FORAYS INTO THE SYNTHESIS OF ZOANTHENOL: INTRIGUING PATTERNS IN REACTIVITY AND SELECTIVITY

Thesis by

Jennifer L. Stockdill

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Dedication

To my parents, Dave and Lucy Stockdill,
who have sacrificed so much for me.

To my sister and brother,
Teresa Barth and Jon Stockdill,
who have been role models to me all of my life.

To my eighth grade science teacher,
Mary Alice Robinson,
who sparked a passion that has not died.

Finally, to my nieces and nephews,
Hudson Barth, Deirdre Stockdill,
Landen Barth, Jonah Stockdill, and Zoe Barth,
who have provided the extra motivation to finish my Ph.D.

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...It is impossible to start....

It cannot be argued with that the most influential person in my graduate career has been my advisor, Brian M. Stoltz. Brian's passion, guidance, and discipline have been indispensable to my growth as a scientist and as a person over these past five and a half years. I am especially grateful to Brian for his devotion to his students' education and success. I have not heard of another professor who goes so far out of his/her way to make sure students are prepared for whatever the next step in their journeys may be. Also, Brian introduced me to my best friend EVER, TLC. After all, it *is* the fastest, cheapest, easiest way to obtain meaningful information about what's going on in your reaction flask!

I am especially indebted to my thesis committee members, who have been simply unreal. Dennis Dougherty, my committee chair, has done a surprising job of keeping Harry in line, not to mention the insights he has provided in discussing my ideas and the depth to which he forces me to think. Harry Gray has been a constant source of support that has proven to be truly invaluable over the past two years when life has seemed so overwhelming. Bob Grubbs, the most recent addition to my committee has been asking me regularly how my research is going for years (I always regret not having a more cheerful reply, but the inquiries have meant a lot to me), and he always remembers to tell me when he's going climbing and I have to stay in lab! In all seriousness, all of my committee members have been very gracious and generous with their time, ideas, and recommendation letters. Thank you so much to all of them.

I have had the great pleasure of working on my project with Dr. Doug Behenna and Dr. Andy McClory. Doug was the single most influential person on my development as a

bench chemist. He taught me everything from what a TBS group is, to how to run a column, to the true meaning of scale-up. His hard work and friendship over the past years have been critical. I am grateful to Andy for helping me to learn that there is more than one way to approach a problem. He is a brilliant scientist, and I am sure he will be an amazing professor.

The various members of the Stoltz group have provided a diverse, if occasionally tumultuous, environment that has not only shaped me as a chemist, but also as a person. Through all of the ups and downs of the 72+ hours/week that we spend together, I wouldn't replace *any* of the people I have had the opportunity to work with in the lab. The early lab members were instrumental to me in learning techniques and in how to think about chemistry. I am especially grateful to Eric Ashley, Eric Ferreira, Doug Behenna, and Raissa Trend for their advice in my early years. Toward the middle and through the end of my graduate career, I had the great fortune of becoming close friends with Dave Ebner and Ryan McFadden, who were both willing to talk endlessly with me about my chemistry and who always tried the ideas that I suggested for their work. They, of course, have both ditched me, and I miss them dearly. (Congratulations to RMAC on the birth of his son, Nathan!! And Dave…you can't escape! I'll be in NYC soon.) I am more and more grateful to Dan Daspi every day as I write my thesis. Dan is so thoughtful in always trying to make the annoying parts of lab life run more smoothly. He has created a macro for everything you might need to do with a spectrum, and I think I'd still be trying to figure out how to get the things into my thesis right now if it weren't for him. My classmates are an awesome crew. I'm grateful to JT, who is a fountain of info from what's the deal with my NMR or the pKa of chemical X to what's the last step of the Rubik's cube algorithm. (Congratulations to JT on the birth of his daughter, Marie!!) Mike Krout always has what I'm looking for, whether it be a reagent or a procedure, and his generosity with both is appreciated. Also, I've always been grateful to

him for being so nice during group sports…I suck at most of them, and he is always patient. Mike Meyer has been a great friend over the years, and he will always hold a special place in my heart. Which brings me to Jenny Roizen…Jenny, I'll put your part at the end. The fou…fifth years are an eclectic bunch, that I have loved having around for the past four years. Nat Sherden has always been good to me, from bringing my mail in that ended up at his house to walking out of his way to walk me home when it's late at night, to apologizing when *I* have done something wrong, his kindness is overwhelming. Also, the emails…I *love* the emails. I hope I don't get taken off the group list right away because I will miss the misspelled sarcasm-rich frustrations. John Enquist is one of the most dedicated people I've known. It has been fun trying to break through his wall of seriousness (the trick is mint-chip ice cream!), and his dry sense of humor really gets me laughing sometimes. I have really enjoyed Kevin Allan's company as a baymate (briefly) and on years of coffee runs. I will always cherish the memory of late night flash columns listening to Ok Go, and I really admire his enthusiasm in the lab. Also, thanks for the cookie. Sandy Ma is one of the more unusual (in a good way) characters I've met. (DOGGIE!) She always makes me laugh and has the most quotable quotes. Brinton Anna Seashore-Ludlow was a fun baymate and is a great friend. I have missed her often since she moved to Sweeden. I've enjoyed getting to know Pam Tadross better over the past 9 months or so, and I'm sad that it took so long. She is a really thoughtful person and devoted friend. Chris Gilmore has always cracked me up. He's a great person to talk about life with, and lately I've enjoyed talking Obama with him as well. It's been awesome to have Hosea in the lab. He has such a different perspective from the status-quo, it's always fun to see what he thinks. I've really enjoyed Narae's company over the past few years. She is a genuine and sweet person, and I've grown to expect her in lab on Saturday over the past 6 months. I always thought she was joking when she said he hobby was sleeping, but she seems to be in lab the rest of the time! :P I've grown to

really enjoy having Allen Hong in 264, and it will be really sad to say goodbye. I'm thankful for all the candy and especially for his concern…he always wants to know how you're doing when he asks. Of course, I'll miss my secret admirer, aka Hahvard, aka Matt Winston. Matt has been a great cheerleader in my thesis effort and his support is really appreciated. Also, he cheers Jenny up, which cheers me up! The first years in the group are a hilarious bunch, and I regret that I won't have the opportunity to get to know them better. Nathan Bennett, my newest baymate, always has something nice to say, and he is very encouraging, even to himself… "Alright, self…" Jonny Gordon is just too cool for school (but he comes anyway). I dig the purple sweatband and the blue glasses. Alex Goldberg is our newest member, and he seems to share my sarcastic sense of humor. Finally, there are the postdocs. There have been many…I'm especially grateful to Amanda Jones, who has been a really good friend, and is always a pleasure to have in lab, but most importantly, hosts the poker night (no boss allowed!). Jan Streuff has been a fun companion over the past year, and I will miss him when he goes back to Deutschland. Also, Corinne Baumgartner has been a fun exercise buddy, and Christian Defieber always tried to speak German with me. If it weren't for Nolan McDougal, I would not be able to say that I've walked from campus to Roscoe's, or worse, I might not know how to properly eat bread at a nice dinner! I'm grateful to him for the fun memories and for introducing me to scallops. I mentioned Andy McClory briefly, but I need to mention here that he is one of the more loyal friends a person could ask for, and I really enjoyed his friendship. A recent addition to the lab, Chris Henry, has fast become one of my closest friends, and I am very thankful to have met him. Thanks also to Xiaoquing Han (X-Dog), Andy Harned, Haiming Zhang, and Kousuke Tani for their kindness and advice.

I need to make a separate paragraph here for my baymates. Eric Ashley was my first baymate, and I am ever grateful to him for all that he taught me those first few years.

Also, I wouldn't know important things like "what ever happened to a good old fashioned passionate *%&-whuppin', getting your shoes, coat and your hat tooken." Brinton Seashore-Ludlow is one of those people that you just love right away. We had lots of fun hiking and going to yoga, and of course running collumm-collummns!! Enough cannot be said about Thomas Jensen, who among other things was the first baymate I had who liked *all* the same music as me. We had a blast jammin' in the lab and talking chemistry. Not to mention playing 10:1 with Dave!

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In addition to the outstanding members of the Stoltz group, I have been warmly welcomed by the Grubbs, Bercaw, Gray, Dougherty, and Reisman labs. To thank each of the people in these groups would be overwhelming, but they are all truly appreciated, and I look forward to seeing them in the future.

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me into a human again. My move to the West Coast would not have been conceived of without Joe Polidan, and my last year of college would have definitely not been as fabulous without Sheila (a.k.a. Pony 2) Gradwell. Boo Shan Tseng and Hari Shroff were indispensable companions in Argentina/Chile. Likewise, Mike Olsen was a blast to have along in Costa Rica. It was a pleasure spending two weeks with each of them in paradise.

Those memories bring me to Tristan Ursell, who was my companion for three of the most challenging, yet adventure-packed years of grad school. Tristan remains one of my closest friends, and I cannot thank him enough for everything that we shared. I will always treasure our many memories in some of the most beautiful places in the world. Tristan also helped me to learn a lot about myself and ultimately led me in the direction of actually paying attention to what's happening in the world. He taught me to look deeper into myself and to become the person I wanted to be instead of wishing things were different.

I've put this off for awhile now, but it comes time to try to thank Jenny Roizen. There aren't words to express my gratitude to Jenny. For the first three years of grad school, Jenny was my roommate, labmate, and friend. We did everything together. I could not possibly have gotten through some of the rougher times of the past five and a half years without Jenny's constant love and support. I have grown to really appreciate her direct candor with me about everything. To put it briefly, Jenny rocks. I'm so sad to be leaving her in the lab without me. I know that she will get through everything fine, but I wish I could be here to support her, as she has so devotedly supported me over this thesis journey.

Most people are lucky to have one friend as constant and close to their heart as Jenny is to mine. I have had the great fortune during my graduate career of having developed two such friends. Professor Dr. Jen Dionne has become a critical appendage over the years. To lose her would be like losing an arm. I am left frustrated again with the

English language for not having the appropriate words to match the quality and magnitude of Jen's friendship. She has become like a twin sister to me, which is exciting because I never had a twin sister! I will just say to both Jen and Jenny, I love you. You are irreplaceable.

Finally, to thank the people who shaped me into who I am. Becky (Doyal) Orrock and Aimee (Dudash) Ketner have been my best friends since I can remember, and it has been awesome watching each other grow from little girls ogling at cute boys at the beach to grown women, ogling at cute boys at the beach. ☺ Sally, I am glad you moved to Virginia. It's been nice having some extended family nearby, and I always enjoy our phone calls, surprisingly also often relating to ogling at boys at the beach! Grandma Stockdill, it has been fabulous visiting with you more often over the past ten years. I'm glad you were persistent about calling. Your support has been treasured. Grandma Vorlicek, I wish I could see you more, but I wanted to take this chance to thank you for working so hard to keep the family together over the years. I know it was challenging raising 8 kids as a single mom, and I'm amazed that you managed to do it so successfully. Teresa and Jon, thanks for all that you have done for me over the years. I have always looked up to you, and I continue to be awed by your talents as you raise your families. You have the 5 coolest kids in the world. I can't wait to be back with you and with them. Mom and Dad, I love you both and I wish you all the happiness and adventure that you have ensured that I had the opportunity to experience. You have all contributed irreversibly to the person I have become. I cannot thank you enough.

ABSTRACT

The zoanthamine family of alkaloids has attracted the attention of synthetic chemists for over two decades, beginning with the first report of their isolation in 1984. Not only are these stereochemically dense polycyclic compounds structurally fascinating, but they also display interesting and important biological activities. Foremost among these is the potent anti-osteoporotic effect of norzoanthamine. To date, norzoanthamine remains the only member to have succumbed to total synthesis, by Miyashita and coworkers in 2004. Our studies began by targeting zoanthenol, a structurally similar natural product that possesses the key stereochemical challenges of norzoanthamine, while offering unique opportunities for strategic development as compared to the other family members.

The synthetic work described herein focuses on approaches to the tricyclic core of zoanthenol, specifically employing an approach by which the stereochemical complexity of the C ring, marked by the challenging vicinal all-carbon quaternary centers, is addressed early in the synthesis. These functionalized C ring synthons are then tethered to an aromatic A ring synthon, and methods to form the final bond of the B ring are explored. Special attention is given to the acid-mediated Friedel-Crafts cyclization approach. In addition to the acid-mediated cyclization approach, an alternative cyclization method is discussed wherein the A ring is substituted with a halogen in order to enable generation of a radical. This radical then undergoes a 1,4-addition into a fully substituted enone to close the B ring and provide the desired stereochemistry both of the two new stereocenters that are generated in the cyclization.

In these efforts, we have learned a great deal about the factors governing selectivity and reactivity in these systems. For each case, stereochemical models are discussed and key structural requirements for future investigations are outlined.

PROLOGUE

The Importance of Natural Products Synthesis

This prologue is primarily for the benefit of readers outside of the field of chemistry, who may not be familiar with the nuances of the field of total synthesis, and thus, the impact of the research described in this thesis.

Natural products are complex molecules that have been isolated from a natural source, such as a tree bark, a fungus, a bacterial species, or even a marine creature. The study of natural products synthesis is essential to the advancement of organic chemistry, as well as to society as a whole. A natural product synthesis involves looking at a structure that has been isolated from nature, and then finding a way to make it from much smaller starting materials. As such, it is an ideal platform for the discovery of new reactions because every natural product presents a unique array of bonds that have likely not been made before. In order to make some of these bonds, new chemistry must be invented. These new reactions are typically applied to related molecules of varying levels of complexity, leading to the development of a new reaction methodology. Thus, total synthesis fuels the discovery of new methodology, while new methodology simultaneously allows for the completion of total syntheses.

The broader impact of these studies is realized largely through the pharmaceutical industry. Although pharmaceutical companies invest a great deal of time and money into their own research programs, they are generally very focused on a specific goal such as finding a drug for breast cancer. This is a large enough problem on its own that the company cannot invest their own man-hours into synthesizing natural products from scratch. Thus, they turn to academic groups for key information about what bonds were the most challenging to make and what disconnections lead to the shortest and most modular synthesis of a compound. Short syntheses are important to pharmaceutical

companies because even if every step of a 30-step synthesis of a compound proceeds with 90% yield (this is not typical), the overall yield for the process is $(.9)^{30}$ or 4%. If the company is going to conduct testing on the compound, they cannot afford to waste 96% of their original materials. Thus, it is important for academic groups to discover as many different types of reactions and ways to disconnect natural products as possible. It is also important to have a modular synthesis, so that analog compounds can be made and tested. In many cases, the best pharmaceutical agents are modified versions of natural products. Natural products offer the great advantage of having already been compatible with at least one living system, the one from which they were isolated. If that creature was able to survive with this compound inside it, it is more likely that a human will be able to tolerate the compound than for a molecule that has been 100% designed. Some important drugs that are natural products or derivatives include the antibiotics penicillin and vancomycin, contraceptives (+)-norgestrel and 17α-ethynylestradiol, the anti-inflammatory agent indomethacin, and the ovarian, breast, and small lung cancer drug paclitaxel (taxol).

The research presented herein centers around the synthesis of a marine alkaloid, zoanthenol, isolated off the coast of the Canary Islands from polyps of the genus *Zoanthus*. A number of very similar compounds were also isolated from the zoanthids, and they comprise a family of natural products called the zoanthamines. As a family, the zoanthamines offer a range of biological activities including inhibition of inflammation in mouse ears, cytotoxicity against murine leukemia cells, broad-spectrum antibacterial activity, and activity against human platelet aggregation. Perhaps the most exciting biological activity is the excellent anti-osteoporotic activity demonstrated by norzoanthamine. In ovarioectomized mice, a good model for post-menopausal osteoporosis, treatment with norzoanthamine hydrochloride prevented the loss of bone mass and strength. Additionally, bone strength can be restored in ovarioectomized mice

by treatment with norzoanthamine hydrochloride without any observed uterine atrophy, a side effect of treatment with 17β-estradiol, the current standard in this type of therapy. This difference points to the possibility of a different mechanism of action than estrogen therapy, making the zoanthamines an important family of natural products to target for synthesis.

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LIST OF ABBREVIATIONS

$[\alpha]_D$	specific rotation at wavelength of sodium D line
Ac	acetyl
ACN	acetonitrile
Ad	adamantyl
add'n	addition
AIBN	2,2'-azobis(*iso*-butyronitrile)
app.	apparent
aq	aqueous
Ar	aryl group
atm	atmosphere
B.	*Bacillus*
BBN	borabicyclo[3.3.1]nonane
BHT	2,6-di-*tert*-butyl-4-methylphenol
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl
bm	broad multiplet
Bn	benzyl
Boc	*tert*-butoxycarbonyl
BOM	benzyloxymethyl
bp	boiling point
br	broad
BRSM	based on recovered starting material
bs	broad singlet
BSA	*N*,*O*-bis(trimethylsilyl)acetamide
Bu	butyl

n-Bu	*n*-butyl
t-Bu	*tert*-butyl
Bz	benzoyl
c	concentration for optical rotation measurement
^{13}C	carbon 13, isotope
/C	supported on activated carbon
°C	degrees Celsius
cat.	catalytic
calc'd	calculated
CAM	ceric ammonium molybdate stain
CAN	ammonium cerium(IV) nitrate
Cbz	benzyloxycarbonyl
CCDC	Cambridge Crystallographic Data Centre
CDI	1,1'-carbonyldiimidazole
c-Hex	cyclohexyl
comb.	combined
comp.	complex
CSA	camphorsulfonic acid
conv	conversion
COSY	correlation spectroscopy
Cy	cyclohexyl
d	doublet, deuterium, diameter, or day(s)
Δ	heat
δ	chemical shift in parts per million
DA	Diels-Alder
dba	dibenzylideneacetone

DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	1,3-dicyclohexylcarbodiimide
DCE	1,2-dichloroethane
DCM	dichloromethane or methylene chloride
DDQ	2,3-dichloro-5,6-dicyano-*p*-benzoquinone
DEAD	diethyl azodicarboxylate
decomp.	decomposes
DIBAL	diisobutylaluminum hydride
DIBAL-H	diisobutylaluminum hydride
DIOP	2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
DIPA	diisopropyl amine
DIPEA	diisopropylethylamine
DMA	N,N-dimethylacetamide
DMAP	4-dimethylaminopyridine
dmdba	3,5,3’,5’-dimethoxydibenzylideneacetone
DMDO	dimethyldioxirane
DME	1,2-dimethoxyethane
DMF	dimethylformamide
DMP	Dess-Martin periodinane
DMPU	N,N'-dimethyl propylene urea
DMS	dimethylsulfide
DMSO	dimethylsulfoxide
DNA	deoxyribonucleic acid
dppb	1,4-bis(diphenylphosphino)butane
DPPE	1,2-bis(diphenylphosphino)ethane

dppp	1,3-bis(diphenylphosphino)propane
dr	diastereomeric ratio
D.-S.	Dean-Stark conditions
ee	enantiomeric excess
E	entgegen olefin geometry
E.	*Escherichia*
EI	electrospray ionization
equiv	equivalent(s)
Et	ethyl
FAB	fast atom bombardment
g	gram
GC	gas chromatography
Grubbs II	Grubbs second-generation metathesis catalyst
[H]	reduction
h	hour(s) or height
hν	light
^{1}H	proton
^{3}H	tritium
HMBC	heteronuclear multiple bond correlation
HMDS	hexamethyldisilazide or hexamethyldisilizane
HMPA	hexamethylphosphoramide
HPLC	high-performance liquid chromatography
HRMS	high-resolution mass spectroscopy
HSQC	heteronuclear single quantum coherence
Hz	hertz
η^n	eta; n = number of atoms coordinated to metal

i	iso
IBX	2-iodoxybenzoic acid
IC_{50}	concentration required for 50% growth inhibition
IL	interleukin
IMDA	intramolecular Diels-Alder
imid.	imidazole
Imid.	imidazole
IR	infrared spectroscopy
J	coupling constant
k	kilo
k_n	rate constant, n refers to various reactions, negative n indicates reverse reaction
kcal	kilocalories
KHMDS	potassium hexamethyldisilazide
L	liter
λ	wavelength
LAH	lithium aluminum hydride
LDA	lithium diisopropylamide
LD_{50}	Lethal Dosage to kill 50% of test population
LiHMDS	lithium hexamethyldisilazide
LITA	lithium tantalate
lut.	lutidine
m	meta
m	multiplet, meter, or milli
μ	micro
M	mega, metal, or molar

m/z	mass to charge ratio
m-CPBA	*meta*-chloroperbenzoic acid
Me	methyl
(*R,R*)-Me-DUPHOS	(-)-1,2-Bis((2R,5R)-2,5-dimethylphospholano)benzene
MEK	methyl ethyl ketone
MH-60	mouse myelohybridoma cells
MIC	minimal inhibitory concetration
min	minute(s)
mol	mole(s)
mol%	percentage used based on moles
MOM	methoxymethyl
(*R*)-MOP	(R)-(+)-2-(Diphenylphosphino)-2'-methoxy-1,1'-binaphthyl
mp or m.p.	melting point
Ms	methanesulfonyl
MS	molecular sieves
M.S.	molecular sieves
MTPA	α-methoxy-α-(trifluoromethyl)phenylacetic acid
MVK	methyl vinyl ketone
N	normal
n	*normal*
n	nano
NBS	*N*-bromosuccinimide
NMP	*N*-methylpyrrolidinone
NMR	nuclear magnetic resonance
nOe	nuclear Overhauser effect

NOESY	2D nuclear Overhauser effect spectroscopy
NR	no reaction
o	ortho
[O]	oxidation
p	para
PCC	pyridinium chlorochromate
PDC	pyridinium dichromate
PG	prostoglandin
Ph	phenyl
pH	hydrogen ion concentration in aqueous solution
PhH	benzene
PhMe	toluene
PHOX	phosphinooxazoline
Phth	phthalamidyl
Piv	pivaloyl
PMA	phorbol myristate acetate
PMB	*p*-methoxybenzyl
PMBM	*p*-methoxybenzyloxymethyl
p.o.	administered orally
ppm	parts per million
PPTS	pyridinium *p*-toluenesulfonate
Pr	propyl
i-Pr	isopropyl
psi	pounds per square inch
Py, py or Pyr	pyridine
q	quartet

QUINAP	(*R*)-(+)-1-(2-diphenylphosphino-1-naphthyl)isoquinoline
R	alkyl group
R	rectus (configurational)
Rearr.	Rearrangement
Red-Al	sodium bis(2-methoxyethoxy)aluminum hydride
R_f	retention factor
RNA	ribonucleic acid
ROESY	rotational nuclear Overhauser effect spectroscopy
s	singlet
S	sinister (configurational)
S.	*Salmonella* or *Staphylococcus*
SAE	Sharpless asymmetric epoxidation
SAR	structure activity relationship
sat.	saturated
sept.	septet
S_N'	allylic nucleophilic substitution
S_N1	unimolecular nucleophilic substitution
S_N2	bimolecular nucleophilic substitution
sp.	*species*
stoich.	stoichiometric
t	triplet
t	*tertiary*
$t_{1/2}$	half-life
TBAC	tetrabutylammonium chloride
TBAF	tetrabutylammonium fluoride

TBAI	tetrabutylammonium iodide
TBAT	tetrabutylammonium triphenyldifluorosilicate
TBDPS	*tert*-butyldiphenylsilyl
TBS	*tert*-butyldimethylsilyl
temp	temperature
TEA	triethylamine
TES	triethylsilyl
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin-layer chromatography
TMEDA	tetramethylethylenediamine
TMS	trimethylsilyl
TOF	turnover frequency
TON	turnover number
TPAP	tetrapropylammonium perruthenate
TROC	trichloroethoxycarbonyl
Ts	*p*-toluenesulfonyl or *p*-toluenesulfonic
UV	ultraviolet
Vis	visual wavelength
v/v	volume per volume
wt%	percent by weight
w/v	weight per volume
X	halide or trifluoromethanesulfonate
Z	zusammen olefin geometry