

TRANSITION METAL CATALYZED APPROACHES TO
THE ASYMMETRIC CONSTRUCTION OF ALL-CARBON
QUATERNARY CENTERS

Thesis by

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In Partial Fulfillment of the Requirements for

the Degree of

Doctor of Philosophy

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California

2026

(Defended June 11th, 2025)

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To my dear mother

ACKNOWLEDGEMENTS

As my time at Caltech comes to an end, I have so many people to thank for enabling my completion of the PhD. First, I would like to express my utmost appreciation to my advisor, Professor Brian Stoltz, who has made me feel welcome at Caltech ever since my visit as a prospective graduate student. I am grateful that you took a chance on me as a member of your lab and appreciate the guidance you have given me over the years. I have learned so much from you and have appreciated our interactions in both professional and casual settings. Indeed, you and your family made me feel like a part of something during my time at Caltech. I look forward to continuing to work with you as you consult with Cytokinetics, and hopefully I will have the privilege of hosting you and the Stoltz's as you visit the better half of California.

In a similar vein, I am extremely indebted to former graduate students and postdocs in the group for making the lab a great place to work for a young researcher with imposter syndrome. While COVID could have completely killed the lab social scene, we found a way to hang out both during and after the strict campus policies, and my first two years at Caltech will be a highlight of my life which I will always look upon fondly. I also had the privilege of being one of a seven student cohort to join the Stoltz group in 2020. It has been an honor growing as a person and as a chemist alongside the rest of you, and we will forever be bonded by our shared experiences during unusual times to do graduate research. I wish you the best in your careers, be they academic or industrial in nature, and I am sure that our paths will overlap in the small world of organic chemistry and Pharma.

I would further like to express my appreciation for the many other faculty and staff at Caltech that made it possible for me to reach this point. Of course, Dr. Scott Virgil has been

indispensable to research in the Stoltz group, maintaining the Catalysis Center and liberally providing his know-how as both a chemist and engineer to the students, even when he is swamped with work. I am so pleased to have met you and Silva and to have been welcomed into your lovely home for your annual holiday celebrations. I am thankful for Leslie for being a positive presence on the floor and working so hard to keep the workplace a clean and safe environment. As a first and second year, I was fortunate enough to take courses with Caltech professors such as Prof. Greg Fu and Prof. Theo Agapie, and I am sure that I will reflect on what I learned in those courses throughout my career.

The journey to reach Caltech was certainly not a linear one, and I have a lot of people to acknowledge for their roles in setting me on this path. My profound gratitude goes out to the teachers who I interacted with throughout my early academic career, as they taught me so much about life and their respective disciplines that I continue to use today. Indeed, it was at an early stage where my passion for science arose, and I would like to thank Ms. Cahatal and Mrs. Nakamatsu for their chemistry courses in high school that refined my interests and gave me the tools I would need to succeed at the next level. I am thankful for Prof. Chueh at Stanford, who generously allowed me to conduct research in his laboratory as a high schooler and for my managers at Applied Materials for giving me insight into the semiconductor industry over the course of three summer internships.

While it was not my dream school coming out of high school, UCSB did turn out to be the school of my dreams. The decision to attend UCSB turned out to be one of the best decisions of my life, followed closely by the leap of faith away from materials science and into organic chemistry. To that end, I am forever grateful to Profs. Aue and Lipshutz for turning a subject I thought I would dread into a calling through their engaging organic

chemistry lectures. I am so fortunate that Prof. Lipshutz took me into his lab and paired me with Nick Lee, who was an excellent mentor for a young chemist and taught me many of the techniques I still use to this day. Prof. Lipshutz has been supportive of my efforts both in and out of the lab, and his tutelage is undoubtedly the main factor leading me to my current position. I am grateful that he has continued to be a reliable point of contact and support system even after my time at UCSB, and I look forward to our paths continuing to cross in the future.

Last, but certainly not least, I have to thank my family for being my support system and for nurturing me throughout my life. During my post-secondary education, our family lost two beloved members in my grandmother, Irandokht, and aunt, Shabnam (or “Shaby Joon”). Though they are not with us to celebrate the completion of my studies, I know they would be so proud and effusive with praise. Their life lessons and love are reflected in everything I accomplish, and I am lucky to have been raised by a group of such incredible women. It is a true shame that only in loss can one fully appreciate a person. I miss you both and hope that we will be reunited one day as a whole, happy family. Shahab, you have been the most caring brother ever since I was born, and I have been so fortunate to have an intelligent and gentle-spirited older brother as a role model. Dad, all the hard work you have done to provide for our family do not go unnoticed. Your work ethic and commitment to the people you love has inspired me and will continue to serve as a model for my future.

Mom...I was questioning whether or not to even write anything here, as no words would do justice to the amount that I love and appreciate you or to what you have meant to my growth. You are the single purest and most loving person I have ever met, and you have loved me as much as anyone can hoped to be loved as a son. You are part of my conscience,

and our hearts are inextricably intertwined. I am so happy that I will be coming home soon and that I will be able to see you on a regular basis again. It has been a long time, but we finally made it.

ABSTRACT

In the Stoltz group, chemical research leverages the interplay between methods development and total synthesis, wherein new synthetic technologies enable the pursuit of novel target compounds and challenges encountered during synthetic campaigns inspire the invention of methodologies. Given the stereochemical complexity of natural products and emerging pharmaceuticals, methods development in our group has focused in particular on the asymmetric construction of all-carbon quaternary centers. Herein is described the development of transition metal catalyzed approaches to the formation of such centers with high levels of stereocontrol. Chapter 1 describes the discovery of an Ir-catalyzed asymmetric allylic alkylation reaction efficiently merging linear, trisubstituted allylic electrophiles with prototypical malonate nucleophiles to generate enantioenriched β -quaternary carbonyl products. The reaction proceeds with low catalyst loadings of iridium and at ambient temperature, marking the first reaction of its kind to be performed under such mild conditions. Appendix 2 highlights recent efforts to develop an Ir-catalyzed process for the doubly stereoselective formation of vicinal quaternary stereocenters. Chapter 2 discloses a more sustainable, Mo-catalyzed alternative to the Ir-catalyzed process in Chapter 1, unveiling thus far unknown reactivity with molybdenum and generating the desired products with outstanding enantioselectivity. This advance was enabled by exhaustive investigation of suitable ligand scaffolds, ultimately leading to the creation of the novel, C1-symmetric ShabyDACH ligand. Chapter 3 discusses the elaboration of a Pd-catalyzed α -vinylation of lactam nucleophiles to forge α -quaternary carbonyls. These products could further be diversified to a range of elusive scaffolds, highlighting their synthetic utility.

PUBLISHED CONTENT AND CONTRIBUTIONS

1. **Moghadam, F. A.**[‡]; Hicks, E. F.[‡]; Sercel, Z. P.; Cusumano, A. Q.; Bartberger, M. D.; Stoltz, B. M. Ir-Catalyzed Asymmetric Allylic Alkylation of Dialkyl Malonates Enabling the Construction of Enantioenriched All-Carbon Quaternary Centers. *J. Am. Chem. Soc.* **2022**, *144*, 7983–7987. DOI:10.1021/jacs.2c02960.
 - F. A. M participated in reaction optimization, experimental work, data analysis, and manuscript preparation.
2. Reimann, C. E.; Kim, K. E.; Rand, A. W.; **Moghadam, F. A.**; Stoltz, B. M. *Tetrahedron* **2023**, *130*, 133176. DOI: 10.1016/j.tet.2022.133176.
 - F. A. M participated in collecting references and manuscript preparation.
3. **Moghadam, F. A.**[‡]; Barbor, J. P.[‡]; Chan, M.[‡]; Jette, C.; Sakurai, S.; Stoltz, B. M. Formation of All-Carbon Quaternary Centers via Enantioselective Pd-catalyzed α -Vinylation of γ -Lactams. *Org. Lett.* **2024**, *26*, 7551–7554. DOI: 10.1021.acs.orglett.4c02551.
 - F. A. M participated in reaction optimization, experimental work, data analysis, and manuscript preparation.
4. **Moghadam, F. A.**[‡]; Cerione, C. S.[‡]; Stoltz, B. M. Mo-Catalyzed Asymmetric Allylic Alkylation Enabling the Construction of Highly Enantioenriched 1,4-Dicarbonyl Scaffolds. *ChemRxiv* **2025**. DOI: 10.26434/chemrxiv-2025-41644.
 - F. A. M participated in reaction optimization, experimental work, data analysis, and manuscript preparation.

5. Xuyu, Y.; Lee, J.; **Moghadam, F. A.**; Steiner, J.; Soo-Kyung, S.; de Almenara, A. J.; Stoltz, B. M. Predicted new molecules followed by experimental validation for protecting human neurons from oxidative stress induced cytotoxicity. *PNAS* **2025**, submitted.
 - F. A. M participated in reaction optimization, experimental work, data analysis, and manuscript preparation.

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APPENDIX 2

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CHAPTER 3

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LIST OF ABBREVIATIONS

$[\alpha]_D$	specific rotation at wavelength of sodium D line
°C	degrees Celsius
Å	Angstrom
λ	wavelength
μ	micro
Aq	aqueous
Ar	aryl
atm	atmosphere
Bn	benzyl
Boc	<i>tert</i> -butyloxycarbonyl
bp	boiling point
br	broad
Bz	benzoyl
<i>c</i>	concentration for specific rotation measurements
calc'd	calculated
cm^{-1}	wavenumber(s)
d	doublet
D	deuterium
dba	dibenzylideneacetone
DIBAL	diisobutylaluminum hydride
DMAP	4-dimethylaminopyridine

DMF	<i>N,N</i> -dimethylformamide
dr	diastereomeric ratio
e.g.	for example (Latin exempli gratia)
<i>ee</i>	enantiomeric excess
EI+	electron impact
equiv	equivalent(s)
ESI	electrospray ionization
Et	ethyl
EtOAc	ethyl acetate
G	grams
GC	gas chromatography
h	hours
HPLC	high-performance liquid chromatography
HRMS	high-resolution mass spectrometry
Hz	hertz
i.e.	that is (Latin id est)
IPA	isopropanol
<i>i</i> -Pr	<i>iso</i> -propyl
IR	infrared (spectroscopy)
<i>J</i>	coupling constant (NMR), exchange coupling constant (diradicals)
K	Kelvin (absolute temperature)

kcal	kilocalorie
KHMDS	potassium hexamethyldisilazide
L	liter; ligand
LDA	lithium diisopropylamide
LHMDS	lithium hexamethyldisilazide
M	multiplet, milli
<i>m/z</i>	mass to charge ratio
<i>m</i> -CPBA	<i>meta</i> -chloroperoxybenzoic acid
Me	methyl
MeCN	acetonitrile
MeOH	methanol
mg	milligram(s)
MHz	megahertz
min	minutes
mol	mole(s)
<i>n</i> -Bu	<i>n</i> -butyl
NMR	nuclear magnetic resonance
Pd/C	palladium on carbon
Ph	phenyl
PHOX	phosphinooxazoline (ligand)
PHOX=O	phosphinooxazoline oxide (ligand)
ppm	parts per million
PTSA	<i>para</i> -toluenesulfonic acid

q	quartet
R	generic for any atom or functional groups
S	singlet
SCF	self-consistent field
SFC	supercritical fluid chromatography
t	triplet
TBS	<i>tert</i> -butyldimethylsilyl
<i>t</i> -Bu	<i>tert</i> -butyl
TES	triethylsilyl
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin-layer chromatography
<i>t</i> _R	retention time
UV	ultraviolet
X	anionic ligand or electronegative element