

Project Summary

Overview

Chemical catalysis is used to produce most commodity chemicals, making catalysis critical to the U.S. economy. Many current catalytic transformations rely on expensive, rare, or toxic metals as catalysts. There is an ongoing need to develop efficient and robust catalysts based on earth-abundant elements as potential replacements for precious metal catalysts. Organocatalytic chemistry has become a prominent alternative to metal catalysts due to its potentially lower environmental impact. Within the context of organocatalysis, both Lewis bases and Brønsted bases have emerged as powerful classes of catalysts for sustainable organic transformations.

This proposal focuses on carbodiphosphoranes, which are metal-free compounds that defy the typical bonding patterns of organic chemistry. While most organic compounds feature carbon atoms that use all four valence electrons in covalent bonds, carbodiphosphoranes feature two phosphorus centers flanking a central carbon with two lone pairs of electrons. Carbodiphosphoranes have long been considered laboratory curiosities; however, most research has focused on their ability to serve as ligands, and their applications as metal-free catalysts are exceptionally rare. We are interested in exploring the organocatalytic potential of carbodiphosphoranes and gaining deeper insight into their steric and electronic properties to help transform carbodiphosphoranes from curiosities into valuable catalysts.

The proposed research targets carbodiphosphorane catalysis in the context of ester derivatization. Esters are ubiquitous in biomass and plant-based oils, making esters promising chemical and fuel feedstocks. Discoveries in the described program will broaden the pool of organocatalysts available to chemists and provide a foundation for applying these catalysts to address challenges in organic and polymer synthesis. This research will be conducted exclusively by undergraduates, which will contribute to the education of future science professionals.

Intellectual Merit

The proposed work aims to demonstrate the synthetic utility of a new class of organocatalysts while simultaneously providing sustainable synthetic methods that use widely available ester substrates. This program will comprehensively study two mechanistic roles for carbodiphosphorane catalysts, which align with the specific aims of this proposal. Reactions involving ester substrates will be studied with the aims of:

1. Elucidating the impact of carbodiphosphorane structure on its *Lewis basicity* by performing ester reduction studies
2. Analyzing carbodiphosphorane *Brønsted basicity* through studies of cyclic ester ring-opening polymerization

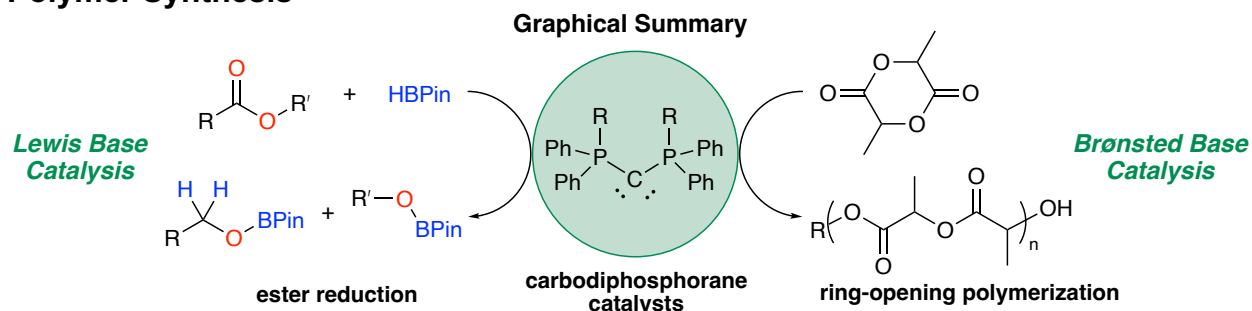
The proposed mechanistic studies and experiments to examine carbodiphosphorane structure and reactivity will improve the understanding of these catalysts, enabling the hypothesis-driven creation of improved synthetic methods.

Broader Impacts

Organocatalysts offer a potentially environmentally benign approach to synthesizing commodity chemicals and polymers. The development of catalytic reduction methods, particularly those featuring earth-abundant catalysts, could significantly improve the sustainability, efficiency, and safety of industrial processes. In addition, the study of cyclic ester polymerization has broader implications for the environment and the U.S. economy, given the vast quantity of plastics generated annually.

Infused in every stage of the proposed research is the involvement and training of undergraduate researchers. The undergraduates who participate in the proposed project will cultivate diverse skill sets, ranging from performing laboratory techniques to disseminating their results. The research objectives are closely tied to efforts to broaden the participation of students from underrepresented minority groups in STEM. The proposed program aims to improve the retention of transfer students in STEM disciplines by creating an orientation program, one-semester research opportunity, and monthly workshop series specifically for STEM transfer students at Chapman University. Opportunities for high school students from neighboring Orange High School to contribute to the proposed research are also included.

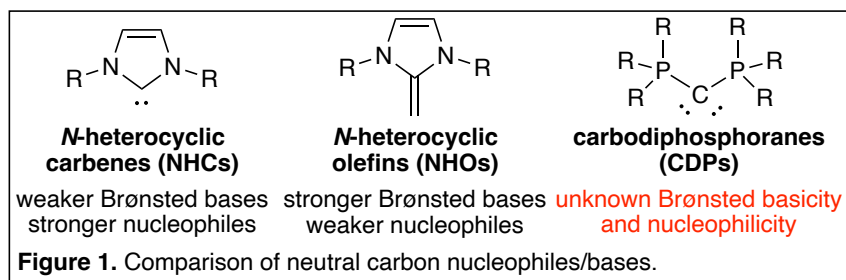
LEAPS-MPS: Development of Carbodiphosphorane Catalysts for Organic and Polymer Synthesis



Significance and Specific Aims

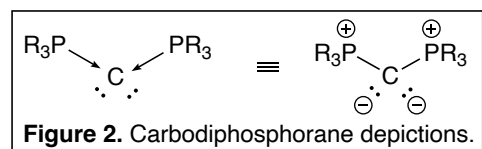
Catalysis is central to chemical industry, with catalytic processes appearing in the production of over 80% of all manufactured products.¹ Over the last three decades, organocatalytic chemistry has achieved prominence as an alternative to metal-catalyzed processes due to the potentially lower cost and lower environmental impact of organic compounds compared to transition metal catalysts. The use of organocatalysts is particularly advantageous in applications that are intolerant of metal contamination such as pharmaceuticals and polymers for biomedical or microelectronics applications.^{2,3}

Carbon nucleophiles have emerged as a powerful class of organocatalysts for organic and polymer synthesis (**Figure 1**). Most prominently, *N*-heterocyclic carbenes (NHCs) have become ubiquitous organocatalysts for a range of transformations.⁴ In an organocatalytic context, NHCs



have been used most extensively as “umpolung” catalysts for reactions involving carbonyl compounds,⁵ however, NHCs can also serve as nucleophilic catalysts for reduction chemistry^{6,7} or as Brønsted base catalysts.^{8,9} Recently, catalytic applications of *N*-heterocyclic olefins (NHOs) as nucleophiles^{10,11} and Brønsted bases¹² have also been demonstrated. The catalytic reactivity of NHOs is attributed to reactivity at the exocyclic α -carbon, which is rendered electron rich due to the strong polarization of the exocyclic C=C double bond.¹³ Rational selection of NHC and NHO catalysts is aided by extensively catalogued nucleophilicities,^{14–16} Brønsted basicities,^{16–18} donor properties,¹⁹ and steric profiles²⁰ of these compounds.

Carbodiphosphoranes constitute an unusual class of molecules featuring a two-coordinate carbon center that is formally zerovalent and possesses two lone pairs (**Figure 2**).^{21,22} As a result, the central carbon of the carbodiphosphorane is strongly donating. There has been significant interest in carbodiphosphoranes as ligands for transition metal complexes,^{23–29} as carbodiphosphoranes are more strongly donating than *N*-heterocyclic carbene ligands based on Tolman electronic parameters.³⁰ However, little is known about the ability of carbodiphosphoranes to serve as catalysts themselves. We believe this represents an opportunity to investigate the catalytic potential of these overlooked compounds and to gain deeper insight into their electronic properties. **We hypothesize that the exceptionally strong donor properties of carbodiphosphoranes will render them highly active as Lewis base and Brønsted base organocatalysts.**



This proposal describes synthetic and mechanistic studies of ester reduction and ring-opening polymerization catalyzed by carbodiphosphoranes. Esters were selected as target substrates because they are ubiquitous in biomass and plant-based oils, making esters a renewable source of chemical and fuel feedstocks.^{31,32} This investigation, which will be performed in collaboration with undergraduate and high school student researchers, will improve understanding of the steric and electronic properties of carbodiphosphoranes while simultaneously providing catalytic methods to derivatize ester compounds.

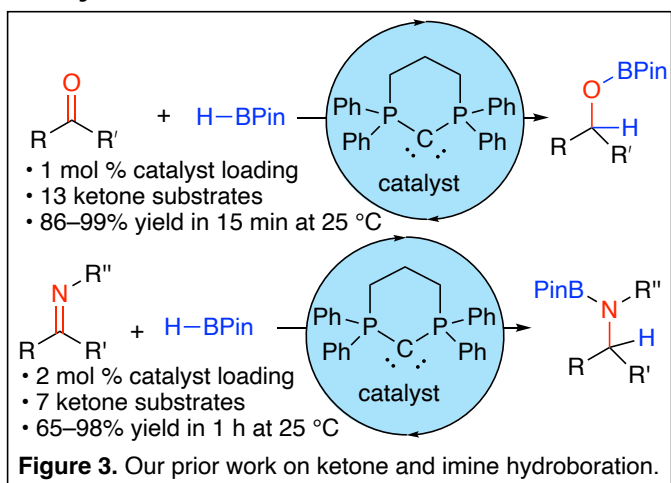
Aim 1. Lewis Base Catalysis – Ester Reduction. We will synthesize a series of six carbodiphosphoranes and evaluate them as catalysts for ester hydroboration. The carbodiphosphorane P–C–P bond angles, $^1J_{CP}$ coupling constants, and donor and steric properties will be measured to determine if a trend exists between these metrics and catalytic efficiency. Stoichiometric experiments of carbodiphosphoranes with borane and ester substrates will be performed to determine reasonable elementary steps in catalysis.

Aim 2. Brønsted-Base Catalysis – Ring-Opening Polymerization of Cyclic Esters. We will compare the catalytic activities of six carbodiphosphorane and four phosphorus ylide catalysts for ring-opening polymerizations of *rac*-lactide, L-lactide, δ -valerolactone (VL), and ϵ -caprolactone (CL) monomers. The Brønsted basicities of carbodiphosphorane catalysts will be measured by ^{31}P NMR titration experiments to determine if a trend exists between catalyst basicity and lactide polymerization rate.

Aim 3: Broadening Participation of Scientists from Underrepresented Groups. STEM transfer students to Chapman University are more racially and ethnically diverse than entering first year students. Concerningly, transfer students have lower retention rates in STEM majors and are underrepresented among students performing research in Schmid College. The implementation of a one-day transfer student orientation event is proposed, along with the creation of a one-semester research opportunity for first-semester transfer students.

Previously Published Work on Related Projects

The first demonstration of organocatalysis using a carbodiphosphorane has recently been reported by our group. Two undergraduate researchers in my group investigated a carbodiphosphorane catalysts for ketone and imine hydroboration.³³ We observed that a cyclic six-membered ring carbodiphosphorane performs these hydroborations with pinacolborane (HBPIn) at room temperature using low catalyst loading (1 or 2 mol %) (**Figure 3**). We compared the catalytic activity of the cyclic carbodiphosphorane and a phosphorus ylide Ph_3PCH_2 . The carbodiphosphorane catalyst showed higher hydroboration activity toward both ketones and imines compared to the phosphorus ylide catalyst. These results validate the viability of carbodiphosphoranes as organocatalysts and demonstrate that the air-sensitive catalytic reactions proposed herein can be performed by Chapman undergraduates.



Aim 1: Lewis Base Catalysis – Ester Reduction

1.1 Introduction

Carbonyl reduction is a ubiquitous method of generating alcohol products, which are widely used in chemical industry.³⁴ Among these reactions, methods for aldehyde and ketone reduction have been most widely developed. Precious metals were the first reported catalysts for aldehyde and ketone hydrogenation;^{35,36} however, significant recent advances have provided highly active non-precious element hydrogenation catalysts.^{37–40} To complement hydrogenation methods, hydroboration and hydrosilylation reactions have emerged as alternative approaches that take advantage of liquid silane and borane reagents that can be used under mild reaction conditions and without the need for high-pressure apparatus.^{41–44}

Compared to their aldehydes and ketone counterparts, ester reduction methods are less widely developed. Traditional methods for ester reduction use powerful reducing agents such as lithium aluminum hydride or sodium borohydride, the latter of which often must be used at elevated temperatures.⁴⁵ Catalytic hydrogenation of esters typically requires conditions that employ high pressure and temperature.⁴⁶ Ester hydroboration has gained recent attention as a milder reduction method. Transition metal, lanthanide, and actinide catalysts have been reported to catalyze ester hydroboration reactions to produce alkoxy boronate products.^{47–52} Furthermore, there are a limited number of reported main group catalysts for ester

hydroboration featuring lithium and magnesium complexes (**Figure 4**).^{53–60} **Notably, none of the previously reported work on ester hydroboration features organocatalysts.** This leaves significant room for the discovery of new ester reduction catalysts that could operate by alternative reaction mechanisms and potentially improve reaction efficiency or functional group tolerance.

1.2 Carbodiphosphorane Selection, Synthesis, and Parameterization

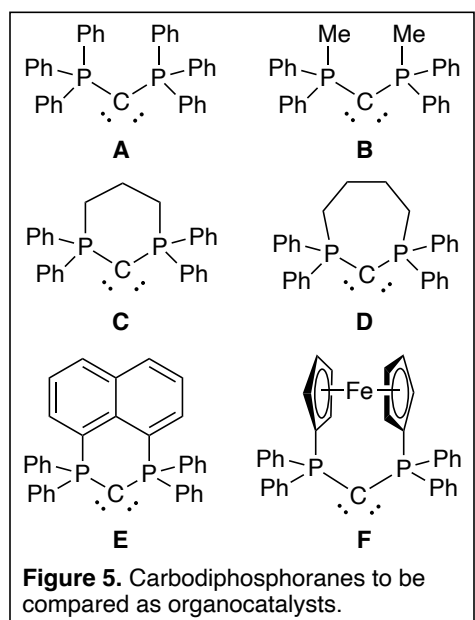
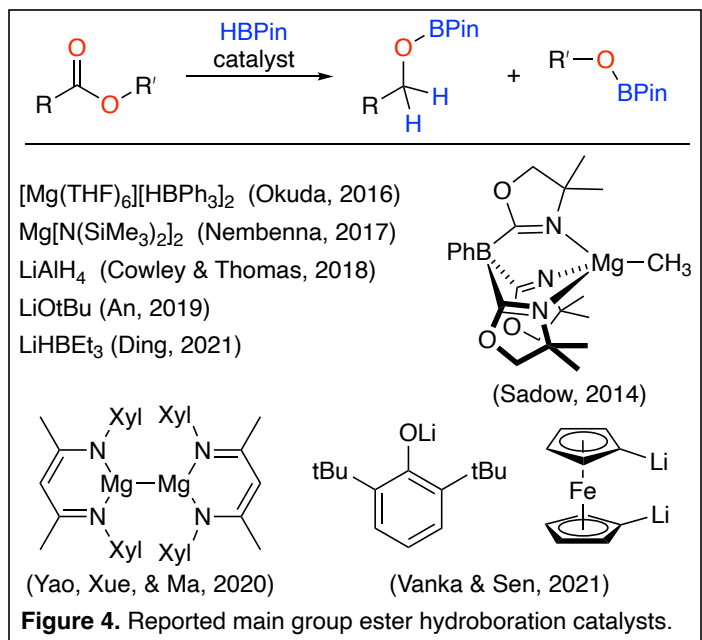
A series of carbodiphosphoranes (**A–F**, **Figure 5**) has been selected to probe the influence of carbodiphosphorane structure on ester reduction activity. These structures will allow comparisons of (i) acyclic carbodiphosphoranes with different steric profiles, (ii) acyclic versus cyclic carbodiphosphoranes, and (iii) ring size effects. Carbodiphosphoranes **A–D** have been previously reported and (i) can be synthesized from commercially available precursors in two reaction steps, and (ii) are indefinitely stable when stored as solids under inert atmosphere.^{33,61–63} These synthetic and storage considerations help make the proposed project accessible for undergraduate researchers.

As a part of these studies, we will attempt to prepare two novel cyclic carbodiphosphoranes (**E**, **F**) featuring 1,8-naphthyl or ferrocenyl backbones. NHCs featuring these backbones are known and have enhanced donor strength relative to imidazolyl NHCs.^{64–66} Ring size and flexibility are known to impact on the steric and electronic properties of NHCs,^{67–70} however, these effects on carbodiphosphorane donor or steric properties are not known. We propose synthesis of these compounds by alkylation of commercially available bisphosphines with diiodomethane, followed by deprotonation of cyclic bisphosphonium salts with benzyl potassium.

One parameter of interest for the carbodiphosphorane series is the central P–C–P angle, which influences the amount of 2s character for the σ -type lone pair orbital.⁷¹ P–C–P angles have been reported for compounds **A** (ranges from 130° to 180°),⁷¹ **B** (122°),⁷² and **C** (117°).⁶³ To allow comparison with these reported values, we will collect single-crystal X-ray crystallographic data for carbodiphosphoranes **D–F** to determine P–C–P angles for these compounds. We anticipate the P–C–P angles will be less flexible for cyclic carbodiphosphoranes than acyclic systems.

The central carbon $^1J_{PC}$ coupling constants for all carbodiphosphoranes will also be measured by ^{13}C NMR spectroscopy and compared. Larger ^{31}P – ^{13}C coupling is indicative of more 2s character in the P–C bond, suggesting less stabilization of lone pairs at the central carbon.⁷³ **We hypothesize that carbodiphosphoranes with larger $^1J_{PC}$ coupling will be more Lewis basic and will exhibit enhanced catalytic activity in hydroboration reactions.**

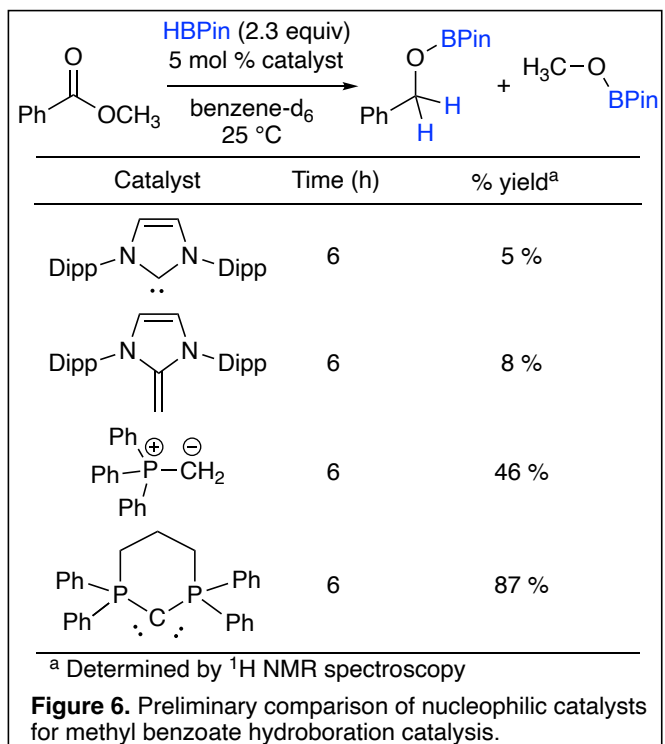
Last, the donor and steric properties of carbodiphosphoranes **B** and **D–F** will be assessed by synthesis of their gallium trichloride complexes and collection of X-ray crystallographic data. The sum of the Cl–Ga–Cl angles is indicative of donor strength, and newly measured angles will be compared to literature values for carbodiphosphoranes **A** and **C**.⁷⁴ The percent buried volume metric of steric bulk will be calculated for



the carbodiphosphorane–GaCl₃ complexes using the SambVca2 web tool for crystallographically-determined structures.⁷⁵

1.3 Optimization of Ester Hydroboration Catalysis

The six carbodiphosphoranes prepared in Aim 1.2 will be compared as catalysts for ester reduction. We are targeting ester cleavage reactions by performing hydroborations with ≥ 2 equiv of borane as a route to generate alkoxy boronate products. To demonstrate the feasibility of the proposed work, we have compared a range of metal-free carbon nucleophiles as potential catalysts for ester hydroboration (**Figure 6**). Excitingly, we have observed that the cyclic carbodiphosphorane **C** can efficiently catalyze methyl benzoate hydroboration at room temperature using 2.3 equiv of pinacolborane (HBPIn) in 86% yield. In contrast, the unsaturated *N*-heterocyclic carbene and *N*-heterocyclic olefin tested showed low catalytic activity, while the phosphorus ylide Ph₃PCH₂ produced a moderate amount (46%) of hydroboration products. These results validate the viability of carbodiphosphoranes as ester reduction catalysts and demonstrate that the air-sensitive catalytic reactions proposed herein are within the capabilities of Chapman undergraduates.



Further experiments will be performed to optimize conditions for methyl benzoate reduction. With all carbodiphosphorane catalysts (**A–F**), the use of alternative reductants will be tested, including other borane reagents (catecholborane and ammonia borane) and silanes (phenylsilane, diphenylsilane, and polymethylhydrosiloxane). Ester hydrosilylation reactions have been reported using transition metal^{76–87} or simple base^{88,89} catalysts; however, there are no reported organocatalysts for these reactions. Yields for catalytic reactions performed in benzene-*d*₆, toluene-*d*₈, dichloromethane-*d*₂, tetrahydrofuran-*d*₈, and under neat conditions will be compared. With the highest performing carbodiphosphorane catalyst, reactions varying catalyst loading (1 mol %, 2.5 mol %, 5 mol %, and 10 mol %) will be performed. Overall, these studies will identify reaction conditions that maximize yield and achieve a reasonable rate of methyl benzoate reduction.

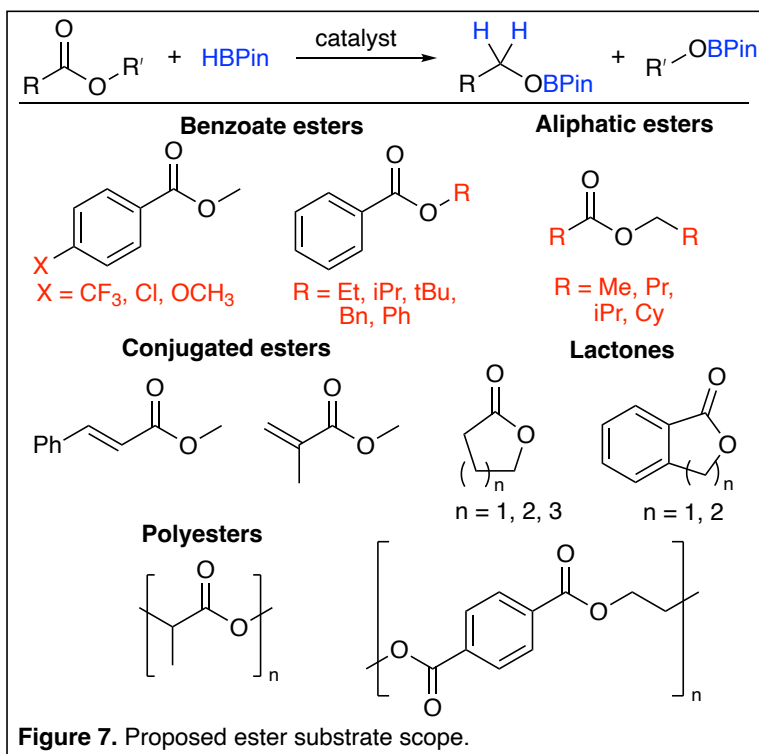
1.4 Ester Hydroboration Substrate Scope

Using the optimal carbodiphosphorane catalyst and reaction conditions identified for methyl benzoate hydroboration (Aim 1.3), hydroboration experiments for a series of commercially available esters will be performed (**Figure 7**). If hydrosilylation reactions are observed to be more efficient in Aim 1.3, those will be performed in place of hydroborations. All catalytic reactions will be performed in J. Young NMR tubes using deuterated solvents, and yields will be calculated by ¹H NMR spectroscopy relative to an internal standard. Products will be characterized by ¹H, ¹¹B, and ¹³C NMR spectroscopy and mass spectrometry.

Para-substituted methyl benzoate derivatives will evaluate electronic effects on the hydroboration yield and rate. We anticipate that electron-poor esters will be reduced more rapidly than electron-rich substrates based on previous studies.^{88,50,49,52} A series of benzoate derivatives featuring varied alkyl substituents and aliphatic esters will be tested to determine steric effects on ester reduction reactivity. In previous studies with magnesium amide catalysts, aliphatic esters were more rapidly reduced than aromatic esters,⁵⁵ and we will determine if this trend is also observed for carbodiphosphorane catalysts. Two conjugated esters will also be studied to determine if ester reduction can be performed selectively over conjugate addition. If 1,4-addition is observed using the carbodiphosphorane catalyst, diborations will be attempted with B₂Pin₂

and B₂Cat₂ reagents. Conjugate additions of diboron reagents to α,β -unsaturated carbonyls can be catalyzed by nucleophilic NHC^{90,91} and phosphine^{92–94} catalysts, and we will compare carbodiphosphorane activity for these reactions. Hydroboration of lactones featuring five-, six-, and seven-membered rings will also be performed.

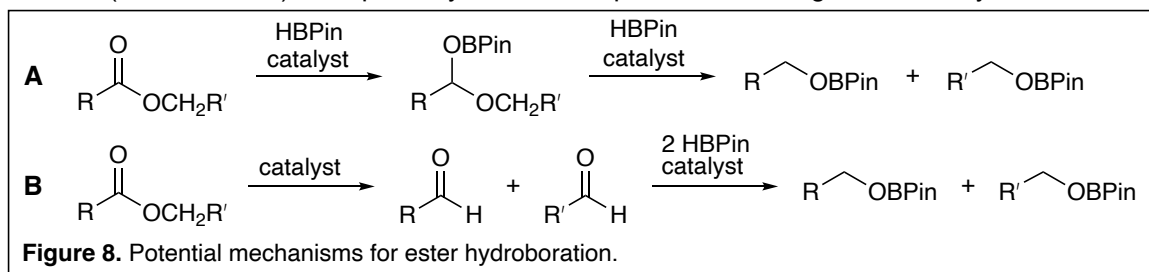
Last, we will attempt reductive depolymerizations of polyesters, and the controlled polymer degradation provides a method to transform plastic waste into value-added products.^{95,96} For these experiments, samples of polylactide (PLA) from a beverage cup and polyethylene terephthalate (PET) from a water bottle will be cut into small (~3 x 3 mm flakes), washed with deionized water, and dried prior to hydroboration reactions.



1.5 Mechanistic Studies of Ester Hydroboration Catalysis

With the knowledge gained from the ester substrate scope in Aim 1.4, we will investigate the mechanism of carbodiphosphorane-catalyzed ester hydroboration. Nucleophilic organic compounds are unprecedented catalysts for these transformations, and the mechanistic insights gained through this work will be valuable for future catalyst development. Both stoichiometric and catalytic experiments will be performed to provide evidence for a plausible catalytic cycle.

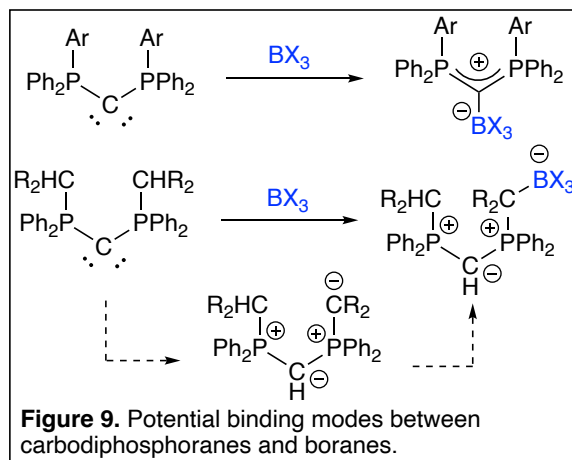
We envision two potential pathways for ester hydroboration (**Figure 8**). The carbodiphosphorane catalyst could catalyze direct ester reduction to initially generate a hemiacetal intermediate, followed by further hydroboration and C–O bond cleavage to form the alkoxy boryl ester product(s) (mechanism **A**). This mechanism has been observed for La[N(SiMe₃)₂]₃-catalyzed ester hydroboration reactions.⁴⁹ Alternatively, the carbodiphosphorane could catalyze the conversion of ester into two equivalents of aldehydes by a reverse-Tishchenko mechanism followed by carbodiphosphorane-catalyzed aldehyde hydroboration (mechanism **B**). This pathway has been implicated for a magnesium catalyst.⁵³



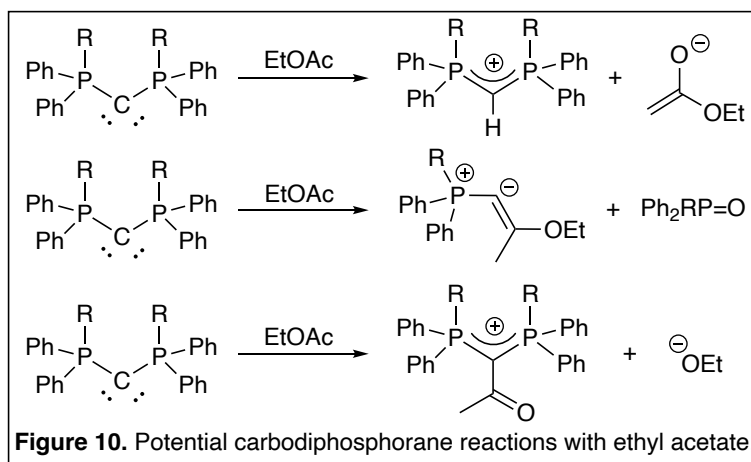
1.5A Stoichiometric Experiments

To determine plausible elementary reaction steps, we will perform stoichiometric experiments of all carbodiphosphoranes (**A–F**, **Figure 5**) with boranes of varying steric and electronic properties, including borane dimethylsulfide (BH₃•SMe₂), triphenylborane (BPh₃), and pinacolborane (HBPIn) (**Figure 9**). Adducts of (Ph₃P)₂C (**A**) with BH₃ and BPh₃ have been previously reported.^{97,98} Borane binding will be conveniently monitored by ¹H, ³¹P, and ¹¹B NMR spectroscopy.

We anticipate that simple coordination of the carbodiphosphorane carbon center to boron will occur for non-tautomerizable carbodiphosphoranes (**A**, **E**, **F**). For carbodiphosphoranes **B**, **C**, and **D**, the presence of α -hydrogens relative to the phosphorus centers allows for potential tautomerization to an unsymmetrical double ylide tautomer prior to borane binding. This binding mode has been observed for coordination of a cyclic double ylide compound to BH_3 .⁹⁹ Furthermore, our prior work investigating carbodiphosphorane-catalyzed ketone hydroboration provided evidence that the cyclic six-membered carbodiphosphorane **C** tautomerizes to a double ylide form prior to a stoichiometric reaction with benzophenone.³³ In borane binding experiments, we will use ^{31}P NMR spectroscopy to identify the tautomeric form (carbodiphosphorane or double ylide) that coordinates to boron. The two phosphorus centers are equivalent in the carbodiphosphorane form, leading to the observation of a singlet in $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. In contrast, the two phosphorus centers are inequivalent in the double ylide form, producing two doublet signals in $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. We anticipate that borane sterics may dictate binding preferences for tautomerizable carbodiphosphoranes.



Separately, we will investigate the stoichiometric reactivity of all carbodiphosphoranes with ethyl acetate and γ -butyrolactone (**Figure 10**). Reactions will be monitored by ^1H , ^{13}C , and ^{31}P NMR spectroscopy. The carbodiphosphorane may deprotonate the ester, a pathway observed between $(\text{Ph}_3\text{P})_2\text{C}$ (**A**) and ethyl bromoacetate.¹⁰⁰ Alternatively, a nucleophilic attack could occur at the ester carbonyl center, which may be followed by Wittig olefination or loss of an alkoxide leaving group. These reactivity patterns have been previously observed for phosphorus ylides.^{101,102} Any products formed in reactions between carbodiphosphoranes and ylides will be isolated and their catalytic activities will be assessed by treatment with excess HBPIn and ester.



1.5B Test for Ester Redistribution

Ester redistribution will be probed in the absence of pinacolborane to determine if carbodiphosphorane catalysts can cause aldehyde formation via a reverse-Tishchenko reaction. Catalytic amounts of carbodiphosphoranes **A–F** will be treated with a 1:1 mixture of $\text{PhCO}_2\text{CH}_2\text{Ph}$ and $\text{CyCO}_2\text{CH}_2\text{Cy}$ and monitored by ^1H NMR spectroscopy. The formation of crossover ester products $\text{PhCO}_2\text{CH}_2\text{Cy}$ and $\text{CyCO}_2\text{CH}_2\text{Ph}$ would suggest the formation of aldehyde intermediates, followed by a Tishchenko reaction to regenerate ester products.⁵³

1.5C Labeling Studies

Deuterium labeling studies using DBPin^{103} under catalytic conditions will be a final method to probe if aldehyde formation occurs during catalysis. Carbodiphosphoranes **A–F** will be treated with excess ethyl benzoate and DBPin , and product formation will be monitored by ^1H and ^2H NMR spectroscopy. If hydroboration of the ester occurs directly (mechanism **A**, **Figure 8**), both deuterides will be delivered to the same carbon, producing $\text{PhCD}_2\text{OBPin}$ and $\text{MeCH}_2\text{OBPin}$ products. Alternatively, if a reverse-Tishchenko reaction occurs (mechanism **B**, **Figure 8**), two non-deuterium labeled aldehydes (PhCHO and MeCHO) will

be produced and will undergo subsequent hydroboration using DBPin to form mono-deutero alkoxy boronate products (PhCHDOBPIn and MeCHDOBPIn).

1.6 Summary of Planned Work

Together, the experiments in Aim 1 will comprehensively investigate carbodiphosphorane-catalyzed ester reduction. We will study a range of carbodiphosphoranes to determine how the structure of a carbodiphosphorane impacts its catalytic activity. The six carbodiphosphoranes will be evaluated by their P–C–P angles, $^1J_{PC}$ coupling constants, and donor and steric measurements for carbodiphosphorane–GaCl₃ complexes. We will look for trends between these metrics and activity in ester hydroboration catalysis. Mechanistic studies will provide a fundamental understanding of catalytic pathways for carbodiphosphoranes that may enable the rational design of future Lewis basic catalysts for ester reduction.

Aim 2: Brønsted-Base Catalysis – Ring-Opening Polymerization of Cyclic Esters

2.1 Introduction

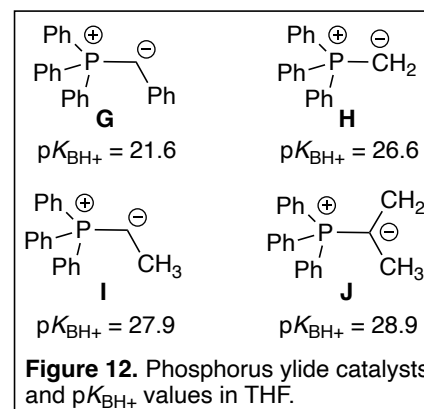
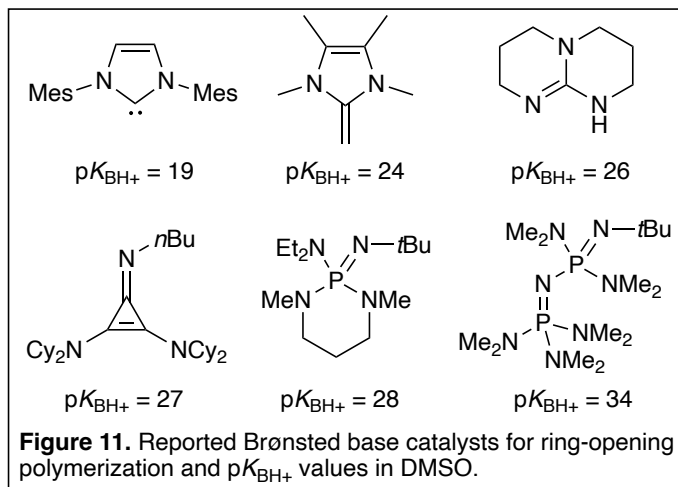
Polymers are ubiquitous in modern society and are produced at a staggering scale,¹⁰⁴ with 368 million tons of polymers were produced worldwide in 2019, and plastics usage expected to grow at a pace of 3% each year.¹⁰⁵ Unfortunately, most plastics end up in landfills or the environment rather than being recycled.¹⁰⁶ A central goal of modern polymer science is to create more sustainable plastics with enhanced degradability or recyclability properties.¹⁰⁷

Aliphatic polyesters are an important class of polymers that are biocompatible, non-toxic, and biodegradable.¹⁰⁸ Ring-opening polymerization (ROP) has emerged as a powerful method to prepare these materials. Because aliphatic polyesters are widely used in tissue engineering and drug delivery, and metallic impurities can be deleterious for these applications, metal-free catalysts for ROP are desirable for preparing polyesters.¹⁰⁹

Strong nucleophiles and Brønsted bases are a prominent class of organocatalysts for the ROP of heterocyclic monomers.¹¹⁰ In the presence of alcohol initiators, Brønsted base catalysts can activate the alcohol initiator and the alcohol group of a growing polymer chain by either hydrogen bonding or deprotonation. Reported Brønsted bases for ROP of lactide or lactones include *N*-heterocyclic carbenes,^{111,112} *N*-heterocyclic olefins,^{113–115} guanidines,¹¹⁶ cyclopropenimines,¹¹⁷ and phosphazenes^{118,119} (Figure 11). Across these catalysts, pK_{BH^+} values vary widely,^{120,121,117,16} and the relationship between catalyst basicity and ROP efficiency or product dispersity is not well understood. This leaves significant room for improvement in catalyst design and mechanistic understanding for Brønsted base catalyzed polymerizations.

2.2 Carbodiphosphorane and Phosphorus Ylide Selection and Brønsted Basicity Measurements

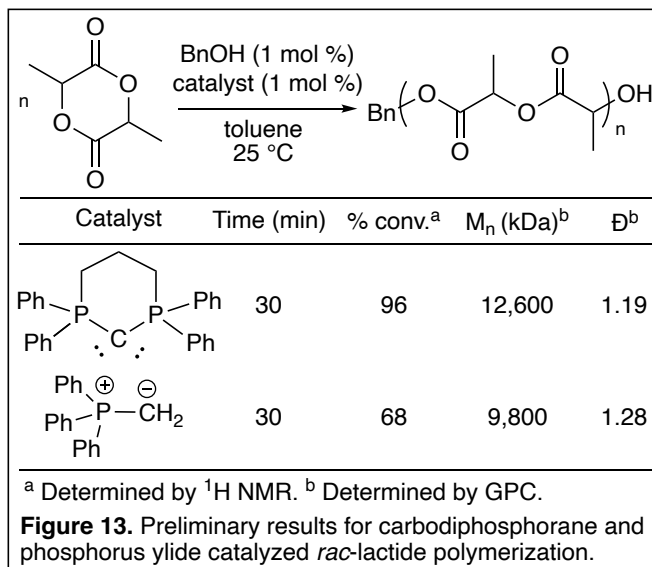
In Aim 2, we will compare the ring-opening polymerization activity of six carbodiphosphoranes (A–F, Figure 5) to a series of phosphorus ylides (G–J, Figure 12). All phosphorus ylides have been previously reported and can be conveniently stored as solids under an inert atmosphere.¹²² By performing reactions in the presence of an alcohol initiator, we will probe the ability of carbodiphosphoranes and phosphorus ylides to serve as Brønsted base catalysts for ring-opening polymerization catalysis. **We hypothesize that more Brønsted basic catalysts will exhibit greater activity in polymerization reactions.**



Experimental basicity measurements have been reported for phosphorus ylide catalysts **G–J** in THF solvent, and pK_{BH^+} values for these compounds are presented in **Figure 12**.¹²³ In contrast, although proton affinities have been calculated for several alkyl/aryl carbodiphosphoranes,¹²⁴ to our knowledge, experimental basicity measurements have not been performed for these compounds. To measure pK_{BH^+} values for carbodiphosphoranes **A–F**, we will perform ³¹P NMR titration experiments against phosphazene and ylide bases with known pK_{BH^+} values in THF-*d*₈.¹²⁵ We anticipate that all carbodiphosphoranes tested will exhibit stronger basicities than phosphorus ylides **G–J**.

2.3 Ring-Opening Polymerizations

The six carbodiphosphoranes (**A–F**) and four phosphorus ylides (**G–J**) will be compared as catalysts for lactide and lactone ring-opening polymerization. To establish the feasibility of these reactions, we have performed *rac*-lactide polymerizations in the presence of a benzyl alcohol initiator using cyclic carbodiphosphorane **C** and phosphorus ylide **H** as catalysts (**Figure 13**). Both catalysts formed polylactide at room temperature, with the carbodiphosphorane showing a higher conversion (96 %) than the phosphorus ylide (68 %) after 30 min. Both catalysts displayed relatively narrow dispersity values (1.19 and 1.29 using catalysts **C** and **H**, respectively). These dispersities are narrower than values recently reported for carbodicarbene catalysts.¹²⁶



We will conduct polymerizations of three types of monomers: lactide (LA), δ -valerolactone (VL), and ϵ -caprolactone (CL) (**Figure 14**). The typical reactivity of these monomers follows the trend $k_{LA} > k_{VL} \gg k_{CL}$.¹²⁷ Conversions will be measured by ¹H NMR spectroscopy, and molecular weights and dispersities of polymer product will be determined by size-exclusion chromatography. Reactions will be performed in both toluene and THF solvents to determine solvent polarity effects on polymerizations. The following experiments will be performed for all carbodiphosphorane and ylide catalysts (**A–J**) using benzyl alcohol as an initiator:

- rac*-LA polymerization with a monomer to initiator ratios $[M]_0/[I]_0 = 100, 200, \text{ and } 500$
- L-LA polymerization with $[M]_0/[I]_0 = 100$
- VL polymerization with $[M]_0/[I]_0 = 100, 200, \text{ and } 500$
- CL polymerization with $[M]_0/[I]_0 = 100, 200, \text{ and } 500$

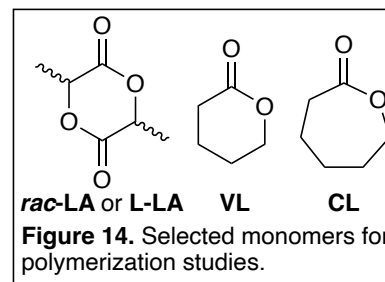
Aliquots of polymerizations with $[M]_0/[I]_0 = 100$ will be taken as reactions proceed to determine if a linear correlation between molecular weight and conversion is observed. A greater than linear increase in number-average molecular weight and a polydispersity increase throughout the reaction may indicate competitive transesterification reactions.¹¹⁸ Analysis of polylactide products by MALDI-TOF mass spectrometry will also be performed to determine if both odd and even numbers of lactic acid units are observed, which is a further indication of transesterification.¹⁰⁹

In addition to experiments in toluene and THF solvents, polymerization of VL and CL, which are liquids at room temperature, will also be attempted under solvent-free conditions. If VL and CL polymerizations are sluggish, polymerizations will be performed with a (thio)urea hydrogen-bond donor co-catalyst.¹²⁸

2.4 Mechanistic Studies for Ring-Opening Polymerizations

2.4A Polymerization Kinetics

Kinetics for *rac*-LA polymerization with a target DP = 100 will be monitored by ¹H NMR spectroscopy for all carbodiphosphorane and phosphorus ylide catalysts. Observed rate constants will be compared with pK_{BH^+} values for catalysts to determine if a trend between Brønsted basicity and polymerization rate. We



anticipate that cyclic carbodiphosphoranes will be the most basic and therefore will exhibit the fastest polymerization rates.

2.4B Investigation of Lactide and Poly lactide Epimerization

The microstructures of *rac*-LA polymerizations will be determined by analysis of the methine region of homodecoupled ^1H NMR spectra, and the probability of forming an isotactic dyad, P_i , will be calculated.¹²⁹ Although the targeted carbodiphosphorane and phosphorus ylide catalysts are achiral, a chain-end control mechanism has been proposed to account for stereoselective ring-opening polymerization of *rac*-LA by other achiral organocatalysts.¹³⁰ We expect isotactic enhancement in the polymerization of *rac*-LA to be influenced by the catalyst's steric hindrance,¹²¹ with greater P_i values expected for bulkier carbodiphosphorane catalysts relative to phosphorus ylides.

We will also collect homodecoupled ^1H NMR spectra for L-LA polymerization products to determine if epimerization occurs in the presence of carbodiphosphorane or phosphorus ylide catalysts. Stoichiometric experiments between catalysts and lactide will be monitored by ^1H NMR spectroscopy to determine if deprotonation to form a lactide enolate occurs, which would cause epimerization.¹¹⁷

2.4C Stoichiometric Experiments with Benzyl Alcohol

To determine the nature of catalyst interactions with the alcohol initiator, stoichiometric experiments will be performed between benzyl alcohol and carbodiphosphorane or phosphorus ylide catalysts **A–J**. In previous work, *N*-heterocyclic carbenes, which are less basic than phosphorus ylides, have been observed to form hydrogen-bonding interactions with aliphatic alcohols^{131,132} and deprotonate aromatic alcohols to form imidazolium aryloxide products.¹³³ We anticipate two analogous interactions between benzyl alcohol and carbodiphosphoranes or phosphorus ylides: (i) hydrogen bonding between the catalyst and benzyl alcohol for weaker bases, or (ii) deprotonation of benzyl alcohol by strong bases to form a hydrogen-bonded phosphonium alkoxides (**Figure 15**).

In a preliminary experiment between cyclic carbodiphosphorane **C** and benzyl alcohol in benzene- d_6 , alcohol deprotonation was observed, as evidenced by strong ^1H – ^{31}P coupling ($^3J_{\text{PH}} = 20$ Hz) for the resulting phosphonium in ^1H NMR spectra.

Catalyst interactions with benzyl alcohol will be determined by ^1H , ^{13}C , and ^{31}P NMR spectroscopy. The NMR spectra for catalyst–alcohol adducts will be compared to spectra for free catalysts and singly protonated phosphonium compounds generated by treatment of catalysts with triflimic acid (HNTf_2). We expect hydrogen-bonded phosphonium alkoxide compounds to display weakened ^1H – ^{31}P coupling than phosphonium triflimidate compounds. As further evidence for non-covalent interactions between reaction components, ^1H – ^1H NOESY experiments will be performed to determine if NOE cross-peaks are observed between catalysts and benzyl alcohol.

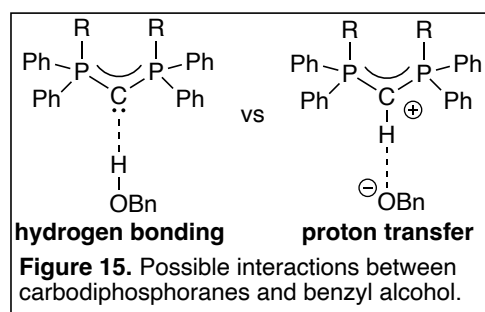
2.5 Summary of Planned Work

The experiments in Aim 2 examine carbodiphosphorane and phosphorus ylide catalysts for ring-opening polymerization of lactide, δ -valerolactone, and ϵ -caprolactone. We will measure the Brønsted basicities of six carbodiphosphoranes to determine if a relationship exists between lactide polymerization rate and catalyst basicity. These studies will provide insight into the fundamental properties of carbodiphosphoranes and provide new catalysts for ring-opening polymerization of cyclic esters.

Aim 3: Broadening Participation of Scientists from Underrepresented Groups

3.1 Introduction

A strong workforce trained in science, technology, engineering, and mathematics (STEM) is essential to U.S. interests in healthcare, national security, transportation, and energy. STEM fields are a significant employment sector, and in 2019, STEM employed 23% of the total U.S. workforce.¹³⁴ The continued underrepresentation of people from marginalized groups in STEM narrows the pipeline of potential scientists and exacerbates social inequalities. Black or African American, Hispanic or Latinx, and American Indian or Alaska Native individuals (the groups considered underrepresented for the purpose of this proposal) comprise 30% of the employed U.S. population yet only make up 15% of the STEM workforce



with a bachelor's degree or higher.¹³⁴ There is an urgent need to create equitable pathways to STEM careers by improving access and retention in STEM education for students from underrepresented minority groups. This Aim describes approaches to foster scientific engagement by creating research and mentoring experiences for transfer students and high school students interested in STEM disciplines.

3.2 Improving the Transition of Transfer Students to Schmid College

Transfer students, particularly those from community colleges, represent a significant population in efforts to improve STEM equity. Community college students are more racially diverse than students enrolled in four-year institutions.¹³⁵ For example, within California, 69% of Hispanic or Latinx students start their post-secondary education at a community college.¹³⁶ However, transfer students face many challenges as they transition to four-year institutions, including unfamiliarity with campus support resources and lack of engagement on campus.¹³⁷ These challenges and others cause 1/3 of STEM transfer students in the U.S. to switch to non-STEM majors shortly after transferring to a four-year institution.¹³⁸

The Schmid College of Science & Technology at Chapman University offers bachelor's degrees in biology, chemistry, physics, environmental science and policy, and mathematics. Schmid College currently enrolls 520 undergraduate students, of whom 12% are transfer students. The transfer student population within Schmid College includes a greater proportion of students who are Black, African American, Hispanic, or Latinx (38%) compared to the general undergraduate population (24%). We observe a concerning trend that Schmid College transfer students have lower retention within science majors compared to non-transfer students. Furthermore, transfer students are underrepresented among Schmid College students who perform undergraduate research, with transfer students only comprising 5% of students registered for course-based research credit despite making up 12% of Schmid College students. The lower retention within STEM majors and research involvement gap for transfer students within Schmid College motivates my interest in creating mentoring and research opportunities specifically for transfer students.

3.2A Creation of a Schmid College Transfer Orientation Program

As a part of the proposed work, the PI will create a one-day pre-orientation Schmid College Transfer Orientation Program to welcome transfer students to campus in collaboration with Dr. Jeremy Hsu, the Biology Program Advisor in Schmid College (see letter). This orientation program will be advertised to incoming Schmid transfer students during the summer or winter before they matriculate at Chapman.

One session of the orientation will provide information about campus resources and STEM student organizations. Faculty for an "Ask a Professor" session will be recruited that teach courses that transfer students are likely to take during their first year at Chapman. Junior and senior transfer student volunteers will be recruited to participate in a panel discussion on experiences and tips for incoming transfer students. Afternoon social activities will also be planned to help transfer students start to build community before beginning their first semester at Chapman.

3.2B Facilitating Early Research Opportunities for Transfer Students

Exposure to research has been shown to spur growth in science identity for students from underrepresented minority groups,¹³⁹ a factor that helps students persist in STEM fields.¹⁴⁰ Traditionally, students participate in research experiences as relatively senior undergraduates. However, there has been a recent push to create more research experiences for beginning undergraduates during the academic year, as students are likely to struggle during their first year of undergraduate study.¹⁴¹ Less is known about the impact of early research experiences on transfer students;¹⁴² however, we **hypothesize that early involvement in authentic research will improve transfer student sense of belonging and retention in STEM majors.**

Incoming transfer students with majors in Schmid College will be recruited to participate in a research project with Schmid faculty mentors during their first semester at Chapman. Emails recruiting transfer students to participate in this research opportunity will be sent approximately one month before their first semester at Chapman (July for fall transfers and December for spring transfers). A session at the transfer student orientation (Aim 3.2A) will have faculty research mentors give 5-minute lightning talks about their research and mentoring style. Students will be surveyed to provide a ranked list of their top three mentor choices so they can be matched with faculty mentors.

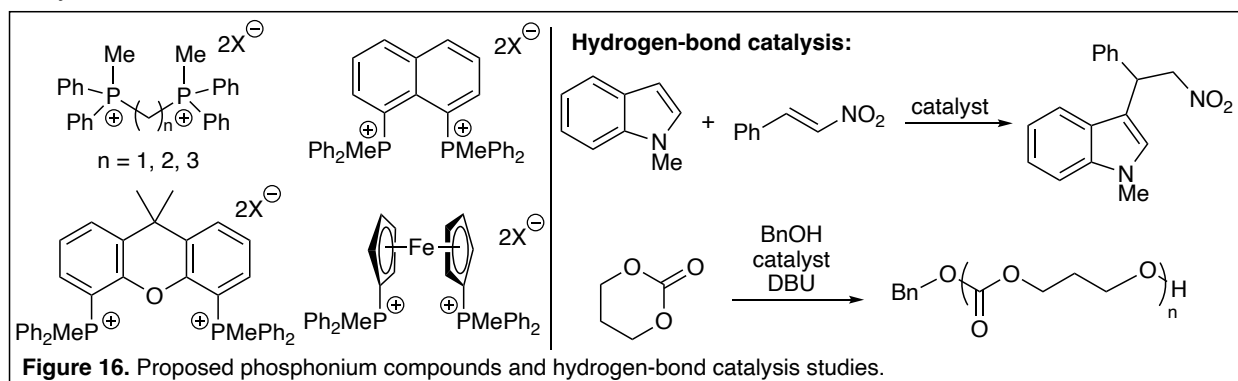
I aim to recruit ten transfer student researchers per academic year to participate in this program during the 2-year grant period. Up to \$1,000 toward the cost of research supplies will be provided for each student participant to offset research costs. While participating in the research program, students will register for 1

credit of 291/491 research credit through the Chapman Center for Undergraduate Excellence. One research credit translates to 3 hours/week of research, designed to be a manageable commitment during a busy first semester. The enrollment for course credit creates accountability between the faculty mentor and student researcher and provides a means of compensating faculty for their mentoring efforts. The 291/491 credit system allows faculty to receive either monetary or course release compensation after accruing research mentorship credits (24 credits translates to a 3-credit course release).⁹⁹

Student researchers will present their results as a poster at a Chapman Student Scholar Symposium, a campus-wide event held at the end of each semester. Participation in this event will allow students to view their work in the larger context of research taking place on campus. Students will be encouraged to continue their research after the one-semester program ends. A workshop will provide students with information about applying for research grants available on campus, including Scholarly/Creative Grants (\$1,000/semester for research supplies) and the Summer Undergraduate Research Fellowship program.

Each year of the grant period, I plan to mentor two participants with interests in chemistry or biochemistry in my research group. For these inexperienced researchers, a significant focus of the one-semester research experience will be on training in basic skills and concepts for a synthetic chemistry laboratory, including safety protocols, notebook keeping, equipment usage, and laboratory calculations. These skills will be contextualized around the use of phosphorus-based organocatalysts, connecting directly to the intellectual merit of this proposal.

To make the research accessible to new chemists, students will investigate the use of bisphosphonium cations as hydrogen-bond catalysts (**Figure 16**). The P₂-dimethylated phosphonium dications are expected to be readily prepared by alkylation of commercially available bisphosphines, and the phosphonium products are anticipated to be air and water stable.¹⁴³ We expect that the alkyl-phosphonium salts can be used as hydrogen-bond catalysts for organic and polymer synthesis.¹⁴⁴ Initial catalytic studies will focus on Friedel-Crafts reactions¹⁴⁵ and ring-opening polymerization of trimethylene carbonate,¹⁴⁶ as both transformations have been reported to be catalyzed by hydrogen-bond catalysts in air. Students will be given significant freedom to choose the types of studies they wish to perform, including comparing different catalyst structures or counteranion effects.



3.2C Cohort Building Efforts Throughout the Academic Year

Establishing a sense of belonging is particularly important in the first year at an institution.¹⁴⁷ Throughout the academic year, transfer students in Schmid College will be invited to monthly lunches to get to know each other and professors in Schmid. Initially, some lunches will be informal opportunities to meet peers and faculty. Others will be thematic opportunities to learn about summer research and internship applications, stress management, or professional development topics. Student lunch attendees will be surveyed to determine which style of lunches they prefer (informal vs. topic-focused) and to solicit suggestions for future themed sessions.

3.2D Assessment of Outcomes for Transfer Student Support Efforts

The combination of an orientation program, research opportunities, and workshop lunches specifically for transfer students in Schmid College are designed to foster campus connectedness, social belonging, and persistence in STEM. To determine the effectiveness of these efforts, I will track transfer student participation in these activities and retention in STEM majors.

At the end of their first semester at Chapman, all Schmid College transfer students will be invited to complete the Sense of Belonging Instrument, a 26-item survey designed to measure participants' sense of belonging in the university environment.¹⁴⁸ The instrument will be modified to include questions probing if students attended the Schmid College transfer student orientation, participated in the research opportunity, or attended monthly lunches. An additional open-ended question asking, "What else would you like to share about your transfer experience?" will also be included.

For transfer students who participate in research during their first semester at Chapman, student perceptions of their growth and achievements from their research experience will be tracked using the Survey of Undergraduate Research Experiences (SURE) assessment instrument.¹⁴⁹ Surveys will be conducted before, during, and six months after students complete the one-semester research experience.

3.3 Mentoring High School Student Researchers

The PI will also mentor public high school students from neighboring Orange High School to participate in the proposed project. Orange High School, Chapman University, and the Simon Foundation have created the Simon-Orange-Chapman STEM Scholars (SOCSS) Program, which brings high school students to Chapman to conduct a short (~10 hours) research project during their Junior and Senior years of high school. Students who complete the two-year program are awarded a full-ride scholarship to Chapman University. Of the ten SOCSS student that matriculate at Chapman University each year, 60% are Hispanic or Latinx and all are Pell Grant recipients.

The PI is currently involved in the SOCSS program as a research mentor to high school students and will continue to host 2-4 high school students each academic year (see letter from program organizer Dr. Elaine Schwartz). To build upon these efforts and facilitate the transition from high school to Chapman, the PI will recruit two SOCSS participants each year to perform full-time research during the summer before they matriculate at Chapman. This pre-matriculation research exposure is designed to provide a pathway for students to quickly become a part of the Chapman academic and scientific community. Summer researchers will participate in a series of professional development and faculty seminars organized by Dr. Julye Bidmead, the Director of the Center for Undergraduate Excellence (see letter). I hope to continue to mentor these summer students throughout their time at Chapman. By working with the same students from their junior year of high school through college, I strive to cultivate a pipeline of researchers that can serve as near-peer mentors for future high school participants in the SOCSS program.

Students who participate in the SOCSS program research with the PI will initially investigate alkyl-phosphonium compounds for hydrogen-bond catalysis (Aim 3.2B). As students gain research experience and confidence in the lab, I will give them more autonomy to choose their research direction and will transition them to working on air-sensitive projects involving carbodiphosphoranes or phosphorus ylides. To gauge student experiences, high school and pre-matriculation researchers will complete the SURE assessment instrument before, during, and six months after their research experience.¹⁴⁹

Proposed Timeline

	Project	Year 1			Year 2		
		Fall	Spring	Summer	Fall	Spring	Summer
Aim 1	Carbodiphosphorane synthesis and parameterization						
	Ester hydroboration catalysis						
	Mechanistic studies						
Aim 2	Phosphorus ylide synthesis and basicity measurements						
	Polymerization catalysis						
	Mechanistic studies						
Aim 3	Transfer student orientation, research, and workshops						
	Host high school researchers						
	Host pre-matriculation researchers						

Products

Submission of a paper on novel carbodiphosphorane synthesis, steric and donor properties, and Brønsted basicities is expected at the end of year 1. Separate papers on ester hydroboration catalysis and ring-opening polymerization catalysis are expected in year 2. Undergraduate researchers will be co-authors on all publications.

The PI will give a yearly presentation at either a national ACS meeting or a Gordon Research Conference. Two undergraduates each year will also present their work as a poster at a national ACS conference. All undergraduates pursuing research in the PI's group will be encouraged to present their work at a regional conference such as the Southern California Conference for Undergraduate Research.

Broader Impacts

The proposed work aims to demonstrate the synthetic utility of carbodiphosphoranes as environmentally benign organocatalysts for ester derivatization reactions. Ester functional groups are ubiquitous in biorenewable feedstocks, and the successful completion of this project could result in more sustainable methods for organic and polymer synthesis. Undergraduate and high school students will be the main drivers of science on this project, providing opportunities to train and recruit new scientists. The research efforts are closely tied to efforts to broaden the participation of students from underrepresented minority groups in STEM through the creation of orientation and research opportunities for transfer students to Chapman University.

Impact Statement

Impact on Chapman University

Institutional Overview

Chapman University is a medium-sized, private, R2 institution located in Southern California. There is a strong emphasis on student-centered learning at Chapman, with a university mission statement of providing a personalized education. The Chemistry and Biochemistry Unit is located within the Schmid College of Science and Technology, a campus leader in research-active faculty as measured by peer-reviewed publications, external funding, and involvement of undergraduates in research. Schmid College is housed in the 140,000 square foot Keck Science and Technology Center, which opened in 2018.

The Chemistry and Biochemistry Unit serves exclusively undergraduate students. The combined number of Chemistry and Biochemistry graduates fluctuates between 20-30 per year, with the total number of declared Chemistry and Biochemistry majors being between 90-110 at a given 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. Students typically perform research for 3–9 hours per week during the academic year for credit and work 40 hours per week during the summer. Chapman University offers several forms of financial support for student research, including competitive \$1,000 student grants for research supplies and \$4,000 student summer research fellowships.

Increased Undergraduate Research Participation

Although Chapman University provides many forms of support, most research activities at Chapman are funded through external grants. A significant impact of the proposed work is an **increased ability to engage a large number of undergraduate students in hands-on research**. Additionally, the proposed work would support the institution's continued emphasis on scholarly research productivity among the faculty.

Since arriving at Chapman in 2018, I have developed an active and dynamic research group that has trained eleven undergraduate students, of which seven are women, three are members of the LGBTQ+ community, two are students of color, and one is a person with a disability. My group typically consists of 5 students at a time, with most students joining as sophomores and continuing their research involvement until graduation.

The requested funds would allow me to expand my group to accommodate 8 students. New students would be recruited as sophomores or juniors to obtain significant research experience and serve as peer mentors for future generations of undergraduates prior to graduation. Full-time summer research

opportunities would be provided to two students per year, and paid part-time (10 hr/week) research positions would be created for two students during the academic year.

My research group is the one at Chapman to offer training in synthetic chemistry or homogeneous catalysis. The proposed work is designed to appeal to a range of student research interests, including novel catalyst synthesis, organic chemistry, polymer synthesis, and analytical measurements. Thus, the funding of this proposal would facilitate further undergraduate research and educational opportunities in synthetic chemistry and contribute to developing the research culture within Schmid College.

Enhanced Infrastructure for Research

The new single-user glovebox requested will supplement the one glovebox currently in the Liberman-Martin Group. This additional equipment will facilitate the expansion of my group to include more undergraduate researchers. The glovebox will also be made available to students in the Inorganic Chemistry laboratory course, allowing for experiments involving air-sensitive complexes. It could also be useful to a physical chemistry research group working with plasmonic nanoparticles.

Institutional Benefits of Broadening Participation Efforts

Chapman University will also benefit from the proposed **efforts to broaden participation of scientists from groups underrepresented in STEM**. Creating a one-day Schmid College transfer student orientation program will strengthen existing campus-wide orientation events, which do not currently specifically target STEM transfer students. The research opportunities and events for STEM transfer students are designed to improve STEM retention, strengthen STEM identity, and build community among transfer students, a cohort containing a greater percentage of students of color than the general Chapman population. The data gained through surveys and tracking student outcomes can help to inform best practices for welcoming transfer students into the Chapman community.

Impact on the PI

I am enthusiastic about my role as a teacher-scholar, in which I am committed to both high-quality undergraduate education and maintaining an active research program that trains undergraduates. I was drawn to Chapman University because the Chemistry and Biochemistry Department at Chapman is solely undergraduate, which allows me to focus on undergraduate education and mentoring. I am currently in my fourth year as an assistant professor, and I will be submitting my tenure application in Summer 2025. In my teaching, I aim to use innovative pedagogical methods, such as a flipped classroom environment, to help students develop confidence as scientists and attain a deep understanding of organic chemistry. My research goals are to (1) foster a thriving undergraduate research group culture in which many students serve as co-authors on publications, (2) develop a national and international reputation as a main-group chemistry researcher, and (3) obtain sustained funding to support my research group. The funding of this proposal would help me advance my group's research on carbodiphosphorane catalysts, expand my research expertise, and strengthen my publication and funding records in pursuit of tenure.

Impact on Preparing Students for Scientific Careers or STEM Graduate Programs

The top priority of my research 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.

Recruitment of Students

I recruit students through short "recruitment presentations" to students enrolled in organic chemistry courses, by participation in a Student Research Expo held each semester, and from referrals by colleagues. In these recruitment efforts, I emphasize that previous research experience is not expected, which is intended to encourage less confident students to express interest in research. Students with interests in careers in science or science education are given preference in joining my group. Undergraduate researchers typically commit to joining my research group for at least one year and plan on completing a full year of organic chemistry coursework.

Student Training

I directly train all undergraduate researchers when they join my research group. As most projects in the group involve air-free techniques, students typically require 2-3 months of training before they can start working more independently. All students are provided copies of group standard operating procedures for basic laboratory safety, Schlenk line use, and cryogen handling, and use of pyrophoric reagents. I review

these documents with each student and supervise students individually until proficiency in each area is achieved. I oversee the use of pyrophoric reagents regardless of the student's experience level.

Laboratory protocols are organized on the group's Google Drive and are updated regularly. Use of an electronic laboratory notebook system (MBook) facilitates sharing of experimental procedures and spectra between lab members. To ensure progress and provide mentorship, I meet with students individually each week and regularly work alongside students while they are in the lab.

Laboratory Research Culture

To accommodate different time commitments by students, I offer different kinds of research experiences, with projects varying in scope and expected duration. Even for a short-term project, students participate in all aspects of research, from literature searches to data analysis. Just one semester of research exposure is valuable in improving scientific literacy by providing hands-on exposure to the scientific method and real-life complications of laboratory work that can only be acquired through research.

I structure projects so that each student takes intellectual ownership of a small piece of a given project. With guidance, students perform literature searches, plan and execute experiments, analyze results, and troubleshoot their projects. I hold structured weekly group meetings throughout the calendar year, at which students present their latest results and analyze literature articles. Students also present their research to the campus community at a Student Scholar Symposium held at the end of each semester.

Students in my group complete Individual Development Plans each semester, which are designed to help students set goals and track their progress toward them. By discussing these plans with each undergraduate researcher, I can better understand their short- and long-term objectives and support students in achieving these goals. To develop their academic portfolios and science communication skills, I encourage students to apply for relevant awards and present results at regional and national conferences.

Student Success

My research students have demonstrated success by several metrics. The three research students to graduate from my research group have all served as co-authors on peer-reviewed publications.^{33,150} Two of these graduates are pursuing Ph.D.s in Chemistry at Caltech and UC San Diego, and one received an NSF Graduate Research Fellowship. Two members of my group have received Chapman Outstanding Senior in Chemistry awards, four have received competitive Center for Undergraduate Excellence research grants, and three have received competitive Summer Undergraduate Research Fellowships.

Development of Future Research and Proposals Related to Proposed Work

Funding from the NSF LEAPS-MPS program would allow me to develop a broad research program on carbodiphosphorane organocatalysts while simultaneously providing research opportunities to undergraduate students. I hope to expand upon these efforts in future applications to the NSF CAREER award and NSF RUI funding mechanisms. Insights gained from our proposed studies of carbodiphosphorane properties, including donor strengths, steric profiles, and Brønsted basicities, will enable hypothesis-driven synthesis of novel carbodiphosphorane structures. Some future carbon(0) catalysts of interest include (i) anionic carbodiphosphoranes to support zwitterionic main-group compounds, (ii) chiral carbodiphosphoranes for use in asymmetric catalysis, and (iii) carbodisulfuranes, the sulfur analogues of carbodiphosphoranes. Furthermore, the knowledge gained from mechanistic studies of ester hydroboration and cyclic ester ring-opening polymerization will allow us to select further organocatalytic applications with a high likelihood of success.

Results from efforts to broaden the participation of students from underrepresented minority groups, including orientation and research opportunities for transfer students, will also guide future programs developed in an NSF CAREER award. Expansions of the current efforts could include the creation of a 1-credit course for STEM transfer students or involvement of transfer students in summer research before they matriculate at Chapman. For the CAREER award, I hope to expand the use of alkyl-phosphonium compounds as hydrogen-bond catalysts by incorporating this work as a course-based undergraduate research experience (CURE) to provide all students enrolled in organic chemistry courses with an authentic research experience.

Results from Prior Support

The PI has not received prior NSF funding.

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Budget Justification

A. Senior/Key Persons

Principal Investigator:

The principal investigator (PI), Dr. Liberman-Martin, requests 1 summer month of salary per year. During this time, the PI will train and mentor undergraduate students on projects described in the proposal as well as independently perform related experiments. The PI will coordinate research related to the project and ensure that undergraduate researchers receive proper safety training, accurately document results in electronic laboratory notebooks, and learn to become independent researchers. The PI has extensive experience in main group chemistry, organometallic chemistry, polymer chemistry, and catalysis. In addition, the PI will evaluate research progress to ensure successful project completion, submit annual and progress reports, attend conferences, and prepare manuscripts for publication. Salary requested includes a 3% annual increase.

B. Other Personnel

A significant impact of the proposed work will be student training. Funds are requested to support undergraduate researchers to work during the 2-year grant period. The student salaries requested include annual increases as mandated by Chapman University. The requested funds will cover:

- A. Two undergraduate students working on research activities for 8 weeks each summer of the two-year grant period. Student salary is based on a pay of \$16/hr for Summer 2023 and \$17/hr for Summer 2024 for students working 40 hr/week.
- B. Two undergraduate students working for 10 hr/week during each 15-week semester of the grant period (Fall 2022, Spring 2023, Fall 2023, and Spring 2024). Student salary is based on a pay of \$15/hr in 2022, \$16/hr in 2023, and \$17/hr in 2024.

Fringe Benefits

Fringe benefits are calculated at the University's rate of 11% for summer appointments for faculty. Academic year undergraduate student benefits are calculated at 5%.

C. Equipment

Glovebox:

Funds to purchase one single station glovebox (with gas purification, oxygen and water sensors, freezer, and cold well) are requested (\$33,000). The additional glovebox will help the PI to expand the size of her research group to enable greater undergraduate and high school student participation in research.

D. Travel

\$3,500 per year is requested for the PI (\$1,600) and two students (\$950 per student) to attend a national conference each year. Funds for the PI will cover conference registration (\$500), airfare (\$500), hotel (\$500), and meals (\$100). Travel funds for students will cover conference registration (\$100), airfare (\$500), hotel (\$250), and meals (\$100). Conference travel will allow students to learn about a wide range of chemistry research topics and job opportunities and will increase the visibility of the proposed research within the chemistry community.

\$1,000 is requested in year 1 of the grant to support the PI's travel to the Washington, DC area for the 1.5-day meeting of grant awardees.

E. Participant support costs

For transfer students to the Schmid College of Science and Technology at Chapman University:

Funds are requested to create a one-day orientation program for STEM transfer students to Chapman University (approximately 15 students per year). These funds will cover lodging (\$50) and food (\$100) for each participant.

Funds are also requested to support incoming STEM transfer students (10 students per academic year) in performing research during their first semester at Chapman. Each transfer student participant will receive \$1,000 toward materials and supplies to complete their research project. The goal of this program is to support the transition of transfer students into the Chapman community.

Funds (\$2,250 per academic year) for a monthly cohort-building lunch series for transfer students are also requested.

For pre-matriculation summer researchers:

Funds are requested to enable two Simon-Orange-Chapman STEM Scholars annually to join the Liberman-Martin Group and perform research activities for 8 weeks each summer of the grant period. Students will receive hands-on research experience and gain familiarity with Chapman faculty and other students before they matriculate at Chapman. The funds requested (\$6,600 per student) will be used toward a stipend (\$4,000), housing (\$1,500), meals (\$500), and participation in the summer professional development and faculty seminar series hosted by the Chapman Center for Undergraduate Excellence (\$600).

F. Other Direct Costs**Materials and Supplies**

Funds (\$17,500/year) for materials and supplies are requested. These will enable the purchase of chemicals and reagents (\$10,000/year), consumables (\$5,000/year), and analytical services (\$2,500/year) related to the proposed research.

G. Modified indirect costs

Indirect costs at Chapman University are calculated at the federally negotiated rate of 36.8% of modified total direct costs.

Facilities, Equipment, and Other Resources

Overview of Research Environment at Chapman University

The PI, Dr. Liberman-Martin, is a part of the Chemistry faculty unit within the Schmid College of Science and Technology at Chapman University. The PI's research laboratory and office are housed in the 140,000 square foot Keck Science and Technology Center, which opened in 2018.

Chapman University is a mid-sized, private, primarily undergraduate institution in Southern California. The university has a goal to provide a personalized education to all students, and research is considered a core component of the undergraduate science curriculum. Chapman has made major investments in its research infrastructure, including creation of a Vice President of Research position to oversee the expanding research capabilities. Chapman's Office of Research supports faculty in seeing external funding and provides opportunities for internal funding. The Center for Undergraduate Excellence offers student grants (up to \$1,000 per semester) to conduct research, hosts a Summer Undergraduate Research Fellowship (SURF) program to support full-time summer research by students, and a Student Scholar Symposium every semester to provide a venue for students to give poster or oral presentations of their research.

Faculty research in Schmid College is further supported by a 2/2 teaching load for tenure-track and tenured faculty, which allows faculty to dedicate a significant amount of time to research during the academic year. Schmid College also provides a vibrant intellectual science environment by regularly inviting speakers to present at the Science Forum seminar series, hosting visiting scientists, providing a peer mentoring program for early career faculty, and offering internal funds to support faculty and student conference travel.

Liberman-Martin Group Facilities and Equipment

The Liberman-Martin laboratory is equipped with all equipment needed to conduct the synthetic and catalytic experiments proposed. The 450 sq. ft. research space is equipped with three four-foot-wide fumehoods, each of which contains a Schlenk line and vacuum pump. The laboratory also contains a dual station MBraun glovebox equipped with a freezer, cold well, solvent removal system, balance, and stir plates. A solvent purification system dispenses six anhydrous and degassed solvents. All standard glassware and equipment needed for organic and inorganic synthesis (including an oven, refrigerator, balances, and two rotary evaporators) are available in the laboratory space along with safety equipment. The laboratory also has a computer workstation.

Shared Equipment

The PI and her research students have access to shared instrumentation through the Keck Science and Technology Center at Chapman. Relevant instruments that are available free of charge include a 400 MHz Bruker NMR spectrometer, a TOSOH EcoSEC gel permeation chromatography system with a refractive index detector and Wyatt DAWN multi-angle light scattering detector, UV-vis spectrophotometers, IR spectrometers, and GC-MS instrumentation.

Other Resources to Support Research Activities

Chapman University has subscriptions to SciFinder Scholar and a vast array of chemistry journals, including publications from the American Chemical Society, Royal Society of Chemistry, and Chemistry Europe. Materials not available through the library collection can be obtained through an interlibrary loan program. Relevant software available to Chapman faculty and students includes ChemDraw and MestReNova.

Instrument support staff maintain analytical instruments, and a Laboratory Operations and Safety Director oversees safety trainings within Schmid College. Administrative support is provided through Schmid College for ordering laboratory and office supplies. Computer support is provided through the Information Systems and Technologies office.

Equipment

Liberman-Martin Group Equipment

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Data Management Plan

Data Types and Formats

Characterization data in both their raw and processed forms will be preserved and stored in multiple locations. Spectroscopic (NMR, IR, UV-Vis) and chromatographic (GPC) data will be collected at Chapman University. Most processed data will be preserved as Excel and .csv files, while NMR data will be stored as .mnova files compatible with the MestReNova software package. X-ray diffraction, high-resolution mass spectrometry, and elemental analysis data will be collected off-site. The Liberman-Martin Group uses an electronic laboratory notebook system (MBook), facilitating data sharing between group members and allowing spectroscopic data to be stored alongside notebook entries.

Data Storage and Preservation

Electronic data will be saved on the computers used for data acquisition. The raw data will also be duplicated to a group computer in the Liberman-Martin laboratory, a password-protected Google Drive provided by Chapman University, and the PI's work desktop computer. Processed data will be stored in these locations as well. The contents of electronic laboratory notebooks are stored to the MBook cloud server, and data is backed up monthly as XML files stored to the group Google Drive and group computer. All instrument computers, the Liberman-Martin group computer, and the PI's desktop computer are backed up external hard drives monthly.

Data Sharing and Public Access

Data will be shared in promptly published peer-reviewed manuscripts. Published experimental data will be available through supplementary information for publications. This data would typically include spectra and spectral data, kinetics plots, and cif files for X-ray crystal structures. Furthermore, X-ray crystallographic data will be deposited in the Cambridge Structural Database at the time of publication. Pre-prints of all manuscripts generated from this project will be uploaded to *ChemRxiv* to make the work searchable and accessible to the public. Unpublished results and data will be shared at conferences that require non-disclosure of presented work by attendees.

Policies for Re-Use and Re-Distribution

The terms and conditions for the distribution of published work will be determined by copyright agreements between the PI and publishers.

Sample Preservation

Chemical samples will be preserved at low temperatures for as long as is feasible based on the stability of the compound and space restrictions. When necessary, these samples will be stored in an air- and moisture-free environment. A rigorous labeling system will ensure that preserved samples are matched to student notebook entries and digitized experimental data.

Roles and Responsibilities

All members of the Liberman-Martin Group will be responsible for ensuring data is saved, backed up, and experimental methods are documented. The PI will routinely check electronic laboratory notebooks to ensure thorough record keeping, such as the inclusion of dates, times, and temperatures for experiments, observations, and procedures. During weekly one-on-one meetings and group meetings, the PI will review data with undergraduate researchers and help them to develop the skills to design reproducible experiments.