

I. SYNTHETIC STUDIES TOWARD THE TOTAL SYNTHESIS OF  
POLYCYCLIC NATURAL PRODUCTS – COMMUNESIN F,  
PEROPHORAMIDINE AND INELEGANOLIDE  
II. NICKEL CATALYZED INTRAMOLECULAR C–O BOND FORMATION

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

2016

(Defended May 13, 2016)

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*To my family,  
for their unwavering support and dedication*

## ACKNOWLEDGEMENTS

First and foremost, I would like to thank my advisor, Professor Brian M. Stoltz, for helping me tremendously during my graduate work. Brian has been very generous and supportive advisor who always encourages me to come up with new ideas. He expects us to be creative, thoughtful and curious in what we do. He has offered a lot of guidance in terms of not only chemistry, but also personal development. Brian is an endless source of knowledge and ideas. Whenever I have discussed my project with Brian, I have always become motivated. It is impossible to thank him enough for his mentorship and kindness. I have been fortunate to have him as an advisor over the last five years.

My committee members Prof. Sarah E. Reisman, Prof. Theodor Agapie, and Prof. Robert H. Grubbs have provided me with valuable advice on my research and career. Sarah has served as a role model for a great female scientist. She is a generous and thoughtful committee member who has helped me to develop my scientific interests. Theo provided me with scientific insights on transition metal-catalyzed transformations. Bob, who is the final member of my committee, has encouraged me to think about my proposals and chemistry from a broader perspective. I am grateful for all the guidance from my thesis committee.

In addition, I would like to thank Dr. Scott C. Virgil of the Caltech Center for Catalysis and Chemical Synthesis. While I was conducting a DKR project with him, he provided me with lots of unique scientific aspects. He also keeps analytical instruments running for us.

I also want to thank my past advisors. I am especially thankful to Prof. Duck-Hyung Lee who was my former advisor at Sogang University. When I was an

undergraduate student, I enjoyed taking his lectures. He motivated me to pursue graduate work in organic chemistry. I learned a great deal of both theoretical and experimental aspects of organic chemistry and developed a stronger synthetic chemistry foundation while I was doing research in his group. Prof. Duck-Hyung Lee deeply cares about his students. He has been a great mentor to me and I cannot thank him enough for his kindness. Dr. Jin Hee Ahn, who was my advisor at Korea Research Institute of Chemical Technology, expanded my interest to medicinal chemistry. He has been supportive and generous to me. I am thankful for all of the patience and guidance from my past advisors.

I have been lucky to work with great individuals in the Stoltz group. When I first joined lab, Dr. Florian Vogt, who was doing a project concerning the synthesis of communesin F and perophoramidine, was preparing to leave for his new job. Although I only spent time with him in the lab for about 10 days, I appreciate his helpful discussion, compounds and chemicals. I also want to thank to Dr. Vikram Bhat, who introduced the DKR project to me. In my 4th year, I took a project concerning the total synthesis of ineleganolide from Dr. Rob Craig. I really appreciate his valuable discussion and all the support. It has also been a pleasure to work with Dr. Ryohei Doi, who was a visiting student from Japan, on Ni-catalyzed etherification reactions. Thanks to the Caltech SURF program, I had opportunities to be a mentor for several undergraduate students. My first undergraduate mentee was Yoobin Koh, who came from GIST, Korea. Yoobin was passionate about learning chemistry. Gabriel Fernando de Melo was another mentee from Brazil in the following year. He helped me to explore a project concerning a new method for the cleavage of nitrobenzyl amides and ethers. I am thankful for his hard work on the

project. I would also like to thank Katherine Bay, who brought a cheerful attitude to the lab.

I need to thank all of the Stoltz group members, past and present, for the help that I have received for last five years. First of all, I would like to thank Kelly Kim and Nicholas O'Connor, who are the members of my class within the Stoltz lab. Kelly and Nick are very kind and always volunteer to help me. When we were the 1st and 2nd years of students, Kelly, Nick, Anton (formal Stoltz group member), and I sometimes hung out, played video games at Kelly's house, and drunk margaritas or beers. I really enjoyed all the activities with them. I also thank Prof. Wen-Bo (Boger) Liu, who was my hoodmate for the last four years. He is a brilliant organic chemist and I really appreciate his helpful discussion and contribution to my development as a chemist. We also enjoyed talking about the cultural differences between USA, Korea, and China. I am certain that he will have a successful career in academia at Wuhan University in China. When I visited Caltech as a prospective student in March 2011, Prof. Jimin Kim, who is a postdoctoral alumnus in the Stoltz group, introduced the Stoltz group to me during the poster session. Jimin and I used to have a lunch together and I enjoyed conversation with her. I am grateful to her for guidance and mentorship. I believe that she will be successful in academia at Chonnam National University in Korea. I also want to thank Dr. Allen Hong, who was one of my baymates. I think he is one of the most diligent people that I have met. He is very brilliant and I appreciate his helpful discussions on my chemistry. In addition, Dr. Chung Whan Lee is thanked for helping me to settle down in the lab in the early days. To Prof. Hosea Nelson, Dr. Alex Goldberg, Dr. Nathan Bennett, Dr. Jeff Holder, Dr. Christopher Haley, Dr. Yoshitaka Numajiri, Doug Duquette, Dr. Doug Behenna, Dr. Corey Reeves, Dr. Yiyang Liu, Dr. Jared Moore, Dr. Eric Welin,

Dr. Daisuke Saito, Dr. Max Klatte, Dr. Caleb Hethcox, Dr. Marchello Cavitt, Dr. Hendrik F. T. Klare, Dr. Guillaume Lapointe, Dr. Marc Linger, Dr. Alex N. Marziale, Dr. Noriko Okamoto, Dr. Grant Shibuya, Dr. Kristy Tran, Dr. Kun-Liang (Phil) Wu, Dr. Xiangyou Xing, Dr. Jonny Gordon, thank you all for your mentorship and guidance. To the younger students I have had the pleasure to work with, Sam, Beau, Shoshana, Kelvin, Eric, Elizabeth, Jiaming, Carina, Steven, Fa, Chris, Alex, David, and Austin, thank you for all of the support and I wish you all best throughout the rest of your time at Caltech. I especially thank to the numerous people who have helped look over my research proposals, manuscripts, and thesis chapters over the years.

I also want to thank to the members of the Reisman group and the Grubbs group for helpful scientific discussion and the sharing of numerous resources. I especially want to acknowledge Kangway Chuang for insightful discussion.

I would like to thank to Hyun Gi Yun, who is a graduate student in the Clemons lab and Dr. Sarah Yunmi Lee, who graduated from the Fu lab. I always enjoyed spending time with them. Hyun Gi and Yunmi have been there since the beginning. I also need to thank one of my best friends, Songi Han, who is a graduate student at Rice University studying bioengineering. Songi has accompanied me during my trips to LA, Houston, and Seattle. Songi and I are on the same wavelength. She has provided me the emotional anchoring during the most difficult moments of graduate school.

I am deeply indebted to the Fulbright for providing me fellowship during my first two years of graduate school. I would also like to thank the Ilju Foundation of Education & Culture for the pre-doctoral research fellowship during the last three years of graduate school.

I also want to thank tremendous support from the Caltech staff. Dr. Dave VanderVelde has helped me to analyze complicated NMR data sets for hours and taught me how to use MestReNova program efficiently. In addition, I must thank Larry Henling for providing lots of crucial X-ray crystal structures for my communesin F and perophoramidine project. Also, thanks Lynne Martinez, who is the administrative assistant for our group and the Reisman group, for keeping things running smoothly on a daily basis. I also want to thank Rick Gerhart for helping repair glassware, Dr. Mona Shahgholi and Naseem for helping to obtain HRMS data, Jeff Groseth for his expertise and service to our group, and Agnes Tong for helping with administrative duties.

Finally, I would like to acknowledge my lovely family who has always supported me. Dad, Mom, and Sangjun, who always pray for me, have been the most warm and supporting family I could ever ask for. Without their dedication and support, I would not be where I am today. I would also like to thank my aunt, Yuri and her husband. They live in LA and we have occasionally met and had a dinner. We had a trip to Sedona during my first vacation. Thanks to them, it has been very easy for me to get used to life in USA.

Without the continued support of all of these people, I would not have made it here.



## ABSTRACT

Expedient synthetic approaches to the highly functionalized polycyclic alkaloids communesin F and perophoramidine are described using a unified approach featuring a key decarboxylative allylic alkylation to access a crucial and highly congested 3,3-disubstituted oxindole. Described are two distinct, stereoselective alkylations that produce structures in divergent diastereomeric series possessing the critical vicinal all-carbon quaternary centers needed for each synthesis. Synthetic studies toward these challenging core structures have revealed a number of unanticipated modes of reactivity inherent to these complex alkaloid scaffolds. Finally, a previously unknown mild and efficient deprotection protocol for the *o*-nitrobenzyl group is disclosed – this serendipitous discovery permitted a concise endgame for the formal syntheses of both communesin F and perophoramidine.

In addition, the atroposelective synthesis of PINAP ligands has been accomplished via a palladium-catalyzed C–P coupling process through dynamic kinetic resolution. These catalytic conditions allow access to a wide variety of alkoxy- and benzyloxy-substituted PINAP ligands in high enantiomeric excess.

An efficient and exceptionally mild intramolecular nickel-catalyzed carbon–oxygen bond-forming reaction between vinyl halides and primary, secondary, and tertiary alcohols has been achieved. This operationally simple method allows direct access to cyclic vinyl ethers in high yields in a single step.

Finally, synthetic studies toward polycyclic ineleganolide are described. The entire fragmented carbon framework has been constructed from this work. Highly (*Z*)-selective olefination was achieved by the method by the Ando group.

**PUBLISHED CONTENT AND CONTRIBUTIONS**

1. Han, S.-J.; Vogt, F.; Krishnan, S.; May, J. A.; Gatti, M.; Virgil, S. C.; Stoltz, B. M. A Diastereodivergent Synthetic Strategy for the Syntheses of Communesin F and Perophoramidine. *Org. Lett.* **2014**, *16*, 3316–3319. DOI: 10.1021/ol5013263.

Han, S.-J. participated in designing the synthesis, synthesized compounds, prepared the data, crystalized the key compounds and wrote the manuscript.

2. Han, S.-J.; Fernando de Melo, G.; Stoltz, B. M. A New Method for the Cleavage of Nitrobenzyl Amides and Ethers. *Tetrahedron Lett.* **2014**, *55*, 6467–6469. DOI: 10.1016/j.tetlet.2014.10.006.

Han, S.-J. optimized reaction conditions, prepared substrates, investigated the new methodology, characterized compounds, and wrote the manuscript.

3. Lee, C. W.; Han, S.-J.; Virgil, S. C.; Stoltz, B. M. Stereochemical evaluation of bis(phosphine) copper catalysts for the asymmetric alkylation of 3-bromooxindoles with  $\alpha$ -arylated malonate esters. *Tetrahedron* **2015**, *71*, 3666–3670. DOI: 10.1016/j.tet.2014.10.065.

Han, S.-J. participated in optimizing reaction conditions, prepared substrates, and participated in the writing of the manuscript.

4. Han, S.-J.; Vogt, F.; May, J. A.; Krishnan, S.; Gatti, M.; Virgil, S. C.; Stoltz, B. M. Evolution of a Unified, Sterodivergent Approach to the Synthesis of Communesin F and Perophoramidine. *J. Org. Chem.* **2015**, *80*, 528–547. DOI: 10.1021/jo502534g.

Han, S.-J. participated in designing the synthesis, synthesized compounds, prepared the data, crystalized the key compounds and wrote the manuscript.

5. Liu, Y.; Han, S.-J.; Liu, W.-B.; Stoltz, B. M. Catalytic Enantioselective Construction of Quaternary Stereocenters: Assembly of Key Building Blocks for the

Synthesis of Biologically Active Molecules. *Acc. Chem. Res.* **2015**, *48*, 740–751.

DOI: 10.1021/ar5004658.

Han, S.-J. participated in the writing of the manuscript.

6. Han, S.-J.; Stoltz, B. M. A mild and efficient approach to enantioenriched  $\alpha$ -hydroxyethyl  $\alpha,\beta$ -unsaturated  $\delta$ -lactams. *Tetrahedron Lett.* **2016**, *57*, 2233–2235.

DOI: 10.1016/j.tetlet.2016.04.022.

Han, S.-J. designed the synthesis, synthesized the compounds, prepared the data and wrote the manuscript.

7. Han, S.-J.; Doi, R.; Stoltz, B. M. Nickel-Catalyzed Intramolecular C–O Bond Formation: Synthesis of Cyclic Enol Ethers. *Angew. Chem., Int. Ed.* **2016**, DOI: 10.1002/anie.201601991; *Angew. Chem.* **2016**, DOI: 10.1002/ange.201601991.

Han, S.-J. participated in optimizing the reaction parameters, synthesized substrates, investigated the new reactions, prepared the data, and wrote the manuscript.

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## **APPENDIX 11**

### *Synthetic Studies Toward Alistonitrine A*

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## LIST OF ABBREVIATIONS

Å	Ångstrom
$\lambda$	wavelength
$\mu$	micro
$\mu$ waves	microwave irradiation
$[\alpha]_D$	specific rotation at wavelength of sodium D line
[H]	reduction
[O]	oxidation
°C	degrees Celsius
Ac	acetyl
acac	acetylacetonate
AcOH	acetic acid
APCI	atmospheric pressure chemical ionization
app	apparent
aq	aqueous
Ar	aryl
atm	atmosphere
B3LYP	3-parameter hybrid Becke exchange/ Lee–Yang–Parr correlation functional
Bn	benzyl
Boc	<i>tert</i> -butyloxycarbonyl
BOP	Bis(2-oxo-3-oxazolidinyl)phospinic
bp	boiling point
br	broad
Bu	butyl
Bz	benzoyl
<i>c</i>	concentration for specific rotation measurements

ca.	about (Latin circa)
calc'd	calculated
CAN	cerium ammonium nitrate
cat	catalytic
CCDC	Cambridge Crystallographic Data Centre
CDI	1,1'-carbonyldiimidazole
cf.	compare (Latin confer)
CI	chemical ionization
cm <sup>-1</sup>	wavenumber(s)
cod	1,5-cyclooctadiene
comp	complex
Cp	cyclopentadienyl
Cy	cyclohexyl
d	doublet
D	deuterium
DABCO	1,4-diazabicyclo[2,2,2]octane
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	<i>N,N'</i> -dicyclohexylcarbodiimide
DCE	1,2-dichloroethane
DDQ	2,3-dichloro-5,6-dicyano- <i>p</i> -benzoquinone
DEAD	diethyl azodicarboxylate
dec	decomposition
DFT	density functional theory
DIBAL	diisobutylaluminum hydride
DIPEA	<i>N,N</i> -diisopropylethylamine
DKR	dynamic kinetic resolution
DMA	<i>N,N</i> -dimethylacetamide
DMAD	dimethyl acetylenedicarboxylate



DMAP	4-dimethylaminopyridine
dmdba	bis(3,5-dimethoxybenzylidene)acetone
DMDO	dimethyldioxirane
DME	1,2-dimethoxyethane
DMF	<i>N,N</i> -dimethylformamide
DMP	Dess–Martin periodinane
DMS	dimethyl sulfide
DMSO	dimethyl sulfoxide
dr	diastereomeric ratio
e.g.	for example (Latin <i>exempli gratia</i> )
$E_A$	activation energy
EC <sub>50</sub>	median effective concentration (50%)
EDC	<i>N</i> -(3-dimethylaminopropyl)- <i>N'</i> -ethylcarbodiimide
ee	enantiomeric excess
EI+	electron impact
equiv	equivalent
ESI	electrospray ionization
Et	ethyl
EtOAc	ethyl acetate
FAB	fast atom bombardment
FID	flame ionization detector
g	gram(s)
GC	gas chromatography
gCOSY	gradient-selected correlation spectroscopy
h	hour(s)
$h\nu$	light
HBPIn	4,4,5,5-tetramethyl-1,3,2-dioxaborolane; pinacolborane
HFIP	1,1,1,3,3,3-hexafluoro-2-propanol

HMDS	1,1,1,3,3,3-hexamethyldisilazane
HMPA	hexamethylphosphoramide
HOBt	hydroxybenzotriazole
HPLC	high-performance liquid chromatography
HRMS	high-resolution mass spectroscopy
Hz	hertz
i.e.	that is (Latin id est)
IBX	2-iodoxybenzoic acid
IC <sub>50</sub>	median inhibition concentration (50%)
IMDA	Intramolecular Diels–Alder reaction
IPA	isopropanol, 2-propanol
<i>i</i> -Pr	isopropyl
IR	infrared (spectroscopy)
IRC	intrinsic reaction coordinate
<i>J</i>	coupling constant
K	Kelvin(s) (absolute temperature)
kcal	kilocalorie
KHMDS	potassium hexamethyldisilazide
L	liter; ligand
LAH	lithium aluminum hydride
LDA	lithium diisopropylamide
LHMDS	lithium bis(trimethylsilyl)amide
lit.	literature value
m	multiplet; milli
<i>m</i>	meta
M	metal; molar; molecular ion
<i>m/z</i>	mass to charge ratio
<i>m</i> -CPBA	<i>meta</i> -chloroperoxybenzoic acid
Me	methyl

mg	milligram(s)
MHz	megahertz
min	minute(s)
MM	mixed method
MMPP	magnesium monoperoxyphthalate
mol	mole(s)
MOM	methoxymethyl
mp	melting point
Ms	methanesulfonyl (mesyl)
MS	molecular sieves
MVK	methyl vinyl ketone
n	nano
N	normal
nbd	norbornadiene
NBS	<i>N</i> -bromosuccinimide
<i>n</i> -Bu	butyl
NHC	<i>N</i> -heterocyclic carbene
NMO	<i>N</i> -methylmorpholine <i>N</i> -oxide
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
NOESY	nuclear Overhauser enhancement spectroscopy
Nosyl	nitrobenzenesulfonyl
Nu	nucleophile
<i>o</i>	ortho
OKR	oxidative kinetic resolution
<i>p</i>	para
PCC	pyridinium chlorochromate
Pd/C	palladium on carbon
PDC	pyridinium dichromate

Ph	phenyl
pH	hydrogen ion concentration in aqueous solution
PHOX	phosphinooxazoline ligand
Piv	pivaloyl
$pK_a$	$pK$ for association of an acid
PMB	<i>p</i> -methoxybenzyl
pmdba	bis(4-methoxybenzylidene)acetone
ppm	parts per million
PPTS	pyridinium <i>p</i> -toluenesulfonate
Pr	propyl
PTU	<i>n</i> -Propylthiouracil
Py	pyridine
q	quartet
R	generic for any atom or functional group
Ref.	reference
$R_f$	retention factor
s	singlet or strong or selectivity factor
sat.	saturated
Selectfluor	1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)
SEM	2-(trimethylsilyl)ethoxymethyl
SFC	supercritical fluid chromatography
$S_N2$	second-order nucleophilic substitution
$S_N2'$	nucleophilic substitution with allylic rearrangement
sp	sparteine
sp.	species
t	triplet
TBAF	tetrabutylammonium fluoride

TBAI	tetrabutylammonium iodide
TBAT	tetrabutylammonium difluorotriphenylsilicate
TBDPS	<i>tert</i> -butyldiphenylsilyl
TBHP	<i>tert</i> -butyl hydroperoxide
TBME	<i>tert</i> -butyl methyl ether
TBS	<i>tert</i> -butyldimethylsilyl
<i>t</i> -Bu	<i>tert</i> -butyl
TES	triethylsilyl
Tf	trifluoromethanesulfonyl (triflyl)
TFA	trifluoroacetic acid
TFAA	trifluoroacetic anhydride
TFE	2,2,2-trifluoroethanol
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin-layer chromatography
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TMS	trimethylsilyl
TOF	time-of-flight
Tol	tolyl
$t_R$	retention time
Ts	<i>p</i> -toluenesulfonyl (tosyl)
UV	ultraviolet
$v/v$	volume to volume
VO(acac) <sub>2</sub>	vanadyl acetoacetate
w	weak
$w/v$	weight to volume
X	anionic ligand or halide