

**RESEARCH CORPORATION FOR SCIENCE ADVANCEMENT  
Cottrell Scholar Award Application**

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**Appointment Date:** August 1, 2018 (research delays due to COVID)

***EDUCATION AND EXPERIENCE:***

- |                       |   |
|-----------------------|---|
| Aug. 2018 – current   | Schmid College of Science and Technology, Chapman University<br>Orange, CA<br>Assistant Professor   |
| Mar. 2016 – Aug. 2018 | Division of Chemistry and Chemical Engineering, California Institute of Technology<br>Pasadena, CA<br>Postdoctoral Researcher, Mentor: Dr. Robert H. Grubbs |
| Aug. 2010 – Dec. 2015 | College of Chemistry, University of California, Berkeley<br>Berkeley, CA<br>Ph.D. in Chemistry, Mentors: Drs. T. Don Tilley and Robert G. Bergman           |
| Aug. 2006 – May 2010  | Scripps College, Claremont, CA<br>B. A. in Chemistry, <i>summa cum laude</i> ; Mentor: Dr. Nancy S. B. Williams   |

***PROPOSAL TITLE:***

Broadening Applications of the Weakly Coordinating Triflimidate Anion in Main Group Catalysis

***ABSTRACT:***

Research: There is an ongoing need for efficient and robust catalysts based on earth-abundant elements as replacements for precious metal catalysts. The use of main group compounds as Lewis acid catalysts has emerged as a powerful strategy for sustainable organic transformations. In the proposed work, undergraduate students in the Liberman-Martin Group will study main group Lewis acids featuring the weakly coordinating triflimidate anion,  $N(SO_2CF_3)_2^-$ . Research projects are structured to provide insight into the role of main group element identity, compound geometry, and anion structure on Lewis acidity and catalytic activity. Simultaneously, the proposed work will provide new methods to transform commodity alkene, alcohol, and carbonyl substrates.

Teaching: Argumentation involves supporting claims with convincing evidence. Although scientific argumentation has cognitive and social benefits for students, pedagogical practices to support students' construction of arguments are not widely implemented. The PI proposes to infuse scaffolded training in argumentation across the organic chemistry curriculum at Chapman University. Organic chemistry is well-suited to these interventions, as over-reliance on memorization in organic chemistry courses leaves students ill-equipped to solve mechanism or reactivity problems. In introductory organic chemistry courses, the PI will incorporate scaffolded argumentation practice across in-class worksheets, problem sets, and exams. In an elective advanced organic chemistry course, students will be further challenged to interpret experimental data when constructing arguments. The emphasis on scientific argumentation is designed to help students develop critical thinking skills and engage in scientific practices.

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**PUBLICATIONS OF PRINCIPAL INVESTIGATOR.** (last 5 years; July 2017–July 2022)

\* Denotes corresponding or co-corresponding authorship

‡ Denotes equal contribution

Undergraduate coauthors are underlined

**Publications Resulting from Work During Tenure-Track Appointment (Independent of Mentors)**

1. Fleener, C. R.; Chang, D. K.; **Lieberman-Martin, A. L.**\* Carbodiphosphorane-Catalyzed Hydroboration of Ketones and Imines. *Organometallics* **2021**, *40*, 4050–4054.
2. Naumann, R. A.; Ziller, J. W.; **Lieberman-Martin, A. L.**\* Crystal Structure of 2-(2,6-diisopropylbenzene)-*N,N*-diethyl-3,3-dimethyl-2-azaspiro[4.5]decan-1-amine: A Diethylamine Adduct of a Cyclic(Alkyl)(Amino)Carbene (CAAC). *Acta Crystallogr.* **2021**, *E77*, 903–906.
3. **Lieberman-Martin, A. L.**;\*‡ Ogba, O. M.\*‡ Midsemester Transition to Remote Instruction in a Flipped College-Level Organic Chemistry Course. *J. Chem. Educ.* **2020**, *97*, 3188–3193. (special issue on “Insights Gained While Teaching Chemistry in the Time of COVID-19”)

**Publications Resulting from Work During Tenure-Track Appointment (With Mentors)**

4. **Lieberman-Martin, A. L.**;‡ Van Vleet, M. J.;‡ Elenberger, T.; Cave, R. J.; Williams, N. S. B.\* Geometric Control of Carbon–Carbon Reductive Elimination from a Platinum(IV) Pincer Complex. (in revision for *Organometallics*, special issue on “Organometallic Chemistry Inspired by Maurice Brookhart”)
5. **Lieberman-Martin, A. L.**;\*‡ Chang, A. B.;‡ Chu, C. K.; Siddique, R. H.; Lee, B.\* Grubbs, R. H.\* Processing Effects on the Self-Assembly of Brush Block Polymer Photonic Crystals. *ACS Macro Letters*, **2021**, *10*, 1480–1486.

**Publications Resulting from Work Prior to Tenure-Track Appointment**

6. Chu, C. K.; Lin, T.-P.; Shao, H.; **Lieberman-Martin, A. L.**; Liu, P.; Grubbs, R. H. Disentangling Ligand Effects on Metathesis Catalyst Activity: Experimental and Computational Studies of Ruthenium–Aminophosphine Complexes. *J. Am. Chem. Soc.* **2018**, *140*, 5634–5643.
7. **Lieberman-Martin, A. L.**; Grubbs, R. H. Ruthenium Olefin Metathesis Catalysts Featuring a Labile Carbodicarbene Ligand. *Organometallics* **2017**, *36*, 4091–4094.
8. Chang, A. B.; Lin, T.-P.; Thompson, N. B.; Luo, S.-X.; **Lieberman-Martin, A. L.**; Chen, H.-Y.; Lee, B.; Grubbs, R. H. Design, Synthesis, and Self-Assembly of Polymers with Tailored Graft Distributions. *J. Am. Chem. Soc.* **2017**, *139*, 17683–17693.

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**Manuscripts in Preparation from Work During Tenure-Track Appointment (Independent of Mentors)**

1. Sullivan, L. P.; Kizirian, V.; **Lieberman-Martin, A. L.**\* Aldehyde and Ketone Hydrosilylation by Carbon(0) Catalysts.
2. Thammavongsy, Z.; Wilson, A.; **Lieberman-Martin, A. L.**\* Organozinc Triflimidate Catalysts for Alkyne Hydrosilylation.

## RESEARCH PROPOSAL

### Broadening Applications of the Weakly Coordinating Triflimidate Anion in Main Group Catalysis

#### Background and Motivation

Catalysis is central to chemical industry, with catalytic processes involved in producing of over 80% of all manufactured products.<sup>1</sup> Main group catalysts have achieved recent prominence as alternatives to transition metals due to the potentially lower cost and environmental impact of these elements.<sup>2</sup> One common catalytic role for main group compounds is as Lewis acids, which can catalyze a broad range of organic reactions.<sup>3</sup>

Charge significantly influences Lewis acidity, with cationic compounds typically displaying greater electrophilicities than neutral variants.<sup>4</sup> To suppress strong cation–anion interactions, cationic Lewis acid fragments must be paired with inert anions possessing highly delocalized charges. Frequently used weakly coordinating anions include carboranes, fluorinated tetraarylborates, and polyfluoroalkoxyaluminates (**Figure 1**);<sup>5</sup> however, the high molecular weights of these anions (MW = 519–967 g/mol) result in the generation of more material waste for a given molar quantity of catalyst. This work will study the triflimidate anion,  $N(\text{SO}_2\text{CF}_3)_2^-$  or  $\text{NTf}_2^-$ , as a lower molecular weight weakly coordinating anion (MW = 280 g/mol). The triflimidate anion has limited applications in well-defined main group compounds,<sup>6</sup> and we believe there is an opportunity to extend the use of triflimidate in the design of potent Lewis acid catalysts.

**Specific Aims** – This work investigates Lewis acids supported by the triflimidate anion, including novel main group compounds, catalytic applications, and fundamental studies assessing Lewis acidity and triflimidate binding.

**In specific aim 1**,  $\text{Cp}^*\text{MNTf}_2$  compounds ( $\text{Cp}^*$  = cyclopentadienyl;  $M = \text{Mg}, \text{Ca}, \text{Zn}, \text{Si}, \text{Ge}$ ) will be prepared. Lewis acidity measurements and application of  $\text{Cp}^*\text{MNTf}_2$  compounds as catalysts for alkene functionalization will elucidate the impact of Lewis acid strength and hardness/softness on catalytic activity.

**In specific aim 2**, Si(IV) triflimidate compounds will be compared to determine the impact of geometry and ligand flexibility on Lewis acidity and catalytic activity toward alcohol deoxygenation.

**In specific aim 3**, the binding of triflimidate and related anions to an aluminum hydride complex will be evaluated. Kinetic measurements for elementary steps relevant to aldehyde hydroboration will determine the impact of anion identity on reaction rates and overall catalytic activity.

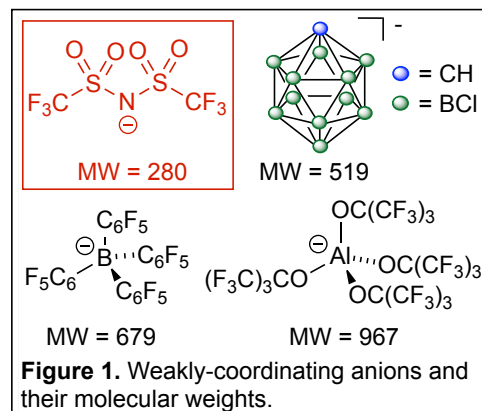
**Evidence of Feasibility** – The PI has significant experience training undergraduates in handling air-sensitive compounds. Students in the Liberman-Martin Group have prepared novel  $\text{RZnNTf}_2$  complexes ( $R = \text{Me}, \text{Et}, \text{Ph}, \text{C}_6\text{F}_5$ ) and studied their activity in alkyne hydrosilylation. Furthermore, as a proof of principle, our group has prepared the  $\text{Cp}^*\text{SiNTf}_2$  and  $\text{Cp}^*\text{GeNTf}_2$  compounds described in Aim 1. These preliminary experiments validate our synthetic strategy for accessing triflimidate-supported Lewis acids and demonstrate that the air-sensitive reactions proposed herein are within the capabilities of Chapman undergraduates.

#### Aim 1: Alkene Hydrosilylation and Cyclopropanation by $\text{Cp}^*\text{MNTf}_2$ Catalysts (Years 1 & 2, 16 months)

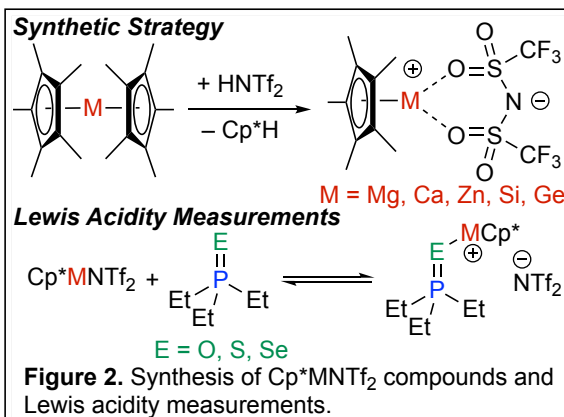
Cyclopentadienyl (Cp) ligands and their derivatives feature prominently in transition metal chemistry, while their use to support main group compounds remains less explored.<sup>7</sup> Within a main group context, hapticity shifts of  $\text{Cp}^*$  ligands have been observed, and  $\eta^1$ ,  $\eta^2$ , and  $\eta^5$  motifs are similar in energy for Group 13–15 compounds.<sup>8</sup> We believe the ability of  $\text{Cp}^*$ -supported main group compounds to undergo hapticity changes may be beneficial in buffering electronic properties upon substrate coordination within a catalytic context.

##### 1.1 $\text{Cp}^*\text{MNTf}_2$ Synthesis and Lewis Acidity Measurements

A series of  $\text{Cp}^*\text{MNTf}_2$  complexes ( $M = \text{Mg}, \text{Ca}, \text{Zn}, \text{Si}, \text{Ge}$ ) will be prepared by treatment of  $\text{Cp}^*_2\text{M}$  species with 1 equiv of commercially available  $\text{HNTf}_2$  (**Figure 2**). The bulky  $\text{Cp}^*$  ligand was selected to discourage unwanted ligand redistribution.<sup>9</sup> Promisingly, we have prepared the  $\text{Cp}^*\text{SiNTf}_2$  and  $\text{Cp}^*\text{GeNTf}_2$  derivatives by this route and do not observe disproportionation. Related  $\text{Cp}^*\text{Si}^+$  and  $\text{Cp}^*\text{Ge}^+$  compounds featuring  $\text{B}(\text{C}_6\text{F}_5)_4^-$  and  $\text{Al}[\text{OC}(\text{CF}_3)_3]_4^-$  anions have been reported,<sup>10</sup> but  $\text{Cp}^*\text{M}^+$  species for Mg, Ca, or Zn incorporating weakly coordinating anions are not known.



**Figure 1.** Weakly-coordinating anions and their molecular weights.



**Figure 2.** Synthesis of  $\text{Cp}^*\text{MNTf}_2$  compounds and Lewis acidity measurements.

NMR spectra of  $\text{Cp}^*\text{MNTf}_2$  compounds will be analyzed for multiple  $\text{Cp}^*$  and  $\text{NTf}_2$  signals to determine if a Schlenk-like equilibrium exists for these heteroleptic species in solution. X-ray crystallographic studies of all complexes will elucidate  $\text{Cp}^*$  hapticity and the triflimidate binding mode, which could involve monodentate coordination ( $\eta^1\text{-N}$  or  $\eta^1\text{-O}$ ) or bidentate interactions ( $\eta^2\text{-O, O'}$  or  $\eta^2\text{-N, O}$ ).<sup>11</sup>

The Lewis acidities of all  $\text{Cp}^*\text{MNTf}_2$  derivatives will be benchmarked by a variation of the Gutmann-Beckett method that involves the binding of triethylphosphine oxide, sulfide, and selenide donors (**Figure 2**).<sup>12</sup> Trends in the magnitudes of  $^{31}\text{P}$  chemical shift changes upon Lewis base binding to  $\text{Cp}^*\text{MNTf}_2$  will evaluate the hardness/softness of the Lewis acid. For comparison, binding studies will also be performed with  $\text{Cp}^*_2\text{M}$  compounds and commercially available  $\text{M}(\text{NTf}_2)_2$  compounds.

### 1.2 Alkene Hydrosilylation Catalysis

Alkene hydrosilylation is among the largest-scale homogeneous reactions performed industrially to produce silicones, which are used in coatings, adhesives, and lubricants.<sup>13</sup> Traditional catalysts for alkene hydrosilylation use precious metals; however, there have been significant advances using base metal and main group catalysts for these transformations. Lewis acids, such as  $\text{B}(\text{C}_6\text{F}_5)_3$ ,

catalyze hydrosilylation reactions by activating the silane substrate via  $\eta^1$ -coordination of the Si-H bond.<sup>14</sup> Although an increasing number of Lewis acid catalysts for alkene hydrosilylation are known, there are no general principles to predict which catalysts will be able to induce  $\eta^1$ -silane coordination and avoid competitive alkene homopolymerization byproducts. **We hypothesize that “soft”  $\text{Cp}^*\text{MNTf}_2$  catalysts will more effectively polarize the silane reagent upon binding, leading to greater hydrosilylation activity.**

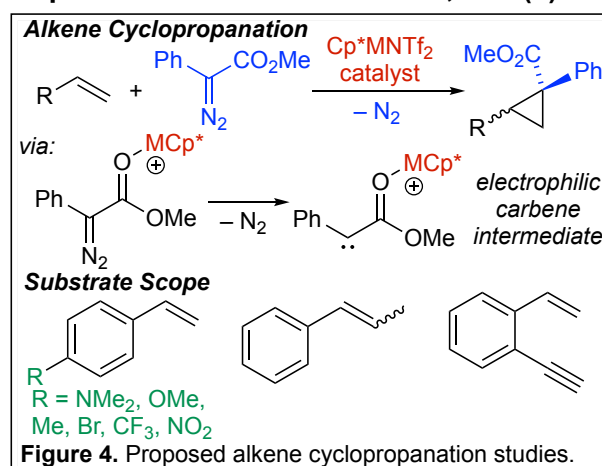
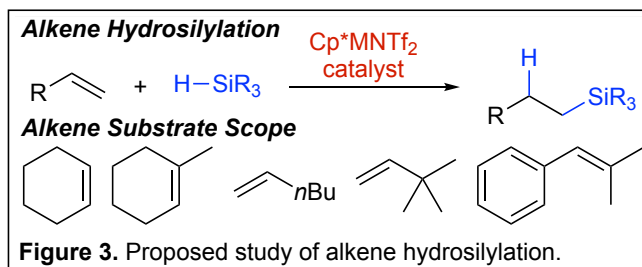
The five  $\text{Cp}^*\text{MNTf}_2$  complexes ( $\text{M} = \text{Mg, Ca, Zn, Si, Ge}$ ; Aim 1.1) will be compared as alkene hydrosilylation catalysts (**Figure 3**). Initial experiments will be performed with cyclohexene and a range of silane substrates ( $\text{HSiEt}_3$ ,  $\text{HSiPh}_3$ ,  $\text{H}_2\text{SiPh}_2$ , and  $\text{H}_3\text{SiPh}$ ). Comparing  $\text{Cp}^*\text{MNTf}_2$  reaction rates to Lewis acidity measurements (Aim 1.1) will uncover if a trend exists between Lewis acid strength (or hardness/softness) and hydrosilylation efficiency.

With the optimal  $\text{Cp}^*\text{MNTf}_2$  catalyst from cyclohexene hydrosilylation studies, the reduction of a series of commercially available alkenes will be performed, including (i) cyclic and acyclic, and (ii) aliphatic and styrenyl substrates (**Figure 3**). Potential silane-Lewis acid interactions will be assessed by  $^1\text{H}$  NMR measurement of coupling between the silicon hydride and the methylene protons of  $\text{HSiEt}_3$  in the presence of Lewis acids.<sup>15</sup> NMR experiments attempting to observe isotopic scrambling between  $\text{DSiPh}_3$  and  $\text{HSiEt}_3$  in the presence of catalytic  $\text{Cp}^*\text{MNTf}_2$  will also be performed.<sup>16</sup> Together, these experiments will determine if  $\text{Cp}^*\text{MNTf}_2$  activates the silane reagent by  $\eta^1$ -coordination, allowing us to identify future catalytic applications with a high chance of success.

### 1.3 Alkene Cyclopropanation Catalysis

Cyclopropane motifs appear in compounds with antibiotic, antiviral, and antimicrobial properties.<sup>17</sup> A common synthetic method to prepare cyclopropanes involves carbene reactions with alkenes. Transition metal catalysts have typically been used to activate the carbene precursors; however, the main group compound  $\text{B}(\text{C}_6\text{F}_5)_3$  was recently shown to activate diazoesters in catalytic reactions, including cyclopropanations.<sup>18,19</sup> The strong Lewis acidity and sterically encumbered nature of the  $\text{B}(\text{C}_6\text{F}_5)_3$  catalyst are believed to be important in enabling catalytic turnover and high diastereoselectivity. **We hypothesize that (i) “harder” Lewis acid  $\text{Cp}^*\text{MNTf}_2$  catalysts will exhibit greater activity due to strong binding to the carbonyl group of the diazoester substrate, and (ii) the bulky nature of the  $\text{Cp}^*$  ligand will discourage product inhibition and enable diastereoselective cyclopropanation.**

The  $\text{Cp}^*\text{MNTf}_2$  derivatives (Aim 1.1) will be compared as catalysts for 4-(trifluoromethyl)styrene cyclopropanation using methyl phenyldiazoacetate (**Figure 4**) using  $^{19}\text{F}$  NMR monitoring. Both product yields and diastereoselectivities will be evaluated to determine optimal reaction conditions. Using the highest performing  $\text{Cp}^*\text{MNTf}_2$  catalyst, cyclopropanation of a series of *para*-substituted styrene derivatives will assess electronic effects on reaction yield and diastereoselectivity. Reactions with *E*- and *Z*- $\beta$ -methylstyrene will evaluate cyclopropanation stereospecificity. Last, the selectivity for cyclopropanation versus cyclopropanation will be determined for a substrate containing both alkene and alkyne functional groups.



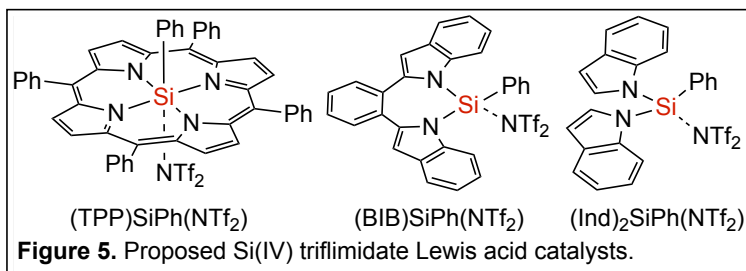
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To provide evidence for the intermediacy of an electrophilic carbene (**Figure 4**), methyl phenyldiazoacetate will be treated with 10 mol % of all Cp\**M*NTf<sub>2</sub> catalysts in the absence of alkene substrate. Observation of alkene products suggests the formation, and subsequent dimerization, of a carbene species.<sup>20</sup> Electronic effects on cyclopropanation will be probed by competition experiments with excess mixtures of styrene and *para*-substituted styrene derivatives to construct a Hammett plot. More electron-rich alkenes are anticipated to exhibit faster relative rates.<sup>18</sup> The proposed investigations will broaden the available main group catalysts for alkene cyclopropanation and provide insight into the impact of Lewis acid strength on catalyst efficiency and diastereoselectivity.

**Aim 2: Alcohol Deoxygenation Catalysis Using Si(IV) Triflimidate Lewis Acids (Years 2 & 3, 12 months)**

Group 13 compounds featuring boron or aluminum are among the most widely used Lewis acid catalysts.<sup>21</sup> There is significant interest in rendering group 14 compounds sufficiently reactive to behave as Lewis acid catalysts, as novel classes of catalysts can uncover distinct reactivity or functional group tolerance.<sup>22</sup> In designing novel group 14 Lewis acid catalysts, two aspects that remain relatively unexplored are the impact of a compound's geometry or ligand rigidity on Lewis acidity.

In Aim 2, we propose to study three Si(IV) compounds featuring triflimidate, phenyl, and nitrogen-based supporting ligands that will be varied as tetraphenylporphyrin (TPP), 1,2-bis(indolyl)benzene (BIB), or di-indolyl (Ind) donors (**Figure 5**). **We hypothesize that the porphyrin-supported compound will display the greatest catalytic activity due to the strong propensity for**



**Si(IV) compounds to form hexacoordinate structures through ligand binding.**<sup>23</sup> Furthermore, comparing the BIB- and Ind-supported compounds will probe the influence of ligand flexibility on Lewis acid strength.

**2.1 Cationic Porphyrin Complex Synthesis and Lewis Acidity Measurements**

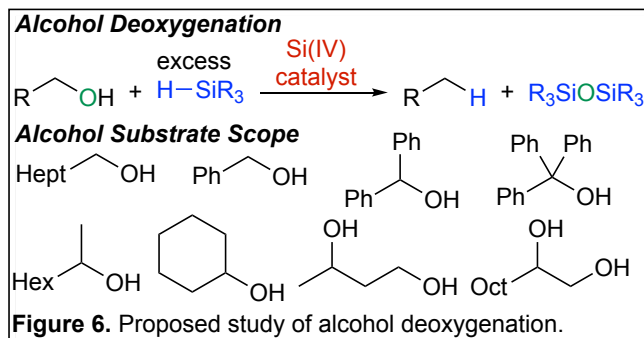
The proposed Si(IV) triflimidate compounds (**Figure 5**) will be prepared by protonolysis of (TPP)SiPh<sub>2</sub>,<sup>24</sup> (BIB)SiPh<sub>2</sub>,<sup>25</sup> or (Ind)<sub>3</sub>SiPh<sup>26</sup> with 1 equiv of HNTf<sub>2</sub>. If protonolysis attempts are unsuccessful, these silicon species could alternatively be prepared by metathesis of Si–Cl bonds with AgNTf<sub>2</sub>. All Si(IV) species will be characterized by NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, and <sup>19</sup>F) and X-ray diffraction. The silicon geometry and triflimidate binding mode are of particular interest in solid-state structures. The diamagnetic ring current for the porphyrin ring of (TPP)SiPh(NTf<sub>2</sub>) will likely complicate the interpretation of chemical shift metrics of Lewis acidity such as the Gutmann-Beckett method.<sup>27</sup> To circumvent this challenge, Lewis acidities will be determined by measuring equilibrium constants for OPEt<sub>3</sub> binding using UV-Vis or NMR spectroscopy.<sup>28</sup>

**2.2 Alcohol Deoxygenation Catalysis**

Defunctionalization reactions, which involve functional groups being replaced by hydrogen atoms, are important for the biomass degradation into value-added feedstocks.<sup>29</sup> Traditional defunctionalization procedures use stoichiometric quantities of metal hydride reductants, which can be pyrophoric or toxic. Some Lewis acids, including B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, can catalyze defunctionalizations using silane reductants.<sup>30</sup> In the proposed work, we will apply novel Si(IV) catalysts for the deoxygenation of alcohols to alkanes.

The three Si(IV) triflimidate catalysts (**Figure 5**) will be compared for 1-octanol deoxygenation using a range of silane reductants. We anticipate that the strongest Lewis acid (Aim 2.1) will exhibit the greatest catalytic activity. With the most active catalyst for 1-octanol reduction, a range of substrates will be examined, including 1°, 2°, and 3° alcohols. Both benzylic and aliphatic substrates will be tested. The reduction of diol reagents will determine if exhaustive or site-selective deoxygenation can occur.

Based on literature precedent for B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, Lewis acid-catalyzed alcohol deoxygenation likely proceeds by initial dehydrocoupling of the alcohol and silane to form a silyl ether intermediate, followed by a slower reduction to an alkane product.<sup>31</sup> For the Si(IV) catalysts described, we will perform a stereochemical study to assess if reduction of the silyl ether intermediate proceeds by an S<sub>N</sub>1 or S<sub>N</sub>2 pathway. The triethylsilyl ether of (*S*)-1-phenylethanol will be prepared and reduced with deuterated silane. Observation of complete or majority inverted stereochemistry in the alkane product implies an S<sub>N</sub>2 reduction step, while substantial racemization suggests an S<sub>N</sub>1 pathway.<sup>31</sup> Through the catalytic and mechanistic studies described, we aim to present new catalysts for alcohol deoxygenation while simultaneously investigating the impact of Si(IV) geometry on Lewis acidity.



**Aim 3: Evaluating Cation–Anion Interactions Involving Triflimidate and Related Anions (Year 3, 8 months)**

Ion-pairing effects can influence processes as varied as supramolecular assembly, charge transfer, and catalysis.<sup>32</sup> Within an organometallic context, fundamental studies of anion interactions with early-metal metallocenes have enabled the development of polymerization catalysts capable of producing >100 megatons of polyolefins annually.<sup>33</sup> Noncovalent interactions between triflimidate and imidazolium cations have been investigated in the context of ionic liquids;<sup>34</sup> however, the relative coordinating ability of triflimidate versus other anions is not well studied from a Lewis acid design perspective.<sup>35</sup>

In Aim 3, we will study a series of (NacNac)AlH(X) complexes (NacNac =  $\beta$ -diketiminate) featuring four commercially available anions (triflate, triflimidate, and two additional sulfonimides; **Figure 7**). Differing trends exist between the acidities of the anion conjugate acids<sup>36</sup> and anion volumes.<sup>37</sup> Stronger Brønsted acids are generally assumed to generate more weakly coordinating anions, yet anion size may be more important in controlling Lewis acidity.<sup>6</sup> **We hypothesize that binding strength will correlate with anion size** and that stronger anion interactions will render Al less Lewis acidic.

**3.1 Aluminum Complexes and Study of Cation–Anion Interactions**

The (NacNac)AlH(OTf) compound is reported,<sup>38</sup> and analogues featuring other anions will be prepared by anion exchange or protonation of (NacNac)AlH<sub>2</sub> with appropriate acids. The selected NacNacAlH(X) framework provides a wealth of spectroscopic data to interrogate cation–anion interactions. The <sup>1</sup>H NMR data for the 2,6-diisopropylphenyl (Dipp) methine position is diagnostic of Al geometry. One signal corresponding to the isopropyl methine position should be observed for a trigonal planar (NacNac)AlH<sup>+</sup> cation with an outer-sphere anion. In contrast, the presence of two methine signals indicates a less symmetrical tetrahedral inner-sphere ion pair (assuming slow rotation of Dipp groups). <sup>1</sup>H–<sup>19</sup>F HOESY spectra will determine if interionic contacts appear between the fluorinated anions and specific positions of the (NacNac)AlH<sup>+</sup> fragment.<sup>39</sup> NMR titration of (NacNac)AlH(X) complexes with added NBu<sub>4</sub>X will establish if fast or slow exchange of bound and free anions is observed and measure equilibrium constants for anion binding. Aluminum Lewis acidity will be determined by the Gutmann-Beckett method.<sup>12</sup> X-ray crystallographic data will assess anion binding modes, and IR measurement of the Al–H stretch will determine if the anion selection impacts the Al–H bond strength. Together, these experiments provide a comprehensive picture of aluminum–anion interactions to determine if ion-pairing effects follow a trend based on anion volume.

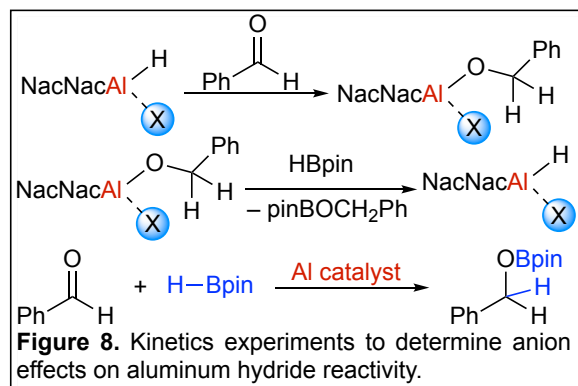
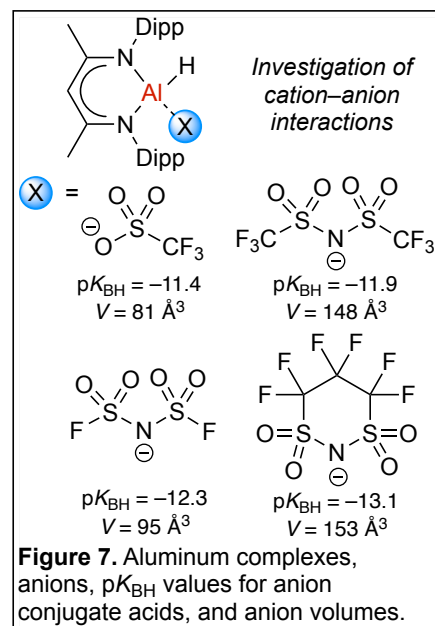
**3.2 Kinetic Experiments Relevant to Aldehyde Hydroboration**

Aluminum hydrides are classic stoichiometric reductants, and recent work has demonstrated that catalytic turnover can occur using suitable hydride sources such as boranes.<sup>40</sup> (NacNac)AlH(OTf) has been reported to catalyze carbonyl hydroboration using pinacolborane (HBpin),<sup>38</sup> and we hope to elucidate the impact of anion interaction strength (Aim 3.1) on hydroboration reactivity.

We will perform kinetics experiments for all (NacNac)AlH(X) compounds to separately measure the rates of (i) insertion of an aldehyde into the Al–H bond to form an alkoxide intermediate, and (ii)  $\sigma$ -bond metathesis between the Al alkoxide and HBpin to regenerate an Al–H bond and form an alkoxyboronate ester product (**Figure 8**). We anticipate that both elementary steps (insertion and  $\sigma$ -bond metathesis) will be faster with more weakly coordinating anions.<sup>41,42</sup> The hydroboration activity of all Al complexes will also be compared under catalytic conditions. The studies described will provide unprecedented insight into ion-pairing effects for a series of sulfonimides and probe the impact of these interactions on common elementary steps for main group catalysts.

**Summary and Significance of the Research Proposal**

This proposal studies main group compounds featuring the weakly coordinating triflimidate anion. These novel compounds will broaden the pool of Lewis acid catalysts available to chemists. A simultaneous focus on probing reaction mechanisms and the role of Lewis acid identity (Aim 1), geometry (Aim 2), and supporting anion (Aim 3) on catalytic activity will improve design principles for main group catalysts, enabling the hypothesis-driven creation of improved catalytic methods.



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**LETTERS OF COLLABORATION.**

Not applicable. All work will be performed using equipment in the PI's laboratory or shared instrument facilities at Chapman University. Details of the space and equipment available to the PI are provided in the Letter of Support from Dean Michael Ibba.

## EDUCATIONAL PROPOSAL

### Strengthening Student Scientific Argumentation Skills in Undergraduate Organic Chemistry Courses

#### Background and Motivation

Proficiency in evaluating if claims are supported by evidence and sound reasoning is an essential skill for adults in making everyday decisions. This ability to justify claims with evidence, referred to as 'argumentation', is also a central aspect of scientific inquiry.<sup>43</sup> A common framework to define argumentation is Toulmin's argument pattern,<sup>44</sup> which was initially developed in a philosophy context but has been extensively applied in science education research (**Figure 1**). In this pattern, a scientific claim must be supported by evidence that is sufficient, relevant, and reasonable.

Scientific argumentation is emphasized in the National Research Council's *Framework for K–12 Science Education*, with "engaging in arguments from evidence" listed as one of eight core science and engineering practices.<sup>45</sup> Research suggests that practicing scientific argumentation has both cognitive and social benefits for students, including helping students develop metacognitive processes and science identities.<sup>46</sup> Despite these assets, pedagogical practices to support students in constructing arguments are not widely implemented. While there have been studies of argumentation in an organic chemistry context,<sup>47–49</sup> *to our knowledge, there are no reported attempts to infuse student argumentation training across the organic chemistry curriculum.*

#### Goals of the Educational Plan and Institutional Fit

The aims of this educational plan are to: (**Aim 1**) integrate the scaffolded practice of argumentation skills within the foundational Organic Chemistry I and II sequence, and (**Aim 2**) develop an upper-division Advanced Organic Chemistry elective course that engages students in building scientific explanations supported by experimental data. **We hypothesize that intentional, scaffolded practice in science argumentation within organic chemistry courses will improve student performance on conceptual tasks and science identity.**

There is a strong emphasis on student-centered learning at Chapman, with a university mission of providing a personalized education, which includes offering curricula that aid students in fostering critical thinking and effective communication skills. Evidence-based teaching strategies are widely used at Chapman, and there is strong institutional support for implementing innovative classroom practices. Chapman's general and organic chemistry courses are taught using an 'atoms-first' approach that emphasizes student problem solving and de-emphasizes rote memorization. Thus, the proposed emphasis on scientific argumentation training is well-aligned with pedagogical practices within the Chemistry and Biochemistry Unit and the wider University.

#### Evidence of Feasibility

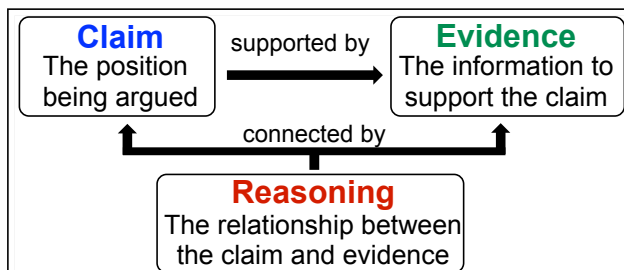
The PI has developed a range of materials for Organic Chemistry I/II and Advanced Organic Chemistry courses, including pre-class videos, pre-class quizzes, and in-class worksheets. The PI has three years of experience teaching using the video-based flipped classroom style, in which students watch videos and complete quizzes before each class session. Class time is spent with students working in small groups through in-class worksheet questions that reinforce skills and concepts from the pre-class videos. This prior experience will enable the PI to have sufficient time to be able to implement the pedagogical practices proposed herein.

#### Aim 1: An Explicit Incorporation of Argumentation Training in Organic Chemistry I/II

Organic chemistry is a widely feared course that traditionally has high withdrawal and failure rates.<sup>50</sup> Chemical education research has shown that organic chemistry students rely heavily on rote memorization, leaving them ill-equipped to select the appropriate conceptual knowledge needed to solve problems.<sup>51</sup> Student reliance on memorized pieces of information produces a fragmented understanding of organic systems, which is insufficient for questions about reactivity and mechanisms.

##### 1.1 Scaffolded Argumentation Practice through In-Class Worksheets and Problem Sets

For students to provide scientific arguments aligned with instructor expectations, they need (i) clearly communicated expectations for the task, and (ii) opportunities to construct arguments at the depth of explanation expected.<sup>51</sup> To address these needs, the PI will provide scaffolded opportunities for students to hone their organic chemistry argumentation skills. At least once a week, an in-class worksheet question will guide students to justify the cause behind a phenomenon or process (the 'why' or causal mechanism). After student groups have completed this question, the PI will engage the class in a discussion of the problem and address misconceptions.



**Figure 1.** Simplified version of Toulmin's argument pattern as a framework for scientific argumentation.

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To provide consistent, individualized feedback on students' argumentation strategies and depth of explanations, the PI will also implement graded problem sets consisting of 1-2 scaffolded questions that require students to construct an argument. These problem sets will be assigned eight times per semester (once a week during weeks without an exam). Together, the weekly ungraded group in-class worksheet questions and graded individual problem sets are designed to emphasize the importance of conceptual understanding within the course and provide an opportunity for students to gain practice performing these high-level tasks.

The PI has identified several promising assessment constructions that can be adapted from the chemical education literature that are designed to scaffold student engagement in organic chemistry argumentation (**Figures 2–4**). All

items explicitly probe scientific reasoning rather than assuming these skills are incorporated in students' answers. In one question style, students are prompted to consider several factors that may impact basicity and determine

those that are relevant or irrelevant (**Figure 2**).<sup>48</sup> Identifying the

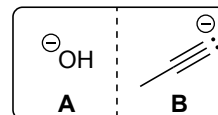
relevance of multiple claims can engage students in scientific modes of thinking and argumentation. Requiring students to consider a range of factors also combats students' tendency to use 'one-reason' decision making, which is often inadequate for organic systems.<sup>51</sup>

Questions that probe reaction mechanisms or products formed in a reaction are also well-suited to being restructured to encourage argumentation practices. In a prompt that forces students to consider alternative answers for a 'predict the products' question (**Figure 3**), after providing their own answer for the product formed in a reaction, students are confronted with other potential answers that challenge them to build alternative arguments and evaluate how plausible the alternatives are.<sup>47</sup>

Another assessment style will be to provide students an observation (for example, the relative rates of two reactions in **Figure 4**) and have students consider multiple factors in their reasoning when constructing an explanation.<sup>49</sup> Thus, a general design principle for the in-class worksheet and problem set items will be to scaffold questions to explicitly probe student analytical reasoning in a way that does not reward rote memorization.

**Task: Distinguish relevant from irrelevant information**

Consider two bases:



1. Identify how each factor affects the stability of the bases, if at all.

<b>Electronegativity</b>	Stabilizes <b>A</b> more than <b>B</b>	Stabilizes <b>B</b> more than <b>A</b>	Not relevant
<b>Atom size</b>	Stabilizes <b>A</b> more than <b>B</b>	Stabilizes <b>B</b> more than <b>A</b>	Not relevant
<b>Resonance</b>	Stabilizes <b>A</b> more than <b>B</b>	Stabilizes <b>B</b> more than <b>A</b>	Not relevant
<b>Hybridization</b>	Stabilizes <b>A</b> more than <b>B</b>	Stabilizes <b>B</b> more than <b>A</b>	Not relevant
<b>Inductive effects</b>	Stabilizes <b>A</b> more than <b>B</b>	Stabilizes <b>B</b> more than <b>A</b>	Not relevant
<b>Charge</b>	Stabilizes <b>A</b> more than <b>B</b>	Stabilizes <b>B</b> more than <b>A</b>	Not relevant

2. The  $pK_a$ s of the conjugate acids are: CA of **A** \_\_\_\_\_ CA of **B** \_\_\_\_\_

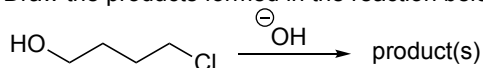
3. Based on  $pK_a$  values, which base is weaker?

4. Which factor(s) have the greatest effect on base stability?

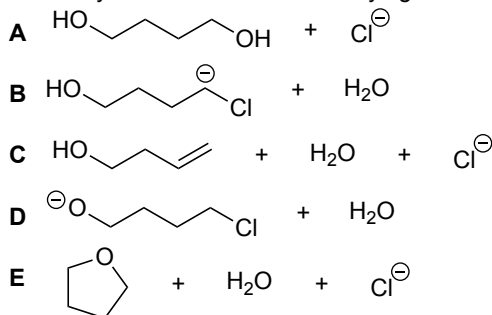
**Figure 2.** Example assessment item prompting students to determine which factors are relevant and irrelevant when comparing two bases.

**Task: Consider alternatives**

1. Draw the products formed in the reaction below.



2. Here are some potential answers. Describe how you think someone came to each solution below. What do you think was their underlying reasoning?



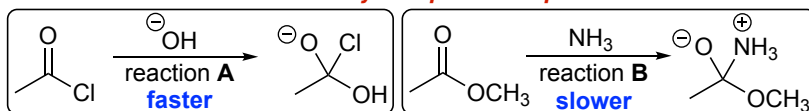
3. After considering these potential products, which do you think is most reasonable, and why?

**Figure 3.** Example assessment item that prompts students to consider alternative answers.

## 1.2 Exam Restructuring

The proposed focus on student argumentation will also be reflected in the Organic Chemistry I/II summative assessments (five exams and one cumulative final exam per semester). Currently, argumentative tasks comprise approximately 10% of exam questions, while these skills represent 25% of course learning outcomes. To better align assessments with the proposed emphasis on critical thinking and argumentation, the PI will adjust exams so that at least 20% of exam questions address these practices.

**Task: Simultaneously compare multiple variables**



1. What does it mean for reaction **A** to be faster than reaction **B**?
2. What changes occur in reactions **A** and **B**? Note changes such as charges, bonds breaking, and bonds forming.
3. What are two differences between reactions **A** and **B**?
4. Describe in as much detail as possible how each difference between these reactions would speed up the reaction, slow it down, or have no effect.
5. Provide a one paragraph in-depth explanation that answers the question:  
*Why do reactions **A** and **B** occur at different rates?*

**Figure 4.** Example assessment item prompting students to consider multiple variables in constructing an explanation.

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#### Aim 2: Analysis of Experimental Data in Argumentation Tasks in an Advanced Organic Chemistry Course

Physical organic chemistry involves the study of structures and mechanisms for organic systems using the techniques of physical chemistry. Coursework in physical organic chemistry is common in Ph.D. programs; however, curricula for undergraduate elective coursework in this area are not well documented in the chemical education literature. The focus on conceptual understanding of organic structure and mechanism in physical organic chemistry is well-aligned with efforts to infuse argumentation practices in the chemistry curriculum.

At Chapman University, the PI has independently designed and taught an elective Advanced Organic Chemistry course that emphasizes physical organic chemistry and the experimental study of reaction mechanisms. During their first iteration of teaching Advanced Organic Chemistry in Fall 2020, the PI received a Chapman Pedagogical Innovation Grant to develop a library of 25 pre-class videos for this course that are publicly available on the PI's YouTube channel with 1500 views as of June 2022.

#### 2.1 Providing Opportunities for Experimental Data Analysis

A major practice of scientists is interpreting data and explaining how these data support a claim. University science students struggle to include authentic data in their arguments, as they often neglect to (i) identify which data are relevant to an argument, or (ii) explicitly rationalize how these data provide evidence for a claim.<sup>52</sup>

Within their elective Advanced Organic Chemistry course, the PI will incorporate experimental data analysis in questions designed to elicit student argument construction. Questions requiring students to examine experimental data will be included at least once a week on in-class worksheets and on all problem sets (6 per semester) and exams (3 per semester). **Table 1** shows select examples of topics amenable to data interpretation and the types of data that will be included. In some tasks, students will be provided spreadsheets of data, while in other cases, students will be trained to analyze X-ray structures or NMR spectra directly. On all assessments requiring students to include data in their explanations, scaffolded questions will prompt students to justify why these data support their claims.

#### 2.2 Incorporation of Primary Literature Articles

Analysis of the primary chemical literature offers students opportunities to apply principles in new contexts, interpret data, and evaluate arguments put forth by authors. These are vital skills for developing scientists, as scientists can spend up to a quarter of their working time reading the scientific literature.<sup>53</sup> As an additional opportunity to guide students in developing scientific argumentation skills, the PI will incorporate student reading of primary literature articles within their Advanced Organic Chemistry course. Two recent articles will be included that apply topics and mechanistic experiments discussed in the course: (i) a study of nucleophilic aromatic substitution by the Jacobsen group that discusses frontier molecular orbitals and kinetic isotope effects,<sup>54</sup> and (ii) a report of nitrogen 'deletion' from amines by the Levin group that includes anomeric effects and various mechanistic experiments (Hammett plots, trapping experiments, radical clocks).<sup>55</sup> Each article will be discussed during a separate class session. Before class, in place of a pre-class video, students will read the literature article and complete a pre-class quiz with straightforward questions establishing that students understand article's topic and recall relevant concepts from earlier in the course. In-class worksheets that guide discussion of the article will require higher-order skills in analyzing data and proposing alternative mechanisms or additional experiments.

#### Summary and Significance of the Educational Proposal

This proposal aims to improve student argumentation skills in organic chemistry courses. Innovations to both the PI's pedagogical approaches and the organic chemistry curriculum at Chapman University are proposed. In Aim 1, for foundational Organic Chemistry I/II courses, the PI will incorporate scaffolded questions that assess student explanations across in-class worksheets, problem sets, and exams. In Aim 2, the PI describes an elective Advanced Organic Chemistry course with an emphasis on physical organic chemistry in which students are challenged to interpret experimental data and primary literature articles while constructing scientific arguments. These practices build upon the argumentation strategies encountered in their earlier organic coursework (Aim 1) and bring additional complexity to the types of evidence students can present supporting their argumentative claims. The proposed activities to strengthen student argumentative skills are grounded in the chemical education literature; however, the emphasis on infusing these practices across the organic chemistry curriculum is novel.

**Table 1.** Example topics for which experimental data will be analyzed by students in an elective advanced organic chemistry course.

Knowledge Area	Experimental Data to be Interpreted
Anomeric effects	Bond length data for cis-2,3-dichloro-1,4-dioxane
Thermodynamic analysis	van't Hoff analysis of keto-enol tautomerization
Kinetic measurements	Eyring analysis for the Claisen rearrangement
Kinetic isotope effects	Primary and secondary isotope effects for alkyl halide S <sub>N</sub> 2 vs E2 reactions
Linear free energy relationships	Hammett analysis of Wittig olefination
Non-classical carbocations	Bond length data for the 2-norbornyl cation

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**EDUCATIONAL PROPOSAL** (continued)

**ASSESSMENT PLAN.**

**Outcomes**

The education plan will result in: (1) fully developed in-class worksheets and problem sets incorporating scaffolded argumentation exercises for the foundational Organic Chemistry I/II curriculum at Chapman, and (2) a complete Advanced Organic Chemistry course incorporating experimental data analysis and literature articles within student argumentation tasks.

The PI plans to publish their method of integrating argumentation practice across organic chemistry courses in a peer-reviewed chemical education journal. All course materials (syllabi, student learning outcomes, pre-class quizzes, in-class worksheets, problem sets, and exams) will be posted on the Organic Chemistry Educational Resources website. Pre-class videos will be made available on YouTube to facilitate implementation by other educators.

Within the Chapman community, the PI will (i) present a seminar on their approach to incorporating scaffolded organic chemistry argumentation tasks and findings from student surveys and performance, and (ii) develop a workshop to help faculty implement similar practices in other science courses.

**Evaluation Design**

The effectiveness of the educational proposal will be evaluated based on:

- 1) Student performance on assessment items that involve explanations, predictions, or reasoning
- 2) Student science identities and attitudes toward organic chemistry

To evaluate student performance, the PI will track student scores on select argumentation-focused questions during the award period (choosing one question each from the earliest exam, a middle exam, and the cumulative final exam during each semester). For these questions, the PI will also use a qualitative coding scheme developed by Flynn and co-workers to track: (i) the concepts students discuss in their answers and if those concepts are discussed correctly or with errors, (ii) the extent to which connections are made between concepts discussed, and (iii) the structure of student arguments.<sup>51</sup> Trends in student scores and argument features will allow the PI to refine course materials and address common misconceptions.

To evaluate student science identities and attitudes toward organic chemistry, the PI will administer the four-item STEM Professional Identity Overlap survey developed by McDonald and co-workers<sup>56</sup> and the Attitudes Toward the Subject of Chemistry Inventory developed by Bauer.<sup>57</sup> For the Advanced Organic Chemistry course, students will also be surveyed on their perceptions of the research literature using a modified version of an instrument developed by Hubbard and Dunbar.<sup>58</sup> By tracking survey instrument responses each semester, the PI hopes to improve the teaching methods used in each iteration of organic chemistry courses.

Identify departmental or institutional colleagues who might play a role in this educational endeavor (as mentors, collaborators, etc.) as appropriate and describe the role they will play.

**Dr. Maduka Ogba**, Assistant Professor, Chapman University

Dr. Ogba teaches in the Organic Chemistry I/II lecture sequence, and Dr. Ogba and the PI co-author and collaboratively grade exams to standardize the summative assessments in their courses. Dr. Ogba supports and will collaborate on the exam restructuring described in Aim 1 of the educational plan.

**Dr. Elaine Schwartz**, Associate Professor, Co-Director of the Chemistry and Biochemistry Program, Chapman University

Dr. Schwartz has been an invaluable mentor to the PI in navigating new pedagogical methods and Chapman's administrative structure. As co-director of the Chemistry and Biochemistry program, Dr. Schwartz provides institutional support for the proposed educational plan.

**Dr. Melissa Rowland-Goldsmith**, Associate Professor, Co-Director of the Institute for Excellence in Teaching and Learning, Chapman University

As co-director of Chapman's Institute for Excellence in Teaching and Learning, Dr. Rowland-Goldsmith will provide a trained classroom observer for the PI to collect Classroom Observation Protocol for Undergraduate STEM (COPUS) data for select class sessions incorporating argumentation in-class worksheet questions (Aim 1) and student discussion of literature articles (Aim 2). COPUS is an established classroom observation tool that provides objective information on how classroom time was spent during these activities.

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**EDUCATIONAL PROPOSAL** (continued)

**COURSES TAUGHT.**

**Organic Chemistry I (CHEM 230);** Sophomore level; Fall 2018 (38 students), Fall 2019 (43 students), Fall 2020 (43 students), Fall 2021 (59 students); Bonding theories, resonance, notation, acid-base chemistry, alkanes, conformational analysis, stereochemistry, kinetics and thermodynamics, substitution and elimination, alkene addition, alkyne addition, alcohol substitution and elimination, ethers and epoxides, radical reactions; Video-based flipped classroom.

**Organic Chemistry I Laboratory (CHEM 230L);** Sophomore level; Fall 2018 (14 students), Fall 2019 (15 students); Computational study of conformational analysis, solubility measurements, recrystallization, distillation, extraction, sublimation, thin-layer chromatography, column chromatography, radical-catalyzed alkene isomerization; Mostly inquiry-based laboratory experiments.

**Organic Chemistry II (CHEM 331);** Sophomore level; Spring 2019 (48 students), Spring 2020 (84 students), Spring 2021 (89 students); Spectroscopy ( $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR, UV-Vis), conjugated  $\pi$  systems, pericyclic and sigmatropic reactions, electrophilic aromatic substitution, nucleophilic addition to aldehydes and ketones, nucleophilic substitution of carboxylic acids and derivatives, alpha carbon reactivity, conjugate addition; Video-based flipped classroom.

**Organic Chemistry II Laboratory (CHEM 331L);** Sophomore level; Spring 2019 (16 students); boiling point determination, IR and  $^1\text{H}$  NMR spectroscopy, alcohol oxidation, Grignard reactions, ester synthesis, amide synthesis, ketone reduction, aldol condensation, polymer synthesis, chemistry literature searches; Mostly inquiry-based laboratory experiments.

**Advanced Organic Chemistry (CHEM 432);** Junior/Senior level; Fall 2020 (16 students); frontier molecular orbital theory, kinetic and thermodynamic experiments, kinetic isotope effects, linear free-energy relationships, cross-over experiments, radical reactions and radical clocks, carbene reactions, aromatic substitution reactions, substitution reactions, rearrangement reactions involving radical or biradical intermediates; Video-based flipped classroom.

**LETTER OF SUPPORT.**

Included after Academic Citizenship Statement

**RESEARCH CORPORATION FOR SCIENCE ADVANCEMENT**  
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**ACADEMIC CITIZENSHIP STATEMENT.**

**Institutional Overview**

Chapman University is a medium-sized, private, R2 institution in Southern California. The Chemistry and Biochemistry Unit at Chapman serves exclusively undergraduate students. The combined number of Chemistry and Biochemistry graduates fluctuates between 20-30 per year, with the total number of declared majors being approximately 90-110 at a time. There is a strong research culture within the Chemistry and Biochemistry Unit at Chapman, and all Chemistry and Biochemistry majors complete a senior Capstone research project as a part of their graduation requirement.

**Curriculum Development Efforts**

Introductory Organic Chemistry Courses – The PI has collaborated with the organic chemistry faculty to re-design the introductory organic chemistry lecture and laboratory sequence. In the time the PI has been at Chapman, the organic chemistry faculty have: (i) selected a new organic chemistry textbook focused on problem-based learning, (ii) developed a detailed list of intended learning outcomes for students to track their progression through the course, and (iii) re-designed the first-semester organic chemistry laboratory course to include more critical-thinking questions in pre-lab and post-lab assignments.

Future Efforts to Improve the Capstone Coursework – As a part of their required senior Capstone project, Chemistry and Biochemistry majors participate in at least 135 hours of research during their senior year, write a Capstone report, and share their findings through poster and oral presentations. The PI is interested in refining the Capstone process to be more uniform and transparent for all Chemistry and Biochemistry majors. In the future, the PI plans to lead faculty efforts to: (i) revise rubrics for Capstone reports and presentations, (ii) incorporate drafting into the Capstone writing process, and (iii) add second readers for each Capstone report. These changes are designed to give students more feedback and structure during their Capstone experience.

**Focus on Enhancing Student Participation in Research**

Overview of the Liberman-Martin Group – Since arriving at Chapman in 2018, the PI has developed a dynamic research group involving eleven undergraduate student members. The top priority of the Liberman-Martin Group is the training and education of undergraduate researchers. All projects focus on sustainable catalysis, and students learn to contextualize their work from the perspective of broader global energy and environmental challenges. Projects are structured so that each student takes intellectual ownership of a small piece of a given research direction. With guidance, students perform literature searches, plan and execute experiments, analyze results, and troubleshoot for their projects. Students present their results and analyze literature articles at structured weekly group meetings throughout the calendar year. The PI's research students have demonstrated success by several metrics, including serving as co-authors on peer-reviewed publications, presenting posters at national ACS meetings, and receiving prestigious scholarships and fellowships (the Goldwater scholarship, Beckman Scholar award, and NSF Graduate Research Fellowship).

Current Efforts to Provide Early Research Exposure for High School and Undergraduate Students – Motivated by findings that early exposure to research spurs growth in science identity and helps students persist in STEM, the PI is committed to providing research experiences to high school students and early undergraduates within their research group. The PI hosts 2-4 students from neighboring Orange High School each spring to conduct a short research project. Through the PI's NSF-funded grant, they are also: (i) creating orientation and research opportunities for STEM transfer students, and (ii) hosting 2 pre-matriculation students per year to participate in full-time summer research the summer between when they graduate high school and begin undergraduate studies at Chapman. In the future, the PI hopes to expand the transfer student research opportunities to begin the summer before transfer students matriculate at Chapman to help incoming transfer students acclimate to campus.

Future Efforts to Provide Research Rotation Opportunities to Students – The PI plans to develop a research rotation system for Chemistry and Biochemistry early undergraduates and transfer students to participate in short rotations through 2-3 research groups. These research rotations will occur during Interterm, a four-week term between the fall and spring semesters at Chapman. During their rotations, a series of professional development workshops will be implemented to assist students in assembling competitive applications for summer research opportunities and internships. This early research exposure is designed to help students identify the types of research they find most interesting and facilitate connections with faculty that could serve as ongoing research mentors and recommendation letter writers. The PI hopes these efforts will help students develop confidence as scientists and remain in STEM majors.

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June 28, 2022

Re: Liberman-Martin Cottrell Scholar Award Application

Dear Committee Members:

As Dean of the Schmid College of Science and Technology at Chapman University, it is my pleasure to provide this letter of support for **Dr. Allegra Liberman-Martin's** Cottrell Scholar Award application entitled "*Broadening Applications of the Weakly Coordinating Triflimidate Anion in Main Group Catalysis.*".

Dr. Liberman-Martin has already enjoyed notable success as a junior faculty member. They have greatly contributed to the renaissance of organic chemistry at Chapman University by creating an exciting and vital research program that has resulted in a renewed enthusiasm for synthetic chemistry in their department. Students consistently comment that they really enjoy the challenge of "working in Allegra's lab and (their) very hands-on mentorship". They guide students through scaffolded meaningful research experiences building student confidence and self-efficacy.

With consideration for the research laboratory space and the safety need for personal supervision, they have maximized the number of students that they can effectively mentor. They have also begun to publish extensively, with three recent independent publications all featuring undergraduate researchers. Their research is outstanding for this career stage. Extensive facilities and support are available to Dr. Liberman-Martin for the research activities proposed here. These include:

- 450 square feet of dedicated research space with three fume hoods containing Schlenk lines for air-free experiments
- A MBraun LabstarPro glove box (four gloves) outfitted with a cold well, solvent removal system, purge functionality, and freezer for the synthesis of air- and moisture-sensitive compounds
- A JCMeyer solvent purification system (dispenses six anhydrous and degassed solvents) and two rotary evaporators

Major Shared Instrumentation with all operational costs paid by the College:

- 400 MHz NMR spectrometer with variable temperature and heteronuclear capabilities
- IR spectrometers (2)
- UV-Visible spectrophotometers (2)
- GC-MS instrumentation

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In addition to the outstanding research program established by Dr. Liberman-Martin, they have also proved to be an exceptional teacher. As an instructor, they have developed an effective teaching approach utilizing a flipped classroom model. Student course evaluations illustrate that students have responded very favorably to this teaching approach. In 2020, Dr. Liberman-Martin launched an Advanced Organic Chemistry elective. Due to their teaching reputation in lower level organic chemistry, Dr. Liberman-Martin was able to cultivate interest in advanced organic. With a Pedagogical Innovation Award, Dr. Liberman-Martin developed a course equipped with pre-lecture videos/quizzes. Dr. Liberman-Martin's new course was praised by students and peers for the "grad school" problem-solving environment created in the class and through assessments. This in-depth course allowed students to really experience the critical thinking that a synthetic chemist develops.

Given Dr. Liberman-Martin's transformative teaching, I am delighted to provide extensive administrative and mentoring support to help ensure the success of the teaching plans in the attached proposal. The College will provide the logistical and structural framework, with the appropriate support staff, to undertake the various activities planned to explicitly incorporate training in argumentation practices so that organic chemistry students can construct more organized and rigorous explanations for organic chemistry phenomena. This, to me, epitomizes the kind of holistic, inclusive, teaching that leads to truly meaningful student outcomes both in Chemistry and in other classes where the knowledge gained will be used. Furthermore, I believe it will provide new mechanisms for effective content delivery that will be of great value for other courses under development in our college outside of Chemistry.

In summary, I confirm my own enthusiastic unreserved endorsement and the full institutional support of Chapman University and the Schmid College of Science for Dr. Liberman-Martin's application for the Cottrell Scholar Award. Dr. Liberman-Martin is an outstanding early career scientist, and I am fully committed to ensuring the success of this important proposal.

Sincerely,

A handwritten signature in black ink that reads "Michael Ibba".

Dr. Michael Ibba, PhD  
Professor of Biochemistry  
Dean  
Schmid College of Science and Technology  
Chapman University

**RESEARCH CORPORATION FOR SCIENCE ADVANCEMENT**  
**Cottrell Scholar Award Application**

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