

DEVELOPMENT OF OXIDATION AND TRANSITION METAL-MEDIATED  
REACTIONS AND APPLICATION TO NATURAL PRODUCT SYNTHESIS

Thesis by

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The logo for the California Institute of Technology (Caltech), featuring the word "Caltech" in a bold, orange, sans-serif font.

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*To Him who made all things*

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## ABSTRACT

Expedient access to complex molecules via chemical synthesis is important for assessing their biological activity and medicinal properties. In one approach, convergent joining of fragments of similar size and complexity is followed by minimal scaffold tailoring steps to rapidly access natural products. This strategy hinges on the ability to (1) tailor peripheral oxidation, ideally via creative redox transformations, and (2) forge strategic bonds within a complex scaffold through C–C bond formation. We disclose efforts to address these aims by developing broadly useful chemical tools and applying them to the preparation of bioactive natural products.

Toward the first aim, we investigated unusual oxidative reactivity mediated by selenium dioxide. To address the second aim, we developed nickel-catalyzed reductive cross-coupling reactions to study: catalyst-controlled enantioselectivity in the preparation of medicinally relevant small molecules, substrate-controlled stereoselectivity, and selectivity for ring formation. The latter studies enabled the exploration of transition metal-mediated cyclization as a convergent annulation strategy toward the rearranged isoryanodane diterpene (+)-cassiabudanol A, as well as the formal synthesis of the macrocyclic cytotoxin (–)-cylindrocyclophane F.

## PUBLISHED CONTENT AND CONTRIBUTIONS

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S.E.D. contributed to the reaction development, conducted experiments, and participated in preparation of the supporting data and writing of the manuscript.

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## LIST OF ABBREVIATIONS

$[\alpha]_D$	angle of optical rotation of plane-polarized light
Å	angstrom(s)
Ac	acetyl
acac	acetylacetonate
aq.	aqueous
atm	atmosphere(s)
bpy	2,2'-bipyridine
Bn	benzyl
BOM	benzyloxymethyl
bp	boiling point
br	broad
Bu	butyl
<sup>i</sup> Bu	<i>iso</i> -butyl
<sup>n</sup> Bu	<i>norm</i> -butyl
<sup>t</sup> Bu	<i>tert</i> -butyl
c	concentration of sample for measurement of optical rotation
<sup>13</sup> C	carbon-13 isotope
°C	degrees Celcius
calcd	calculated
CAN	ceric ammonium nitrate
Cbz	benzyloxycarbonyl

<i>cf.</i>	consult or compare to (Latin: <i>confer</i> )
<i>cis</i>	on the same side
cm <sup>-1</sup>	wavenumber(s)
CM	cross-metathesis
CO	carbon monoxide
COD	1,5-cyclooctadiene
conv.	conversion
COSY	homonuclear correlation spectroscopy
CSA	camphor sulfonic acid
Δ	heat or difference
δ	chemical shift in ppm
d	doublet
<i>d</i>	deutero or dextrorotatory
D	deuterium
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	<i>N,N'</i> -dicyclohexylcarbodiimide
DCE	1,2-dichloroethane
DCM	dichloromethane
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
<i>de novo</i>	starting from the beginning; anew
DIBAL	diisobutylaluminum hydride
diglyme	bis(2-methoxyethyl) ether

DMA	<i>N,N</i> -dimethylacetamide
DMAP	4-(dimethylamino)pyridine
DME	1,2-dimethoxyethane
DMF	<i>N,N</i> -dimethylformamide
DMPU	1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone
DMSO	dimethylsulfoxide
dppf	1,1'-bis(diphenylphosphino)ferrocene
dr	diastereomeric ratio
dtbbpy	4,4'-di-tert-butyl-2,2'-dipyridyl
ee	enantiomeric excess
<i>E</i>	<i>trans</i> (entgegen) olefin geometry
EDC	<i>N</i> -(3-dimethylaminopropyl)- <i>N'</i> -ethylcarbodiimide hydrochloride
e.g.	for example (Latin: <i>exempli gratia</i> )
EI	electron impact
<i>ent</i>	enantiomer of
<i>epi</i>	epimeric
equiv	equivalent(s)
ESI	electrospray ionization
Et	ethyl
<i>et al.</i>	and others (Latin: <i>et alii</i> )
FAB	fast atom bombardment
FD	field desorption
FI	field ionization

FTIR	fourier transform infrared spectroscopy
g	gram(s)
glyme	dimethoxyethane
h	hour(s)
$^1\text{H}$	proton
[H]	reduction
HFIP	hexafluoroisopropanol
HMBC	heteronuclear multiple-bond correlation spectroscopy
HMDS	hexamethyldisilazide
HMPA	hexamethylphosphoramide
$h\nu$	irradiation with light
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectrometry
HSQC	heteronuclear single quantum coherence spectroscopy
Hz	hertz
i.e.	that is (Latin: <i>id est</i> )
<i>in situ</i>	in the reaction mixture
<i>iso</i>	isomeric
$J$	coupling constant in Hz
$k$	rate constant
kcal	kilocalorie(s)
L	liter
$l$	levorotatory

LCMS	liquid chromatography–mass spectrometry
LDA	lithium diisopropylamide
m	multiplet or meter(s)
M	molar or molecular ion
<i>m</i>	<i>meta</i>
μ	micro
Me	methyl
MeOH	methanol
MeCN	acetonitrile
mg	milligram(s)
MHz	megahertz
min	minute(s)
mL	milliliter(s)
mol	mole(s)
MOM	methoxymethyl
Ms	methanesulfonyl (mesyl)
<i>m/z</i>	mass-to-charge ratio
NBS	<i>N</i> -bromosuccinimide
nm	nanometer(s)
nM	nanomolar
NMO	<i>N</i> -methylmorpholine <i>N</i> -oxide
NMR	nuclear magnetic resonance
nOe	nuclear Overhauser effect

NOESY	nuclear Overhauser enhancement spectroscopy
<i>o</i>	<i>ortho</i>
[O]	oxidation
OMe	methoxy
<i>p</i>	<i>para</i>
PCC	pyridinium chlorochromate
Ph	phenyl
pH	hydrogen ion concentration in aqueous solution
PhH	benzene
PhMe	toluene
pin	pinacol
$pK_a$	acid dissociation constant
pm	picometer(s)
PMB	<i>para</i> -methoxybenzyl
ppm	parts per million
PPTS	pyridinium <i>para</i> -toluenesulfonate
Pr	propyl
<sup>i</sup> Pr	isopropyl
<sup>n</sup> Pr	propyl or <i>norm</i> -propyl
psi	pounds per square inch
pyr	pyridine
q	quartet
quant.	quantitative

R	generic group
<i>R</i>	rectus
RCM	ring-closing metathesis
ref	reference
<i>R<sub>f</sub></i>	retention factor
rgt.	reagent
rr	regioisomeric ratio
rt	room temperature
sat.	saturated
s	singlet or seconds
<i>S</i>	sinister
SAR	structure-activity relationship
sat.	saturated
SFC	supercritical fluid chromatography
t	triplet
TBACl	tetra- <i>n</i> -butylammonium chloride
TBAF	tetra- <i>n</i> -butylammonium fluoride
TBAI	tetra- <i>n</i> -butylammonium iodide
TBS	<i>tert</i> -butyldimethylsilyl
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography



TMS	trimethylsilyl
TOF	time-of-flight
Tol	tolyl
<i>trans</i>	on the opposite side
Ts	<i>para</i> -toluenesulfonyl (tosyl)
UV	ultraviolet
<i>vide infra</i>	see below
<i>vide supra</i>	see above
w/v	weight per volume
X	anionic ligand or halide
xs	excess
Z	<i>cis</i> (zusammen) olefin geometry