterogeneous Catalysts* (dissertation).
5. Bhattacharya, M. , Sebghati S., VanderLinden R. T., and Saouma C. T. *J. Am. Chem. Soc.* **2020** *142*, 17589.
6. Cunningham D. W., Barlow J. M., Velazquez R. S., Yang J. Y., *Angew. Chem. Int. Ed.* **2020**, *59*, 4443.