

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

Thesis by

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*To my dear mother*

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## 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  $\beta$ -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  $\alpha$ -vinylation of lactam nucleophiles to forge  $\alpha$ -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.**<sup>‡</sup>; Hicks, E. F.<sup>‡</sup>; 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.
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3. **Moghadam, F. A.**<sup>‡</sup>; Barbor, J. P.<sup>‡</sup>; Chan, M.<sup>‡</sup>; Jette, C.; Sakurai, S.; Stoltz, B. M. Formation of All-Carbon Quaternary Centers via Enantioselective Pd-catalyzed  $\alpha$ -Vinylolation of  $\gamma$ -Lactams. *Org. Lett.* **2024**, *26*, 7551–7554. DOI: 10.1021.acs.orglett.4c02551.
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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.
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## LIST OF ABBREVIATIONS

$[\alpha]_D$	specific rotation at wavelength of sodium D line
$^{\circ}\text{C}$	degrees Celsius
$\text{\AA}$	Angstrom
$\lambda$	wavelength
$\mu$	micro
Aq	aqueous
Ar	aryl
atm	atmosphere
Bn	benzyl
Boc	<i>tert</i> -butoxycarbonyl
bp	boiling point
br	broad
Bz	benzoyl
<i>c</i>	concentration for specific rotation measurements
calc'd	calculated
$\text{cm}^{-1}$	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 <i>exempli gratia</i> )
<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 <i>id est</i> )
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
$m/z$	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
$t_R$	retention time
UV	ultraviolet
X	anionic ligand or electronegative element