ARYNE ANNULATION REACTIONS TOWARD THE SYNTHESIS OF HETEROCYCLIC MOLECULES

Thesis by

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To Oliver Francis Fredericks,
and his daughter, Jane,
who gave up a career for this.

ACKNOWLEDGMENTS

As anyone who has written a thesis certainly knows, the run up to submission is one of the most frenetic, stressful, and intensely satisfying times of your life. After reading my predecessors' acknowledgements, I had vowed to not open mine with some hackneyed line like "this is the most difficult part of my thesis to write." But truthfully, I have no idea how to properly acknowledge the countless, selfless contributions made by so many people over such a long period of time in a few short sentences. So, with all that being said, this was the most difficult part of my thesis to write.

First, I want to thank my committee for their support. I've had the opportunity to interact with Prof. John Bercaw, my committee chairman, in another capacity as well. He was, while I was a GLA in the NMR facility, the faculty head of the instrumentation committee. He was honest, unflinchingly supportive, and a visionary for what small changes we could make to bring about a big difference in that crucial aspect of the Division's administration. John has been exceptionally supportive of me in his capacity as my committee chairman, writing what must have been a large number of recommendation letters as a result of my protracted job search. He is the very embodiment of the traits that make Caltech an excellent institution for research and place it first among equals on the world stage.

Prof. Linda Hsieh-Wilson has been tremendous as well, in her support and flexibility as I've progressed through my studies. I've also interacted with her in her capacity as department safety committee chair, and she was excellent, open, firm, and fair in her oversight of our lab's move from Crellin/Church/Gates to Schlinger in the spring of 2010. To Prof. Peter Dervan, a fellow Boston College alumnus, I would like to thank for being helpful on such short notice in getting me out of here. I accidentally ducked my 4^{th}($/5^{th}/6^{th}$)-year meetings when we should have otherwise been introduced, but when I showed up to schedule my proposal and thesis defenses, he could not have been more understanding.

Much of what happens here wouldn't be possible without the contributions of numerous staff, operating sometimes invisibly to make sure that the instrumentation works. In my capacity as GLA (of HgBI, Hg2, FID and Siena), I have seen the NMR facility morph from a functional afterthought into something that has taken center stage

for many researchers in the department. That is almost entirely due to the contributions of two people: Dr. David VanderVelde and Tom Dunn. Dave came in 2009 and provided a much needed injection of energy and new ideas. He has converted the facility into highly functioning laboratory through his labors. I am proud to have known him, and profoundly grateful for what I have learned from him. While Dave's Herculean effort turned the facility around, Tom Dunn's equally impressive exertions largely kept things running in the times when we were a ship without a captain. He is one of the nicest, most genuine, most helpful people I have ever met, and I am proud to call him a friend.

Among other members of the staff, Lynne Martinez, Steve Gould, Chris Smith, Anne Penney, Agnes Tong, and Leah Mentch have been extremely supportive in those stressful times that have me scrambling to figure out what to do next. They had the answers I needed, when I needed them. Dian Buchness, the former division graduate office head, was wonderful my first two years here, and a source of positivity whenever things got rough. Joe Drew, frankly, is the man. He's the kind of guy you go to if nothing works, and you need a couple *completely professional* jokes to help cheer you up. Rick Gerhart is an artist. If you don't know why, I recommend that you break some glassware and take it to him. Paul Carroad, the former division administrator, is a man whose competence and impact were often overlooked, but I've found that not only was he the heartbeat of the department, he was also generous, kind, and enthusiastic about helping the faculty and students perform research at the highest level.

The experience of designing our labs in Schlinger with Brian and Pam was exceptional. It was fundamentally interesting, and at its root, extremely frustrating. But, it was rewarding and a great success; rarely as a graduate student do you get to see something as concrete as a building go from design to construction in your time there. Moreover, it introduced me to competent people like Tony Parker, Mike Maiese, Patty Cully, Alex Muñoz and Rich Kalish.

By a quirk of timing, I've managed to meet two remarkable people at the beginnings of their careers here at Caltech: Dr. Scott Virgil and Prof. Sarah Reisman. Both of them are perfect examples of why Caltech, year in and year out, maintains its high standard of excellence in research. Sarah has been tremendously helpful and generous to me and to Pam with her time and advice. From my perspective, she has

transformed from a promising post-doc who was friends with Bekka, to an astonishingly bright rising star in the synthetic community overnight. I wish she, her wonderful husband Andy, and their adorable baby boy, Oliver, a lifetime of delight in Pasadena. Scott, the head of the CCCS, is one of the most interesting people I have ever met. If not for his biography alone, he is one of the most intelligent, insightful, and curious individuals on earth. And perhaps most amazing, he does it all without a hint of ego or pretense. We are lucky to have him as a department. Scott has become a good friend, and has welcomed Pam and I both into his new family, with his lovely wife, Silva. From the importance of the "Well-Tempered Clavier" to opera, to the delights of an Armenian wedding, their unflinching generosity has been a tremendous gift to me, for which I can never thank them enough.

Finally, I'd be remiss to not thank my two most professionally significant people on this list—Scott Miller and Brian Stoltz.

When Scott took me into his lab in January of 2003, I wasn't sure I wanted to do chemistry seriously. I had lucked my way into the tutelage of one of the most fundamentally decent, intelligent, and thoughtful people in the world of chemistry. Through the lens of the Miller lab (and the direction of my mentors, Drs. Melissa Vasbinder, Adam Morgan, and Steve Mennen), I developed an incredible enthusiasm for synthesis. Scott himself was an effective but distant advisor while I worked for him. My full appreciation for him has come since I moved to Calfornia. He has been a source of advice, a sounding board, and a pillar of support for me. He emphasized the importance of striving to be the consummate gentleman, which is a notion I continue to pursue (and struggle with).

The second person on that list, Brian Stoltz, has been nothing short of a spectacular boss, and has become something much closer to a friend as time has gone on. It took me nearly 7 years to graduate, but that was not because Brian was holding me back. His generosity toward me could not be better exemplified in the fact that he kept me on as a graduate student while I slogged through the bad job market for more than a year. Such an act of generosity (which ultimately led me to Dow) is uncommon, and rarer still in an extremely tight funding environment. His impact on me, of course, is much more profound than a recommendation letter, or even chemistry. What he brought

was an implicit trust in talented individuals that are highly motivated to accomplish their goals, which led him to intervene only occasionally to bump us in the right direction. That's how we develop into the best possible scientists that we could be. That trust, which has endowed our lab with exceptional creativity and wide ranging interests, is how an unexpected result became a project around which I could build a thesis. Though the lab is going through a difficult time presently, there is not a shred of doubt in my mind that Brian will capably navigate through these troubled waters. Out the other side, will emerge a leaner, meaner, more productive Stoltz lab that will be better than ever, and closer to reaching Brian's ultimate goal of being the best synthetic chemistry lab in the world.

On a more personal level, I'd like to thank Brian for being a friend to me, and being supportive of Pam and I throughout graduate school. It's been a long road to walk, but I can't think of a better person to follow. It helps that he's a Sox fan, and hates losing as much as I do. The one thing that really brings home the tremendous character Brian has is my experience in organizing his 40th birthday party. We wanted alumni to put on the uniform—khakis, blue polo, glasses— and send us photos for a montage. Not only did 80% of the people I sent the email to respond with photos, but about a dozen alumni (and his Ph.D. advisor, Prof. John Wood) cleared their schedules to fly in and attend the party. The man is a great boss and a loyal friend, which is reflected in the loyalty his students, past and present alike, have to him.

Brian's wife, Erna, and his two sons, Harry and Teddy, Have been delightful additions to the lab. Erna is always quick with a punch line, and quicker still with a supportive word. As for Harry and Teddy, well, go meet them, so I don't have to tell you why seeing them around would always lift my spirits.

When you've been in a large research group as long as I have, literally hundreds of people pass through, and contribute in their own small way to this chaotic organism. Each group member feels the ebbs and flows of every other; nobody works in a vacuum. So, to all members of the group, thank you for creating an environment that is hard working and professional, while being fun and supportive. Thank you for keeping the instrumentation running, and the solvents stocked, and the advice, large and small, that pointed me and so many others in the right direction along our ways.

Naturally, some members had more significant impacts on my time here than others. First to mind are Dan Caspi, Mike Krout, and J. T. Mohr, who inculcated me with the importance of being a team player in the group. Those three really defined what being a group member and eventually, group leader really meant. Likewise, Dave Ebner and Uttam Tambar, talented chemists both, were crucial in getting the aryne projects off of the ground, for which I am forever thankful. Mike Meyer was the prototypical baymate for me, and definitely helped me appreciate the value of hard work and good partnership.

Also in the isolated lab of 364 Crellin with Meyer and I were Carolyn Woodroofe, Jeff Servesko, Amanda Jones, Andy McClory, and Doug Behenna. Amanda and her husband John have become good friends, and were excellent poker hosts. Will will not be repeating Risk night, however. Doug, the prodigal grad student, could not have timed his 2 year return to the group any better. As the group grew to truly gargantuan proportions (topping out at 33, I believe), it was Doug that held us together. Always willing to help with a good piece of advice or a well-timed punchline, Doug's coming departure will leave a void that will be dearly missed.

Andy McClory is simply one of the most intelligent, endearing people I've ever met, and became one of my closest friends, even if he is Canadian. He has an encyclopædic chemical knowledge that I plumb every day. He was one of a few bright spots during some of the toughest times I've had in graduate school.

Since moving to Schlinger, I've seen the night and day difference between an open and closed lab environment. I've come to revel in the tight space and chaotic environment of our new labs, an experience that is largely made tolerable by the people around me. Allen Hong, Nathan Bennett, Max Loewinger, and Nat Sherden have been a mixture of entertaining and helpful in making the lab more fun. In the adjacent space, Alex Goldberg, Kristy Tran, Corey Reeves, Doug Duquette, Chung-Whan Lee, and Doug Behenna (again!) have been invaluable in keeping an upbeat, relaxed, if loud and chaotic, vibe going, replete with jokes, debates, and music of all varieties (good and bad).

My one and only hoodmate, Florian Vogt, made working the long hours a fantastic, musical, and cross-cultural experience. Mein Deutsche tolerated 2 straight weeks of questions about WW2 Germany, and then became a great friend. He is a willing, patient font of technical knowledge, but he has a rare empathy that made working

2 feet away from me for 15 hours a day tolerable. Our long-time neighbor, Chris Henry, is tremendously selfless. Our conversations (not pertaining to Duke-UNC) were mutually beneficial in many ways, but I will forever remember Chris as a kind, quiet voice of reason in times of heated exchange.

It's been incredible to see Rob Craig, Corey Reeves, Jeff Holder and Christopher Haley mature into the bright future leaders of the group. I leave them with heavy hearts, but the knowledge that their contributions will keep the Stoltz lab competitive in the coming years. Russell Smith, he of the intense drive to perform, is one of the most gold-hearted people I've ever met, and brought with him into the lab both high expectations and a pedagogical enthusiasm that was contagious. Our Great Dane, Thomas Jensen, loved the group so much as a visiting graduate student, he came back for a post-doc. Along the way, it's been tremendously rewarding to bond with some quiet, intense members of the group, whose hard work often goes on quietly, and whose quiet resolve is a wonder to behold in the pressure-cooker of graduate school. Among those are Hideki Shimizu, John Enquist, Josh Day, Phil Wu, John Phillips, Grant Shibuya and Ryan McFadden, all of whom have moved on to succeed at bigger things. Kathrin Hoeferl-Prantz and Kim Petersen were both critical and supportive, shepherding me along in my growth as a labmate and a person as well.

The spouses club—Kami Hoeferl, Lindsay Smith, John Eilbes, Megan McClory—over the course of years did the little things that made me feel at home away from home, and let 'couples' night' work.

Kevin Allan, more than anyone else, has dealt with my strengths and weaknesses as a coworker and a friend, taking them all in stride through the highs and the lows of our collaborations. There were times when Kevin and I fed into each other and made a simple project something great. There were times when Kevin strapped me to his back and carried me to the end of a project. He's an inspiration, and someone whose talent and capacity for learning seem completely without limit. I can never repay him for his contributions, patience, and generosity.

Beyond the Stoltz lab, I have benefitted from completely undeserved acts of generosity from so many people in the greater Los Angeles area and beyond. Kathe Marshall, her brother Greg Bonann, and his partner Tai Collins, all offered me a family

away from mine, and later a respite from the stresses of grad school in a beautiful Malibu getaway. Paul Clark and Kelly (Dusinberre) Matzen were friends and patient roommates, and I'm excited to be joining Paul at Dow in the coming weeks. In the Reisman lab across the hall, have been good friends, and seeing Roger Nani, Lindsay Repka and Jay Codelli grow with the group has been a tremendous pleasure for me. Throughout the department, I owe many thanks to Chris and Kristina Daeffler, Paul and Stephanie Oblad, Ted Weintrob, Ian Tonks, and, the MVP of my closing-the-books stretch run, Shannon Stone. And my college buddies, most notably Chip Bell, Pete Mazzone, MichaelAaron Flicker, Ross Ericson and Dr. Jacob Soumerai, have been tremendously diligent in keeping up with me, and amazingly supportive when they do. One of my very best friends, Dr. Rebekka Klausen, has been instrumental in my transition from pharma-oriented chemist to someone about to enter into the world of electronic materials, and has been the non-pareil for support from a distance.

From afar, my aunt Lynne, her husband John Casey, and my uncle George Fredericks have supported me constantly. George has reminded me of how awesome it is to go to school in a place where you can literally trip over Nobel Laureates. Karen, Tony, and Vicky Tadross have surprisingly approved of me over the last 7 years, and have let me marry Pam. I couldn't think of a better family to join, and cannot thank them enough for welcoming me into theirs.

Zach Marshall, known to many as 'Malibu Zach' embodies to me what the Caltech experience should be. Ironically, as a high energy particle physicist, he only spent a year here. But, even from Geneva, Zach's centeredness was a point of gravity for me through my duration in Pasadena. Perhaps, with one exception, he is the closest friend I've made at Caltech. The graduate experience would be worth it for that alone.

In August 2009, my family moved to Pasadena, right as the Station Fire overtook the San Gabriels. This led to no shortage of grumbles as the smoke filled the new house. Omens aside, I couldn't have thought of a better way to grow closer to my parents, and my sister. Seeing them weekly (and now daily) has been a reminder of how lucky I am to have my family. When I left for college, my sister was 8 years old; now, she is a beautiful young woman, venturing forth on her own adventure. Had they not moved, I would have forever had that image of 8 year old Ellen in my head, so the timing was

priceless. During the move, my brother spent a month out here with me, and in addition to proving that he was the smarter Gilmore brother by getting into Duke Med School on scholarship, he's become one of my best friends, and certainly my best man—someone of whom I am proud to call my brother, and lucky to think of as my equal. My mother, one of the smartest people I know, has been a model for so much of what I look for in my own life. And my father, wise enough to marry the smartest woman he knew, is a mold for who I strive to become more like, personally and professionally. Without their insistence that I do things that challenge me, I would never have crossed the threshhold into Caltech. And without them, I don't know if I could be writing these words right now, leaving a school that I love. So, Mom and Dad, this is all because of you both, and thank you for every day I've had with you since you bought the money pit.

Finally, there's Pam. So many things have been said to describe her, but even after growing to know her better than anyone else over the last 6 years, 5 months, and 16 days, words simply cannot capture everything she is. Quite literally, I would not have made it through graduate school without her love, her forgiveness, her kindness, intelligence, selflessness, anxiety, humor, support, loyalty, ambition, perfectionism, patience, and generosity. She is one of the most creative people I have met, and one of the most beautiful people who has graced my life with their presence. Her warmth of spirit has touched so many people, but nobody more than me. Writing this now, I consider myself to be the luckiest man on the face of the earth to have met her, to have been loved by her, and to have loved her back. I guess it's a good thing we're getting married.

Caltech is an amazing place. If you're a second year, bored, with nothing to do, browsing through old theses, asking 'why am I doing this?' the answer doesn't come at the end. The journey itself is the answer. If your experience is $1/10^{th}$ as good as mine was, you will emerge from your time here a smarter, more generous, more enlightened, more fulfilled person, with tried and true friendships that will last a lifetime. If your experience is as good as mine, you'll be leaving Pasadena with a heavy heart, hoping that someday you can come back and relive what was, without question, the intellectual and personal experience of a lifetime.

– Chris Gilmore, March 14, 2012

ABSTRACT

The last decade has seen an outgrowth in the development of synthetic methodologies exploiting benzyne. The unique ability of this reactive intermediate to directly furnish *ortho*-difuntionalized aromatic systems first stoked interest in this research group as a possible partner in asymmetric arylation reactions. Since our initial forays, we have expanded our synthetic strategies to include bond insertions, cycloadditions, condensations, and multicomponent reactions.

The first project discussed in this volume is the development of an aryne annulation strategy for constructing common, synthetically useful heterocyclic structures in a convergent manner. We have developed a convergent approach to indoles and indolines. Likewise, through an orthogonal functional group intallation upon an enamine substrate, isoquinolines, quinolines, and isoquinolones can all be accessed as well. In this manner, we have been able to generate an array of functionalized heterocycles, including some that are prohibited by traditional means of synthesis. We have also begun to understand some of the reactivity trends in this context for the elusive aryne reaction partner.

The development of the aryne annulation strategy for the synthesis of isoquinolines directly led to the shortest reported total synthesis of the opiate alkaloid papaverine, and the tetrahydroisoquinoline anticancer antibiotic quinocarcin. Our more recent, ongoing efforts toward the synthesis of the bis-tetrahydroisoquinoline antitumor molecule jorumycin and its many structural relatives are detailed herein. Jorumycin has been targeted through a combination of aryne annulation and acyl-alkylation/condensation methodologies aimed at the synthesis of a functionalized bis-isoquinoline intermediate. Reduction of this key bis-isoquinoline to a bis-tetrahydroisoquinoline and subsequent lactamization will provide the pentacyclic core of jorumycin and related natural products in only three steps from simple isoquinoline building blocks.

The final project described is the development of several different aryne multicomponent reactions to form novel carbo- and heterocyclic scaffolds, including iminoisobenzfurans, iminoindenones, dibenzoketocaprolactams, and 2-quinolones.

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LIST OF ABBREVIATIONS

A	adenine
$[\alpha]_D$	angle of optical rotation of plane-polarized light
Å	angstrom(s)
p-ABSA	*para*-acetamidobenzenesulfonyl azide
Ac	acetyl
AIBN	azobisisobutyronitrile
APCI	atmospheric pressure chemical ionization
app	apparent
aq	aqueous
Ar	aryl group
At	benztriazolyl
atm	atmosphere(s)
BHT	2,6-di-*tert*-butyl-4-methylphenol ("butylated hydroxytoluene")
BINAP	(1,1'-binaphthalene-2,2'-diyl)bis(diphenylphosphine)
Bn	benzyl
Boc	*tert*-butoxycarbonyl
bp	boiling point
br	broad
Bu	butyl
i-Bu	*iso*-butyl
n-Bu	butyl or *norm*-butyl
t-Bu	*tert*-butyl

Bz	benzoyl
C	cytosine
c	concentration of sample for measurement of optical rotation
^{13}C	carbon-13 isotope
^{14}C	carbon-14 isotope
/C	supported on activated carbon charcoal
°C	degrees Celcius
calc'd	calculated
CAN	ceric ammonium nitrate
Cbz	benzyloxycarbonyl
CCDC	Cambridge Crystallographic Data Centre
CDI	1,1'-carbonyldiimidazole
cf.	consult or compare to (Latin: *confer*)
cm^{-1}	wavenumber(s)
cod	1,5-cyclooctadiene
comp	complex
conc.	concentrated
Cy	cyclohexyl
CSA	camphor sulfonic acid
d	doublet
d	dextrorotatory
D	deuterium
DABCO	1,4-diazabicyclo[2.2.2]octane

dba	dibenzylideneacetone
DBDMH	*N*,*N*'-dibromo-5,5-dimethylhydantoin
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	dicyclohexyl carbodiimide
DCE	1,2-dichloroethane
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
de	diastereomeric excess
DIAD	diisopropyl azodicarboxylate
DIBAL	diisobutyl aluminum hydride
DMA	dimethylacetamide
DMAD	dimethyl acetylenedicarboxylate
DMAP	4-dimethylaminopyridine
DME	1,2-dimethoxyethane
DMF	*N*,*N*-dimethylformamide
DMSO	dimethylsulfoxide
DMTS	dimethylthexylsilyl
DNA	deoxyribonucleic acid
DPPA	diphenylphosphorylazide
dppp	1,3-bis(diphenylphosphino)propane
dr	diastereomeric ratio
DTT	dithiothreitol
ee	enantiomeric excess
E	methyl carboxylate (CO_2CH_3)

E^+	electrophile
E	trans (entgegen) olefin geometry
EC_{50}	median effective concentration (50%)
EDCI	*N*-(3-Dimethylaminopropyl)-*N*-2-ethylcarbodiimide hydrochloride
e.g.	for example (Latin: *exempli gratia*)
EI	electron impact
eq	equation
ESI	electrospray ionization
Et	ethyl
et al.	and others (Latin: *et alii*)
FAB	fast atom bombardment
Fmoc	fluorenylmethyloxycarbonyl
g	gram(s)
G	guanine
h	hour(s)
^1H	proton
^2H	deuterium
^3H	tritium
[H]	reduction
HATU	2-(7-aza-1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate
HMDS	hexamethyldisilamide or hexamethyldisilazide
HMPT	hexamethylphosphoramide
$h\nu$	light

HPLC	high performance liquid chromatography
HRMS	high resolution mass spectrometry
Hz	hertz
IBX	2-iodoxybenzoic acid
IC_{50}	half maximal inhibitory concentration (50%)
i.e.	that is (Latin: *id est*)
iNOS	human-inducible nitric oxide synthase
IR	infrared spectroscopy
J	coupling constant
k	rate constant
kcal	kilocalorie(s)
kg	kilogram(s)
KHMDS	potassium bis(trimethylsilyl)amide
L	liter or neutral ligand
l	levorotatory
LA	Lewis acid
LD_{50}	median lethal dose (50%)
LDA	lithium diisopropylamide
LHMDS	lithium bis(trimethylsilyl)amide
LICA	lithium isopropylcyclohexylamide
LTMP	lithium 2,2,6,6-tetramethylpiperidide
m	multiplet or meter(s)
M	molar or molecular ion

m	meta
μ	micro
m-CPBA	*meta*-chloroperbenzoic acid
Me	methyl
mg	milligram(s)
MHz	megahertz
MIC	minimum inhibitory concentration
min	minute(s)
mL	milliliter(s)
MM	mixed method
mol	mole(s)
MOM	methoxymethyl
mp	melting point
Ms	methanesulfonyl (mesyl)
MS	molecular seives
m/*z*	mass-to-charge ratio
N	normal or molar
NBS	*N*-bromosuccinimide
nm	nanometer(s)
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
NOESY	nuclear Overhauser enhancement spectroscopy
Nu^-	nucleophile

o	ortho
[O]	oxidation
t-Oct	*tert*-octyl (1,1,3,3-tetramethylbutyl)
p	para
PCC	pyridinium chlorochromate
PDC	pyridinium dichromate
Ph	phenyl
pH	hydrogen ion concentration in aqueous solution
Piv	pivalate
pK_a	acid dissociation constant
PKS	polyketide synthase
PMB	*para*-methoxybenzyl
ppm	parts per million
PPTS	pyridinium *para*-toluenesulfonate
Pr	propyl
i-Pr	isopropyl
n-Pr	propyl or *norm*-propyl
psi	pounds per square inch
py	pyridine
q	quartet
R	alkyl group
R	rectus
RCM	ring-closing metathesis

REDAL	sodium bis(2-methoxyethoxy)aluminum hydride
ref	reference
R_f	retention factor
RNA	ribonucleic acid
s	singlet or seconds
s	selectivity factor = $k_{rel(fast/slow)} = \ln[(1 - C)(1 - ee)]/\ln[(1 - C)(1 + ee)]$, where C = conversion
S	sinister
sat.	saturated
SEM	2-(trimethylsilyl)ethoxymethyl
SOD	superoxide dismutase
Su	succinimide
t	triplet
T	thymine
TBAF	tetra-*n*-butylammonium fluoride
TBAT	tetra-*n*-butylammonium difluorotriphenylsilicate
TBDPS	*tert*-butyldiphenylsilyl
TBHP	*tert*-butyl hydroperoxide
TBS	*tert*-butyldimethylsilyl
TCA	trichloroacetic acid
temp	temperature
TES	triethylsilyl
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid

TFAA	trifluoroacetic anhydride
TFE	2,2,2-trifluoroethanol
THF	tetrahydrofuran
THIQ	tetrahydroisoquinoline
TIPS	triisopropylsilyl
TLC	thin layer chromatography
TMEDA	*N*,*N*,*N*',*N*'-tetramethylethylenediamine
TMP	2,2,6,6-tetramethylpiperidine
TMS	trimethylsilyl
TOF	time-of-flight
tol	tolyl
Tr	triphenylmethane (trityl)
Troc	2,2,2-trichloroethoxycarbonyl
Ts	*para*-toluenesulfonyl (tosyl)
UV	ultraviolet
w/v	weight per volume
v/v	volume per volume
X	anionic ligand or halide
Z	cis (zusammen) olefin geometry