

THE DESIGN AND DEVELOPMENT OF PALLADIUM-CATALYZED
AEROBIC OXIDATIVE TRANSFORMATIONS

Thesis by

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To my parents

ACKNOWLEDGMENTS

I should have written this days ago. “No,” I kept telling myself. “Save it for the end. You should end on the acknowledgments.” And now here I am, late to turn this thing in, rushing. But it’s important to get this right. This is the part that everyone reads. Sure, there’s the person who wants to look up this specific reference or that similar procedure, but come on, it’s this, followed by the remark, “It seems kinda long.”

I have to first thank Professor Brian Stoltz for his support, guidance, and enthusiasm. For an assistant professor to take on so many responsibilities and put forth such a tremendous effort in everything he does is truly remarkable. I appreciate the personal interactions I have had with him over the years, both as a mentor and as a friend. I’ve been thankful for his continuous interest in science, and for allowing me to forge my own research path with a pretty long leash. I’ve learned so much from him and his advice, and he has really provided me with an excellent model of what an advisor should be. I also want to thank his wife Erna for her supportive discussions during my time here.

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I've had three baymates while in the group. Sarah Spessard was the first back in the days of 264 Crellin. I enjoyed playing tennis a bunch with Sarah Spessard in the early days. Though she kicked my butt most of the time, it helped to release some of the built up tension from the day-to-day lab stuff. In 204 Church, I then had the luxury (yes, that's the right word) of working next to Richmond Sarpong. I could have done with less Steely Dan or Hall & Oates, but he was an excellent coworker. His enthusiasm about chemistry was contagious, and I thoroughly enjoyed the scientific discussions we had in the years he was here. I hope he does great as a professor at Berkeley; I can't think of anyone more deserving of success. Mike Krout has been my baymate for almost a year. Although we haven't had too much time to work next to each other, it's been a pleasure working near him. I'm also grateful to him for putting up with way more Sonic Youth than he should have felt obligated to.

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Hmm. Even my acknowledgments section is too long.

ABSTRACT

Oxidation is a fundamental process in chemistry and biology. In synthetic chemistry, several developments have been made in catalytic asymmetric oxidative transformations that involve a heteroatom transfer from a reagent to a substrate (e.g., epoxidations, dihydroxylations). Enantioselective oxidations that do not involve a heteroatom transfer have been relatively less explored. These types of oxidative transformations were investigated using a general palladium(II) catalyst system.

A palladium-catalyzed oxidative kinetic resolution of secondary alcohols was developed. This catalytic system utilizes (–)-sparteine as the chiral ligand and molecular oxygen as the sole stoichiometric oxidant. Benzylic and allylic alcohols can be resolved to high enantiomeric excesses in excellent yields. The same selective process has been applied to the desymmetrization of meso diols.

This general palladium(II) oxidative system was applied to intramolecular Wacker oxidations to form a variety of heterocycles. Lactones, lactams, tetrahydrofurans, dihydrobenzofurans, and dihydrobenzopyrans were all accessed by this methodology. Importantly, this work provided entry into the development of asymmetric variants. Highly enantioselective cyclizations of phenolic substrates were realized with a palladium-sparteine catalyst, analogous to the kinetic resolution chemistry. The heterocyclization chemistry was employed in the context of the total synthesis of the *Cephalotxaxus* alkaloids.

Oxidative annulations for the synthesis of carbocycles were developed utilizing this general palladium system. Indoles with pendant olefin tethers were oxidatively

cyclized under palladium(II) catalysis to form annulated indoles. Electron-rich aromatic systems were also investigated, culminating in the syntheses of benzofurans and dihydrobenzofurans. These reactions were demonstrated to proceed by an initial C-H bond functionalization event, followed by olefin insertion and β -hydride elimination.

Enantioselective heterocyclizations using the general oxidative system were further explored. Promising results were realized in the heterocyclizations of sulfonamide-based compounds. Key experiments allowed for a firmer understanding of how the reaction was progressing and, specifically, how enantioselectivity was being induced by the palladium catalyst.

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LIST OF ABBREVIATIONS

[α]_D	specific rotation at wavelength of sodium D line
Ac	acetyl
AIBN	2,2'-azobisisobutyronitrile
<i>t</i> -Am	<i>tert</i> -amyl
app.	apparent
aq.	aqueous
Ar	aryl
atm	atmosphere
BBN	borabicyclo[3.3.1]nonane
Bn	benzyl
Boc	<i>tert</i> -butyloxycarbonyl
BOM	benzyloxymethyl
bp	boiling point
br	broad, broadened
Bu	butyl
<i>i</i> -Bu	isobutyl
<i>n</i> -Bu	<i>n</i> -butyl
<i>t</i> -Bu	<i>tert</i> -butyl
Bz	benzoyl
<i>c</i>	concentration for specific rotation measurements
° C	degrees Celsius
calc'd	calculated
cat.	catalytic
comp	complex
conv	conversion
Cy	cyclohexyl
d	doublet
dba	dibenzylideneacetone

DCC	dicyclohexylcarbodiimide
DCE	1,2-dichloroethane
DIAD	diisopropyl azodicarboxylate
DIBAL	diisobutylaluminum hydride
DMAP	4-dimethylaminopyridine
DMF	<i>N,N</i> -dimethylformamide
DMFDA	<i>N,N</i> -dimethylformamide dimethyl acetal
DMSO	dimethylsulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene
dr	diastereomeric ration
ee	enantiomeric excess
EI	electrospray ionization
equiv	equivalents
er	enantiomeric ratio
Et	ethyl
FAB	fast atom bombardment
g	grams
GC	gas chromatography
[H]	reduction
h	hours
HMDS	hexamethyldisilazane or hexamethyldisilazide
hν	light
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectroscopy
Hz	hertz
imid.	imidazole
IR	infrared
<i>J</i>	coupling constant
kcal	kilocalories
L	liter

LAH	lithium aluminum hydride
LDA	lithium dicyclohexylamide
M	metal or molar
m	milli or multiplet or meters
<i>m/z</i>	mass to charge ratio
μ	micro
Me	methyl
Mes	mesityl
MHz	megahertz
min	minutes
mol	moles
mp	melting point
MS	molecular sieves
Ms	methanesulfonyl
N	normal
ν	frequency
nbd	norbornadiene
NBS	<i>N</i> -bromosuccinimide
NMO	<i>N</i> -methylmorpholine <i>N</i> -oxide
NMR	nuclear magnetic resonance
NOE	Nuclear Overhauser Effect
[O]	oxidation
<i>o</i>	ortho
OKR	oxidative kinetic resolution
<i>p</i>	para
PCC	pyridinium chlorochromate
<i>n</i> -Pent	<i>n</i> -pentyl
Ph	phenyl
pH	hydrogen ion concentration in aqueous solution
PhH	benzene
Piv	pivaloyl (trimethylacetyl)

pK_a	acidity constant
PPA	polyphosphoric acid
ppm	parts per million
PPTs	pyridinium <i>p</i> -toluenesulfonate
<i>i</i> -Pr	isopropyl
py	pyridine
pyr	pyridine
q	quartet
ref	reference
R_F	retention factor
s	singlet or selectivity factor
sat.	saturated
SEM	(trimethylsilyl)ethoxymethyl
stoich.	stoichiometric
Sub	substrate
t	triplet
TBAF	tetrabutylammonium fluoride
TBHP	<i>tert</i> -butyl hydroperoxide
TBS	<i>tert</i> -butyldimethylsilyl
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy, free radical
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid or trifluoroacetate
TFAA	trifluoroacetic anhydride
THF	tetrahydrofuran
THP	tetrahydropyran
TLC	thin-layer chromatography
TMG	1,1,3,3-tetramethylguanidine
TMS	trimethylsilyl
TOF	turnover frequency
TON	turnover number
TPAP	tetrapropylammonium perruthenate

Ts	<i>p</i> -toluenesulfonyl or tosyl
TsOH	<i>p</i> -toluenesulfonic acid or tosic acid
UV	ultraviolet
v/v	volume to volume
w/v	weight to volume