Synthesis of Tetrapetalone A-Me Aglycon

by

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To my wife and family for all their love and support

Biographical Sketch

The author was born in Taipei, Taiwan in 1987. He lived in Southeast Asia for 10 years before moving to the U.S. He attended Duke University in Durham, N. C. from 2005 to 2009, and graduated with a Bachelor of Science in Chemistry with Distinction. He began doctoral studies at the University of Rochester in 2009. He was awarded Sherman Clarke Fellowships in 2009, 2010, and 2011, an NSF Graduate Research Fellowship Honorable Mention in 2011, a Robert and Marian Flaherty DeRight Fellowship in 2012, and an Elon Huntington Hooker Fellowship in 2013. He has tutored financially disadvantaged, first-generation college, and underrepresented minority students in organic chemistry through the David T. Kearns Center at the University of Rochester since 2012. He pursued his research in synthetic organic chemistry under the direction of Professor Alison J. Frontier. After receiving his doctoral degree from the University of Rochester, the author will pursue his postdoctoral studies at Harvard University under the direction of Professor Andrew G. Myers.

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Abstract

The work presented here is a detailed account of the strategies used toward the first synthesis of tetrapetalone A-Me aglycon, a derivative of the natural product tetrapetalone A. Chapter 1 describes the isolation, biological activity, and derivatization studies on tetrapetalone A by Hirota and co-workers, as well the numerous synthetic approaches from the research groups of Porco, Hong, Sarpong, Pettus, and Frontier. Chapter 2 describes the use of Nazarov cyclization to form the AB ring system as well as the use of Buchwald-Hartwig coupling to form the key aryl C-N bond. Chapter 3 describes the use of ring-closing metathesis to form the ABC ring system. Chapter 4 describes the installation of the tetramic acid D ring *via* a conjugate reduction/intramolecular aldol cascade as well as the installation of the C15-O bond through oxidative dearomatization. The completion of the synthesis is also described. Chapter 5 describes the remaining studies toward the enantioselective total synthesis of tetrapetalone A, namely the installation of the β -D-rhodinose moiety as well as the development of an asymmetric Nazarov cyclization protocol.

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List of Symbols and Abbreviations

+	rotates plane-polarized light clockwise
–	rotates plane-polarized light counterclockwise
±	rotates plane-polarized light clockwise and counterclockwise equally
2D	two-dimensional
Å	angstrom
°C	degrees Celsius
[O]	oxidation
α	alpha
β	beta
δ	delta
μL	microliter
μM	micromolar
Ac	acetate
Acac	acetylacetate

Ad	adamantyl
Ag	silver
AHBA	3-amino-5-hydroxybenzoic acid
Al	aluminum
Ar	aromatic moiety
ATR	attenuated total reflectance
B	boron
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
Boc	<i>tert</i> -butoxycarbonyl
Bn	benzyl
Br	bromine
br	broad
Brsm	based on recovered starting material
BSA	benzene selenenic anhydride
Bu	butyl
Bz	benzoyl

C	carbon
cap	caprolactamate
cat.	catalytic
Cd	cadmium
Cl	chlorine
COD	1,5-cyclooctadiene
Cu	copper
Cy	cyclohexane
COSY	correlation spectroscopy
CSA	camphorsulfonic acid
<i>d</i>	deutero-
d	doublet
D	dexter
dd	doublet of doublets
dq	doublet of quartets
DABCO	1,4-diazabicyclo[2.2.2]octane

Davephos

Dba

dibenzylideneacetone

DCC

N,N'-dicyclohexylcarbodiimide

DCE

dichloroethane

DEPT

distortionless enhancement by polarization

Transfer

DIAD

diisopropyl azodicarboxylate

DIBAL

diisobutylaluminum hydride

DIPEA

diisopropylethylamine

DMAP

4-dimethylaminopyridine

DMF

dimethylformamide

DMI

dimethylimidazole

DMP

Dess-Martin periodinane

DMSO

dimethylsulfoxide

dr

diastereomeric ratio

DTBBP

di(*tert*-butyl)-2-biphenylphospined^tbpy4,4'-di-*tert*-butyl-2,2'-dipyridyl

E

entgegen

EDC

1-Ethyl-3-(3-

dimethylaminopropyl)carbodiimide

eq

equivalents

ESI

electrospray ionization

Et

ethyl

F

fluorine

Fe

iron

FTIR

Fourier transform infrared spectroscopy

g

grams

Grubbs 2nd generation catalyst

Grubbs II

Grubbs 2nd generation catalyst

H

hydrogen

h	hour
h ν	photonic energy
HFIP	hexafluoroisopropanol
Hg	mercury
HLO	human lipoxygenase
HOBT	1-hydroxybenzotriazole
HMBC	heteronuclear multiple-bond correlation spectroscopy
HMPA	hexamethylphosphoramide
HRFAB MS	high resolution fast-atom bombardment mass spectroscopy
HRMS	high resolution mass spectroscopy
HSQC	heteronuclear single-quantum correlation spectroscopy
Hz	hertz
I	iodine
IBX	2-iodoxybenzoic acid

IC ₅₀	half maximal inhibitory concentration
Imid	imidazole
In	indium
INADEQUATE	incredible natural-abundance double- quantum transfer experiment
iPr	isopropyl
IR	infrared
<i>J</i>	coupling constant
Jones reagent	a solution of chromium trioxide in dilute sulfuric acid and acetone
K	potassium
KHMDS	potassium hexamethyldisilazide
L	liter
LA	Lewis acid
LAH	lithium aluminum hydride
LDA	lithium diisopropylamide

LHMDS	lithium hexamethyldisilazide
Li	lithium
LTA	lead tetraacetate
LTBH	lithium triethylborohydride
M	molarity
m	multiplet/medium
M/z	mass-to-charge ratio
mM	millimolarity
mmol	millimoles
MAP	monoaryloxide pyrrolide
<i>m</i> -CPBA	<i>meta</i> -chlorobenzoic acid
Me	methyl
Mes	mesityl
Mg	magnesium
mg	milligram
MHz	megahertz

min	minute
mL	milliliter
Mn	manganese
Mo	molybdenum
mol	moles
MOM	methoxymethyl
MS	molecular sieves
N	nitrogen
<i>n</i>	normal
Na	sodium
Nap	naphthoate
NBS	N-bromosuccinimide
NDGA	nordihydroguaiaretic acid
Ni	Nickel
NMO	N-methylmorpholine N-oxide
NMR	nuclear magnetic resonance

NOE	nuclear Overhauser effect
NOESY	nuclear Overhauser effect spectroscopy
O	oxygen
ORTEP	Oak Ridge Thermal Ellipsoid Plot
<i>o</i> -Tol	<i>ortho</i> -tolyl
Oxone	potassium peroxymonosulfate
<i>p</i>	para
Pb	lead
Pd	palladium
PDC	pyridinium dichromate
Ph	phenyl
PIDA	phenyliodonium diacetate
PIFA	phenyliodine bis(trifluoroacetate)
Pin	pinacolato
PPA	polyphosphoric acid
ppm	parts per million

PMP	<i>para</i> -methoxyphenyl
Pyr	pyridine
q	quartet
<i>R</i>	rectus
R	undefined functional group
RCM	ring-closing metathesis
<i>rac</i>	racemic
Red-Al	sodium bis(2-methoxyethoxy)aluminum hydride solution
Rh	rhodium
ROM	ring-opening metathesis
rt	room temperature
Ru	ruthenium
S	sulfur
<i>S</i>	sinister
s	singlet/strong

sat	saturated
Sc	scandium
Si	silicon
SLO	soybean lipoxygenase
Sm	samarium
Sn	tin
<i>t</i>	tertiary
t	triplet
TBAF	tetrabutylammonium fluoride
TBHP	<i>tert</i> -butyl hydroperoxide
TBS	<i>tert</i> -butyldimethylsilyl
Tc	thiophenecarboxylate
<i>tert</i>	tertiary
TES	triethylsilyl
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid

TFAA	trifluoroacetic anhydride
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin-layer chromatography
TMS	trimethylsilyl
TPAP	tetrapropylammonium perruthenate
Ts	<i>para</i> -toluenesulfonyl
UV	ultraviolet
V	vanadium
w	weak

Weitz's triarylammonium salt

Wilkinson's catalyst

Xantphos

Z

zusammen

Zn

Zinc

Chapter 1. Introduction

1.1. Isolation, Biological Activity, and Structural Determination

In 2003, Hirota and co-workers discovered that a strain of *Streptomyces* bacteria found in the soil of Japan could inhibit soybean lipoxygenase (SLO).¹ The SLO inhibitor was isolated from a culture broth and designated tetrapetalone A (**1**, Figure 1.1). The moderate inhibitory activity of Tetrapetalone A ($IC_{50} = 190 \mu M$) is comparable to known SLO inhibitors kojic acid ($IC_{50} = 110 \mu M$) and nordihydroguaiaretic acid (NDGA) ($IC_{50} = 290 \mu M$).² Human lipoxygenase (HLO) catalyzes the first step in the arachidonic acid pathway, and the resultant leukotrienes, lipoxins, and prostaglandins have been implicated in many diseases.³ Since the catalytic domain of plant and mammalian lipoxygenases is highly conserved,⁴ the study of an SLO inhibitor like tetrapetalone A could lead to the identification of new HLO inhibitors.

Figure 1.1. Initial Proposed Structure of Tetrapetalone A

The structural elucidation of **1** began with HRFAB MS data giving a molecular formula of $C_{26}H_{33}O_7N$.¹ IR spectroscopy revealed the presence of ketone and hydroxyl

groups. The ^1H NMR, ^{13}C NMR, and DEPT spectra, in addition to ^1H - ^1H COSY, HSQC, and HMBC data, revealed partial structure **2** (Figure 1.2). 2D-INADEQUATE data revealed two additional fragments, which, when combined with **2**, led to partial structure **3**. Methylation of the vinologous carbamic acid of **1** with CH_2N_2 gave tetrapetalone A-Me (**4**, Figure 1.3), and analysis of this material's HMBC spectrum revealed an OH group connected to C3. Two new signals were observed in the ^1H NMR spectrum of **1** using $\text{DMSO-}d_6$; these were assigned as an amide proton and a hydroxyl proton. ^1H - ^1H COSY and HMBC spectra suggested that C4' is connected to the hydroxyl group and C15 to the amide. C1 is also connected to the amide to close the ring. Based on the ^{13}C NMR spectrum and the molecular formula, C15 and C4 are connected *via* an oxygen atom.

Figure 1.2. Partial Structures Derived from Spectroscopic Analysis

Figure 1.3. Initial Proposed Structure of Tetrapetalone A-Me

The spectral data corresponding to the 2-methyltetrahydropyran ring is consistent with β -rhodinosose.¹ Treatment of **4** with Mosher's acid chloride revealed the absolute stereochemistry of C4' to be *R*, and the remaining stereochemistry in the ring was determined relative to this stereocenter. Furthermore, acid hydrolysis of **4** produced tetrapetalone A-Me aglycon (**5**, Figure 1.4). This revealed a hydroxyl group at C9, which, when added to Mosher's acid chloride, revealed the absolute stereochemistry of C9 as *S*. The remaining stereochemistry was determined relative to C9, with the exception of C4 and C15, which were left undetermined.

Figure 1.4. Initial Proposed Structure of Tetrapetalone A-Me Aglycon

Further investigation into the stereochemistry at C4 and C15 using ^1H - ^{15}N HMBC led to a revision of the structure of tetrapetalone A (**6**, Figure 1.5).⁵ Key to this revision was the realization that the amide proton in the DMSO- d_6 ^1H NMR spectrum was actually from a hydroxyl group at C15. Compound **6** was then methylated with $\text{CH}_3\text{I}/\text{Ag}_2\text{O}$ at C2 and C15-OH; analysis of the NOESY spectrum of this material along with knowledge of the absolute stereochemistry of C9 led to the assignment of all the remaining stereocenters of **6**. Hirota shortly thereafter reported the isolation and characterization of tetrapetalones B (**7**), C (**8**), and D (**9**), which also exhibit inhibitory activity toward SLO (Figure 1.5, Table 1.1).² The structures of tetrapetalone A-Me (**10**) and tetrapetalone A-Me aglycon (**11**) were also revised.⁶ The low inhibitory activity of **10** revealed that the tetramic acid moiety plays a crucial role in inhibiting SLO.⁶

Figure 1.5. Revised Structures of Tetrapetalones A, B, C, D, Tetrapetalone A-Me and Tetrapetalone A-Me aglycon

Table 1.1. Inhibitory Activity of Compounds **6-10** against SLO

Entry	Compound	IC ₅₀ (μM)
1	6	190-460
2	7	320
3	8	360
4	9	340
5	10	>1000
6	Kojic acid (positive control)	110-280
7	NDGA (positive control)	190-290

Hirota also conducted a study on the biosynthesis of tetrapetalones in 2007.⁷ *Streptomyces* were fed ¹³C-enriched sodium propanoate, sodium butanoate, glucose, and 3-amino-5-hydroxybenzoic acid (AHBA). ¹³C-NMR analysis indicated that **6** is constructed from three molecules of propanoate, one molecule of butanoate, one molecule of AHBA, and one molecule of glucose. Furthermore, the authors inferred that

7, **8**, and **9** are derived from **6**; **6** can be oxidized to form **8**, or it can be hydroxylated at C17 and then acetoxylation to form **7**. Compound **7** can be oxidized similarly to form **9** (Scheme 1.1).

Scheme 1.1. Proposed Biosynthesis of the Tetrapetalones

1.2. Prior Synthetic Approaches to Tetrapetalone A

The tetrapetalone natural products possess a β -D-rhodinose moiety connected to a uniquely complex tetracyclic core. Key features of this core include a *para*-quinol A ring, a five-membered B ring containing four contiguous stereocenters, a 7-membered C ring containing a bridging trisubstituted olefin, and a tetramic acid D ring. To date, a total synthesis of tetrapetalone A has not been reported, though several laboratories have published synthetic approaches.

In 2005, Porco and co-workers reported an approach toward the synthesis of the core of tetrapetalone A.^{8a} They hypothesized that the tetrapetalones derive from the

macrocyclic ansamycins (**10**, Figure 1.6) due to structural similarities between the two compounds, and the retrosynthetic analysis reflected this biomimetic approach (Scheme 1.2). Hence, **6** would be produced by a formal [4+3] transannular cyclization of intermediate **11**. This carbocation would be generated from oxidation of hydroquinone **12**.⁹ **12** would be derived by ring-closing metathesis (RCM)¹⁰ on compound **13**, and **13** would be derived from condensation of acid **14** and aniline **15**.

Figure 1.6. Core of the Ansamycins

Scheme 1.2. Porco Group's Retrosynthetic Analysis of Tetrapetalone A

The forward synthesis proceeded smoothly until the RCM step.^{8a} Compound **13** was found to be unreactive under typical conditions. The lack of metathesis was attributed to the prohibitively large distance spanned by the two olefinic appendages when in a *meta* relationship. Thus, a revised retrosynthetic analysis was envisaged in which the RCM step would be conducted on olefinic appendages in an *ortho* relationship, followed by an acyl transfer to yield macrocycle **16** (Scheme 1.3).

Scheme 1.3. Porco Group's Revised Retrosynthetic Analysis

From here, the forward synthesis proceeded without incident, and the key [4+3] transannular oxidative cyclization appeared to be successful, producing the tetracyclic carbon skeleton of **6** (Scheme 1.4).^{8a} A later correction, however, revealed that the cyclization product was incorrectly assigned; the revised compound, **22**, was simply the product of oxidation to the quinone (Figure 1.7).^{8b}

HC C OTBS

Q. OTBS

Scheme 1.5. Hong Group's Key Iminium Ion Cyclization **Scheme 1.6.** Hong Group's Synthesis of the Tetracyclic Core of Tetrapetalone A

In 2010, Sarpong and co-workers reported an approach toward the tetracyclic core of the tetrapetalones.^{12a} They envisioned the formation of target compound **6** from late-stage oxidative dearomatization of **29**, which could be generated from pyrrole **30** using reductive alkylation (Scheme 1.7). This tetracycle could be synthesized from aryl dienone **31** using Nazarov cyclization.

Scheme 1.7. Sarpong Group's Retrosynthetic Analysis of Tetrapetalone A

The forward synthesis proceeded smoothly with the preparation of pyrrole **36** in multigram quantities (Scheme 1.8).^{12a} Key transformations include the Nazarov cyclization of aryl dienone **31** to form bicycle **34** with 13:1 regiocontrol and reduction of **34** followed by Paal-Knorr conditions to form pyrrole **36**. Notably, the authors misassigned the stereochemistry of the NaBH_4 reduction product of **34**.^{12b} Additionally, they were unable to successfully install the aryl C-N bond using transition metal catalysis.

Scheme 1.8. Sarpong Group's Synthesis of Intermediate **36**

The next major synthetic transformation was formation of the C ring. It was envisaged that an intramolecular Friedel-Crafts acylation would accomplish this; thus, hydroboration of olefin **36** gave alcohol **37**, which, upon Dess-Martin oxidation, unexpectedly produced tetracycle **40** (Scheme 1.9). The authors hypothesized that the initial product of oxidation was activated by residual hypervalent iodine or acetic acid and attacked by the pyrrole. The resultant secondary alcohol (**39**) was then oxidized further to yield tetracycle **40**.^{12a}

Scheme 1.9. Formation of Key Tetracycle **40** *via* Oxidation/Friedel-Crafts

Acylation/Oxidation Cascade

The next few steps in the synthesis involved the transformation of the pyrrole ring in **40** to the tetramic acid D ring present in **6** (Scheme 1.10).^{12a} The key step in this sequence involved the regioselective and diastereoselective alkylation of the pyrrole ring in compound **40** under dissolving metal conditions.

Scheme 1.10. Elaboration to Tetracycle **45**

In 2014, Pettus and co-workers reported an approach toward the tetracyclic core of the tetrapetalones that combined two methodologies developed in their group.¹³ First, they developed a method for the mild construction of 3-methyl tetramic acid derivatives which could be applied toward the D ring (Scheme 1.11).¹⁴ Second, they developed a method for the construction of substituted *meta*-amino phenols which could be applied toward the A ring (Scheme 1.12).¹³

Scheme 1.11. Pettus Group's Construction of 3-Methyl Tetramic Acids

Scheme 1.12. Pettus Group's Construction of Substituted *meta*-Amino Phenols

They took known compound **51** and acylated with 2-bromopropionyl bromide to yield amide **52** (Scheme 1.13).¹³ This material was subjected to the conditions for tetramic acid derivative construction developed in their group, then elaborated to tetramic acid derivative **54** after two successive alkylations. Tetramic acid **54** was then transformed to tetramic acid **55**, containing the desired protected *meta*-amino phenol.

Scheme 1.13. Synthesis of Tetramic Acid **55**

1.3. Preliminary Studies (Frontier Group)

The Frontier group has developed a methodology that can be used to synthesize substituted indanones: first, alkynoate **56** and nitron **57** are subjected to [3+2] cycloaddition followed by oxidative extrusion of nitrosomethane to yield aryl enone **59**;¹⁵ then, a Nazarov cyclization is used to generate the cyclopentanone ring in **60** under mild Lewis acidic conditions (Scheme 1.14).¹⁶ This bicyclic structure provides a convenient starting point toward the synthesis of **6** due to the close structural similarities between **60** and the AB ring system of **6**.

Scheme 1.14. Prior Methodology Developed in the Frontier Group for Indanone Synthesis

The first member of the Frontier group to work on the synthesis of **6** was Ildiko Herrick.¹⁷ Her retrosynthetic disconnections first involved RCM to form the C ring

(Scheme 1.15). The D ring would be introduced by a Buchwald-Hartwig coupling¹⁸ between aryl triflate **63** and tetramic acid **62**. The A and B rings would then be constructed from the methodology described above.

Scheme 1.15. Frontier Group's First Generation Retrosynthetic Analysis

For the forward synthesis, construction of the AB ring system proceeded without incident as shown in Scheme 1.14.¹⁷ Compound **60** was decarbalkoxylated, methylated, and finally subjected to global deprotection to yield diol **65** (Scheme 1.16).¹⁷ Monoprotection of **65** was regioselective due to the steric hindrance of the pendant cinnamyl group; triflation of the more hindered hydroxyl group resulted in aryl triflate **66**. At this point, both Buchwald-Hartwig amination with tetramic acid derivative **67** and transformation into bromide **69** were unsuccessful. A significant problem was base-

promoted cleavage of the triflate group, which prompted preparation of the corresponding aryl bromide for further cross-coupling studies.

Scheme 1.16. Initial Efforts Toward Pd-Catalyzed Cross-Coupling

Chao Jiang continued work on the forward synthesis and attempted to utilize an intramolecular Buchwald-Hartwig amination as a means of overcoming the apparent steric issues seen in previous attempts at cross-coupling (Scheme 1.17).¹⁹

Scheme 1.17. Tricycle Formation Using an Intramolecular Buchwald-Hartwig Amination

The hypothesis was that the inherent bond strain of cyclopropene **71** would enhance reactivity toward olefin metathesis.¹⁹ While the Steglich esterification of cyclopropene **71** with bicyclic phenol **76** was successful, the subsequent olefin metathesis step yielded only ring-opened products (Scheme 1.18). These results implied that the trisubstituted olefin in the cinnamyl group was too unreactive for RCM.

Scheme 1.18. Esterification and ROM/RCM Products from **77**

These preliminary studies showed that the AB ring system of tetrapetalone A could be accessed reliably using Nazarov cyclization. From there, a synthetic roadblock

was reached as several strategies toward C-N bond formation and C ring construction failed. It was at this juncture that I joined the project and initiated studies.

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Chapter 2. Synthesis of Aniline 116 (AB Ring System)

2.1. Synthesis of Aryl Bromide **91**

At the onset of my studies toward the synthesis of **6**, the most immediate challenge was to solve the problem of poor aryl C-N bond formation using Buchwald-Hartwig coupling. Exchange of the triflyl group with a bromide was thought to solve this problem, as the triflyl group seemed to decompose under the strongly basic reaction conditions (see Chapter 1). Thus, a synthetic route toward aryl bromide **91** was desired (Scheme 2.1), and this material would be subjected to the [3+2] cycloaddition/oxidative extrusion and Nazarov cyclization processes described in Chapter 1. It is worth noting that the inclusion of an electron-withdrawing aryl bromide would diminish reactivity in the Nazarov cyclization step.

Commercially available arene **88** was subjected to iridium-catalyzed C-H bond activation, borylation and oxidation to give phenol **89**.¹ TIPS protection and Sonogashira coupling of ethynyltrimethylsilane yielded alkyne **90**.² Next, removal of the TMS group proceeded cleanly to yield a terminal alkyne. This alkyne was deprotonated by butyllithium and alkylated with methyl chloroformate to give ynoate **91**, despite fears of competing lithium-halogen exchange.

Scheme 2.1. Synthesis of Aryl Bromide **91**

A second-generation route to **91** was devised, whereby coupling methyl propiolate directly to the aryl iodide reduced the number of steps (Scheme 2.2).³

Scheme 2.2. Second-Generation Synthesis of Aryl Bromide **91**

2.2. Synthesis of B Ring Using Nazarov Cyclization

In analogy to the procedures described in Chapter 1, aryl bromide **91** was cyclized with several nitrones, and the resulting adducts were treated with *m*-CPBA to furnish aryl dienones **94-97** (Scheme 2.3).⁴ Nitron **57** was chosen due to its simple synthesis and availability in the laboratory. If the vinyl phenyl group prevented the anticipated RCM on a steric basis, then a sterically smaller group, such as a methyl group, may be successful,

hence the use of nitrone **92** (synthesized from tiglic aldehyde). The TMS or TBS groups of nitrones **84** (previously synthesized by Chao Jiang; see Scheme 1.19) and **93** could be unmasked at a later stage to reveal a terminal olefin, which would likely enhance the facility of the anticipated RCM even more. The synthesis of nitrone **93** was carried out in a manner analogous to the synthesis of **84**.

Scheme 2.3. Synthesis of Indanones **101** and **102**

Several Lewis acids were screened in the Nazarov cyclization of aryl dienones **94-97** (Table 2.1). Catalytic Sc(OTf)₃ was unable to catalyze the transformation of **94** to **98** (Entry 1). The bromide moiety was thought to deactivate the A ring toward Nazarov cyclization. The use of Li(ClO₄) as a co-catalyst has been shown to enable “unreactive” Nazarov cyclizations,⁵ and its use resulted in the successful formation of **99** (Entry 2).

Table 2.1. Conditions Screened in the Nazarov Cyclization of **94-97**

Entry	Starting Material	Conditions	Product	Yield
1	94	cat. Sc(OTf) ₃ , DCE, 45 °C	No reaction	--
2	94	cat. Sc(OTf) ₃ /Li(ClO ₄), DCE, 45 °C	98	81%
3	95	cat. Cu(OTf) ₂ , DCE, 45 °C	Decomposition	--
4	95	AlCl ₃ , DCE, 0 °C	99	71%
5	96	cat. Sc(OTf) ₃ /Li(ClO ₄), DCE, 45 °C	Decomposition	--
6	96	cat. (TMS)NTf ₂ , DCE, 45 °C	Decomposition	--
7	96	AlCl ₃ , DCE, 0 °C	100	79%
8	96	Sc(OTf) ₃ , DCE, rt	100	46%
9	97	cat. Sc(OTf) ₃ /Li(ClO ₄), DCE, 45 °C	Decomposition	--
10	97	cat. Cu(OTf) ₂ /Li(ClO ₄), DCE, 45 °C	Decomposition	--
11	97	cat. Al(OTf) ₃ , DCE, 45 °C	Decomposition	--
12	97	cat. (TMS)NTf ₂ , DCE, 45 °C	Decomposition	--
13	97	AlCl ₃ , DCE, 0 °C	100	Not Determined

Nazarov cyclization on **95** using $\text{Cu}(\text{OTf})_2$ resulted in decomposition (Entry 3). The use of stoichiometric AlCl_3 ,⁶ however, was found to be successful (Entry 4). With **96**, the conditions used in Entry 2 resulted in decomposition (Entry 5). Furthermore, the use of $(\text{TMS})\text{NTf}_2$ ^[7] resulted in decomposition (Entry 6). The use of either stoichiometric AlCl_3 ^[6] or $\text{Sc}(\text{OTf})_3$ furnished indanone product **100** (Entries 7 and 8). Aryl dienone **96** underwent protodesilylation during the reaction, presumably due to trace acid in the reaction mixture.⁸ If the initial protodesilylation is the cause of decomposition in entries 5 and 6, then a bulkier vinyl silane, such as in **97**, may prevent decomposition. Unfortunately, the use of catalytic $\text{Sc}(\text{OTf})_3/\text{Li}(\text{ClO}_4)$, cat. $\text{Cu}(\text{OTf})_2/\text{Li}(\text{ClO}_4)$, cat. $\text{Al}(\text{OTf})_3$, and cat. $(\text{TMS})\text{NTf}_2$ all resulted in decomposition (Entries 9-12). Use of stoichiometric AlCl_3 resulted in desilylated cyclization product **100** (Entry 13). Thus, the bulkier TBS group did not appear to have an effect on desilylation. Decarbalkoxylation of **98** and **99** with DABCO⁹ proceeded smoothly to yield indanones **101** and **102**, respectively.

2.3. Aryl C-N Bond Formation Using Buchwald-Hartwig Coupling

Several test reactions exploring the Buchwald-Hartwig coupling of amines with **101** were conducted (Figure 2.1).¹⁰ Dimethylglycine methyl ester (**103**) was initially chosen as a coupling partner due to having a quaternary center analogous to the C4 quaternary center in **6**. The reaction between **101** and **103** did not give any cross-coupled products (Equation 1). It was believed that the strong base, sodium *tert*-butoxide, was reacting with the methyl ester, and not with the catalytic center. Unfortunately, a weaker

base, potassium phosphate, did not afford cross-coupled products (Equation 2). Only *tert*-butylamine (**105**) cross-coupled successfully, though in low yield (Equation 3). It was theorized that the steric hindrance of the *tert*-butyl group was the reason for the low yield. Hence, coupling of sterically less hindered benzophenone imine (**107**) was successful and subsequent hydrolysis furnished aniline **108** in modest overall yield (Equation 4).¹¹

Figure 2.1. Test Reactions on **101** Using Buchwald-Hartwig Cross-Coupling

The aniline nitrogen of **108** could be used as a handle for further synthesis toward **6**. The yield of **108** (27% over two steps) could also be improved, mainly by exploring

cross-coupling with ammonia, which is considerably less sterically hindered. Rather than exploring this reaction with indanone **104**, the B ring was first functionalized to have it more closely resemble **6**.

Methylation of **100** proceeded smoothly, though the phenolic oxygen was unexpectedly desilylated and methylated under the reaction conditions (Scheme 2.4). Decarboxylation under a variety of conditions (DABCO, LiOH, NaOH) failed, likely due to the steric congestion of the five-membered ring. Notably, the use of NaCN in HMPA provided the desired decarboxylated product, which was then isomerized with K₂CO₃ to give the thermodynamic *anti* product as the major isomer. Aryl bromide **110** was then subjected to the direct cross-coupling with ammonia under palladium catalysis to furnish aniline **112** in 37% yield.¹¹

Scheme 2.4. Synthesis of Aniline **112** *via* Palladium Catalyzed Cross-Coupling of Ammonia

The yield of the decarbalkoxylation or Buchwald-Hartwig coupling steps was unsatisfyingly low. Decarbalkoxylation prior to methylation was thought to be smoother, and that removal of the enolizable ketone would enhance the facility of the Buchwald-Hartwig coupling step.

Thus, **100** was decarbalkoxylated to furnish **113** (Scheme 2.5). Methylation of this material and subsequent reduction with NaBH₄ smoothly furnished alcohol **114** in 67% over two steps. Both of these steps were found to be completely diastereoselective; single-crystal x-ray crystallography confirmed that the alkylation and reduction steps both occurred on the diastereoface of the B ring *anti* to the isopropenyl group (Figure 2.2). Hence, the steric bulk of this isopropenyl group appeared to direct the stereoselectivity of the alkylation and reduction steps. This relative stereochemistry also matched the desired stereochemistry present in **6**. Protection of the secondary alcohol as a TBS group followed by Buchwald-Hartwig amination using the conditions described in Scheme 2.4 yielded aniline **116** in excellent yield.

Scheme 2.5. Synthesis of Aniline **116** *via* Palladium Catalyzed Cross-Coupling of Ammonia

Figure 2.2. ORTEP Diagram of **114**

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Chapter 3. Synthesis of Tetracycle 152a (ABC Ring System)

3.1. Synthesis of Ring-Closing Metathesis Precursors

With the aryl C-N bond constructed, the next goal was to construct the C ring through RCM. First, functionality off the aniline nitrogen would need to be built that could provide a handle toward this end (Scheme 3.1). This handle would have to include an olefin for the requisite RCM, in addition to a fully substituted carbon which would map onto C4 of **6**. This fully substituted carbon might make RCM difficult on steric basis; nevertheless, overcoming this potential obstacle would provide the most direct route to the C ring.

Scheme 3.1. General Synthetic Strategy for C Ring Construction

One strategy investigated was to convert the aniline nitrogen into an isocyanate and treat with a vinyl epoxide under palladium catalysis to form a 4-vinyl oxazolidinone. Seminal studies by Trost¹ provided excellent precedent for this type of transformation (Scheme 3.2).

Scheme 3.2. Synthesis of Oxazolidinone **119** *via* Pd-Catalyzed Cycloaddition of Isoprene Monoepoxide with Tosyl Isocyanates

As proof of concept, aniline **108** was treated with triphosgene, and the resultant isocyanate was immediately treated with commercially available isoprene monoepoxide under palladium catalysis to furnish oxazolidinone **120** as a 1.5:1 mixture of diastereomers (Scheme 3.3). The poor diastereomeric ratio despite the use of a chiral phosphine ligand was disconcerting, though RCM on this material would in theory form the desired 7-membered C ring.

Scheme 3.3. Synthesis of Oxazolidinone **120** *via* Pd-catalyzed cycloaddition of isoprene monoepoxide with **108**

The same strategy was applied to aniline **112** to furnish oxazolidinone **121** as a 1:1 mixture of diastereomers, which was expected since an achiral phosphine ligand was used (Scheme 3.4).

Scheme 3.4. Synthesis of Oxazolidinone **121** via Pd-catalyzed cycloaddition of isoprene monoepoxide with **112**

Since the previous two results had poor yields, alternate strategies were investigated. One strategy was to perform Buchwald-Hartwig coupling and oxazolidinone formation prior to the Nazarov cyclization step. The yields of the cycloaddition were thought to increase with less sterically hindered reactive sites. The high yield in the formation of aryl bromide **123** confirmed this hypothesis (Scheme 3.5). The Negishi coupling of methyl propiolate to **123** was unsuccessful, so the Sonogashira coupling protocol from Scheme 2.1 was used. Elaboration to aryl dienone **125** proceeded smoothly, but this material unfortunately decomposed on exposure to AlCl₃.

Scheme 3.5. Synthesis and Attempted Nazarov Cyclization on **125**

To address the poor diastereoselectivity seen in Scheme 3.3, the construction of a 4,4-divinyl oxazolidinone was explored, with the intention of controlling diastereoselectivity in the RCM step. Indeed, such a strategy was exploited by the Hoveyda group in their total synthesis of quebrachamine (**129**) (Scheme 3.6).²

Scheme 3.6. Key Stereoselective RCM in the Total Synthesis of Quebrachamine

Hence, vinyl epoxides **133** and **134** were envisioned. These materials would later undergo elimination to generate the desired divinyl functionality. Thus, alcohol **131** was

generated from known dibromide **130**,³ followed by directed epoxidation⁴ and tosylation/etherification to form epoxides **133/134** (Scheme 3.7). Cyclization of epoxides **133/134** with isocyanate **135** was not successful and unfortunately resulted in decomposition to the aniline.

Scheme 3.7. Synthesis of **133** and **134** and Attempted Cycloaddition with Isocyanate **135**

Another strategy considered was a two-step workaround for oxazolidinone formation rather than a single cycloaddition step. Berkowitz has reported a Ni-catalyzed intramolecular allylic amination reaction to form oxazolidinones (Scheme 3.8).⁵

Scheme 3.8. Ni-Catalyzed Intramolecular Allylic Amination of Carbamate **137**

Following this precedent, the isocyanate derived from **116** was trapped with allylic alcohol **139** to form carbamate **140** (Scheme 3.9). Then, this material was subjected to Pd⁰-catalyzed intramolecular allylic amination to furnish oxazolidinone **141**. Gratifyingly, the presence of a conjugated dienyl system in **140** did not result in the formation of undesired byproducts. This reaction could also be carried out without the addition of exogenous base.

Scheme 3.9. Synthesis of **138** via Pd-Catalyzed Intramolecular Allylic Amination

To synthesize alcohol **139**, known vinyl iodide **142**^{6,7} was subjected to Stille coupling with tributyl(vinyl)tin,⁸ followed by allylic carbonate installation and TBAF deprotection (Scheme 3.10).

Scheme 3.10. Synthesis of Alcohol 139

The construction of a lactam instead of an oxazolidinone was also investigated. This was done in case the transformation of the oxazolidinone into the desired tetramic acid seen in **6** failed. Additionally, the carbon skeleton of **6** would be set with the incorporation of a lactam and successful RCM. To this end, carboxylic acid **144** was synthesized using a route similar to the synthesis of alcohol **139** (Scheme 3.11). EDC coupling between aniline **116** and acid **144** proceeded to very low conversion, likely due to the poor nucleophilicity and steric congestion of the aniline nitrogen (Scheme 3.12). Nevertheless, enough material was acquired to perform the intramolecular allylic amination to form triene **146**. In contrast to the oxazolidinone formation (see Scheme 3.9), this reaction required the addition of exogenous base.

Scheme 3.11. Synthesis of Carboxylic Acid 144

Scheme 3.12. Synthesis of Triene **146** via Pd-Catalyzed Intramolecular Allylic Amination

One last set of experiments conducted prior to initiating RCM studies was to functionalize oxazolidinone **141** into a divinyl tetramic acid. RCM on such a substrate would be closer to the original retrosynthetic vision. Thus, ring-opening of the oxazolidinone under basic conditions was explored. First, the TIPS group was deprotected with TBAF(^tBuOH)₄^[9] and re-protected with a MOM group to form **147**. Then, this material was treated with sodium hydroxide to form amino alcohol **148** (Scheme 3.13). Both alcohols of **148** were protected as TBS ethers to furnish amine **149**. This amine was unfortunately inert to acylation, and hence the development of this route was halted.

Scheme 3.13. Synthesis of Amine **149** Toward Divinyl Tetramic Acid **150**

3.2. C Ring Construction Using Ring-Closing Metathesis

Oxazolidinone **121** was subjected to a 25% loading of Hoveyda-Grubbs' 2nd generation catalyst (**151**),¹⁰ and olefin metathesis was complete in 4h with 66% isolated yield of tetracycle **152** (Scheme 3.14). Since the existing stereocenters were not affected during the reaction, **152** was produced as a 1:1 mixture of diastereomers. This result provided good proof of concept on the utility of RCM in forming the ABC ring system.

Scheme 3.14. RCM on Triene **121** with **151** to Form Tetracycle **152**

RCM studies on oxazolidinone **141** and lactam **146** were performed with several commercially-available catalysts (Table 3.1). In contrast to the smooth RCM of substrate **121**, catalyst **151**, Grela's catalyst (**155**),¹¹ and Schrock's catalyst (**156**)¹² gave no reaction with **141** even at elevated temperatures (Entries 1-3). It was only with near-stoichiometric loading (90 mol %) of **151** that a 2.4:1 mixture of **153a**:**153b** was obtained in 58% yield (Entry 4). Similarly high catalyst loading with the Stewart-Grubbs catalyst¹³ (**157**) (80 mol%) was required for high conversion (Entry 5). No reaction occurred when **146** was treated with near-stoichiometric **151** or **155** (Entries 6 and 7). The subtle

Table 3.1. RCM on **141** and **146** with Commercially Available Catalysts

Entry	Substrate	Catalyst; mol%	Temp. (°C); time (h)	% Conversion; % Yield	Product Ratio (a:b)
1	141	151 ; 25%	80; 24	No reaction	--
2	141	 155 ; 25%	80; 24	No reaction	--
3	141	 156 ; 25%	80; 24	No reaction	--
4	141	151 ; 90%	85; 9	89; 58	2.4:1
5	141	 157 ; 80%	85; 9	89; 58	2.4:1
6	146	151 ; 90%	80; 24	No reaction	--
7	146	155 ; 90%	80; 24	No reaction	--

electronic differences in the structures of **146** and **141** (CH_2 vs. O) were enough to completely shut down the reaction.

Since the synthesis of tetracycle **153** required near-stoichiometric levels of **151** and provided the desired diastereomeric product in modest ratio (2.4:1), alternatives that could yield better results were explored. A collaboration with Prof. Amir Hoveyda of Boston College was initiated to see if his group could screen some of their Mo-based complexes similar to **128** to enable efficient and diastereoselective formation of the C ring. Several catalysts were screened by his student, Tyler Mann, with triene **141** (Table 3.2).¹⁵ While Mo-based bis-aryloxide **158**^[16] furnished ring-closed products in excellent conversion and yield with catalytic loading, the diastereoselectivity unfortunately favored the undesired diastereomer **153b** (Entry 1). Mo-based monoaryloxide pyrrolide (MAP)^{14a} complexes **159** and **160** both furnished ring-closed products in excellent conversion and yield with catalytic loading, favoring exclusively the desired diastereomer **153a** (Entries 2-5). Heating of the reaction helped improve the conversion and yield (Entries 3 and 5). Notably, the conditions in Entry 5 were replicated at the University of Rochester on gram scale. Slightly modified catalysts **161** and **162** gave diminished conversion and diastereoselectivity, respectively (Entries 6 and 7). It is interesting to note that slight modifications to the electronic properties of the Mo complexes can engender major differences in the outcome of the RCM reaction.

Table 3.2. RCM on 141 with Mo-Based Complexes

Entry	Catalyst; mol%	Temp. (°C); time (h)	% Conversion; % Yield	Product Ratio (153a:153b)
1	 158 ; 12.5%	22; 25	98; 90	1:3
2	 159 ; 25%	22; 25	50; not determined	>25:1
3	159 ; 25%	40; 25	63; 63	>25:1

4	; 25%	25; 25	58; not determined	>25:1
5	160 ; 25%	65; 20	83; 82	>25:1
6	; 25%	22; 25	28; Not determined	>25:1
7	; 25%	22; 25	49; 40	1:1

153a was derivatized to determine if it contained stereochemistry congruent with **6**. Thus, **153a** was chemoselectively hydrogenated with Wilkinson's catalyst¹⁸ to furnish tetracycle **163** (Scheme 3.15). The TIPS group was selectively and smoothly deprotected with TBAF to furnish phenol **164**. The structure of this material was confirmed by single-crystal X-ray crystallography and showed that **153a** contained the desired stereochemistry (Figure 3.1).

Scheme 3.15. Derivatization of **152a** to Phenol **164**

Figure 3.1. ORTEP Diagram of **164**

3.3. References

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Chapter 4. Synthesis of Tetrapetalone A-Me Aglycon (ABCD Ring System)

4.1. Transformation of Oxazolidinones into Tetramic Acids

The next major transformation was to install the tetramic acid D ring, which appeared to be fairly straightforward. Tetramic acid derivatives have been synthesized previously in the Frontier group *via* the acylation of amino esters with methyl 2-(triphenylphosphoranylidene)acetate followed by intramolecular Wittig olefination (Scheme 4.1).¹

Scheme 4.1. Frontier Lab Synthesis of Tetramic Acid Derivative **165** *via*

Acylation/Intramolecular Wittig Olefination

To incorporate this strategy in the current work, the oxazolidinone ring of **153a** would first be opened to reveal an amino alcohol, followed by oxidation to an ester, acylation with methyl 2-(triphenylphosphoranylidene)propanoate,² and then intramolecular Wittig olefination to secure the tetramic acid D ring (Scheme 4.2).

Scheme 4.2. Initial Strategy Toward Securing the Tetramic Acid D Ring

Compound **153a** was subjected to reductive conditions to open the oxazolidinone ring as aqueous basic conditions would likely cleave the silyl protecting groups. Treatment of **153a** with an equimolar mixture of DIBAL and *n*-BuLi³ resulted in no reaction. Treatment with LAH resulted in amino alcohol **166** in 32% yield, while treatment with LTBH raised the yield to 80% (Scheme 4.3).⁴ A mild procedure was sought to convert the alcohol to a methyl ester due to the presence of the highly oxidizable amino group. While treatment of **166** with DMP, IBX, and PDC resulted in decomposition, oxidation under Swern conditions afforded aldehyde **169** in 39% yield.⁵ Then, a mild I₂-mediated oxidation procedure afforded methyl ester **167** in 91% yield.⁶ Following the strategy outlined in Scheme 4.2 to convert amine **167** into tetramic acid derivative **168** unfortunately resulted in decomposition. Acylation with propionyl chloride under similar conditions also resulted in decomposition.

Scheme 4.3. Attempted Synthesis of Tetramic Acid Derivative **168** via

Acylation/Intramolecular Wittig Olefination

The inability to acylate **167** was disconcerting, as the current synthetic strategy hinged on this reactivity to form the tetramic acid moiety. Thus, several acylation studies were initiated. Alcohol **166** was acylated with an excess of propionyl chloride, and the product of this reaction was exclusively the O-acylated compound **170** (Scheme 4.4). An intramolecular acyl transfer with trimethylaluminum⁷ was attempted, but this resulted in deacylation back to **166**.

Scheme 4.4. Attempted Intramolecular Acyl Transfer on Ester **170**

The alcohol in **166** was next protected as a TES ether to isolate the nitrogen as the only reactive center. Then, several acylation conditions were screened (Table 4.1). Initial attempts resulted in desilylation of the TES group, and in some cases acylation of the liberated hydroxyl (Entries 1-4). Another strategy was N-alkylation with an allyl or propyl species, but this proved to be nonselective or resulted in O-alkylation (Entries 5-6). Acylation with phosgene was successful according to an NMR spectrum of the crude reaction mixture, but the carbamoyl chloride product was unstable to silica gel chromatography. Nevertheless, when the crude product was treated with ethyl cuprate (formed *in situ*), desilylation followed by ring-closure occurred to yield oxazolidinone

Table 4.1. Acylation and Alkylation Studies on Amine **171**

Entry	Conditions	Product
1	NaH, THF,	$R^1 = R^2 = \text{H}$ (166)
2	EDCI, Et ₃ N, CH ₂ Cl ₂ ,	$R^1 = R^2 = \text{H}$ (166)
3	BuLi, THF, -78 °C, 	$R^1 = \text{H}$, $R^2 = $ (170)
4	DMAP, CH ₂ Cl ₂ ,	$R^1 = R^2 = \text{H}$ (166)
5	BuLi, allyl iodide, THF, -78 °C	<p> $R^1 = R^2 = \text{H}$, $R^3 = \text{allyl}$, 172 $R^1 = R^3 = \text{H}$, $R^2 = \text{allyl}$, 173 $R^2 = R^3 = \text{H}$, $R^1 = \text{allyl}$, 174 </p>
6	NaH, propyl iodide, DMF, 0 °C to rt	<p> $R^1 = \text{TIPS}$, $R^2 = \text{Pr}$, 175 $R^1 = R^2 = \text{Pr}$, 176 </p>
7	Phosgene, Et ₃ N, THF, 0 °C; CuCN, EtMgBr, Et ₂ O, -30 °C	$R_1 = R_2 = \text{C(O)}$ (153a)
8	Phosgene, Et ₃ N, THF, 0 °C; Pd(PPh ₃) ₂ , Bu ₃ Sn(vinyl), THF, 0 °C	$R_1 = R_2 = \text{H}$ (166)

153a (Entry 7). Additionally, when the crude carbamoyl chloride was subjected to Stille coupling conditions with tributyl(vinyl)tin, decarbonylation occurred to yield amino alcohol **166** (Entry 8).

Since the proposed reaction in Entry 8 was over two steps, a single step process was envisioned. To this end, amine **171** was subjected to acylation conditions with acryloyl chloride,⁸ and gratifyingly the reaction successfully afforded amide **177** in 57% yield (Scheme 4.5). Acylation of amine **167** with acryloyl chloride under the same conditions as **171** resulted in no reaction. Clearly, what appeared to be minor structural changes had a profound effect on the reactivity of this sterically crowded region.

Scheme 4.5. Synthesis of Amide **177** *via* acylation with acryloyl chloride

Given the success of acylation with acryloyl chloride, the strategy was now to take amide **177**, oxidize the alcohol to a methyl ester, and perform a conjugate reduction/Dieckmann condensation cascade to form the tetramic acid D ring (Scheme 4.6).⁹

Scheme 4.6. Synthetic Plan for the Conversion of **177** to Tetramic Acid Derivative **168**

The TES group of amide **177** was removed under acidic conditions to furnish alcohol **179** (Scheme 4.7). Oxidation of alcohol **179** with IBX and under Swern conditions failed, but was successful with Ley oxidation to furnish aldehyde **180**.¹⁰ When **180** was subjected to the I₂-mediated oxidation procedure⁶ used in Scheme 4.3, decomposition resulted. Furthermore, treatment of aldehyde **180** with PDC/MeOH or under Lindgren oxidation conditions¹¹ also resulted in decomposition.

Scheme 4.7. Synthesis of Aldehyde **180**

Amine **171** was also subjected to chemoselective hydrogenation using Wilkinson's catalyst to furnish amine **181** (Scheme 4.8).¹² The resulting product was then subjected to acylation with acryloyl chloride, followed by desilylation, to afford alcohol **182**. The structure was confirmed by single-crystal x-ray crystallography (Figure 4.1).

Scheme 4.8. Synthesis of Alcohol **182**

Alcohol **182** was subjected to Ley oxidation¹⁰ to furnish aldehyde **183** (Scheme 4.9). Since the oxidation of aldehyde **180** to the carboxylic acid oxidation state resulted in decomposition, **183** was treated with Stryker's reagent to initiate a conjugate reduction/aldol condensation cascade instead of the planned conjugate reduction/Dieckmann condensation cascade.⁹ This process smoothly produced alcohol **185** as a mixture of four diastereomers in 94% combined yield.

Figure 4.1. ORTEP Diagram of 182

Scheme 4.9. Synthesis of Alcohol **185** *via* Conjugate Reduction/Aldol

Condensation Cascade

Oxidation of secondary alcohol **185** under Swern conditions using oxalyl chloride furnished chlorinated tetracycle **187** as a single diastereomer (Scheme 4.10). The stereochemistry of **187** was determined from later derivatization (see Figure 4.2). Presumably, oxidation to tetramic acid **186** occurred, and this intermediate then trapped electrophilic chlorine present in the reaction mixture.¹³ Ley oxidation¹⁰ on **185** produced tertiary alcohol **188** as a 5:1 mixture of diastereomers. Like the formation of **187**, the initially formed tetramic acid **186** trapped electrophilic oxygen, though this trapping was not completely stereoselective. This “over-oxidation” strategy may be useful in the synthesis of tetrapetalone C and may be biomimetic. To circumvent this trapping of electrophilic chlorine species, DMSO-based oxidations on **185** with $\text{SO}_3\cdot\text{pyridine}$ and TFAA were conducted; the result was no reaction and an unknown product inconsistent with oxidation, respectively.

Scheme 4.10. Synthesis of Tetracycles **187** and **188** via Oxidation

Tetracycle **187** was smoothly dechlorinated with zinc dust under acidic conditions¹⁴ to give tetramic acid **186** (Scheme 4.11). To ensure that the tetramic acid would not over-oxidize, the enol OH was methylated with TMSCHN₂^[15] to give tetracycle **189**.

Scheme 4.11. Synthesis of Tetramic Acid Derivative **189**

4.2. Installation of C15-O Bond and Completion of the Synthesis

With the tetramic acid D ring secured, the only major remaining synthetic challenge was to functionalize the A ring from a phenol to a *para*-quinol at C15 (Scheme 4.12).

Scheme 4.12. Endgame Strategy for the Synthesis of Tetrapetalone A-Me Aglycon

Several synthetic approaches were considered. First, nitroso groups are known to undergo [4+2] cycloadditions with dienes and anthracene (Scheme 4.13).¹⁶ No examples, however, are known of nitroso group cycloadditions with phenyl rings. Nevertheless, if a nitroso group could be tethered to the phenolic A ring, a similar [4+2] cycloaddition may occur that would create the desired C15-O bond (Scheme 4.14). Then, reductive cleavage of the N-O bond followed by hydrolysis would furnish the desired *para*-quinol.

Scheme 4.13. [4+2] Cycloaddition between Nitroso Group and Dienes

Scheme 4.14. Proposed Installation of C15-O Bond *via* Intramolecular [4+2] Cycloaddition

141 was thus deprotected and alkylated with methyl bromoacetate to furnish **193** (Scheme 4.15). Amination with hydroxylamine furnished **194**. This material unfortunately underwent hydrolysis of the N-hydroxy acetamide group under Swern oxidation conditions.

Scheme 4.15. Attempted Nitroso Group Installation

Another strategy for C15-O bond formation would be to utilize the oxidative dearomatization of phenols.¹⁷ Pettus and workers have shown that when phenol **196** is treated with PhI(OCOCF₃)₂ (PIFA), intramolecular attack by a tethered nucleophile forms bicycle **197** (Scheme 4.16).¹⁸

Scheme 4.16. Oxidative Dearomatization of Phenols/Intramolecular Trapping Cascade

Following this strategy, tetracycle **153a** was chemoselectively desilylated with TFA to furnish alcohol **198** (Scheme 4.17). This alcohol was subjected to a Mitsunobu inversion reaction¹⁹ to furnish ester **199**. The newly formed ester was planned to be the trapping agent in an oxidative dearomatization reaction. First, deprotection with TBAF(^tBuOH)₄^[20] furnished phenol **200**. Treatment of this phenol with PIFA in HFIP solvent unfortunately resulted in decomposition.

Scheme 4.17. Synthesis of **200** in Preparation for Oxidative Dearomatization and Trapping with a Tethered Ester

A more nucleophilic trapping agent, such as a carbamate, might have greater success in the oxidative dearomatization reaction. Thus, ester **199** was hydrolyzed to furnish alcohol **201** (Scheme 4.18). **201** was treated with phenyl isocyanate, followed by deprotection with TBAF(^tBuOH)₄^[20] to furnish phenol **203**. This compound unfortunately also decomposed when treated with PIFA in HFIP solvent.

Scheme 4.18. Synthesis of Phenol **203** in Preparation for Oxidative Dearomatization with a Tethered Carbamate

The oxidative dearomatization was also attempted using water as an exogenous nucleophile. When treated with various oxidants¹⁷ such as PIFA,²¹ PhI(OAc) $_2$ (PIDA),²¹ Pb(OAc) $_4$,¹⁷ benzeneseleninic anhydride (BSA),¹⁷ and singlet oxygen,¹⁷ phenol **164** unfortunately decomposed (Scheme 4.19).

Scheme 4.19. Attempted Oxidative Dearomatization of **164** with Water as an Exogenous Nucleophile

Further oxidative dearomatization studies were explored with chlorinated tetracycle **186**. This material was treated with TBAF, which chemoselectively deprotected the TIPS group (Scheme 4.20). Phenol **205** was treated with PIFA, which

surprisingly resulted in oxidation at C7 rather than C15, in addition to epoxidation of the trisubstituted olefin. To confirm this result, the TBS group was unmasked with TBAF to furnish alcohol **207**, whose structure was confirmed by X-ray crystallography (Figure 4.2). Treatment of **205** with singlet oxygen (formed from the basic decomposition of Oxone)²² gave no reaction, and treatment with $\text{Pb}(\text{OAc})_4$ ^[17] resulted in decomposition. Interestingly, treatment of **205** with singlet oxygen (formed from photosensitization)¹⁷ resulted in **206**. Oxidation of **186** with PIFA, singlet oxygen (from Oxone),²² and Weitz's triarylammonium salt²³ resulted in no reaction.

Scheme 4.20. Synthesis of Phenol **207** *via* Oxidative Dearomatization Conditions

Figure 4.2. ORTEP Diagram of **207**

Oxidative dearomatization studies were next attempted on substrates containing the tetramic acid moiety. It was hypothesized that by changing the electronics of the D ring, oxidation at undesired positions may be prevented. Thus, tetracycle **189** was chemoselectively deprotected with TBAF(^tBuOH)₄^[20] to yield phenol **208** (Scheme 4.21). To confirm the identity of phenol **208**, a sample was submitted for X-ray crystallographic analysis (Figure 4.3). When phenol **208** was subjected to oxidative dearomatization conditions using PIFA or PIDA,²¹ the ¹H NMR of the product showed the same characteristic chemical shifts and splitting patterns present in epoxide **206**. Namely, the C5 proton resonance moved to 3.25 ppm (consistent with epoxidation of an alkene) and the C7 proton resonance disappeared (consistent with replacement of H with OH).

Scheme 4.21. Synthesis of Phenol **209** *via* Oxidative Dearomatization

Figure 4.3. ORTEP Diagram of **208**

If epoxidation of the double bond were occurring initially, then the epoxide could be directing oxidation at C7. To test this, the trisubstituted olefin was removed by hydrogenation to give phenol **210**, which was subjected to oxidative dearomatization conditions using PIFA (Scheme 4.22).²¹ Once again, the ¹H NMR of **211** showed the characteristic loss of the C7-H resonance.

Scheme 4.22. Synthesis of Phenol **211** *via* Oxidative Dearomatization

A plausible mechanism for the oxidation is shown below (Scheme 4.23). Addition of PIFA to the phenolic OH proceeds as expected, but elimination at C7 to form an extended quinone methide occurs rather than attack by water at the *para* position. Attack by water occurs at C7, and the resultant C7 hydroxyl group promotes epoxidation of the trisubstituted double bond (if present).

Scheme 4.23. Plausible Mechanism for Formation of Phenols **206**, **209**, and **211**

Since oxidative dearomatization with hypervalent iodine reagents was furnishing undesired products, other synthetic strategies were investigated. The greatest success in C15-O bond formation came when **208** was treated with catalytic Rh₂(cap)₄ and *tert*-butyl hydroperoxide to furnish peroxide **212** as a 1.3:1 mixture of diastereomers (Scheme 4.24).²⁴ The major diastereomer was found to contain the desired C15 stereochemistry from characterization of a later intermediate (see Figure 4.4). Peroxide **212** could also be secured by treating **208** with catalytic RuCl(PPh₃)₃ and *tert*-butyl hydroperoxide, though in lower yield.²⁵

Scheme 4.24. Rh-Catalyzed Oxidation of **208** to Secure Key C15-O Bond

With the C15-O bond secured, the last major hurdle was to cleave the peroxide O-O bond to furnish the desired *para*-quinol. Several conditions for peroxide O-O bond cleavage were screened: when **212** was treated with Mg^0/MeOH ,^{26,27} Zn^0/HOAc ,²⁷ or $\text{Al}(\text{Hg})$,²⁸ the result was, surprisingly, clean and quantitative conversion back to phenol **208**. These conditions could be used to recycle the undesired C15 epimer of **212**, which would greatly increase the throughput of the oxidative dearomatization step. Treatment of **212** with thiourea²⁷ resulted in no reaction.

10% Cd/Pb couple²⁹ cleanly cleaved the O-O bond in **212** to furnish **192** (Scheme 4.25). This material was subjected to X-ray crystallographic analysis to confirm its structure (Figure 4.4). Deprotection with $\text{HF}\cdot\text{pyridine}$ smoothly furnished tetrapetalone A-Me aglycon (**11**). This material was also subjected to X-ray crystallographic analysis (Figure 4.5). Furthermore, the characterization data of **11** matched the characterization data reported in the literature.³⁰ With this milestone, only a few steps remain to secure tetrapetalone A though synthesis.

Scheme 4.25. Reductive Conditions Leading to Completion of the Synthesis of Tetrapetalone A-Me Aglycon (**11**)

Figure 4.4. ORTEP Diagram of **192**

Figure 4.5. ORTEP Diagram of **11**

4.3. References

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Chapter 5. Studies Toward The Enantioselective Synthesis of Tetrapetalone A

5.1. Coupling Tetrapetalone A-Me Aglycon with Rhodiose Precursor

With **11** secured, the last remaining synthetic steps are the stereoselective installation of a rhodiose moiety on the C9 oxygen followed by demethylation of the D ring to reveal the natural product tetrapetalone A (**6**) (Scheme 5.1). The most straightforward way to install the glycosidic bond would be to couple **11** with a D-rhodosyl donor to give the β -O-glycoside tetrapetalone A-Me (**10**).

Scheme 5.1. Endgame Synthetic Strategy toward **6**

Unfortunately, there are very few reports of coupling rhodosyl donors with acceptors. Boeckman¹ and Schlessinger² have reported β -N-glycosidic linkages with L-rhodiose due to a “reverse” anomeric effect³ (Scheme 5.2).

Scheme 5.2. Boeckman’s Synthesis of β -N-glycoside **215**

On the other hand, the only examples in the literature of O-glycosidic linkages between rhodinosyl donors⁴⁻⁶ or rhodnose glycols^{7,8} with acceptors are in the α configuration. One recent example from Saikawa and Nakata highlights the exclusive α selectivity of this glycosidic linkage in natural product synthesis (Scheme 5.3).⁶

Scheme 5.3. Coupling of Lactonamycin Aglycon with Rhodinosyl Donor Yields

Exclusively α -O-glycoside

It is clear that a strategy for forming a β -O-glycosidic linkage with rhodnose would have to override the donor's inherent stereoelectronic predisposition. Indeed, Lee has reported the use of palladium to catalyze O-glycosylation of glycols where the anomeric selectivity is under catalyst control (Scheme 5.4).⁹

Scheme 5.4. Pd-Catalyzed O-Glycosylation with Glycols

In a preliminary exploration of this type of chemistry, known glycal **220**^[10] was combined with *rac*-**114** under palladium catalysis to yield two diastereomeric coupling products **221a/b** (Scheme 5.5). Since *rac*-**114** was synthesized as the racemate and **220** as a single enantiomer, it stands to reason that one of the diastereomeric products derives from the coupling of (+)-**114** and **220**, and the other product derives from the coupling of (-)-**114** and **220**. In other words, the anomeric carbon was installed stereoselectively, and is likely in the desired β configuration following the example of Lee in Scheme 5.4. Further characterization of **221a/b** and coupling studies on a more advanced intermediate such as **11** are currently underway.

Scheme 5.5. Pd-Catalyzed Coupling of Glycal **220** with Alcohol **114**

5.2. Synthesis of AB Ring using Enantioselective Nazarov Cyclization

The formation of a mixture of diastereomeric products in Scheme 5.5 can be avoided by coupling an enantiopure acceptor with the enantiopure donor **220**. Since the Nazarov cyclization established the first stereocenter on C7 (See Chapter 2), and since all subsequent relative stereochemistry on the aglycon was relayed from this stereocenter, an

asymmetric Nazarov cyclization¹¹ would enable an enantioselective synthesis of **11** and the formation of a β -O-glycoside as a single stereoisomer.

One strategy explored was the use of chiral auxiliaries to afford high levels of enantioselectivity. Since the methyl ester on indanone **104** was eventually removed (See Chapter 2), studies were initiated where this methyl ester was replaced with a chiral sulfoxide.¹² In theory, when β -keto sulfoxide **222** is treated with Lewis acid, the ketone and the sulfoxide would both coordinate to the Lewis acid (Scheme 5.6). A Nazarov cyclization would be initiated, and the chiral presence at sulfur would hopefully lead to torquoselectivity. The chiral auxiliary would then be removed immediately after the Nazarov cyclization to furnish **113** as a single enantiomer.

Scheme 5.6. Enantioselective Nazarov Cyclization Enabled by Chiral Sulfoxide

Commercially available (–)-menthyl (*S*)-*p*-toluenesulfinate was treated with (2-methyl-1-butene-3-yne)magnesium bromide to yield sulfoxide **225** (Scheme 5.7).¹² This material was subjected to hydrostannylation to yield vinyl stannane **226**.¹³ Stille coupling

with acid chloride **227** using CuTc^{14} yielded aryl enone **228**. This material unfortunately decomposed on exposure to AlCl_3 .

Scheme 5.7. Synthesis of Aryl Dienone **228** *via* Stille Coupling

An approach using Evans' auxiliary was explored due to having more direct precedent in the literature.^{15,16} Enantioinduction using Evans' auxiliary would be analogous to using the chiral sulfoxide (Scheme 5.8).

Scheme 5.8. Enantioselective Nazarov Cyclization Enabled by Evans' Auxiliary

Construction of aryl enones using this approach was similar to the approach using the sulfoxide auxiliary. Thus, Cu-catalyzed oxidative coupling of **231** with (*S*)-4-phenyloxazolidin-2-one yielded ynamide **232** (Scheme 5.9).¹⁷ This material was subjected to hydrostannylation to yield vinyl stannane **233**.¹⁵ Stille coupling with acid chloride **227** produced aryl enone **234**.¹⁶ This material unfortunately decomposed on exposure to AlCl_3 .

Scheme 5.9. Synthesis of Aryl Dienone **234** *via* Stille Coupling

At the same time, aryl enone **237**, which incorporated the auxiliary (*S*)-4-isopropoxyloxazolidin-2-one, was synthesized in a manner analogous to **234** (Scheme 5.10). The use of superstoichiometric CuCl compared to catalytic CuTc was found to be essential for high yield in the Stille coupling.

Scheme 5.10. Synthesis of Aryl Dienone **237** *via* Stille Coupling

Several Lewis acids were screened in the Nazarov cyclization of **237** (Table 5.1). The best result, which used AlCl_3 , furnished indanone **238** as a 9:1 mixture of diastereomers (entry 5). The major isomer was isolated by recrystallization from hexanes/ether, and a single-crystal X-ray diffraction experiment unambiguously confirmed its structure and absolute stereochemistry (Figure 5.1).

Table 5.1. Conditions Screened in the Nazarov Cyclization of **237**

Entry	Conditions	Yield	dr
1	MeSO ₃ H (10 eq), DCE, rt	Decomposition	--
2	Cu(OTf) ₂ (2 eq), DCE, 55 °C	Decomposition	--
3	Mg(OTf) ₂ (1.6 eq), DCE, 85 °C	No Reaction	--
4	Al(OTf) ₃ (1.6 eq), DCE, 85 °C	Decomposition	--
5	AlCl ₃ (1.5 eq), DCE, 35 °C	45%	9.0:1
6	In(OTf) ₃ (1.1 eq), DCE, 65 °C	35%	5.0:1
7	Sc(OTf) ₃ (1.1 eq), DCE, 55 °C	55%	3.2:1
8	Y(OTf) ₃ (1.1 eq), DCE, 55 °C	Not determined (75% Conversion)	3.4:1
9	SnCl ₄ (1.1 eq), DCE, 45 °C	36%	6.8:1
10	TiCl ₄ (1.1 eq), DCE, rt	Decomposition	--

Figure 5.1. ORTEP Diagram of **238**

The chiral auxiliary was cleaved with either lithium naphthalenide or SmI_2 ^[16] to furnish indanone (**S**)-**136**, containing a stereocenter with absolute configuration congruent to C7 of **6** (Scheme 5.11). Since all further stereochemistry of the aglycon is relayed from C7, this material could, in theory, be elaborated to enantiopure **11**.

Scheme 5.11. Auxiliary Cleavage to Furnish (**S**)-**113** and Potential Elaboration to Enantiopure **11**

5.3. Conclusions

The work presented in this thesis is a detailed account of the strategies used toward the first synthesis of tetrapetalone A-Me aglycon, a derivative of the natural product tetrapetalone A. A graphical summary of this synthetic sequence is depicted below (Scheme 5.12). Key bond-forming reactions include Nazarov cyclization to form the AB ring system, diastereoselective ring-closing metathesis to form the ABC ring system, a tandem conjugate reduction-intramolecular aldol condensation to form the ABCD ring system, and an oxidative dearomatization to finalize the *para*-quinol A ring. An asymmetric Nazarov cyclization protocol was developed that could, in theory, deliver enantiopure tetrapetalone A-Me aglycon (**11**). Then, the completion of the total synthesis of tetrapetalone A would involve palladium-catalyzed β -glycosidic bond formation between **11** and glycal **220**, chemoselective hydrogenation, and demethylation of the tetramic acid (Scheme 5.13).

This work overcomes several of the shortcomings of previously reported synthetic approaches. In the Porco approach, their key oxidative [4+3] cyclization failed and was unable to furnish the tetracyclic skeleton. This work was able to construct the tetracyclic skeleton as well as install the *para*-quinol moiety using an oxidative dearomatization reaction. While the Hong approach produced the tetracyclic carbon framework of the tetrapetalones, their advanced intermediate lacked the required oxidation present in the tetrapetalones. This work produced the tetrapetalone aglycon containing all of the requisite oxidation and functional groups. The Sarpong approach produced an advanced

Scheme 5.12. Summary of the Synthesis of Tetrapetalone A-Me Aglycon

Scheme 5.13. Proposed Completion of the Total Synthesis of Tetrapetalone A

intermediate that seemed to be only a few steps away from the tetrapetalone aglycon; they still needed to install the C ring trisubstituted olefin and convert the A ring from a phenol to a *para*-quinol. While late-stage oxidation of the A ring should be possible, given its successful execution in this work, it may be that the Sarpong group could not successfully execute a late-stage installation of the trisubstituted olefin. In contrast, this work installs the C ring trisubstituted olefin midway through the synthesis. The Pettus approach successfully installed the D ring and linked it to the phenolic A ring precursor; their group still has to report the successful installation of the B and C rings. Lastly, Chao Jiang and Ildiko Herrick, the former graduate students on this project, never had success in progressing past the AB ring system; this work installs the remaining C and D rings and culminates in the synthesis of tetrapetalone A-Me aglycon.

This work also describes the beginnings of a second-generation synthesis to address several of the problems encountered en route toward the total synthesis of tetrapetalone A. First, the goal of developing an enantioselective approach has already been solved (see section 5.2). The next major goal is to achieve a more convergent Buchwald-Hartwig coupling between the AB ring system and a functionalized amide or

oxazolidinone, in line with the original retrosynthetic vision. Indeed, protocols for Pd-catalyzed¹⁸ and Cu-catalyzed^{19,20} cross-couplings of oxazolidinones with aryl halides have been reported, and these should be explored. Another approach to streamline the synthesis would be to reinvestigate the acylation/intramolecular Wittig olefination process seen in Scheme 4.3. Amine **167** would be treated with methyl 2-(triphenylphosphoranylidene)acetate, and the reaction would be halted after acylation but prior to Wittig olefination (Scheme 5.14). The acylation with methyl 2-(triphenylphosphoranylidene)acetate would be facile since methyl 2-(triphenylphosphoranylidene)acetate is known to eliminate to form a highly electrophilic ketenylidene triphenylphosphorane.²¹ After the acylation, methylation followed by intramolecular Wittig olefination would furnish tetramic acid derivative **168**.

Scheme 5.14. Reinvestigation of the Acylation/Wittig Olefination Cascade to form Tetramic Acid Derivative **168**

Another goal would be to find ways of lowering the catalyst loading of the RCM step; while the reaction is an amazing success given the steric crowding around the olefins and functional group tolerance, a 25% loading of catalyst is still not amenable to scale. Approaches to this problem are currently under investigation with our collaborators in the Hoveyda group. The last major goal would be to investigate ways of enhancing the diastereomeric ratio of the oxidative dearomatization step. When this step was achieved, there was very little starting phenol available to conduct such a study. With an increased availability of phenol, the modulation of reaction conditions would be investigated (in particular the use of chiral rhodium catalysts) to enhance the diastereomeric ratio even further. A graphical summary of the above plans for a second-generation, enantioselective synthesis of tetrapetalone A is given below (Scheme 5.15).

Once tetrapetalone A is secured through synthesis, the next step would be to assay it against HLO and to explore its activity against other important human diseases, such as cancer. Assuming tetrapetalone A has some degree of potency toward fighting a human disease, the synthesis of analogs can be explored by modifying steps in the synthetic sequence. Analogs having increased potency, increased metabolic half-life, and simplified structures compared to the natural product would be desired. Ideally, a tetrapetalone A analog optimized for these and other criteria would be on the road to drug candidacy.

Scheme 5.15. Proposed Second-Generation Enantioselective Synthesis of
Tetrapetalone A

5.4. References

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Chapter 6. Experimental Procedures and Compound Characterization Data

6.1. General Information

All reactions were carried out under an argon or N₂ atmosphere in flame-dried glassware with magnetic stirring unless otherwise noted. All substrates were dried by azeotropic distillation with benzene prior to use with Mo-based complexes. Reagents were used as obtained from commercial suppliers without further purification unless otherwise noted. Tetrahydrofuran, diethyl ether, methylene chloride, 1,2-dichloroethane, and toluene were purchased from Fisher and dispensed using the Glass Contour solvent purification system. Benzene was purchased from Alfa Aesar and dispensed using a modified Innovative Technologies solvent purification system. 4Å molecular sieves (activated powder, <5 micron) were purchased from Aldrich and dried in an oven overnight prior to use. Celite 545 was purchased from EMD. ACS grade hexanes and ethyl acetate were used for column chromatography. Thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F254 glass-supported plates from EMD, and visualization was performed with a UV lamp followed by staining with potassium permanganate, *p*-anisaldehyde, ninhydrin, or ceric ammonium molybdate solution followed by heating. Column chromatography was carried out on EM Science 60 Å silica gel (230-400 mesh). Methanol-*d*₄ and chloroform-*d* were purchased from Cambridge Isotope Laboratories.

¹H NMR spectra were recorded on a 400 MHz Bruker Avance spectrometer or a 500 MHz Bruker Avance spectrometer at room temperature. Chemical shifts are given in parts per million (ppm) from tetramethylsilane, referenced to solvent residual proton

resonance ($\delta = 7.26$ for CHCl_3 , $\delta = 3.31$ for CH_3OH). Some NMR spectra contain tetramethylsilane as an internal reference. NMR data are reported as: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dq = doublet of quartets, br = broad), coupling constants (J) given in Hz, and integration. ^{13}C NMR spectra were recorded on a 100 MHz Bruker Avance spectrometer or a 125 MHz Bruker Avance spectrometer at room temperature with proton decoupling. Chemical shifts are given in parts per million (ppm) from tetramethylsilane, referenced to solvent carbon resonance ($\delta = 77.16$ for CHCl_3 , $\delta = 49.00$ for CH_3OH). Infrared spectra (IR) were recorded on a Shimadzu FTIR 8400S (ATR Mode) spectrometer. Absorbance frequencies are given in cm^{-1} at the peak maximum as strong (s), medium (m), weak (w), or broad (br). High resolution mass spectra (HRMS) were measured by the Mass Spectrometry Lab of the University of Illinois, Urbana, IL 61801. X-ray crystallography data were collected by the X-ray Crystallographic Facility of the University of Rochester, Rochester, NY 14627 and by the X-ray Crystallographic Laboratory of the University of Minnesota, Minneapolis, MN 55455.

6.2. Experimental Procedures from Chapter 2

89 was prepared according to the literature.¹ To a 50 ml round-bottom flask was added **89** (0.120 g, 0.401 mmol), imidazole (0.0817 g, 1.20 mmol, 3 eq), TIPSCl (0.215 ml, 1.00 mmol, 2.5 eq), and THF (4 ml). After stirring at room temperature overnight, the reaction was quenched with H₂O and extracted three times with Et₂O. The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude material was purified by flash column chromatography (hexanes) to afford **S1** (0.181 g, 99%). ¹H NMR (400 MHz, CDCl₃) δ 7.50 (s, 1H), 7.26 (s, 1H), 7.08 (s, 1H), 1.38 – 1.24 (m, 3H), 1.16 (d, *J* = 7.4 Hz, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 157.18, 132.49, 128.01, 122.92, 122.84, 94.17, 17.97, 12.65; IR (neat, cm⁻¹): 2943 (m), 2866 (m), 1570 (s), 1543 (s), 1462 (m), 1423 (s), 1261 (s), 1072 (w), 995 (w), 945 (s), 879 (s), 837 (s), 748 (s), 725 (s), 667 (s); HRMS (ESI): Calculated for C₁₅H₂₅BrIOSi ([M+H]⁺): *m/z* 454.9903, found: 454.9897.

To a 10 ml round-bottom flask was added **S1** (0.050 g, 0.11 mmol), Pd(PPh₃)₂Cl₂ (0.0023 g, 0.0033 mmol, 0.03 eq), and dry CuI (0.0013 g, 0.0066 mmol, 0.06 eq). The flask was purged with argon for 30 minutes. Dry THF (5 ml) was added, followed by ethynyltrimethylsilane (0.17 ml, 1.2 mmol, 11 eq) and Et₃N (0.35 ml, 2.5 mmol, 23 eq), and the solution was stirred at room temperature for two hours. The reaction mixture was diluted with EtOAc, washed two times with sat. NH₄Cl, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude material was purified by flash column chromatography (neat hexane) to afford **90** (0.0453 g, 93%) as translucent, square crystals. ¹H NMR (400 MHz, CDCl₃) δ 7.20 (s, 1H), 6.99 (t, *J* = 2.0 Hz, 1H), 6.87 (t, *J* = 2.0 Hz, 1H), 1.36 – 1.18 (m, 3H), 1.09 (d, *J* = 7.3 Hz, 18H), 0.24 (s, 9H).

To a 50 ml round-bottom flask was added **90** (2.4 g, 5.65 mmol), K₂CO₃ (0.08 g, 0.565 mmol, 0.1 eq), CH₂Cl₂ (12 ml), and MeOH (12 ml). The reaction mixture was stirred overnight. The reaction mixture was quenched with H₂O, extracted with CH₂Cl₂, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue (80% crude yield) was taken to the next step without further purification. ¹H NMR (400 MHz, CDCl₃) δ 7.21 (t, *J* = 1.5 Hz, 1H), 7.03 (t, *J* = 2.0 Hz, 1H), 6.91 (dd, *J* = 2.0, 1.5 Hz, 1H), 3.08 (s, 1H), 1.33 – 1.15 (m, 3H), 1.09 (d, *J* = 7.2 Hz, 18H).

To a flame-dried 50 ml round-bottom flask was added **S2** (1.6g, 4.53 mmol) from the previous step and THF (22 ml). The flask was cooled to $-78\text{ }^\circ\text{C}$, then *n*-butyllithium (3.125 ml, 1.6 M in hexanes, 5 mmol) was added dropwise. Stirring continued for one hour. Then, methyl chloroformate (0.63 ml, 8.15 mmol, 1.8 eq) was added dropwise and stirring continued overnight as the reaction mixture was raised to room temperature. The solution was quenched with water, extracted with ethyl acetate, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (19:1 hexane: ethyl acetate) to yield 1.207 g (65%) of **91** as a translucent oil. ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.29 (m, 1H), 7.12 (t, $J = 2.0$ Hz, 1H), 7.01 – 6.97 (m, 1H), 3.83 (s, 3H), 1.31 – 1.18 (m, 3H), 1.09 (d, $J = 7.3$ Hz, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.89, 154.26, 128.45, 126.25, 122.83, 122.67, 121.92, 84.63, 80.89, 53.04, 17.94, 12.69; IR (neat, cm^{-1}): 2947 (s), 2866 (s), 2230 (s), 1717 (s), 1586 (s), 1555 (s), 1462 (w), 1424 (s), 1319 (m), 1292 (w), 1231 (s), 1196 (w), 1157 (s), 976 (m), 883 (s), 853 (m), 810 (m), 733 (s), 675 (s), 648 (w), 621 (w); HRMS (ESI): Calculated for $\text{C}_{19}\text{H}_{28}\text{BrO}_3\text{Si}$ ($[\text{M}+\text{H}]^+$): m/z 411.0991, found: 411.0990.

To a flame-dried 10 ml round-bottom flask in a glove box was added ZnBr_2 (0.270 g, 1.20 mmol, 1.2 eq). The flask was removed from the glove box and dry THF (5 ml) and Et_3N (0.669 ml, 4.80 mmol, 4.8 eq) were added. This mixture was stirred for two minutes, followed by the addition of aryl iodide **S1** (0.455 g, 1.00 mmol), methyl propiolate (0.107 ml, 1.2 mmol, 1.2 eq), and $\text{Pd(PPh}_3)_2\text{Cl}_2$ (0.0351 g, 0.05 mmol, 0.05 eq). The reaction mixture was stirred at 60 °C overnight. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted three times with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (neat hexanes, then 19:1 hexanes:ethyl acetate) to afford unreacted **S1** (0.077 g, 0.169 mmol, 17% yield) and **91** (0.309 g, 0.751 mmol 75% yield) as a translucent oil.

57 was synthesized from α -methyl-*trans*-cinnemaldehyde.² To a 10 ml round-bottom flask was added **91** (0.617 g, 1.5 mmol), **57** (0.289 g, 1.65 mmol, 1.1 eq), and toluene (5 ml). The flask was purged with argon for 10 minutes and heated at 80 °C overnight. The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford **S3** (0.847 g, 90%). ¹H NMR (400 MHz, CDCl₃) δ 7.58 (t, J = 1.5 Hz, 1H), 7.36 – 7.21 (m, 6H), 7.13 (t, J = 2.0 Hz, 1H), 4.66 (s, 1H), 3.67 (s, 3H), 2.97 (s, 3H), 1.93 (d, J = 1.2 Hz, 3H), 1.33 – 1.21 (m, 3H), 1.11 (d, J = 7.3 Hz, 18H).

To a 10 ml round-bottom flask was added **S3** (0.75 g, 1.28 mmol) and CH₂Cl₂ (5 ml). The flask was cooled to 0 °C. *m*-CPBA (77%, 0.8625 g, 5 mmol, 3 eq) was added and the reaction mixture was stirred for 30 minutes. The reaction mixture was quenched with a saturated aqueous solution of Na₂SO₃, extracted with ether, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford **94** (0.67 g, 94%). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 0.6 Hz, 1H), 7.69 (t, J = 1.5 Hz, 1H), 7.52 – 7.20 (m, 7H),

7.00 (s, 1H), 3.72 (s, 3H), 1.79 (d, $J = 0.9$ Hz, 3H), 1.35 – 1.17 (m, 3H), 1.08 (d, $J = 7.3$ Hz, 18H).

To a flame-dried 25 ml round-bottom flask in a glove box was added Sc(OTf)_3 (0.03 g, 0.06 mmol, 0.05 eq) and $\text{Li(ClO}_4\text{)}$ (0.03 g, 0.18 mmol, 0.15 eq). The flask was removed from the glove box and dry DCE (12 ml) was added. **94** (0.67 g, 1.2 mmol) was added, and the reaction mixture was heated at 45 °C overnight. The reaction mixture was quenched with water, extracted with ether, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (9:1 hexane:ethyl acetate) to afford **98** as a 3:1 mixture of *anti:syn* isomers (0.546 g, 81%). For major (presumably *anti*) isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 2.2$ Hz, 1H), 7.37 – 7.20 (m, 5H), 7.18 (d, $J = 2.2$ Hz, 1H), 6.38 (s, 1H), 4.47 (d, $J = 3.0$ Hz, 1H), 3.81 (s, 3H), 3.61 (d, $J = 3.0$ Hz, 1H), 1.70 (d, $J = 1.1$ Hz, 3H), 1.35 – 1.23 (m, 3H), 1.11 (d, $J = 7.2$ Hz, 18H).

To a 25 ml round-bottom flask was added DABCO (0.142 g, 1.26 mmol, 1.43 eq), toluene (8 ml), H₂O (0.8 ml), and **98** (0.491 g, 0.882 mmol). The flask was purged with argon for 10 minutes. The reaction mixture was refluxed overnight. The reaction mixture was diluted with water and ether, extracted with ether, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 ether:hexane) to afford **101** (0.371 g, 84%). ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 2.2 Hz, 1H), 7.34 – 7.20 (m, 5H), 7.19 (d, *J* = 2.2 Hz, 1H), 6.39 (s, 1H), 4.15 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.08 (dd, *J* = 19.3, 8.0 Hz, 1H), 2.61 (dd, *J* = 19.3, 2.0 Hz, 1H), 1.63 (s, 3H), 1.40 – 1.20 (m, 3H), 1.11 (d, *J* = 7.3 Hz, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 204.98, 157.16, 147.42, 140.36, 137.89, 137.30, 131.25, 128.86, 128.23, 126.52, 122.57, 112.37, 44.44, 18.02, 17.89, 12.72.

To a 100 ml round-bottom flask was added MgSO₄ (6.00 g, 50.0 mmol 2.5 eq), NaHCO₃ (9.24 g, 110 mmol, 5.5 eq), *N*-methylhydroxylamine hydrochloride (5.01g, 60.0 mmol, 3 eq), tiglic aldehyde, (1.93 ml, 20.0 mmol), and CH₂Cl₂ (40 ml). The solution was stirred at RT overnight. The reaction mixture was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (9:1 ethyl acetate:methanol) to afford **92** (0.48 g, 21% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.30 (q, *J* = 7.2 Hz, 1H), 6.75 (s, 1H), 3.71 (s, 3H), 1.93 (s, 3H), 1.80 (d, *J* = 7.2 Hz, 3H).

To a 10 ml round-bottom flask was added **91** (1.58 g, 3.86 mmol), **92** (0.48 g, 4.25 mmol, 1.1 eq), and toluene (40 ml). The flask was purged with argon for 10 minutes and heated at $80\text{ }^\circ\text{C}$ overnight. The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford **S4** (1.28 g, 63%) and unreacted **91** (0.37 g, 19%). ^1H NMR (400 MHz, CDCl_3) δ 7.53 (t, $J = 1.5\text{ Hz}$, 1H), 7.21 – 7.16 (m, 1H), 7.11 (t, $J = 2.0\text{ Hz}$, 1H), 5.49 (q, $J = 6.5\text{ Hz}$, 1H), 4.46 (s, 1H), 3.64 (s, 3H), 2.88 (s, 3H), 1.68 (s, 3H), 1.65 (d, $J = 6.5\text{ Hz}$, 3H), 1.38 – 1.15 (m, 3H), 1.10 (d, $J = 7.3\text{ Hz}$, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.25, 156.29, 134.18, 125.37, 125.16, 122.88, 121.83, 119.78, 101.74, 80.59, 51.23, 17.85, 13.51, 12.54, 12.12.

To **S4** (1.28 g, 2.43 mmol) was added CH_2Cl_2 (25 ml). The flask was cooled to $0\text{ }^\circ\text{C}$. $m\text{-CPBA}$ (77%, 0.6 g, 2.68 mmol, 1.1 eq) was added and the reaction mixture was stirred for one hour at $0\text{ }^\circ\text{C}$. The reaction mixture was quenched with a saturated aqueous

solution of Na_2SO_3 and extracted three times with CH_2Cl_2 . The combined organic extracts were added to a larger solution of saturated aqueous Na_2SO_3 and extracted three times with CH_2Cl_2 . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford aryl dienone **95** (0.899 g, 75% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.36 (s, 1H), 7.19 (t, J = 1.9 Hz, 1H), 7.10 – 7.03 (m, 1H), 6.92 (s, 1H), 6.08 (q, J = 7.0 Hz, 1H), 3.83 (s, 3H), 1.83 (d, J = 10.0 Hz, 3H), 1.82 (s, 3H), 1.34 – 1.19 (m, 3H), 1.09 (d, J = 7.3 Hz, 18H).

To a 3ml vial in a glove box was added AlCl_3 (0.014 g, 0.106 mmol, 1.1 eq). The vial was capped with a pierceable PFTE seal and removed from the glove box. DCE (1 ml) was added. The vial was cooled to 0 °C. Aryl dienone **95** (0.048 g, 0.096 mmol) was added, and the reaction mixture was stirred for 30 minutes. The reaction mixture was quenched with saturated aqueous potassium sodium tartrate. The reaction mixture was extracted three times with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford **99** as a 7:1 mixture of *anti:syn* isomers (0.034 g, 71% yield). Major isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, J = 2.2 Hz, 1H), 7.14 (d, J = 2.2 Hz, 1H), 5.33 (q, J = 6.5 Hz,

1H), 4.26 (d, $J = 2.8$ Hz, 1H), 3.77 (s, 3H), 3.47 (d, $J = 2.8$ Hz, 1H), 1.60 (d, $J = 6.5$ Hz, 3H), 1.44 (s, 3H), 1.33 – 1.21 (m, 3H), 1.09 (d, $J = 7.3$, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 198.24, 168.97, 157.25, 146.85, 138.65, 133.34, 131.97, 123.72, 122.37, 112.98, 61.07, 53.00, 52.22, 17.98, 13.66, 13.12, 12.70.

To a 25 ml round-bottom flask was added **99** (0.693 g, 1.4 mmol), DABCO (0.078 g, 0.7 mmol, 0.5 eq), toluene (14 ml), and H_2O (1.4 ml). The solution was heated at 80 °C overnight. The solution was quenched with saturated aqueous NH_4Cl and extracted three times with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford indanone **102** (0.430 g, 0.983 mmol, 70%). ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 2.2$ Hz, 1H), 7.13 (d, $J = 2.2$ Hz, 1H), 5.30 (q, $J = 6.6$ Hz, 1H), 4.00 – 3.85 (m, 1H), 2.94 (dd, $J = 19.3$, 8.0 Hz, 1H), 2.46 (dd, $J = 19.3$, 2.0 Hz, 1H), 1.58 (d, $J = 6.6$ Hz, 3H), 1.37 (s, 3H), 1.32 – 1.22 (m, 3H), 1.09 (d, $J = 7.3$ Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.49, 156.90, 147.85, 140.21, 134.45, 131.05, 122.48, 122.34, 112.21, 65.98, 47.59, 44.62, 17.96, 15.40, 12.68.

Nitrone **84** was synthesized from (*E*)-2-methyl-3-(trimethylsilyl)acrylaldehyde.^{3,4} To a 25 ml round-bottom flask was added alkynoate **91** (0.950 g, 2.31 mmol), nitrone **84** (0.435 g, 2.54 mmol, 1.1 eq), and toluene (10 ml). The flask was heated at 80 °C overnight. The reaction mixture was concentrated under reduced pressure and taken to the next step without further purification. Alternatively, purification by flash column chromatography (19:1 hexanes:ethyl acetate) afforded isoxazoline **S5** (1.21 g, 2.08 mmol, 90% yield) as a translucent oil. ¹H NMR (400 MHz, CDCl₃) δ 7.56 (t, *J* = 1.5 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.12 (t, *J* = 1.5 Hz, 1H), 5.47 (s, 1H), 4.46 (s, 1H), 3.64 (s, 3H), 2.90 (s, 3H), 1.84 (s, 3H), 1.33 – 1.22 (m, 3H), 1.10 (d, *J* = 7.3 Hz, 18H), 0.12 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 164.29, 160.06, 156.47, 151.33, 130.01, 127.62, 125.60, 125.29, 122.02, 119.87, 102.23, 82.76, 51.26, 47.35, 18.01, 17.49, 12.70, 0.01. IR (neat, cm⁻¹): 2947 (s), 2897 (m), 2870 (s), 1709 (s), 1624 (w), 1589 (s), 1559 (s), 1439 (s), 1335 (w), 1281 (m), 1246 (s), 1192 (w), 1092 (s), 1045 (w), 995 (w), 972 (m), 910 (s), 837 (s), 729 (s), 687 (s), 648 (w); HRMS (ESI): Calculated for C₂₇H₄₅BrNO₄Si₂ ([M+H]⁺): *m/z* 582.2071, found: 582.2064.

To the crude isoxazoline **S5** from the previous step was added CH₂Cl₂ (10 ml). The flask was cooled to 0 °C. *m*-CPBA (77%, 1.55 g, 6.93 mmol, 3 eq) was added and the reaction mixture was stirred for one hour at 0 °C. The reaction mixture was quenched with a saturated aqueous solution of Na₂SO₃ and extracted three times with CH₂Cl₂. The combined organic extracts were added to a larger solution of saturated aqueous Na₂SO₃ and extracted three times with CH₂Cl₂. The combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford aryl dienone **96** (1.12 g, 2.02 mmol, 88% yield) as an inseparable mixture of geometric isomers (1.7:1) and vibrant yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (s, 1H, maj. isomer), 7.49 (s, 1H maj. isomer), 7.39 (s, 1H, min. isomer), 7.29 (s, 1H, maj. isomer), 7.24 (t, *J* = 1.9 Hz, 1H, maj. isomer), 7.20 (t, *J* = 1.9 Hz, 1H, min. isomer), 7.08 (s, 1H, min. isomer), 6.86 (s, 1H, min. isomer), 6.09 (s, 1H, maj. isomer), 6.02 (s, 1H, min. isomer), 3.82 (s, 3H, min. isomer), 3.70 (s, 3H, maj. isomer), 1.97 (s, 3H, min. isomer), 1.68 (s, 3H, maj. isomer), 1.31 – 1.19 (m, 3H), 1.15 – 1.05 (m, 18H), 0.16 (s, 9H, min. isomer), 0.08 (s, 9H, maj. isomer); ¹³C NMR (100 MHz, CDCl₃) δ 193.81, 192.54, 167.28, 165.69, 157.38, 156.93, 150.29, 149.10, 146.88, 146.67, 146.42, 139.92,

139.55, 128.44, 128.31, 127.01, 124.63, 123.31, 122.86, 119.23, 119.12, 52.63, 52.58, 20.01, 18.70, 17.99, 17.95, 17.59, 12.70, -0.39, -0.47; IR (neat, cm^{-1}): 2947 (s), 2893 (w), 2866 (s), 1728 (s), 1593 (s), 1562 (s), 1435 (s), 1385 (w), 1366 (w), 1343 (w), 1281 (s), 1250 (s), 1215 (w), 1169 (w), 1099 (w), 1057 (w), 995 (w), 972 (w), 941 (w), 914 (w), 880 (m), 845 (s), 752 (m), 733 (m), 687 (s), 648 (w); HRMS (ESI): Calculated for $\text{C}_{26}\text{H}_{42}\text{BrO}_4\text{Si}_2$ ($[\text{M}+\text{H}]^+$): m/z 553.1805, found: 552.1814.

To a 25 ml round-bottom flask in a glove box was added AlCl_3 (0.231 g, 1.73 mmol, 1.1 eq). The flask was removed from the glove box and DCE (15 ml) was added. The flask was cooled to 0°C . Aryl dienone **96** (0.869 g, 1.57 mmol) was added, and the reaction mixture turned deep red. The reaction mixture was stirred for 30 minutes. The reaction mixture was quenched with saturated aqueous potassium sodium tartrate, which turned the reaction mixture green, then yellow. The reaction mixture was extracted three times with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford **110** as a 3.6:1 mixture of *anti:syn* isomers (0.597 g, 1.24 mmol, 79% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, $J = 2.2$ Hz, 1H, maj. isomer), 7.15 (d, $J = 2.2$ Hz, 1H, maj. isomer), 7.09 (d, $J = 2.2$ Hz, 1H, min. isomer), 7.06 (d, $J = 2.2$ Hz, 1H, min. isomer), 5.19 (s, 1H,

min. isomer), 5.09 (s, 1H, min. isomer), 4.92 (s, 1H, maj. isomer), 4.69 (s, 1H, maj. isomer), 4.30 (s, 1H, min. isomer), 4.28 (d, $J = 2.7$ Hz, 1H, maj. isomer), 3.82 (s, 3H, min. isomer), 3.78 (s, 3H, maj. isomer), 3.50 (d, $J = 2.7$ Hz, 1H, maj. isomer), 2.34 (d, $J = 4.5$ Hz, 1H, min. isomer), 1.64 (s, 3H), 1.35 – 1.20 (m, 3H), 1.15 – 1.05 (m, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.82, 168.72, 157.41, 157.30, 156.72, 146.72, 143.52, 139.76, 139.38, 138.48, 131.91, 125.57, 123.67, 122.40, 119.91, 117.07, 114.25, 113.05, 111.15, 107.44, 107.15, 61.23, 53.09, 52.98, 51.46, 50.48, 48.17, 20.53, 18.63, 17.96, 17.59, 17.39, 16.94, 13.00, 12.69. IR (neat, cm^{-1}): 2947 (s), 2866 (s), 1721 (s), 1651 (s), 1586 (s), 1555 (m), 1458 (s), 1377 (m), 1292 (s), 1219 (s), 1157 (w), 1134 (w), 1069 (w), 961 (s), 883 (s), 799 (w), 729 (s), 687 (s), 648 (w); HRMS (ESI): Calculated for $\text{C}_{23}\text{H}_{34}\text{BrO}_4\text{Si}$ ($[\text{M}+\text{H}]^+$): m/z 481.1410, found: 481.1402.

To a 3 ml vial in a glove box was added Sc(OTf)_3 (0.0155 g, 0.0314 mmol, 1.1 eq). The vial was removed from the glove box and aryl dienone **96** (0.0158 g, 0.0286 mmol) dissolved in DCE (0.286 ml) was added. The reaction mixture was stirred for 60 minutes. The reaction mixture was quenched with water. The reaction mixture was extracted three times with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue

was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford **110** as a 4.5:1 mixture of *anti:syn* isomers (0.0063 g, 46% yield).

To a flame-dried 250 ml round-bottom flask was added EtMgBr (3M in Et₂O, 40 ml, 120 mmol, 3 eq) and dry THF (150 ml). The solution was cooled to 0 °C. Propargyl alcohol (2.3 ml, 40 mmol) was added dropwise, and the reaction mixture was stirred and warmed to room temperature for one hour. TBSCl (18 g, 120 mmol, 3 eq) was added, and the reaction mixture was stirred overnight. The reaction mixture was quenched with saturated aqueous NH₄Cl, diluted and extracted with ether, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was then dissolved into MeOH (200 ml) in a 500 ml round-bottom flask. Concentrated HCl (10 ml) was added, and the reaction was stirred for two hours. The reaction was quenched with saturated aqueous NaHCO₃, diluted and extracted with ether, dried over MgSO₄, filtered, and concentrated under reduced pressure to afford crude **S6** (6.81 g, quantitative). ¹H NMR (400 MHz, CDCl₃) δ 4.28 (d, *J* = 6.0 Hz, 1H), 1.61 – 1.48 (m, 1H), 0.94 (s, 9H), 0.11 (s, 6H).

To a flame-dried 50 ml round-bottom flask was added **S6** (0.95 g, 5.588 mmol), CuI (0.106 g, 0.559 mmol, 0.1 eq), and Et₂O (17 ml). The solution was cooled to 0 °C and MeMgCl (3M in THF, 4.1 ml, 12.294 mmol, 2.2 eq) was added dropwise. The reaction mixture was heated at reflux overnight. The reaction mixture was quenched with saturated aqueous NaHCO₃, diluted and extracted with ether, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (3:1 hexane:ethyl acetate) to afford **S7** (1.02g, 98%). ¹H NMR (400 MHz, CDCl₃) δ 5.52 (d, *J* = 0.7 Hz, 1H), 4.03 (d, *J* = 4.5 Hz, 2H), 1.77 (s, 3H), 0.94 (s, 1H), 0.89 (s, 9H), 0.10 (s, 6H).

To a 100 ml round-bottom flask was added **S7** (1.0g, 5.376 mmol), MnO₂ (18.7 g, 215 mmol, 40 eq), and CH₂Cl₂ (50 ml). The reaction mixture was stirred overnight. The solution was filtered and concentrated under reduced pressure. The crude residue was taken to the next step without further purification.

To a 25 ml round-bottom flask was added the product of the previous step, N-methyl-N-hydroxylamine hydrochloride (1.345g, 16.116 mmol, 3 eq), MgSO₄ (1.617g, 13.43 mmol, 2.5 eq), NaHCO₃ (2.48g, 29.546 mmol, 5.5 eq), and CH₂Cl₂ (10 ml). The reaction mixture was stirred overnight. The solution was filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 ethyl

acetate:methanol) to afford unreacted starting material (0.1816 g, 18.4%) and **93** (0.533 g, 46.5%). ^1H NMR (400 MHz, CDCl_3) δ 6.87 (s, 1H), 6.86 (s, 1H), 3.71 (s, 3H), 2.14 (s, 3H), 0.91 (s, 9H), 0.13 (s, 6H).

To a 50 ml round-bottom flask was added **93** (0.533 g, 2.5 mmol), **91** (1.028 g, 2.5 mmol), and toluene (25 ml). The flask was purged with argon for 10 minutes. The reaction mixture was heated at 80 °C overnight. The solution was concentrated under reduced pressure, and the crude residue was purified by flash column chromatography (97:3 hexane:ethyl acetate) to afford **S8** (1.4 g, 90%). ^1H NMR (500 MHz, CDCl_3) δ 7.57 (d, $J = 1.5$ Hz, 1H), 7.22 (d, $J = 1.5$ Hz, 1H), 7.12 (d, $J = 1.8$ Hz, 1H), 5.47 (s, 1H), 4.49 (s, 1H), 3.63 (s, 3H), 2.91 (s, 3H), 1.84 (s, 3H), 1.35 – 1.21 (m, 3H), 1.15 – 1.04 (m, 18H), 0.88 (s, 9H), 0.10 (s, 6H).

To a 50 ml round-bottom flask was added **S8** (1.4 g, 2.24 mmol) and CH_2Cl_2 (25 ml). The solution was cooled to 0°C . *m*-CPBA (77%, 1.00 g, 5.82 mmol, 2 eq) was added, and the solution stirred for 30 minutes. The reaction was quenched with a saturated aqueous solution of Na_2SO_3 , diluted and extracted with ether, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford **97** (1.147 g, 86%). ^1H NMR (400 MHz, CDCl_3) δ 7.63 (s, 1H), 7.51 (s, 1H), 7.32 – 7.28 (m, 1H), 7.23 (t, $J = 1.9$ Hz, 1H), 6.09 (s, 1H), 3.70 (s, 3H), 1.70 (s, 3H), 1.33 – 1.17 (m, 3H), 1.08 (d, $J = 7.3$ Hz, 18H), 0.83 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.74, 165.70, 157.36, 149.29, 147.51, 143.56, 139.41, 128.34, 128.28, 124.66, 123.30, 119.25, 52.66, 26.42, 20.35, 17.94, 17.23, 12.68, -4.65.

To a flame-dried 25 ml round-bottom flask in a glove box was added AlCl_3 (0.134 g, 1 mmol). The flask was removed from the glove box and DCE (10 ml) and **97** (0.593 g, 1 mmol) were added. The reaction was stirred for 15 minutes, then quenched with a saturated aqueous solution of NH_4Cl . The mixture was diluted and extracted with ether, dried over MgSO_4 , filtered, then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (3:1 hexanes:methylene chloride, then 19:1 hexanes:ethyl acetate) to afford **100** (0.350 g, 73%).

To a flame-dried 3 ml vial in a glove box was added $\text{Pd}_2(\text{dba})_3$ (0.0046 g, 0.005 mmol, 0.05 eq), P^tBu_3 (10% in hexanes, 0.025 mmol, 0.25 eq), and NaO^tBu (0.0115 g, 0.12 mmol, 1.2 eq). The vial was capped with a pierceable PTFE seal. The vial was removed from the glove box and dry toluene (0.2 ml) was added. The mixture was stirred for five minutes. **105** (0.016 ml, 0.15 mmol, 1.5 eq) and **101** (0.050 g, 0.1 mmol) were added by syringe, and the vial was heated at 110 °C behind a blast shield overnight. The reaction mixture was diluted with ether, filtered over celite, concentrated under reduced pressure, and purified by flash column chromatography (9:1 hexane:ethyl acetate) to afford **106** (0.0032 g, 6.5%). ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.20 (m, 5H), 6.67 (s, 1H), 6.59 (s, 2H), 4.32 (s, 1H), 3.98 (dd, $J = 7.8, 2.7$ Hz, 1H), 2.98 (dd, $J = 19.3, 7.8$ Hz, 1H), 2.49

(dd, $J = 19.3, 2.7$ Hz, 1H), 1.58 (s, 3H), 1.32 (s, 9H), 1.30 – 1.17 (m, 3H), 1.11 (d, $J = 7.2$ Hz, 18H).

To a flame-dried 3 ml vial in a glove box was added Pd₂(dba)₃ (0.0046 g, 0.005 mmol, 0.05 eq), BINAP (0.011 g, 0.015 mmol, 0.15 eq), and NaO^tBu (0.0115 g, 0.12 mmol, 1.2 eq). The vial was capped with a pierceable PFTE seal. The vial was removed from the glove box and dry toluene (0.6 ml) was added. The mixture was stirred for five minutes. **107** (0.025 ml, 0.15 mmol, 1.5 eq) and **101** (0.050 g, 0.1 mmol) were added by syringe, and the vial was heated at 110 °C behind a blast shield overnight. The reaction mixture was concentrated under reduced pressure, and taken onto the next step without further purification.

The crude residue from above was dissolved in THF (0.33 ml) in a 5 ml round-bottom flask. 1M aqueous HCl was added (0.033 ml) and the reaction was stirred for 15 minutes. The reaction was quenched with aqueous saturated NaHCO₃, diluted and extracted with ether, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude material was purified by flash column chromatography (9:1 hexane:ethyl acetate) to afford aniline **108** (11.6 mg, 27% over two steps). ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.13 (m, 5H), 6.69 (d, *J* = 2.0 Hz, 1H), 6.64 (s, 1H), 6.45 (d, *J* = 2.0 Hz, 1H), 4.07 (dd, *J*

= 7.8, 2.6 Hz, 1H), 3.99 (s, 2H), 3.01 (dd, J = 19.3, 7.8 Hz, 1H), 2.53 (dd, J = 19.3, 2.6 Hz, 1H), 1.67 (d, J = 0.9 Hz, 3H), 1.36 – 1.18 (m, 3H), 1.10 (d, J = 7.2 Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 206.09, 157.66, 145.81, 139.68, 138.78, 137.29, 133.96, 128.90, 128.39, 127.69, 127.49, 126.84, 103.48, 103.28, 43.46, 18.09, 17.96, 12.75.

To a 100 ml round-bottom flask was added acetone (40 ml), **100** (3.7g, 7.69 mmol), K_2CO_3 (1.28g, 9.23 mmol), and MeI (1.28g, 27 mmol). The reaction was stirred at room temperature overnight. The mixture was diluted with water and extracted with ether, washed with brine, dried over MgSO_4 , filtered, then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford **109** (2.63g, 97%). ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, J = 2.3 Hz, 1H), 7.23 (d, J = 2.3 Hz, 1H), 5.02 (s, 1H), 4.59 (s, 1H), 3.86 (s, 3H), 3.73 (s, 1H), 3.61 (s, 3H), 1.71 (s, 3H), 1.59 (s, 3H).

To a 10 ml round-bottom flask was added HMPA (10 ml), **109** (0.6g, 1.7 mmol), and NaCN (0.33g, 6.8 mmol). The solution was heated to 80 °C for 2.5h. 0.136 g NaOH (3.4 mmol) in 2.5 ml H₂O was added, and the reaction was stirred for an additional 30 minutes. The mixture was diluted and extracted with ether, washed with brine, dried over MgSO₄, filtered, then concentrated under reduced pressure. The crude mixture was carried to the next step unpurified.

To a 10 ml round-bottom flask was added dioxane (6 ml), the crude residue from the previous step, and K₂CO₃ (0.26 g, 1.9 mmol). The mixture was heated to 80 °C overnight. The mixture was diluted and extracted with ether, washed with brine, dried over MgSO₄, filtered, then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 to 4:1 hexanes:ethyl acetate) to afford **110** as a 4:1 mixture of *anti/syn* diastereomers (0.171 g, 34% over two steps). Major isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, *J* = 2.3 Hz, 1H), 7.18 (d, *J* = 2.3 Hz, 1H), 4.88 (s, 1H), 4.76 (s, 1H), 3.84 (s, 4H), 3.51 (d, *J* = 2.8 Hz, 1H), 2.49 (qd, *J* = 7.5, 2.8 Hz, 1H), 1.60 (s, 2H), 1.33 (d, *J* = 7.5 Hz, 5H).

To a flame-dried 25 ml two-necked round-bottom flask in a glove box was added Pd(allyl)₂Cl₂ (0.103g, 0.028 mmol), **111** (0.0522 g, 0.1126 mmol), and NaO^tBu (0.108 g,

1.689 mmol). The flask was taken out of the glove box and charged with 2.25 ml dry toluene. The solution was stirred at room temperature for 10 minutes. **110** (0.166 g, 0.563 mmol) was added, followed by ammonia (0.5 M in dioxane, 3.38 ml). The solution was refluxed for 45 minutes. The mixture was diluted and extracted with ether, washed with brine, dried over MgSO_4 , filtered, then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford **112** as a 3:1 mixture of diastereomers (0.048 g, 37%). Major diastereomer: ^1H NMR (400 MHz, CDCl_3) δ 6.66 (d, $J = 2.1$ Hz, 1H), 6.42 (d, $J = 2.2$ Hz, 1H), 5.08 (s, 1H), 4.97 (s, 1H), 3.99 (s, 2H), 3.78 (s, 3H), 3.44 (d, $J = 3.4$ Hz, 1H), 2.44 (qd, $J = 7.4$, 3.4 Hz, 1H), 1.58 (s, 3H), 1.30 (d, $J = 7.4$ Hz, 3H).

To a 25 ml round-bottom flask was added **100** (0.475 g, 0.987 mmol), DABCO (0.055 g, 0.493 mmol, 0.5 eq), toluene (10 ml), and H_2O (1 ml). The solution was heated at 80 °C overnight. The solution was quenched with saturated aqueous NH_4Cl and extracted three times with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford indanone **113** (0.382 g, 0.902 mmol 91% yield).

LDA was prepared according to the following: to a 50 ml round-bottom flask was added THF (15 ml) and diisopropylamine (1.37 ml, 9.74 mmol, 1.21 eq). The solution was cooled to -40°C , and *n*-BuLi (3.66 ml, 2.42M in hexanes, 1.1 eq) was added. The solution was stirred at -40°C for 40 minutes. Then, indanone **113** (3.41 g, 8.05 mmol), in THF (38 ml) was added dropwise. The solution was stirred and maintained at -40°C for three hours. Then, MeI (24.9 ml, 400 mmol, 50 eq) was added to the solution, which was slowly raised to room temperature overnight. The reaction was quenched the next day with 1M aqueous HCl and extracted three times with Et₂O. The combined organic fractions were washed with saturated NaHCO₃, concentrated under reduced pressure, and taken to the next step without further purification.

The crude material from the previous step was dissolved in MeOH (80 ml) and cooled to 0°C . NaBH₄ (0.610 g, 16.1 mmol, 2 eq) was added. The reaction was stirred at 0°C for 2 hours, then quenched with water. The solution was extracted three times with Et₂O, and the combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford alcohol **114** (2.37 g, 5.39 mmol, 67% over two steps) as a crystalline solid. ¹H NMR (400 MHz, CDCl₃) δ 6.99 (s, 1H), 6.88 (s, 1H), 4.86 (s, 1H), 4.62 (s, 1H), 4.55 (dd, *J* = 8.5, 4.9 Hz, 1H), 3.19 (d, *J* = 5.4 Hz,

1H), 2.18 (d, $J = 8.5$ Hz, 1H), 2.14 – 2.07 (m, 1H), 1.74 (s, 3H), 1.30 – 1.21 (m, 3H), 1.16 (d, $J = 6.9$ Hz, 3H), 1.10 (d, $J = 7.4$ Hz, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.59, 147.61, 147.12, 134.96, 124.24, 120.96, 115.16, 112.45, 82.41, 58.76, 49.23, 20.49, 17.99, 17.89, 12.70. IR (neat, cm^{-1}): 3287 (br), 3075 (w), 2943 (s), 2866 (s), 1605 (s), 1555 (s), 1458 (s), 1412 (w), 1377 (w), 1285 (s), 1211 (m), 1177 (m), 1142 (s), 1057 (s), 999 (s), 880 (s), 845 (s), 814 (w), 760 (s), 733 (m), 683 (s), 644 (w); HRMS (ESI): Calculated for $\text{C}_{22}\text{H}_{35}\text{BrO}_2\text{SiNa}$ ($[\text{M}+\text{H}+\text{Na}]^+$): m/z 461.1487, found: 461.1492.

To a 100 ml round-bottom flask was added **114** (2.54 g, 5.78 mmol), TBSCl (3.48 g, 23.1 mmol, 4 eq), imidazole (3.15 g, 46.2 mmol, 8 eq), and THF (57 ml). The solution was stirred at room temperature overnight. The reaction was quenched with saturated aqueous NH_4Cl and extracted three times with Et_2O . The combined organic fractions were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford aryl bromide **115** (2.90 g, 5.24 mmol, 91% yield) as a translucent oil. ^1H NMR (400 MHz, CDCl_3) δ 6.94 (d, $J = 2.2$ Hz, 1H), 6.74 (d, $J = 2.2$ Hz, 1H), 4.88 (s, 1H), 4.86 (s, 1H), 4.58 (d, $J = 6.3$ Hz, 1H), 3.20 (d, $J = 7.2$ Hz, 1H), 2.08 – 1.97 (m, 1H), 1.62 (s, 3H), 1.31 – 1.19 (m, 3H), 1.15 (d, $J = 6.9$ Hz, 3H), 1.09 (d, $J = 7.2$ Hz, 18H), 0.93 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.27, 148.76, 145.74,

134.25, 123.99, 120.63, 114.67, 113.31, 82.12, 58.89, 49.43, 25.92, 19.39, 18.13, 18.03, 17.25, 12.78, -3.95, -4.12. IR (neat, cm^{-1}): 2951 (s), 2931 (w), 2893 (w), 2866 (s), 1605 (s), 1559 (m), 1458 (s), 1362 (m), 1296 (s), 1254 (s), 1180 (w), 1146 (m), 1115 (s), 1067 (m), 999 (s), 868 (s), 833 (m), 772 (s), 733 (s), 683 (s), 671 (w).

To a 100 ml Schlenk bomb was added $[\text{Pd}(\text{allyl})\text{Cl}]_2$ (0.0192 g, 0.0524 mmol, 0.01 eq), **111** (0.0974 g, 0.210 mmol, 0.04 eq), NaO^tBu (1.01 g, 10.5 mmol, 2 eq), and toluene (52 ml). The solution was stirred for 10 minutes. Then, **115** (2.9 g, 5.24 mmol) was added, followed by NH_3 (0.5 M solution in 1,4-dioxane, 31.4 ml, 3 eq.). The Schlenk bomb was sealed and heated at 110 $^\circ\text{C}$ for 1 hour. The reaction vessel was cooled, quenched with saturated aqueous NH_4Cl , and extracted three times with Et_2O . The combined extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford aniline **116** (2.48 g, 5.06 mmol, 97% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.24 (d, $J = 2.0$ Hz, 1H), 6.05 (d, $J = 2.0$ Hz, 1H), 5.05 (d, $J = 2.0$ Hz, 1H), 4.94 (s, 1H), 4.56 (d, $J = 7.4$ Hz, 1H), 3.75 (s, 2H), 3.15 (d, $J = 8.4$ Hz, 1H), 2.10 – 1.98 (m, 1H), 1.64 (s, 3H), 1.32 – 1.16 (m, 3H), 1.14 (d, $J = 6.8$ Hz, 3H), 1.09 (d, $J = 7.0$ Hz, 18H), 0.95 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ

156.72, 147.94, 147.28, 144.22, 118.61, 113.66, 106.24, 105.50, 82.18, 56.32, 49.05, 26.01, 18.26, 18.20, 18.12, 16.32, 12.86, -3.91, -4.00; IR (neat, cm^{-1}): 2951 (s), 2928 (w), 2893 (w), 2866 (s), 1613 (s), 1470 (s), 1362 (s), 1254 (m), 1204 (m), 1157 (s), 1096 (w), 1009 (m), 837 (s), 683 (w); HRMS (ESI): Calculated for $\text{C}_{28}\text{H}_{52}\text{NO}_2\text{Si}_2$ ($[\text{M}+\text{H}]^+$): m/z 490.3537, found: 490.3531.

6.3. Experimental Procedures from Chapter 3

To a 50 ml round-bottom flask was added **108** (0.060 g, 0.138 mmol), Na_2CO_3 (0.031 g, 0.290 mmol, 2.1 eq), CH_2Cl_2 (10 ml), and H_2O (10 ml). The reaction mixture was cooled to 0°C . Triphosgene (0.016 g, 0.0552 mmol, 0.4 eq) was added, and the reaction mixture was stirred rapidly at 0°C for 30 minutes, then warmed to room temperature over an hour. The reaction was then diluted and extracted with CH_2Cl_2 and concentrated under reduced pressure to afford crude isocyanate (0.067g) which was taken to the next step without further purification.

To a flame-dried 5-ml vial was added $\text{Pd}_2(\text{dba})_3$ (0.013 g, 0.0145 mmol, 0.1 eq) and (R)-BINAP (0.019 g, 0.0307 mmol, 0.06 eq) in a glove box. The vial was capped with a pierceable PTFE seal and removed from the glove box. Dry THF (2.5 ml) was added and the solution was stirred for five minutes. Isoprene monoepoxide (0.014 ml, 0.145 mmol, 1 eq) was added by syringe, followed by the isocyanate prepared from the previous step. The reaction mixture was stirred for 70 hours. The reaction was quenched with saturated aqueous NH_4Cl , diluted and extracted with ether, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford **120** as a 1.5:1 mixture of isomers

(0.019 g, 25% over 2 steps). Major isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.42 – 7.17 (m, 6H), 6.90 (d, $J = 2.2$ Hz, 1H), 6.61 (s, 1H), 6.23 (dd, $J = 17.4, 10.7$ Hz, 1H), 5.41 (d, $J = 10.7$ Hz, 1H), 5.21 (d, $J = 17.4$ Hz, 1H), 4.53 (s, 1H), 4.44 (s, 1H), 4.06 (t, $J = 6.7$ Hz, 1H), 3.08 – 2.88 (m, 1H), 2.58 (d, $J = 2.3$ Hz, 1H), 1.61 (s, 3H), 1.54 (s, 3H), 1.36 – 1.15 (m, 3H), 1.09 (d, $J = 6.7$ Hz, 18H).

To a 5ml round-bottom flask was added **112** (0.048g, 0.208 mmol), triethylamine (0.058ml, 0.416 mmol), and CH_2Cl_2 (2ml). The solution was cooled to 0 °C and charged with triphosgene (0.123g, 0.416 mmol). The solution was brought to rt, stirred for 1h, then refluxed for 1h. The solution was then cooled and filtered through a plug of celite. The crude residue was taken to the next step unpurified.

To a flame-dried 5ml round-bottom flask in a glove box was added $\text{Pd}_2(\text{dba})_3$ (0.0095g, 0.0104 mmol). The flask was taken out of the glove box and charged with anhydrous THF (2ml), triisopropyl phosphite (0.0287ml, 0.125 mmol), and isoprene epoxide (0.0224 ml, 0.229 mmol). The solution was stirred for 10 minutes. The crude product of the previous reaction was then added, and the solution was allowed to stir overnight. The mixture was diluted and extracted with ethyl acetate, washed with brine, dried over MgSO_4 , filtered, then concentrated under reduced pressure. The crude residue was

purified by flash column chromatography (3:1 hexanes:ethyl acetate) to afford **121** as a 1:1 mixture of diastereomers (0.018g, 25% over two steps). ^1H NMR (400 MHz, CDCl_3) δ 7.18 (s, 1H), 7.16 (s, 1H), 7.12 (s, 1H), 6.93 (d, $J = 2.4$ Hz, 1H), 6.21 (dd, $J = 17.3, 10.6$ Hz, 1H), 5.81 (dd, $J = 17.6, 10.8$ Hz, 1H), 5.43 (d, $J = 10.8$ Hz, 2H), 5.29 (d, $J = 10.8$ Hz, 2H), 5.04 (s, 2H), 4.89 (d, $J = 8.7$ Hz, 2H), 4.61 (dq, $J = 12.6, 6.2$ Hz, 1H), 4.18 (d, $J = 8.0$ Hz, 2H), 4.10 (d, $J = 8.2$ Hz, 1H), 4.05 (d, $J = 8.0$ Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 2.49 (qt, $J = 7.4, 3.5$ Hz, 2H), 1.45 (s, 3H), 1.43 (s, 3H), 1.35 – 1.28 (m, 12H).

To a flame-dried 5ml vial in a glove box was added $\text{Pd}_2(\text{dba})_3$ (0.045g, 0.05 mmol), BINAP (0.100 g, 0.15 mmol), and NaO^tBu (0.134g, 1.4mmol). The vial was capped with a PTFE seal and removed from the glove box. The vial was charged with 2ml anhydrous toluene and stirred for 10 minutes. The vial was then charged with **S1** (0.455g, 1mmol) and benzophenone imine (0.217g, 1.2mmol). The solution was stirred overnight at room temperature. The mixture was diluted and extracted with ether, washed with brine, dried over MgSO_4 , filtered, then concentrated under reduced pressure. The crude residue was taken to the next step unpurified.

The crude product was dissolved in THF (2.5ml) and charged with 0.25ml 1M HCl. The solution was mixed at room temperature for 20 minutes, then basified with NaHCO_3 . The mixture was diluted and extracted with ether, washed with brine, dried over MgSO_4 ,

filtered, then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford **122** (0.151g, 44%). ^1H NMR (400 MHz, CDCl_3) δ 6.45 (t, $J = 1.8$ Hz, 1H), 6.43 (t, $J = 1.8$ Hz, 1H), 6.13 (t, $J = 1.8$ Hz, 1H), 3.65 (s, 2H), 1.35 – 1.17 (m, 3H), 1.10 (d, $J = 7.2$ Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.73, 148.56, 122.91, 113.62, 111.29, 105.57, 17.98, 12.70.

To a flame-dried 100ml round-bottom flask is added **122** (1.9g, 5.52mmol), Na_2CO_3 (1.23g, 11.6 mmol), and anhydrous CH_2Cl_2 , (55ml). The solution is cooled to 0 °C. Phosgene is added (3ml, 20% solution in toluene), and the solution is stirred at 0 °C for 1 hour, then refluxed for 1 hour. The solution is concentrated under reduced pressure, filtered through celite, and taken on to the next step unpurified.

To a flame-dried 100ml round-bottom flask is added $\text{Pd(PPh}_3)_4$ (0.329g, 0.285mmol), isopropyl phosphite, (0.1311ml, 0.570mmol), and anhydrous THF (40 ml) under an atmosphere of argon. The solution is stirred at room temperature for 10 minutes. Then isoprene epoxide (0.838ml, 8.55 mmol) was added, followed by the product of the previous reaction. The reaction is usually finished upon addition of isocyanate. . The mixture was diluted and extracted with ether, washed with brine, dried over MgSO_4 , filtered, then concentrated under reduced pressure. The crude residue was purified by

flash column chromatography (9:1 hexanes:ethyl acetate) to afford **123** (2.42g, 96%). ^1H NMR (400 MHz, CDCl_3) δ 7.09 (t, $J = 1.6$ Hz, 1H), 6.92 (s, 1H), 6.76 (t, $J = 1.6$ Hz, 1H), 6.04 (dd, $J = 17.4, 10.7$ Hz, 1H), 5.33 (d, $J = 10.7$ Hz, 1H), 5.26 (d, $J = 17.4$ Hz, 1H), 4.20 (d, $J = 8.5$ Hz, 1H), 4.10 (d, $J = 8.5$ Hz, 1H), 1.47 (s, 3H), 1.28 – 1.16 (m, 3H), 1.07 (d, $J = 7.3$ Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.99, 155.95, 139.45, 137.48, 122.30, 121.78, 121.74, 117.45, 116.35, 74.38, 63.72, 21.28, 17.90, 12.60.

To a flame-dried 100ml two-neck round-bottom flask was added $\text{PdCl}_2(\text{PPh}_3)_2$ (0.304g, 0.433 mmol) and CuI (0.082g, 0.433mmol) under an atmosphere of argon. Then **123** (1.97g, 4.33 mmol) was added in 43ml acetonitrile. Triethylamine was added, (10.9ml, 78.373mmol), followed by ethynyltrimethylsilane (6.12ml, 43.3mmol), and the solution was raised to 70 $^\circ\text{C}$ and ran overnight. The mixture was cooled, diluted and extracted with ether, washed with brine, dried over MgSO_4 , filtered, then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford **S8** (1.32g, 65%). ^1H NMR (400 MHz, CDCl_3) δ 7.22 – 6.96 (m, 1H), 6.85 (dd, $J = 2.1, 1.3$ Hz, 1H), 6.77 (t, $J = 2.1$ Hz, 1H), 6.04 (dd, $J = 17.4, 10.7$ Hz, 1H), 5.30 (d, $J = 10.7$ Hz, 1H), 5.23 (d, $J = 17.4$ Hz, 1H), 4.20 (d, $J = 8.5$ Hz,

1H), 4.09 (d, $J = 8.5$ Hz, 1H), 1.45 (s, 3H), 1.32 – 1.16 (m, 3H), 1.07 (d, $J = 7.1$ Hz, 18H), 0.22 (s, 9H).

To a 50ml round-bottom flask was added K_2CO_3 (0.034g, 0.247mmol), **S8**, (1.163g, 2.47mmol), and 25ml MeOH. After stirring for 30 minutes, the mixture was diluted and extracted with ether, washed with brine, dried over MgSO_4 , filtered, then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford **124** as a brown oil (0.693g, 70%). ^1H NMR (400 MHz, CDCl_3) δ 6.95 (s, 1H), 6.76 (s, 2H), 5.93 (dd, $J = 17.3, 10.7$ Hz, 1H), 5.18 (d, $J = 10.7$ Hz, 1H), 5.11 (d, $J = 17.3$ Hz, 1H), 4.06 (d, $J = 8.5$ Hz, 1H), 3.97 (d, $J = 8.5$ Hz, 1H), 2.99 (s, 1H), 1.33 (s, 3H), 1.25 – 1.08 (m, 3H), 0.97 (d, $J = 7.5$ Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.74, 155.55, 139.17, 136.53, 123.05, 122.15, 121.28, 118.29, 116.71, 82.46, 77.65, 73.86, 63.20, 20.75, 17.48, 12.18.

To a flame-dried 25ml round bottom flask was added 13m anhydrous THF and **124** (0.520g, 1.303 mmol) under an atmosphere of argon. The solution was cooled to -78 °C. LHMDS (1.7ml, 1M in THF, 1.694mmol) was added dropwise and the solution was stirred at -78 °C for one hour. Methyl chloroformate (0.131ml, 1.694mmol) was added dropwise, and the solution was raised to rt. After an additional hour of stirring, the mixture was quenched with saturated NH₄Cl, extracted with ether, washed with brine, dried over MgSO₄, filtered, then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (4:1 hexanes:ethyl acetate) to afford **S9** (0.482g, 81%). ¹H NMR (400 MHz, CDCl₃) δ 7.13 – 7.02 (m, 1H), 6.88 (t, *J* = 2.1 Hz, 1H), 6.87 – 6.79 (m, 1H), 5.97 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.25 (d, *J* = 10.7 Hz, 1H), 5.17 (d, *J* = 17.4 Hz, 1H), 4.12 (d, *J* = 8.5 Hz, 1H), 4.03 (d, *J* = 8.5 Hz, 1H), 3.71 (s, 3H), 1.39 (s, 3H), 1.22 – 1.10 (m, 3H), 0.98 (d, *J* = 7.3 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 156.19, 155.68, 153.95, 139.12, 137.06, 122.60, 121.94, 120.48, 120.15, 117.24, 85.18, 80.20, 74.12, 63.45, 52.59, 20.92, 17.60, 12.33.

To a 5ml round-bottom flask was added **S9** (0.039g, 0.0853mmol, **84** (0.016g, 0.094mmol), and toluene (0.8ml). The solution was heated to 80 °C and left to stir

overnight. The mixture was diluted and extracted with ether, washed with brine, dried over MgSO_4 , filtered, then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (3:1 hexanes:ethyl acetate) to afford **S10** as a 1:1 mixture of diastereomers (0.045g, 85%). ^1H NMR (400 MHz, CDCl_3) δ 7.42 (t, J = 1.6 Hz, 1H), 7.40 (t, J = 1.6 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.18 – 7.15 (m, 1H), 6.95 (t, J = 2.1 Hz, 1H), 6.93 (t, J = 2.1 Hz, 1H), 6.15 – 6.02 (m, 2H), 5.46 (s, 2H), 5.37 – 5.22 (m, 4H), 4.45 (s, 2H), 4.27 – 4.10 (m, 4H), 3.64 (s, 3H), 3.63 (s, 3H), 2.88 (s, 6H), 1.83 (s, 6H), 1.52 (s, 3H), 1.51 (s, 3H), 1.30 – 1.20 (m, 6H), 1.09 (d, J = 7.2 Hz, 36H), 0.11 (s, 18H).

To a 5ml round-bottom flask was added **S10** (0.100g, 0.159mmol) and CH_2Cl_2 (1.6ml). The solution was cooled to $0\text{ }^\circ\text{C}$. The solution was charged with $m\text{-CPBA}$ (0.0713g, 0.3184mmol) and stirred at $0\text{ }^\circ\text{C}$ for 30 minutes. The reaction was quenched with 10% aqueous Na_2SO_3 , extracted with ether, washed with brine, dried over MgSO_4 , filtered, then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate to 4:1 hexanes:ethyl acetate) to afford **125** (0.080g, 84%). ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, J = 0.7 Hz, 1H), 7.43 – 7.38

(m, 1H), 7.27 (dd, $J = 2.2, 1.5$ Hz, 1H), 7.17 (t, $J = 2.2$ Hz, 1H), 6.21 – 5.88 (m, 2H), 5.32 (d, $J = 10.7$ Hz, 1H), 5.24 (d, $J = 17.4$ Hz, 1H), 4.22 (d, $J = 8.5$ Hz, 1H), 4.12 (d, $J = 8.5$ Hz, 1H), 3.67 (s, 3H), 1.67 (s, 3H), 1.47 (s, 3H), 1.35 – 1.15 (m, 3H), 1.07 (d, $J = 7.1$ Hz, 18H), 0.07 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.37, 165.76, 157.00, 155.99, 148.71, 146.81, 146.20, 139.57, 138.62, 137.35, 128.74, 122.83, 118.70, 118.41, 117.51, 74.42, 63.73, 52.55, 21.26, 19.93, 17.94, 12.67, -0.46.

130 was prepared as described in the literature.⁵ To a 100ml round-bottom flask was added indium metal (3.4 g, 29.6 mmol, 3 eq), **130** (3.14 g, 14.8 mmol, 1.5 eq), EtOH (50 ml), and freshly distilled acetaldehyde (0.55 ml, 9.87 mmol). The mixture was stirred at 30°C for 1 hour. The resulting white suspension was extracted with ether, washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford **131** (0.247 g, 2.52 mmol, 26%). ^1H NMR (400 MHz, CDCl_3) δ 6.28 (dd, $J = 17.8, 11.2$ Hz, 1H), 5.25 (d, $J = 17.8$ Hz, 1H), 5.21 (s, 1H), 5.04 (d, $J = 11.2$ Hz, 1H), 5.03 (s, 1H), 4.51 (q, $J = 6.4$ Hz, 1H), 2.80 (s, 1H), 1.28 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.34, 136.35, 114.02, 113.16, 66.95, 22.84.

To a 50 ml flame-dried round-bottom flask is added V(O)(acac)_2 (0.055 g, 0.209 mmol, 0.1 eq), **131** (0.205 g, 2.09 mmol), and DCM (21 ml). The blue solution is stirred and cooled to 0 °C. Then $t\text{BuOOH}$ is added dropwise (0.76 ml, 5.5M in decanes, 2 eq) and solution turns red. After stirring at 0 °C for 1 hour, the reaction is quenched with 10% aqueous Na_2SO_3 . The solution is extracted with ether, washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford **132** (0.056g, 0.49 mmol, 24%). ^1H NMR (400 MHz, CDCl_3) δ 5.95 (dd, $J = 17.3, 10.9$ Hz, 1H), 5.39 (dd, $J = 17.3, 1.3$ Hz, 1H), 5.27 (dd, $J = 10.9, 1.3$ Hz, 1H), 3.92 (q, $J = 6.3$ Hz, 1H), 3.00 (d, $J = 5.4$ Hz, 1H), 2.67 (d, $J = 5.4$ Hz, 1H), 2.34 (s, 1H), 1.24 (d, $J = 6.3$ Hz, 3H).

To a 5 ml round-bottom flask was added **132** (0.028 g, 0.246 mmol), TsCl (0.141 g, 0.738 mmol), Et_3N (0.154 ml, 1.107 mmol), DMAP (0.004 g, 0.012 mmol) and DCM (1.23ml). The solution was stirred overnight. The reaction was quenched with a saturated solution of aqueous NH_4Cl . The solution was extracted with ether, washed with brine,

dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford **133** (0.0168 g, 25%). ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.2$ Hz, 1H), 7.34 (d, $J = 8.2$ Hz, 1H), 6.04 (dd, $J = 17.2, 10.9$ Hz, 1H), 5.37 (dd, $J = 17.2, 1.2$ Hz, 1H), 5.25 (dd, $J = 10.9, 1.2$ Hz, 1H), 4.26 (q, $J = 6.5$ Hz, 1H), 2.74 (d, $J = 5.5$ Hz, 1H), 2.59 (d, $J = 5.5$ Hz, 1H), 2.45 (s, 3H), 1.28 (d, $J = 6.5$ Hz, 3H).

To a 10 ml round-bottom flask was added **132** (0.065 g, 0.572 mmol), MOMCl (0.174 ml, 2.29 mmol), DIEPA (0.598 ml, 3.43 mmol), NaI (0.155g, 1.03 mmol), and DCM (2.8 ml). The solution was stirred at reflux overnight. The reaction was quenched with saturated solution of aqueous NaHCO_3 . The solution was extracted with ether, washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford **134** (0.0171 g, 38%). ^1H NMR (400 MHz, CDCl_3) δ 6.10 (dd, $J = 17.3, 10.9$ Hz, 1H), 5.40 (dd, $J = 17.3, 1.7$ Hz, 1H), 5.24 (dd, $J = 10.9, 1.7$ Hz, 1H), 4.71 (d, $J = 6.8$ Hz, 1H), 4.64 (d, $J = 6.8$ Hz, 1H), 3.51 (q, $J = 6.4$ Hz, 1H), 3.37 (s, 3H), 2.92 (d, $J = 5.8$ Hz, 1H), 2.68 (d, $J = 5.8$ Hz, 1H), 1.25 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 133.03, 117.07, 95.49, 74.83, 59.66, 55.94, 55.58, 17.48.

To a 20 ml scintillation vial was added $[\text{Pd}(\text{allyl})\text{Cl}]_2$ (0.0083 g, 0.0226 mmol, 0.05 eq), **111** (0.0419 g, 0.0903 mmol, 0.2 eq), NaO^tBu (0.0864 g, 0.903 mmol, 2 eq), and toluene (6.3 ml). The solution was stirred for 10 minutes. Then, **113** (0.191 g, 0.452 mmol) was added, followed by NH_3 (0.5 M solution in 1,4-dioxane, 2.71 ml, 3 eq.). The vial was sealed and heated at $110\text{ }^\circ\text{C}$ for 1 hour. The reaction vessel was cooled, quenched with saturated aqueous NH_4Cl , and extracted three times with Et_2O . The combined extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford aniline **S11** (0.057 g, 0.159 mmol, 35% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.65 (d, $J = 2.0$ Hz, 1H), 6.41 (d, $J = 2.0$ Hz, 1H), 5.02 (s, 1H), 4.94 (d, $J = 1.3$ Hz, 1H), 4.10 – 3.80 (m, 3H), 2.92 (dd, $J = 19.3, 7.9$ Hz, 1H), 2.44 (dd, $J = 19.3, 2.7$ Hz, 1H), 1.53 (s, 3H), 1.39 – 1.17 (m, 3H), 1.08 (d, $J = 7.3$ Hz, 18H).

To a 10 ml round-bottom flask was added **S11** (0.057 g, 0.159 mmol), CH_2Cl_2 (1.6 ml), and saturated aqueous NaHCO_3 (1.6 ml). The solution was stirred vigorously for 5 minutes at $0\text{ }^\circ\text{C}$. Then, the stirring was halted and the layers were allowed to separate. Then, phosgene (0.2 ml, 1.94 M solution in toluene, 2.5 eq) was added via syringe into the organic (bottom) layer. The biphasic system was stirred vigorously for 1 hour at $0\text{ }^\circ\text{C}$. Then, the solution was extracted three times with CH_2Cl_2 , dried over MgSO_4 , and

concentrated under reduced pressure. The crude material was used without further purification.

To a 1L round-bottom flask was added **116** (11.1 g, 22.7 mmol), CH_2Cl_2 (225 ml), and saturated aqueous NaHCO_3 (225 ml). The solution was stirred vigorously for 5 minutes at $0\text{ }^\circ\text{C}$. Then, the stirring was halted and the layers were allowed to separate. Then, phosgene (29.3 ml, 1.94 M solution in toluene, 2.5 eq) was added via syringe into the organic (bottom) layer. The biphasic system was stirred vigorously for 1 hour at $0\text{ }^\circ\text{C}$. Then, the solution was extracted three times with CH_2Cl_2 , dried over MgSO_4 , and concentrated under reduced pressure. The crude material was taken to the next step without further purification.

The crude isocyanate was dissolved in CH_2Cl_2 (225 ml), and added to a 500 ml round bottom flask containing alcohol **139** (4.30 g, 25.0 mmol, 1.1 eq), DMAP (2.77 g, 22.7 mmol 1 eq), and $4\text{\AA}$ molecular sieves (11.3 g). The solution was stirred at room temperature and monitored by TLC for the complete consumption of starting material. The reaction was filtered through a plug of celite, poured into water, and extracted three

times with Et₂O. The combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (39:1 hexanes:ethyl acetate to 19:1 hexanes:ethyl acetate) to afford carbamate **140** (10.7 g, 15.6 mmol, 69% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.46 (s, 1H), 7.26 (s, 1H), 6.59 (dd, *J* = 17.6, 11.3 Hz, 1H), 6.53 (d, *J* = 1.4 Hz, 1H), 5.77 (t, *J* = 6.8 Hz, 1H), 5.38 (d, *J* = 17.6 Hz, 1H), 5.31 (d, *J* = 11.3 Hz, 1H), 5.14 (s, 1H), 5.05 (s, 1H), 4.85 (d, *J* = 6.8 Hz, 2H), 4.81 (s, 2H), 4.59 (d, *J* = 7.4 Hz, 1H), 3.79 (s, 3H), 3.21 (d, *J* = 8.6 Hz, 1H), 2.16 – 2.02 (m, 1H), 1.61 (s, 3H), 1.32 – 1.23 (m, 3H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.10 (d, *J* = 7.2 Hz, 18H), 0.95 (s, 9H), 0.19 (s, 3H), 0.15 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.63, 155.82, 152.85, 147.54, 146.91, 136.47, 135.62, 130.07, 124.19, 121.04, 117.74, 115.08, 110.20, 81.79, 64.87, 63.54, 56.31, 55.03, 49.05, 25.98, 18.18, 18.11, 18.01, 16.09, 12.84, -3.92, -4.01; IR (neat, cm⁻¹): 2951 (s), 2932 (w), 2893 (w), 2866 (s), 1748 (s), 1593 (s), 1532 (s), 1458 (s), 1443 (s), 1362 (w), 1335 (w), 1258 (s), 1207 (s), 1150 (s), 1111 (s), 1072 (w), 1011 (m), 980 (m), 837 (s), 772 (m), 737 (w), 683 (m); HRMS (ESI): Calculated for C₃₇H₆₂NO₇Si₂ ([M+H]⁺): *m/z* 688.4065, found: 688.4063.

Using $\text{Pd}_2(\text{dba})_3$: To a 5 ml round-bottom flask was added $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (0.0164 g, 0.0158 mmol, 0.05 eq), BINAP (0.0395 g, 0.0634 mmol, 0.2 eq), Cs_2CO_3 (0.103 g, 0.317 mmol, 1 eq), and THF (1.6 ml). The mixture was allowed to stir for 5 minutes. Then **140** (0.218 g, 0.317 mmol) was added and the reaction was stirred at 60 °C overnight. The reaction was quenched with saturated aqueous NH_4Cl and extracted three times with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. TLC analysis showed near-overlap of bands corresponding to dba and product. Thus, the crude residue was dissolved in MeOH (3 ml) and cooled to 0 °C. To this solution was added NaBH_4 (0.0240 g, 0.634 mmol, 2 eq), and the reaction was stirred for 1 hour. The reaction was quenched with saturated aqueous NH_4Cl and extracted three times with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford oxazolidinone **141** (0.127 g, 0.208 mmol, 66%) as a crystalline solid.

Using $\text{Pd}(\text{PPh}_3)_4$: To a 250 ml round-bottom flask was added $\text{Pd}(\text{PPh}_3)_4$ (1.08 g, 0.938 mmol, 0.05 eq), **140** (12.9 g, 18.7 mmol), and THF (100 ml). The reaction was heated at 40°C for one hour. The reaction was quenched with saturated aqueous NH_4Cl and extracted three times with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford oxazolidinone **141** (8.05 g, 13.2 mmol, 71%) as a crystalline solid. ^1H NMR (400 MHz, CDCl_3) δ 6.71 (s, 1H), 6.55 (d, J = 2.1 Hz, 1H), 6.19 (dd, J = 17.3, 10.8 Hz, 1H), 5.76

(dd, $J = 17.0, 11.0$ Hz, 1H), 5.56 – 5.38 (m, 2H), 5.36 (d, $J = 11.0$ Hz, 1H), 5.32 (d, $J = 17.8$ Hz, 1H), 5.01 (s, 1H), 4.87 (s, 1H), 4.66 (d, $J = 7.8$ Hz, 1H), 4.22 – 4.00 (m, 2H), 3.54 – 3.36 (m, 1H), 2.11 – 1.99 (m, 1H), 1.49 (s, 3H), 1.22 – 1.13 (m, 6H), 1.05 (dd, $J = 7.3, 2.6$ Hz, 18H), 0.96 (s, 9H), 0.18 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.23, 154.41, 149.32, 144.14, 136.98, 134.45, 132.65, 130.02, 120.59, 118.05, 114.09, 113.63, 81.52, 73.34, 68.58, 56.86, 48.93, 25.97, 19.18, 18.17, 17.98, 16.07, 12.68, -3.96, -4.08; IR (neat, cm^{-1}): 2951, 2932, 2893, 2866, 1755, 1609, 1470, 1381, 1362, 1277, 1254, 1215, 1180, 1150, 1103, 907, 883, 837, 772, 729, 683, 648; HRMS (ESI): Calculated for $\text{C}_{35}\text{H}_{58}\text{NO}_4\text{Si}_2$ ($[\text{M}+\text{H}]^+$): m/z 612.3904, found: 612.3903.

Vinyl iodide **142** was prepared in two steps from commercially available 2-butyne-1,4-diol according to the literature.⁶ To a 25 ml round-bottom flask was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.397 g, 0.566 mmol, 0.2 eq), vinyl iodide **142** (0.928 g, 2.83 mmol), degassed DMF (10 ml), and $\text{Bu}_3\text{Sn(vinyl)}$ (1.24 ml, 4.25 mmol, 1.5 eq). The reaction was stirred at room temperature overnight. The brown reaction mixture was quenched the next day with 10 ml 10% aqueous NH_4OH solution and stirred for 15 minutes. The solution turned bright yellow. The solution was extracted three times with Et_2O . The combined organic extracts were washed five times with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (3:1

hexanes:ethyl acetate) to afford diene **S12** (0.524 g, 2.29 mmol, 81% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.57 (dd, $J = 17.7, 11.3$ Hz, 1H), 5.86 (t, $J = 6.5$ Hz, 1H), 5.22 (d, $J = 17.7$ Hz, 1H), 5.14 (d, $J = 11.3$ Hz, 1H), 4.30 (s, 4H), 1.87 (br s, 1H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.51, 130.83, 127.22, 115.23, 63.38, 58.59, 26.03, 18.48, -5.24; IR (neat, cm^{-1}): 3341 (br), 2955 (s), 2928 (s), 2886 (w), 2859 (s), 1462 (m), 1389 (w), 1362 (w), 1319 (w), 1254 (s), 1119 (w), 1080 (s), 991 (s), 907 (m), 833 (s), 775 (s), 737 (w), 710 (w), 667 (w); HRMS (ESI): Calculated for $\text{C}_{12}\text{H}_{24}\text{O}_2\text{Si}_2\text{Na}$ ($[\text{M}+\text{H}+\text{Na}]^+$): m/z 251.1443, found: 251.1447.

To a 250 ml round-bottom flask was added **S12** (6.08 g, 26.6 mmol), CH_2Cl_2 (133 ml), methyl chloroformate (6.17 ml, 79.8 mmol, 3 eq), and pyridine (8.57 ml, 106 mmol, 4 eq). The solution was stirred at 0°C for 30 minutes. The solution was quenched with a 1M aqueous solution of HCl and extracted three times with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude material was taken to the next step without further purification.

To a 500 ml round-bottom flask cooled to 0°C was added the crude material from the previous step, THF (260 ml), and TBAF (53.2 ml, 1M in THF, 2 eq) at 0°C . The solution was brought to room temperature and stirred for 1 hour. The reaction was quenched with

saturated aqueous NH_4Cl and extracted three times with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (3:1 hexanes:ethyl acetate) to afford alcohol **139** (4.23 g, 24.6 mmol, 92% over two steps) as a pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 6.55 (dd, $J = 17.7, 11.3$ Hz, 1H), 5.76 (t, $J = 6.7$ Hz, 1H), 5.33 (d, $J = 17.7$ Hz, 1H), 5.24 (d, $J = 11.3$ Hz, 1H), 4.78 (d, $J = 6.7$ Hz, 2H), 4.26 (s, 2H), 3.73 (s, 3H), 2.42 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.78, 140.61, 130.22, 121.96, 117.10, 63.56, 63.21, 54.88; IR (neat, cm^{-1}): 3402 (br), 3094 (w), 3013 (w), 2959 (m), 2928 (w), 2870 (w), 1744 (s), 1659 (w), 1601 (w), 1443 (s), 1377 (w), 1350 (w), 1254 (s), 1115 (w), 1072 (m), 1038 (w), 984 (w), 934 (s), 856 (w), 791 (s), 691 (w); HRMS (ESI): Calculated for $\text{C}_8\text{H}_{12}\text{O}_4\text{Na}$ ($[\text{M}+\text{H}+\text{Na}]^+$): m/z 195.0633, found: 195.0643.

To a 250 ml round-bottom flask was added commercially available pent-4-yn-1-ol (10 g, 118.88 mmol), CH_2Cl_2 (150 ml), TBSCl (20 g, 133 mmol, 1.12 eq), Et_3N (37 ml, 266 mmol, 2.24 eq), and DMAP (0.726 g, 5.94 mmol, 0.05 eq). The reaction was stirred at room temperature overnight. The reaction was quenched with water, extracted three times with Et_2O , and the combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was taken to the next step without further purification.

To a flame-dried 250 ml round bottom flask under argon atmosphere was added the crude residue from the previous step and dry THF (157 ml). The reaction mixture was cooled to -78 °C. BuLi was added (2.5 M solution in hexanes, 52.3 ml, 1.1 eq) dropwise and the reaction mixture stirred at -78 °C for 1 hour. Then paraformaldehyde (5.7 g, 190.2 mmol, 1.6 eq) was added as the reaction mixture slowly warmed to room temperature overnight. The reaction was quenched with saturated aqueous NH₄Cl, extracted three times with Et₂O, and the combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford alcohol **S13** (23.9 g, 104 mmol, 87% yield over two steps). ¹H NMR (400 MHz, CDCl₃) δ 4.24 (dt, *J* = 6.0, 2.2 Hz, 2H), 3.68 (t, *J* = 6.0 Hz, 2H), 2.30 (tt, *J* = 7.1, 2.2 Hz, 2H), 1.81 – 1.63 (m, 2H), 1.49 (t, *J* = 6.0 Hz, 1H), 0.89 (s, 9H), 0.05 (s, 6H).

To a flame dried 50 ml round-bottom flask was added alcohol **S13** (1.32 g, 5.75 mmol) and dry THF (14.4 ml). The reaction mixture was cooled to 0 °C and Red-Al (3.3 M in toluene, 2.79 ml, 1.6 eq) was added dropwise. Upon complete addition, the solution was stirred for 30 minutes. Then the reaction was cooled to -78 °C and a solution of I₂ (2.77 g, 1.9 eq) in dry THF (7.2 ml) was added dropwise. The reaction mixture was warmed to 0 °C and quenched with saturated aqueous Rochelle's salt solution and saturated aqueous sodium thiosulfate solution. The reaction mixture was extracted three times with Et₂O,

and the combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (19:1 benzene:ethyl acetate) to afford iodide **143** (0.926 g, 2.59 mmol, 45% yield) and unreacted starting material (23% yield). ^1H NMR (400 MHz, CDCl_3) δ 5.86 (t, J = 5.8 Hz, 1H), 4.19 (d, J = 5.8 Hz, 2H), 3.61 (t, J = 6.1 Hz, 2H), 2.58 (t, J = 7.2 Hz, 2H), 2.40 – 2.19 (m, 2H), 1.78 – 1.69 (m, 1H), 0.89 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 133.94, 110.18, 67.42, 61.42, 41.82, 32.38, 26.06, -5.16.

To a 25 ml round-bottom flask was added iodide **143** (0.953 g, 2.66 mmol), $\text{Pd(PPh}_3)_2\text{Cl}_2$ (0.093 g, 0.133 mmol, 0.05 eq), and DMF (8.86 ml). The reaction mixture was sparged with argon for 1 hour. Tributylvinyltin was added (0.933 ml, 3.19 mmol, 1.2 eq) and the solution was stirred at room temperature overnight. The reaction was quenched with 9:1 10% aqueous NH_4OH solution:saturated aqueous NH_4Cl solution. The reaction mixture was extracted three times with Et_2O , and the combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate to 9:1 hexanes:ethyl acetate) to afford diene **S14** (0.403 g, 1.56 mmol, 59% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.62 (dd, J = 17.4, 11.0 Hz, 1H), 5.59 (t, J = 6.8 Hz, 1H), 5.33 (d, J = 17.4 Hz, 1H), 5.18 (d, J = 11.0 Hz, 1H), 4.30 (d, J = 6.8 Hz, 2H), 3.62 (t, J = 6.3 Hz, 2H), 2.44 – 2.18 (m, 2H), 1.80 – 1.55 (m, 2H), 1.20 (t, J = 6.8 Hz, 1H), 0.90 (s,

9H), 0.05 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.58, 132.19, 128.09, 115.70, 62.84, 58.71, 31.93, 29.62, 26.09, 18.46, -5.15.

To a 25 ml round-bottom flask cooled to 0 °C was added diene **S14** (0.387 g, 1.5 mmol), CH_2Cl_2 (7.5 ml), methyl chloroformate (0.348 ml, 4.5 mmol, 3 eq), and pyridine (0.483 ml, 6 mmol, 4 eq). The reaction was stirred for one hour. The reaction was quenched with water. The reaction mixture was extracted three times with Et_2O , and the combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford diene **S15** (0.461 g, 1.46 mmol, 97% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.58 (dd, J = 17.4, 11.0 Hz, 1H), 5.48 (t, J = 7.0 Hz, 1H), 5.32 (d, J = 17.4 Hz, 1H), 5.19 (d, J = 11.0 Hz, 1H), 4.73 (d, J = 7.0 Hz, 2H), 3.71 (s, 3H), 3.56 (t, J = 6.2 Hz, 2H), 2.51 – 2.14 (m, 2H), 1.72 – 1.51 (m, 2H), 0.85 (s, 9H), -0.01 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.75, 142.08, 131.83, 121.95, 116.53, 63.63, 62.44, 54.63, 31.62, 29.57, 25.92, 18.26, -5.36.

To a 25 ml round-bottom flask is added diene **S15** (0.403 g, 1.27 mmol) and acetone (12.7 ml). The solution was cooled to 0 °C and Jones reagent was added dropwise until a

red color persisted in the solution. The reaction was quenched with a few drops of iPrOH. The reaction mixture was diluted with EtOAc, washed with brine, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (3:1 hexanes:ethyl acetate to 1:1 hexanes:ethyl acetate) to afford acid **144** (0.161 g, 0.753 mmol, 59% yield). ^1H NMR (400 MHz, CDCl_3) δ 10.75 (s, 1H), 6.58 (dd, $J = 16.9, 11.3$ Hz, 1H), 5.53 (s, 1H), 5.33 (d, $J = 16.9$ Hz, 1H), 5.25 (d, $J = 11.3$ Hz, 1H), 4.76 (s, 2H), 3.74 (s, 3H), 2.53 (s, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.10, 155.78, 140.27, 131.34, 122.76, 116.95, 63.55, 54.86, 33.04, 28.06.

To a 10-ml round-bottom flask was added acid **144** (0.137 g, 0.638 mmol, 1.2 eq), EDC · HCl (0.153 g, 0.797 mmol, 1.5 eq), Et₃N (0.22 ml, 1.6 mmol, 3 eq), DMAP (0.100 g, 0.819 mmol, 1.5 eq), HOBT (0.108 g, 1.5 eq), and CH₂Cl₂ (5 ml). The reaction mixture was stirred for 10 minutes, then aniline **116** was added (0.240 g, 0.532 mmol). The reaction mixture was stirred for four days. The reaction was quenched with aqueous 1M HCl solution, extracted three times with Et₂O, and the combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (39:1

hexanes:ethyl acetate to 9:1 hexanes:ethyl acetate) to afford amide **145** (0.0487 g, 0.0710 mmol, 13% yield) and unreacted starting material (0.150 g). ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, $J = 13.7$ Hz, 1H), 6.62 (dd, $J = 17.4, 11.1$ Hz, 1H), 6.57 (d, $J = 13.7$ Hz, 1H), 5.56 (t, $J = 6.8$ Hz, 1H), 5.40 (d, $J = 17.4$ Hz, 1H), 5.29 (d, $J = 11.1$ Hz, 1H), 5.16 (s, 1H), 5.06 (s, 1H), 4.77 (d, $J = 6.8$ Hz, 2H), 4.59 (d, $J = 7.5$ Hz, 1H), 3.76 (s, 3H), 3.22 (d, $J = 8.6$ Hz, 1H), 2.74 – 2.55 (m, 2H), 2.41 – 2.28 (m, 2H), 2.13 – 2.00 (m, 1H), 1.62 (s, 3H), 1.34 – 1.20 (m, 3H), 1.15 (d, $J = 6.8$ Hz, 3H), 1.10 (d, $J = 7.2$ Hz, 18H), 0.95 (s, 9H), 0.19 (s, 3H), 0.15 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.99, 156.50, 155.82, 147.77, 147.32, 140.95, 135.74, 131.45, 122.78, 120.86, 117.12, 114.83, 113.35, 111.34, 110.78, 81.68, 63.63, 56.35, 54.93, 49.00, 36.84, 29.09, 25.95, 18.09, 15.98, 12.81, -3.94, -4.02.

To a flame dried 5-ml round-bottom flask under an atmosphere of argon was added $\text{Pd(PPh}_3)_4$ (0.010 g, 0.0087 mmol, 0.1 eq), dry, degased THF (0.871 ml), and amide **145** (0.0598 g, 0.0871 mmol). The reaction mixture was cooled to 0 °C. LHMDS (1M in THF, 0.087 ml, 1 eq) was added, and the reaction was allowed to warm to room temperature overnight. The reaction was quenched with saturated aqueous NH_4Cl

under rotary evaporation. The crude residue was purified by flash column chromatography (3:1 hexanes:ethyl acetate) to afford phenol **S16** (0.326 g, 0.715 mmol, 85% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.62 (s, 1H), 6.51 (s, 1H), 6.26 – 6.12 (m, 1H), 5.85 – 5.71 (m, 1H), 5.60 – 5.43 (m, 2H), 5.39 (d, J = 10.9 Hz, 1H), 5.34 (d, J = 17.7 Hz, 1H), 5.02 (s, 1H), 4.88 (s, 1H), 4.74 (s, 1H), 4.65 (d, J = 7.8 Hz, 1H), 4.15 (s, 1H), 4.11 (s, 1H), 3.42 (d, J = 5.7 Hz, 1H), 2.12 – 2.00 (m, 1H), 1.51 (s, 3H), 1.16 (d, J = 6.7 Hz, 3H), 0.97 (s, 9H), 0.20 (s, 3H), 0.16 (s, 3H).

To a 25 ml round-bottom flask at 0 °C was added phenol **S16** (0.301 g, 0.661 mmol), CH_2Cl_2 (6.6 ml), DIEPA (0.53 ml, 3.05 mmol, 4.6 eq), and MOMCl (0.26 ml, 3.44 mmol, 5.2 eq). The reaction was raised to rt slowly overnight. The next day, the reaction was quenched with water. The reaction mixture was extracted three times with Et_2O , and the combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (7:1 hexanes:ethyl acetate) to afford triene **147** (0.296 g, 0.592 mmol, 90% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.91 (s, 1H), 6.72 (d, J = 1.4 Hz, 1H), 6.18 (dd, J = 16.7, 10.7 Hz, 1H), 5.88 – 5.67 (m, 1H), 5.63 – 5.31 (m, 4H), 5.11 – 4.96 (m, 3H), 4.88 (s, 1H), 4.66 (d, J = 8.0 Hz, 1H), 4.14 (s, 1H), 4.10 (s, 1H), 3.41 (s, 3H), 2.17 –

1.93 (m, 1H), 1.51 (s, 3H), 1.16 (d, $J = 6.7$ Hz, 3H), 0.96 (s, 9H), 0.20 (s, 3H), 0.15 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.78, 154.40, 149.36, 143.73, 137.00, 134.16, 132.82, 130.70, 121.01, 118.16, 114.33, 111.25, 109.64, 94.90, 81.46, 73.38, 68.52, 56.69, 55.78, 49.00, 25.97, 19.24, 18.15, 15.86, -4.06.

To a 10 ml round bottom flask was added triene **147** (0.164 g, 0.328 mmol), NaOH (0.131 g, 3.28 mmol, 10 eq), and wet Ethanol (3.28 ml). The flask was heated at reflux overnight. The reaction was quenched with saturated aqueous NH_4Cl solution. The reaction mixture was extracted three times with Et_2O , and the combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (3:1 hexanes:ethyl acetate) to afford amino alcohol **148** (0.037 g, 0.103 mmol, 31% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.43 (d, $J = 1.7$ Hz, 1H), 6.09 (d, $J = 2.0$ Hz, 1H), 5.97 – 5.82 (m, 2H), 5.39 – 5.19 (m, 4H), 5.13 – 5.03 (m, 3H), 5.00 (s, 1H), 4.99 (s, 1H), 4.57 (d, $J = 6.6$ Hz, 1H), 3.47 (s, 2H), 3.44 (s, 3H), 3.20 (d, $J = 7.5$ Hz, 1H), 2.11 – 1.97 (m, 1H), 1.70 (s, 3H), 1.21 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.74, 146.80, 146.30, 143.40, 137.80, 137.47, 120.40, 117.75, 117.66, 114.24, 103.78, 99.25, 94.81, 82.22, 68.82, 63.36, 56.82, 56.06, 49.45, 18.67, 16.73.

To a 3 ml vial were added amino alcohol **148** (0.037 g, 0.103 mmol), DMF (1.03 ml), TBSCl (0.034 g, 0.227 mmol, 2.2 eq), and imidazole (0.021 g, 0.309 mmol, 3 eq). The reaction was stirred at rt overnight. The reaction was quenched with water the next day. The reaction mixture was extracted three times with Et₂O, and the combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford amine **149** (0.0577 g, 0.0981 mmol, 95%). ¹H NMR (400 MHz, CDCl₃) δ 6.35 (d, *J* = 1.6 Hz, 1H), 6.10 (d, *J* = 1.6 Hz, 1H), 5.99 – 5.81 (m, 2H), 5.29 – 5.23 (m, 3H), 5.21 (d, *J* = 5.7 Hz, 1H), 5.13 – 5.01 (m, 4H), 4.95 (s, 1H), 4.61 (d, *J* = 7.1 Hz, 1H), 3.52 (d, *J* = 9.7 Hz, 1H), 3.47 (d, *J* = 9.7 Hz, 1H), 3.44 (s, 3H), 3.14 (d, *J* = 8.1 Hz, 1H), 2.19 – 1.96 (m, 1H), 1.69 (s, 3H), 1.16 (d, *J* = 6.8 Hz, 3H), 0.96 (s, 9H), 0.89 (s, 9H), 0.20 (s, 3H), 0.15 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H).

To a flame-dried 10ml round bottom flask was added **121** (0.016 g, 0.0472 mmol), commercially available Hoveyda-Grubbs' 2nd generation catalyst (**151**, 0.0074 g, 0.25 eq), and anhydrous toluene (5ml). The solution was heated to 60 °C for four hours. The mixture was concentrated under reduced pressure and purified by flash column chromatography (3:1 hexanes:ethyl acetate) to afford **152** as a 1:1 mixture of diastereomers (0.098g, 66%). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 2.5 Hz, 1H), 7.41 (d, *J* = 2.4 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.08 (d, *J* = 2.5 Hz, 1H), 5.77 (q, *J* = 1.6 Hz, 1H), 5.28 (q, *J* = 1.6 Hz, 1H), 4.33 (d, *J* = 8.3 Hz, 1H), 4.28 – 4.25 (m, 1H), 4.23 (d, *J* = 8.3 Hz, 1H), 4.20 (d, *J* = 8.3 Hz, 1H), 4.12 (d, *J* = 8.3 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 3.75 (s, 1H), 2.88 – 2.78 (m, 1H), 2.78 – 2.68 (m, 1H), 1.98 (t, *J* = 1.6 Hz, 3H), 1.94 (t, *J* = 1.6 Hz, 3H), 1.45 (d, *J* = 7.4 Hz, 3H), 1.42 (d, *J* = 7.1 Hz, 3H), 1.33 (s, 3H), 1.32 (s, 3H).

To a flame-dried 500 ml round-bottom flask under argon atmosphere was added Hoveyda-Grubbs 2nd generation catalyst (**151**, 0.1 g, 5 mol %), **141** (1.96g, 3.20 mmol), and dry, degassed toluene (320 ml). The solution was heated to 85 °C and continuously sparged with argon. Additional catalyst (0.1g) was added every 30 minutes. At 90% catalyst loading, TLC showed the complete consumption of starting material, and the reaction mixture was cooled and concentrated. NMR analysis of the crude material showed a 2.4:1 ratio of diastereomeric products. The crude material was purified by flash column chromatography (19:1 hexanes:ethyl acetate to 9:1 hexanes:ethyl acetate) to afford unreacted starting material (0.297 g, 9%), fractions containing only the major diastereomer of **153a** (0.577 g, 31% yield) and fractions containing both diastereomers of **153** (0.517 g, 27%). **153a**: ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 1.6 Hz, 1H), 6.58 (s, 1H), 5.98 (dd, *J* = 17.4, 10.5 Hz, 1H), 5.74 (s, 1H), 5.26 (d, *J* = 3.0 Hz, 1H), 5.23 (d, *J* = 3.0 Hz, 1H), 4.50 (d, *J* = 8.1 Hz, 1H), 4.22 (d, *J* = 8.2 Hz, 1H), 4.01 (d, *J* = 8.2 Hz, 1H), 3.76 (d, *J* = 9.9 Hz, 1H), 2.37 – 2.22 (m, 1H), 1.90 (s, 3H), 1.38 – 1.20 (m, 6H), 1.10 (dd, *J* = 7.3, 1.4 Hz, 18H), 0.97 (s, 9H), 0.20 (s, 4H), 0.16 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 155.82, 155.33, 146.81, 146.03, 136.17, 134.95, 126.74, 120.55, 117.42,

113.78, 111.63, 81.33, 75.26, 65.21, 49.01, 47.87, 25.99, 21.37, 18.56, 18.10, 18.02, 12.79, -3.74, -3.87. IR (neat, cm^{-1}): 2947 (s), 2928 (s), 2893 (m), 2866 (s), 2361 (s), 2342 (m), 1755 (s), 1609 (m), 1582 (m), 1470 (s), 1380 (s), 1366 (s), 1257 (s), 1227 (m), 1200 (w), 1150 (m), 1103 (s), 1069 (m), 1009 (m), 907 (m), 872 (s), 837 (s), 760 (m), 733 (s), 683 (m); HRMS (ESI): Calculated for $\text{C}_{33}\text{H}_{54}\text{NO}_4\text{Si}_2$ ($[\text{M}+\text{H}]^+$): m/z 584.3591, found: 584.3589.

Note: The following reaction is extremely air and moisture sensitive. It is recommended to purify **141** using recrystallization from hexanes. Furthermore, substrate and ligand should be azeotroped three times from dry, degassed benzene. Catalyst **160** was prepared according to the literature to give a 0.025M stock solution.⁴ To an oven-dried 25 ml round-bottom flask was added triene **141** (0.500 g, 0.817 mmol) and catalyst stock solution (8.17 ml, 25 mol % catalyst loading). The flask was sealed with a polyethylene cap and the interface between cap and flask was wrapped first with Teflon tape and then Parafilm. The flask was heated to 65 °C for 20 h in the glove box. The reaction was then concentrated under reduced pressure and purified by flash column chromatography (19:1

hexanes:ethyl acetate) to afford oxazolidinone **153a** as a single diastereomer (0.391 g, 0.667 mmol, 82% yield) as well as unreacted **141** (0.083 mg, 17%).

To a flame-dried 10 ml round-bottom flask in an argon atmosphere was added Wilkinson's catalyst (0.093 g, 0.100 mmol, 0.25 eq), **153a** (0.235 g, 0.402 mmol), and dry, degassed benzene (4 ml). The solution was sparged for 1 hour with H₂ (1 atm) and then stirred at RT under an atmosphere of H₂ (1 atm) for 5 hours. The reaction mixture was loaded directly onto a flash column and purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford oxazolidinone **163** (0.221 g, 0.376 mmol, 94% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 2.2 Hz, 1H), 6.60 (d, *J* = 2.2 Hz, 1H), 5.60 (s, 1H), 4.54 (d, *J* = 8.4 Hz, 1H), 4.18 (d, *J* = 8.2 Hz, 1H), 4.10 (d, *J* = 8.2 Hz, 1H), 3.76 (d, *J* = 10.1 Hz, 1H), 2.41 – 2.19 (m, 2H), 2.00 – 1.82 (m, 4H), 1.34 (d, *J* = 6.4 Hz, 3H), 1.31 – 1.19 (m, 3H), 1.10 (dd, *J* = 7.4, 2.0 Hz, 18H), 0.97 (s, 9H), 0.90 (t, *J* = 7.5 Hz, 3H), 0.21 (s, 3H), 0.17 (s, 3H).

To a 3 ml vial was at 0 °C was added **163** (0.030 g, 0.0511 mmol), CH₂Cl₂ (0.5 ml), and TBAF (0.0562 ml, 1M in THF, 1.1 eq). The reaction was stirred for 1 hour, then quenched with saturated aqueous NH₄Cl. The reaction mixture was extracted three times with Et₂O, and the combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (3:1 hexanes:ethyl acetate) to afford oxazolidinone **164** (0.222 g, 0.0516 mmol, quantitative yield). ¹H NMR (400 MHz, DMSO) δ 9.44 (s, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 6.46 (s, 1H), 5.76 (s, 1H), 4.59 (d, *J* = 8.4 Hz, 1H), 4.34 (d, *J* = 8.4 Hz, 1H), 4.14 (d, *J* = 8.4 Hz, 1H), 3.82 (d, *J* = 10.3 Hz, 1H), 2.35 – 2.08 (m, 2H), 1.96 – 1.77 (m, 4H), 1.30 (d, *J* = 6.3 Hz, 3H), 0.95 (s, 9H), 0.81 (t, *J* = 7.3 Hz, 3H), 0.21 (s, 3H), 0.16 (s, 3H).

6.4. Experimental Procedures from Chapter 4

Using LAH: To a 5-ml round-bottom flask was added tetracycle **153a** (0.0483 g, 0.0824 mmol) and THF (0.824 ml). The solution was cooled to 0 °C. LAH (0.0063 g, 0.165 mmol, 2 eq) was added, and additional LAH was added (approximately 0.028 g) until the complete consumption of starting material was observed by TLC. The reaction was quenched initially with 0.05 ml water, then 0.2 ml 1M aqueous NaOH solution and allowed to warm to rt while stirring for 15 minutes. MgSO_4 was added, and the mixture was allowed to stir for an additional 15 minutes. The solution was filtered, concentrated, and purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford amino alcohol **166** (0.0147 g, 0.0263 mmol, 32% yield).

Using LTBH: To a 100-ml round-bottom flask was added tetracycle **153a** (3.08 g, 5.26 mmol) and dry THF (52 ml). The reaction mixture was cooled to 0 °C. To the reaction mixture was added LTBH (1M in THF solution, 21 ml, 4 eq) dropwise. The reaction mixture was stirred for 30 minutes at 0 °C. The solution was quenched with saturated aqueous NH_4Cl . The reaction mixture was extracted three times with EtOAc, and the combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column

chromatography (19:1 hexanes:ethyl acetate to 9:1 hexanes:ethyl acetate) to afford amino alcohol **166** (2.34 g, 4.19 mmol, 80% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.20 (s, 1H), 6.05 (d, $J = 1.9$ Hz, 1H), 5.83 (dd, $J = 17.2, 10.4$ Hz, 1H), 5.27 (d, $J = 11.1$ Hz, 1H), 5.25 (s, 1H), 5.16 (d, $J = 17.2$ Hz, 1H), 4.50 (d, $J = 8.2$ Hz, 1H), 4.36 (s, 1H), 3.61 (d, $J = 9.5$ Hz, 1H), 3.50 (t, $J = 10.7$ Hz, 1H), 3.43 (dd, $J = 10.6, 2.0$ Hz, 1H), 2.32 – 2.19 (m, 1H), 1.86 (s, 3H), 1.66 (dd, $J = 10.8, 2.5$ Hz, 1H), 1.32 – 1.17 (m, 6H), 1.09 (d, $J = 7.0$ Hz, 18H), 0.96 (s, 9H), 0.18 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.19, 147.12, 144.18, 142.92, 138.73, 124.58, 117.03, 116.65, 106.98, 105.38, 82.03, 77.36, 69.03, 59.95, 48.47, 47.67, 26.04, 21.78, 18.74, 18.14, 12.84, -3.73, -3.83; IR (neat, cm^{-1}): 3395 (w), 2928 (s), 2893 (w), 2866 (s), 2361 (s), 2342 (s), 1609 (s), 1589 (s), 1462 (s), 1362 (m), 1304 (m), 1254 (m), 1207 (m), 1165 (s), 1150 (w), 1111 (m), 1072 (w), 1045 (m), 1007 (m), 833 (s), 772 (m), 737 (m), 667 (m); HRMS (ESI): Calculated for $\text{C}_{32}\text{H}_{56}\text{NO}_3\text{Si}_2$ ($[\text{M}+\text{H}]^+$): m/z 558.3799, found: 558.3790.

To a 5-ml round-bottom flask was added $(\text{COCl})_2$ (0.0153 ml, 0.176 mmol, 1.5 eq) and CH_2Cl_2 (0.27 ml). The mixture was cooled to -78°C . In a separate vial, DMSO (0.024 ml, 0.351 mmol, 3 eq) was dissolved in CH_2Cl_2 (0.109 ml) and this solution was added dropwise to the $(\text{COCl})_2$ solution. The reaction mixture was stirred for 20 minutes at -78°C .

To a 5-ml round-bottom flask was added I₂ (0.0519 g, 0.204 mmol, 4.5 eq), KOH (0.0250 g, 0.447 mmol, 9.7 eq), and MeOH (0.94 ml). This solution was stirred for 10 minutes. Then, aldehyde **169** (0.0256 g, 0.0459 mmol) dissolved in MeOH (0.188 ml) was added to the mixture. The reaction mixture was stirred for 30 minutes and quenched with saturated aqueous sodium thiosulfate solution and saturated aqueous NH₄Cl solution. The reaction mixture was extracted three times with Et₂O, and the combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford amino ester **167** (0.0244 g, 0.0415 mmol, 91% yield). ¹H NMR (400 MHz, CDCl₃) δ 6.20 (s, 1H), 6.12 (s, 1H), 6.01 (dd, *J* = 17.0, 10.2 Hz, 2H), 5.77 (s, 1H), 5.26 (d, *J* = 17.0 Hz, 1H), 5.20 (d, *J* = 10.2 Hz, 1H), 4.98 (s, 1H), 4.49 (d, *J* = 7.9 Hz, 1H), 3.80 (s, 3H), 3.62 (d, *J* = 8.1 Hz, 1H), 2.30 – 2.23 (m, 1H), 1.87 (s, 3H), 1.30 – 1.19 (m, 6H), 1.09 (d, *J* = 6.7 Hz, 18H), 0.96 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H).

To a 3-ml vial was added DMAP (0.0111 g, 0.091 mmol, 2.3 eq), 4Å MS, amino alcohol **166** (0.0222 g, 0.0396 mmol), and CH₂Cl₂ (0.396 ml). The reaction mixture was cooled to 0 °C, then propionyl chloride was added (0.00726 ml, 0.0832 mmol, 2.1 eq). The

reaction mixture was stirred overnight and allowed to warm to room temperature. The reaction was quenched with water, extracted three times with Et₂O, and the combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford amino ester **170** (0.0174 g, 0.0283 mmol, 71% yield). ¹H NMR (400 MHz, CDCl₃) δ 6.22 (d, *J* = 1.3 Hz, 1H), 6.06 (d, *J* = 1.3 Hz, 1H), 5.82 (dd, *J* = 17.4, 10.3 Hz, 1H), 5.34 (s, 1H), 5.23 – 5.12 (m, 2H), 4.50 (d, *J* = 8.0 Hz, 1H), 4.22 (d, *J* = 11.0 Hz, 1H), 4.15 (s, 1H), 3.80 (d, *J* = 11.0 Hz, 1H), 3.59 (d, *J* = 9.6 Hz, 1H), 2.37 (q, *J* = 7.5 Hz, 2H), 2.24 (ddd, *J* = 9.6, 8.0, 6.6 Hz, 1H), 1.87 (s, 3H), 1.27 (d, *J* = 6.6 Hz, 3H), 1.25 – 1.80 (m, 3H), 1.15 (t, *J* = 7.5 Hz, 3H), 1.09 (dd, *J* = 7.3, 2.3 Hz, 18H), 0.96 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H).

To a 50 ml round-bottom flask was added alcohol **166** (0.614 g, 1.10 mmol), DMF (11 ml), TESCl (0.554 ml, 3.30 mmol, 3 eq), and imidazole (0.374 g, 5.5 mmol, 5 eq). The reaction was stirred at 40 °C for one hour. The reaction mixture was diluted with Et₂O and washed five times with brine solution. The solution was dried over MgSO₄, filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (49:1 hexanes:ethyl acetate) to afford amine **171** (0.652 g, 0.970

mmol, 89% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.19 (s, 1H), 6.05 (s, 1H), 5.83 (dd, $J = 17.0, 10.6$ Hz, 1H), 5.22 (s, 1H), 5.17 – 5.13 (m, 1H), 5.10 (d, $J = 10.6$ Hz, 1H), 4.51 (d, $J = 8.1$ Hz, 1H), 4.44 (s, 1H), 3.65 (d, $J = 9.5$ Hz, 1H), 3.53 (d, $J = 9.3$ Hz, 1H), 3.46 (d, $J = 9.3$ Hz, 1H), 2.33 – 2.15 (m, 1H), 1.86 (d, $J = 0.9$ Hz, 3H), 1.34 – 1.16 (m, 6H), 1.10 (d, $J = 7.2$ Hz, 18H), 1.00 – 0.93 (m, 18H), 0.63 (q, $J = 8.1$ Hz, 6H), 0.19 (s, 3H), 0.15 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.05, 146.89, 144.66, 141.89, 139.83, 125.04, 117.46, 115.19, 107.40, 105.09, 82.16, 70.19, 59.80, 48.51, 47.76, 26.05, 22.12, 18.84, 18.14, 12.88, 6.90, 4.58, -3.72, -3.82. HRMS (ESI): Calculated for $\text{C}_{38}\text{H}_{70}\text{NO}_3\text{Si}_3$ ($[\text{M}+\text{H}]^+$): m/z 672.4664, found: 672.4655.

To a flame-dried 3-ml vial was added **171** (0.0248 g, 0.0368 mmol), and THF (0.368 ml). The vial was cooled to -78°C . BuLi was added dropwise (2.5 M in hexanes, 0.0147 ml, 1 eq) and the reaction was stirred at -78°C for one hour. The reaction was quenched at -78°C by the dropwise addition of allyl iodide. The reaction was diluted with water and extracted three times with Et_2O . The combined organic extracts were washed with brine,

dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography to afford allylated compounds **172**, **173** and **174** (yield not recorded). For **172**: ^1H NMR (400 MHz, CDCl_3) δ 6.43 (s, 1H), 6.36 (s, 1H), 5.93 (dd, $J = 17.5, 10.7$ Hz, 1H), 5.85 – 5.73 (m, 1H), 5.44 (s, 1H), 5.22 – 5.06 (m, 4H), 4.53 (d, $J = 7.2$ Hz, 1H), 3.94 (d, $J = 5.0$ Hz, 2H), 3.61 – 3.44 (m, 3H), 2.30 – 2.18 (m, 1H), 1.87 (s, 3H), 1.33 – 1.16 (m, 6H), 1.08 (d, $J = 7.2$ Hz, 18H), 0.95 (s, 8H), 0.91 (t, $J = 8.0$ Hz, 9H), 0.54 (q, $J = 8.0$ Hz, 6H), 0.16 (s, 3H), 0.14 (s, 3H). For **173**: ^1H NMR (400 MHz, CDCl_3) δ 6.18 (s, 1H), 5.94 – 5.83 (m, 1H), 5.79 (dd, $J = 17.1, 10.4$ Hz, 1H), 5.22 (s, 1H), 5.17 – 4.95 (m, 4H), 4.61 (s, 1H), 4.50 (d, $J = 8.0$ Hz, 1H), 3.74 (d, $J = 10.0$ Hz, 1H), 3.69 – 3.57 (m, 1H), 3.55 (d, $J = 9.1$ Hz, 1H), 3.44 (d, $J = 9.1$ Hz, 1H), 3.17 (dd, $J = 16.0, 6.5$ Hz, 1H), 2.28 – 2.17 (m, 1H), 1.84 (s, 3H), 1.39 – 1.18 (m, 6H), 1.13 – 1.05 (m, 18H), 0.96 (d, $J = 1.8$ Hz, 18H), 0.61 (q, $J = 7.8$ Hz, 6H), 0.17 (s, 3H), 0.14 (s, 3H). For **174**: ^1H NMR (400 MHz, CDCl_3) δ 6.09 (s, 1H), 5.98 – 5.78 (m, 2H), 5.26 (d, $J = 16.0$ Hz, 1H), 5.17 (d, $J = 10.4$ Hz, 1H), 5.02 (s, 1H), 4.92 – 4.80 (m, 2H), 4.73 (d, $J = 2.9$ Hz, 1H), 3.66 (s, 1H), 3.49 (d, $J = 9.2$ Hz, 1H), 3.44 – 3.35 (m, 3H), 2.40 (s, 1H), 1.86 (s, 3H), 1.36 – 1.17 (m, 6H), 1.17 – 1.01 (m, 18H), 0.96 (t, $J = 7.9$ Hz, 6H), 0.88 (s, 9H), 0.60 (q, $J = 7.9$ Hz, 9H), 0.14 (s, 3H), 0.11 (s, 3H).

To a flame-dried 3-ml vial was added NaH (0.0018 g, 0.046 mmol, 2.2 eq) and dry DMF (0.209 ml) at 0 °C. Then, **171** was added (0.0141 g, 0.0209 mmol) and the reaction stirred for one hour. The reaction was quenched by the addition of propyl iodide (0.006 ml, 3 eq). The reaction was diluted with water and extracted three times with Et₂O. The combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography to afford compounds **175** (0.0019 g, 15%) and **176** (0.0028 g, 22%). For **175**: ¹H NMR (500 MHz, CDCl₃) δ 6.18 (s, 1H), 6.05 (d, *J* = 1.9 Hz, 1H), 5.88 (dd, *J* = 17.2, 10.5 Hz, 1H), 5.25 (s, 1H), 5.18 – 5.11 (m, 2H), 4.49 (d, *J* = 8.2 Hz, 1H), 4.37 (s, 1H), 3.63 (d, *J* = 9.2 Hz, 1H), 3.47 – 3.39 (m, 2H), 3.33 (d, *J* = 8.8 Hz, 1H), 3.29 (d, *J* = 8.8 Hz, 1H), 2.29 – 2.17 (m, 1H), 1.85 (s, 3H), 1.68 – 1.57 (m, 2H), 1.30 – 1.17 (m, 6H), 1.08 (dd, *J* = 7.4, 2.7 Hz, 18H), 0.99 – 0.88 (m, 12H), 0.17 (s, 3H), 0.14 (s, 3H). For **176**: ¹H NMR (500 MHz, CDCl₃) δ 6.22 (d, *J* = 1.5 Hz, 1H), 6.05 (d, *J* = 2.1 Hz, 1H), 5.89 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.25 (s, 1H), 5.20 – 5.13 (m, 2H), 4.52 (d, *J* = 8.0 Hz, 1H), 4.49 (s, 1H), 3.85 (td, *J* = 6.6, 2.2 Hz, 2H), 3.67 (d, *J* = 9.7 Hz, 1H), 3.51 – 3.37 (m, 2H), 3.34 (d, *J* = 8.8 Hz, 1H), 3.30 (d, *J* = 8.8 Hz, 1H), 2.30 – 2.21 (m, 1H), 1.85 (s, 3H), 1.80

– 1.71 (m, 2H), 1.66 – 1.57 (m, 2H), 1.26 (d, $J = 6.6$ Hz, 3H), 1.03 – 0.96 (m, 12H), 0.93 (t, $J = 7.4$ Hz, 3H), 0.20 (s, 3H), 0.15 (s, 3H).

To a 3 ml vial was added **171** (0.0216 g, 0.0321 mmol) and PhCH_3 (0.321 ml). The solution was cooled to $0\text{ }^\circ\text{C}$. Et_3N (0.00624 ml, 0.045 mmol, 1.4 eq) and acryloyl chloride (0.0039 ml, 0.0482 mmol, 1.5 eq) were added, and the reaction was stirred overnight. Additional Et_3N and acryloyl chloride were added as necessary to consume all starting material (up to extra 5 equivalents each). The reaction mixture was quenched with saturated aqueous NaHCO_3 solution. The solution was diluted and extracted with ether, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford amide **177** (0.0133 g, 0.0183 mmol, 57% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.81 (d, $J = 1.9$ Hz, 1H), 6.75 (s, 1H), 6.36 (dd, $J = 17.7, 11.1$ Hz, 1H), 6.28 (dd, $J = 16.7, 2.0$ Hz, 1H), 6.12 (dd, $J = 16.7, 10.1$ Hz, 1H), 5.66 (s, 1H), 5.39 (dd, $J = 10.1, 2.0$ Hz, 1H), 5.18 (d, $J = 17.7$ Hz, 1H), 5.12 (d, $J = 11.1$ Hz, 1H), 4.64 (d, $J = 6.5$ Hz, 1H), 3.27 (d, $J = 10.0$ Hz, 1H), 3.17 (d, $J = 9.6$ Hz, 1H), 3.15 (d, $J = 10.0$ Hz, 1H), 2.37 – 2.15 (m, 1H), 1.89 (s, 3H), 1.36 (d, $J = 6.7$ Hz, 3H), 1.32 – 1.19 (m, 3H), 1.11 (dd, $J = 7.3, 1.9$ Hz, 18H), 0.95 (s, 9H), 0.83 (t, $J = 7.9$ Hz, 9H), 0.44 (q, $J = 7.9$ Hz, 6H), 0.19 (s, 3H), 0.16 (s, 3H). ^{13}C

NMR (101 MHz, CDCl_3) δ 166.60, 156.13, 145.48, 143.44, 137.63, 136.08, 134.25, 129.94, 127.06, 126.16, 121.79, 114.79, 109.22, 82.49, 69.65, 65.07, 50.57, 49.50, 25.92, 25.55, 20.23, 18.11, 18.04, 12.78, 6.82, 4.40, -3.67, -3.85.

To a 3 ml vial was added **171** (0.100 g, 0.149 mmol), PhCH_3 (1.49 ml), 4Å MS (0.075 g, 500 mg/mmol), DIEPA (0.26 ml, 1.49 mmol, 10 eq), and acryloyl chloride (0.013 ml, 0.163 mmol, 1.1 eq). The solution was heated to 40 °C. Additional DIEPA and acryloyl chloride were added as necessary to consume all starting material (up to extra 10 equivalents each). The reaction mixture was concentrated under rotary evaporation and dissolved in MeOH (1.5 ml). Concentrated HCl was added dropwise until complete desilylation was observed by TLC analysis. The reaction was quenched with saturated aqueous NaHCO_3 solution. The solution was dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate to 7:1 hexanes:ethyl acetate) to afford amide **179** (0.0601 g, 0.0982 mmol, 66% yield over two steps). ^1H NMR (400 MHz, CDCl_3) δ 6.79 (s, 1H), 6.73 (s, 1H), 6.31 (d, J = 16.7 Hz, 1H), 6.22 (dd, J = 17.7, 11.0 Hz, 1H), 6.06 (dd, J = 16.7, 10.2 Hz, 1H), 5.44 (d, J = 10.2 Hz, 1H), 5.34 (s, 1H), 5.30 – 5.19 (m, 2H), 4.64 (d, J = 5.7 Hz, 1H), 3.35 (s, 2H), 3.27 (d, J = 6.7 Hz, 1H), 2.41 (s, 1H), 2.35 –

2.27 (m, 1H), 1.88 (s, 3H), 1.33 (d, $J = 6.8$ Hz, 3H), 1.29 – 1.20 (m, 3H), 1.09 (d, $J = 7.2$ Hz, 18H), 0.94 (s, 9H), 0.19 (s, 3H), 0.16 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.93, 156.50, 145.88, 141.19, 136.96, 130.06, 127.73, 126.20, 121.23, 115.59, 111.05, 82.46, 67.79, 66.44, 50.19, 48.67, 25.95, 25.17, 20.25, 18.16, 18.01, 12.72, -3.77, -3.93.

To a flame-dried 5 ml round-bottom flask under argon atmosphere was added alcohol **179** (0.140 g, 0.229 mmol), NMO (0.080 g, 0.686 mmol, 3 eq), 4Å MS (0.114 g, 500 mg/mmol), CH_2Cl_2 (2.29 ml), and MeCN (0.229 ml). The reaction mixture was stirred at 0 °C for 10 minutes. Then, TPAP was added (0.008 g, 0.0229 mmol, 0.1 eq) and the reaction mixture stirred at 0 °C. Upon complete consumption of starting material by TLC analysis, the reaction mixture was filtered through a plug of celite and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate to 9:1 hexanes:ethyl acetate) to afford aldehyde **180** (0.0806 g, 0.132 mmol, 57%). ^1H NMR (400 MHz, CDCl_3) δ 9.13 (s, 1H), 6.73 (s, 1H), 6.54 (s, 1H), 6.40 – 6.18 (m, 3H), 5.71 (s, 1H), 5.59 (dd, $J = 9.9, 2.1$ Hz, 1H), 5.32 (d, $J = 10.0$ Hz, 1H), 5.23 (d, $J = 16.8$ Hz, 1H), 4.52 (d, $J = 7.8$ Hz, 1H), 3.51 (d, $J = 9.8$ Hz, 1H), 2.44 – 2.24 (m, 1H), 1.93 (s, 3H), 1.33 (d, $J = 6.4$ Hz, 3H), 1.31 – 1.18 (m, 3H), 1.10 (d, $J = 7.2$ Hz, 18H), 0.97 (s, 9H), 0.21 (s, 3H), 0.18 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ

1173 (m), 1076 (m), 1045 (w), 1007 (s), 880 (w), 837 (s), 814 (w), 775 (m), 737 (s), 667 (m); HRMS (ESI): Calculated for $C_{38}H_{72}NO_3Si_3$ ($[M+H]^+$): m/z 674.4820, found: 674.4828.

To a 100 ml round-bottom flask was added aniline **181** (2.25 g, 3.33 mmol), toluene (33.3 ml), 4Å molecular sieves (1.66 g), acryloyl chloride (2.7 ml, 33.3 mmol, 10 eq), and diisopropylethylamine (11.6 ml, 66.6 mmol, 20 eq). The reaction mixture was heated at 50°C for two hours. The reaction mixture was cooled to room temperature and filtered through a plug of celite into aqueous 1M HCl solution. The reaction mixture was extracted three times with Et₂O, and the combined organic extracts were washed with brine and concentrated under reduced pressure. The crude residue was taken to the next step without further purification

To a 100 ml round-bottom flask was added the crude amide from the previous reaction, THF (16.7 ml), MeOH (3.33 ml), and HCl (1M in H₂O, 10 ml, 3 eq). The reaction was stirred for 5 hours. The reaction was quenched with saturated aqueous NaHCO₃ solution and extracted three times with Et₂O. The combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude

residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate to 9:1 hexanes:ethyl acetate) to afford alcohol **182** (1.45 g, 2.36 mmol, 71% yield over two steps) as a crystalline solid. ^1H NMR (400 MHz, CDCl_3) δ 6.73 (d, $J = 1.7$ Hz, 1H), 6.54 (d, $J = 1.7$ Hz, 1H), 6.27 (dd, $J = 16.8, 1.8$ Hz, 1H), 5.93 (dd, $J = 16.8, 10.2$ Hz, 1H), 5.41 (dd, $J = 10.2, 1.8$ Hz, 1H), 4.99 (s, 1H), 4.65 (d, $J = 4.9$ Hz, 1H), 3.52 (dd, $J = 11.2, 4.9$ Hz, 1H), 3.44 – 3.33 (m, 2H), 2.94 (dd, $J = 14.1, 7.1$ Hz, 1H), 2.81 (t, $J = 4.9$ Hz, 1H), 2.46 – 2.28 (m, 1H), 2.03 – 1.93 (m, 1H), 1.89 (s, 3H), 1.28 (d, $J = 7.0$ Hz, 3H), 1.26 – 1.18 (m, 3H), 1.08 (d, $J = 7.1$ Hz, 18H), 1.00 – 0.91 (m, 12H), 0.18 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.47, 156.35, 145.19, 138.64, 137.61, 135.73, 131.57, 127.14, 126.86, 121.79, 115.10, 82.62, 68.74, 68.27, 49.80, 47.47, 28.04, 25.97, 24.69, 20.38, 18.20, 18.01, 12.72, 8.73, -3.86, -4.02; IR (neat, cm^{-1}): 3445 (s), 2928 (s), 2866 (s), 2735 (w), 2361 (s), 2342 (s), 1655 (s), 1609 (s), 1589 (m), 1474 (s), 1443 (w), 1408 (s), 1345 (s), 1316 (m), 1254 (s), 1215 (s), 1076 (w), 1049 (s), 984 (w), 918 (m), 880 (s), 833 (s), 772 (s), 652 (w); HRMS (ESI): Calculated for $\text{C}_{35}\text{H}_{60}\text{NO}_4\text{Si}_2$ ($[\text{M}+\text{H}]^+$): m/z 614.4061, found: 614.4069.

To a 10 ml round-bottom flask was added alcohol **182** (0.237 g, 0.386 mmol), CH_2Cl_2 (3.86 ml), MeCN (0.386 ml), 4Å molecular sieves (0.194 g), and NMO (0.0904 g, 0.772

To a 5 ml round-bottom flask cooled to 0°C was added aldehyde **183** (0.176 g, 0.287 mmol), toluene (2.87 ml), and [PPh₃CuH]₆ (0.112 g, 0.057 mmol, 1.2 eq H⁻). The reaction mixture was stirred for 30 minutes, during which the color of the mixture turned from brick red to orange. The reaction mixture was quenched with a 9:1 saturated aqueous NH₄Cl/10% aqueous NH₄OH solution and stirred for 30 minutes. The reaction

mixture was extracted three times with Et₂O. The combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate to 7:1 hexanes:ethyl acetate to 5:1 hexanes:ethyl acetate) to afford alcohol **185** which could be isolated as two sets of two diastereomers (0.166 g, 0.270 mmol, 94% combined yield). Major diastereomer in set 1: ¹H NMR (400 MHz, CDCl₃) δ 7.11 (s, 1H), 6.62 (d, *J* = 3.2 Hz, 1H), 5.45 (s, 1H), 4.53 (d, *J* = 8.3 Hz, 1H), 4.06 (s, 1H), 3.90 – 3.55 (m, 1H), 2.94 – 2.81 (m, 1H), 2.54 (dq, *J* = 13.9, 6.9 Hz, 1H), 2.39 (td, *J* = 15.1, 7.6 Hz, 1H), 2.33 – 2.18 (m, 1H), 1.87 (s, 3H), 1.34 (d, *J* = 6.3 Hz, 3H), 1.33 – 1.22 (m, 3H), 1.10 (d, *J* = 7.3 Hz, 21H), 0.96 (s, 9H), 0.91 (t, *J* = 7.6 Hz, 3H), 0.21 (s, 3H), 0.17 (s, 3H). Major diastereomer in set 2: ¹H NMR (400 MHz, CDCl₃) δ 7.38 (s, 1H), 6.62 (s, 1H), 6.06 (s, 1H), 4.53 (d, *J* = 8.2 Hz, 1H), 4.29 (d, *J* = 4.1 Hz, 1H), 3.73 (d, *J* = 10.0 Hz, 1H), 2.83 (p, *J* = 7.6 Hz, 1H), 2.35 – 2.24 (m, 2H), 1.92 (s, 3H), 1.78 (dt, *J* = 14.4, 7.2 Hz, 1H), 1.34 (d, *J* = 6.3 Hz, 3H), 1.32 – 1.20 (m, 6H), 1.10 (d, *J* = 7.3 Hz, 18H), 0.96 (s, 9H), 0.93 (t, *J* = 7.6 Hz, 3H), 0.21 (s, 3H), 0.17 (s, 3H).

To a 5 ml round-bottom flask cooled to $-78\text{ }^{\circ}\text{C}$ was added $(\text{COCl})_2$ (0.0401 ml, 0.459 mmol, 3 eq) and CH_2Cl_2 (0.375 ml). A solution of DMSO (0.0651 ml, 0.918 mmol,

6 eq) in CH_2Cl_2 (0.375 ml) was added dropwise. The reaction mixture was stirred at -78°C for 1 hour. Alcohol **185** (0.0937 g, 0.153 mmol) dissolved in CH_2Cl_2 (0.75 ml) was added dropwise. The reaction mixture was stirred for another 1 hour at -78°C . Et_3N (0.256 ml, 1.84 mmol, 12 eq) was added and the reaction mixture was stirred for 1 hour at -78°C and then allowed to slowly warm to RT over three hours. The reaction mixture was quenched with saturated aqueous NaHCO_3 and extracted three times with Et_2O . The combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford chlorinated tetracycle **187** as a single diastereomer (0.0730 g, 0.113 mmol, 74% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 1.6$ Hz, 1H), 6.71 (s, 1H), 5.68 (s, 1H), 4.53 (d, $J = 8.2$ Hz, 1H), 3.82 (d, $J = 10.3$ Hz, 1H), 2.43 – 2.30 (m, 2H), 2.21 – 2.17 (m, 1H), 1.91 (s, 3H), 1.78 (s, 3H), 1.36 (d, $J = 6.3$ Hz, 3H), 1.33 – 1.22 (m, 3H), 1.12 (d, $J = 6.0$ Hz, 18H), 0.97 (s, 9H), 0.73 (t, $J = 7.2$ Hz, 3H), 0.22 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 205.89, 167.35, 155.59, 147.42, 143.38, 133.36, 125.46, 121.84, 116.32, 113.51, 81.12, 74.17, 56.81, 50.36, 49.21, 30.46, 25.95, 24.24, 22.28, 20.73, 18.66, 18.10, 12.82, 9.20, -3.64, -3.83; IR (neat, cm^{-1}): 2947 (w), 2932 (s), 2893 (w), 2866 (s), 2361 (s), 2342 (w), 1778 (s), 1713 (s), 1613 (s), 1578 (m), 1470 (s), 1362 (s), 1304 (m), 1288 (w), 1254 (m), 1223 (m), 1173 (m), 1103 (s), 1065 (m), 910 (w), 880 (m), 837 (s), 775 (s), 679 (br); HRMS (ESI): Calculated for $\text{C}_{35}\text{H}_{57}\text{NO}_4\text{Si}_2\text{Cl}$ ($[\text{M}+\text{H}]^+$): m/z 646.3515, found: 646.3524.

To a 3 ml vial was added alcohol **185** (0.010 g, 0.0162 mmol), CH_2Cl_2 (0.32 ml), MeCN (0.0162 ml), 4Å molecular sieves (8.1 mg, 500mg/mmol), and NMO (0.0038 g, 0.0324 mmol, 2 eq). The reaction mixture was stirred at 0 °C for 10 minutes. Then, TPAP (spatula tip) was added. The reaction mixture was allowed to come to room temperature and stirred overnight. The reaction mixture was filtered through a plug of celite and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford alcohol **188** as a 5:1 mixture of diastereomers (0.0023 g, 0.0037 mmol, 26% yield) and unreacted starting material (0.0026 mg). Major diastereomer: ^1H NMR (500 MHz, CDCl_3) δ 7.53 (d, $J = 2.2$ Hz, 1H), 6.69 (d, $J = 1.2$ Hz, 1H), 5.55 (s, 1H), 4.53 (d, $J = 8.3$ Hz, 1H), 3.80 (d, $J = 10.3$ Hz, 1H), 2.63 (s, 1H), 2.36 – 2.18 (m, 3H), 1.89 (s, 3H), 1.55 (s, 3H), 1.35 (d, $J = 6.4$ Hz, 3H), 1.32 – 1.24 (m, 3H), 1.12 (dd, $J = 7.4, 1.7$ Hz, 18H), 0.97 (s, 9H), 0.88 (t, $J = 6.9$ Hz, 3H), 0.22 (s, 3H), 0.18 (s, 3H).

To a 20 ml scintillation vial was added tetracycline **187** (0.580 g, 0.897 mmol), CH_2Cl_2 (8.97 ml), AcOH (1.03 ml, 17.9 mmol, 20 eq), and zinc dust (0.565 g, 8.97 mmol, 10 eq). The reaction was stirred at rt for 1 hour. The reaction mixture was filtered through a plug of celite and concentrated under reduced pressure. The crude residue was taken to the next step without further purification. Alternatively, purification by flash column chromatography (9:1 hexanes:ethyl acetate to 3:1 hexanes:ethyl acetate) afforded tetramic acid **186**. ^1H NMR (500 MHz, MeOD) δ 7.86 (d, J = 1.6 Hz, 1H), 6.57 (s, 1H), 5.71 (s, 1H), 4.59 (d, J = 8.6 Hz, 1H), 3.96 (d, J = 10.4 Hz, 1H), 2.44 – 2.35 (m, 1H), 2.29 – 2.20 (m, 1H), 1.92 (s, 4H), 1.72 (s, 3H), 1.38 (d, J = 6.3 Hz, 3H), 1.33 – 1.23 (m, 3H), 1.12 (dd, J = 7.4, 2.8 Hz, 18H), 1.00 (s, 9H), 0.61 (t, J = 7.3 Hz, 3H), 0.25 (s, 3H), 0.21 (s, 3H). ^{13}C NMR (126 MHz, MeOD) δ 174.29, 172.10, 156.56, 148.29, 142.41, 136.64, 126.45, 120.95, 114.54, 111.45, 101.55, 82.44, 69.05, 51.01, 50.53, 26.43, 24.07, 22.14, 18.91, 18.47, 18.45, 18.41, 13.91, 5.94, -3.55, -3.70. IR (neat, cm^{-1}): 2947 (s), 2932 (s), 2893 (w), 2866 (s), 2361 (s), 2342 (m), 1778 (w), 1680 (w), 1632 (s), 1560 (w), 1470 (s), 1381 (s), 1304 (m), 1254 (m), 1223 (m), 1173 (w), 1103 (m), 1065 (m), 1002

(w), 910 (m), 880 (m), 837 (m), 775 (m), 679 (m); HRMS (ESI): Calculated for $C_{35}H_{58}NO_4Si_2$ ($[M+H]^+$): m/z 612.3904, found: 612.3904.

To a 25 ml round-bottom flask was added crude tetramic acid **186** from the previous step (0.52 g), CHCl_3 (6 ml), and MeOH (2 ml). Commercially available TMSCHN_2 (2M in Et_2O) was added dropwise until a yellow color persisted (approximately 1.5 ml). The yellow reaction mixture was stirred at 0 °C for 30 minutes. The reaction was quenched with a few drops of AcOH. The reaction mixture was concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate to 9:1 hexanes:ethyl acetate) to afford tetracycle **189** (0.340 g, 0.544 mmol, 61%). ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 1.6 Hz, 1H), 6.55 (d, J = 1.6 Hz, 1H), 5.60 (s, 1H), 4.51 (d, J = 8.3 Hz, 1H), 4.12 (s, 3H), 3.84 (d, J = 10.0 Hz, 1H), 2.41 – 2.19 (m, 2H), 2.05 (s, 3H), 1.87 (s, 3H), 1.83 – 1.76 (m, 1H), 1.33 (d, J = 6.3 Hz, 3H), 1.29 – 1.22 (m, 3H), 1.11 (dd, J = 7.3, 2.0 Hz, 18H), 0.97 (s, 9H), 0.61 (t, J = 7.2 Hz, 3H), 0.21 (s, 3H), 0.16 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.17, 168.87, 155.54, 146.66, 140.90, 135.50, 125.45, 119.24, 113.83, 110.48, 101.99, 81.36, 67.51, 59.10, 49.91, 49.04, 26.00, 23.65, 21.99, 18.68, 18.16, 12.84, 8.58, 7.72, -3.67, -3.83. IR

(neat, cm^{-1}): 2947 (m), 2866 (m), 1663 (m), 1605 (m), 1470 (m), 1451 (w), 1381 (m), 1316 (m), 1254 (w), 1215 (m), 1188 (w), 1103 (w), 1065 (w), 1003 (m), 880 (m), 837 (m), 752 (s), 667 (m). HRMS (ESI): Calculated for $\text{C}_{36}\text{H}_{60}\text{NO}_4\text{Si}_2$ ($[\text{M}+\text{H}]^+$): m/z 626.4061, found: 626.4055.

TBAF($^t\text{BuOH}$)₄ was prepared according to literature procedures.⁷ To a 3-ml vial was added **141** (0.095 g, 0.155 mmol), MeCN (1.5 ml), and TBAF($^t\text{BuOH}$)₄ (0.086 g, 0.155 mmol, 1 eq). The reaction was stirred for 1 hour, then quenched with saturated aqueous NH_4Cl . The reaction mixture was extracted three times with Et_2O , and the combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified flash column chromatography (3:1 hexanes:ethyl acetate) to afford a phenolic product (0.060 g, 0.132 mmol, 85%).

To a 3-ml vial was added the phenolic material (0.060 g, 0.132 mmol), DMF (1.32 ml), methyl bromoacetate (0.050 ml, 4 eq), K_2CO_3 (0.036 g, 2 eq), and NaI (0.080 g, 4 eq). The reaction was stirred at rt overnight. The next day the reaction mixture was diluted with Et_2O (20 ml) and washed 5x with brine (2 ml). The organic layer was dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (3:1 hexanes:ethyl acetate) to afford **193** (0.069

g, 99% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.66 (s, 1H), 6.60 (s, 1H), 6.18 (dd, J = 16.2, 10.9 Hz, 1H), 5.77 (dd, J = 16.4, 11.7 Hz, 1H), 5.58 – 5.29 (m, 4H), 5.01 (s, 1H), 4.89 (s, 1H), 4.66 (d, J = 7.7 Hz, 1H), 4.53 (s, 2H), 4.15 (s, 1H), 4.11 (s, 1H), 3.78 (s, 3H), 3.42 (s, 1H), 2.03 (s, 1H), 1.50 (s, 3H), 1.15 (d, J = 6.5 Hz, 3H), 0.95 (d, J = 9.0 Hz, 9H), 0.19 (s, 3H), 0.15 (s, 3H).

To a 3-ml vial was added **193** (0.0092 g, 0.0174 mmol), MeOH (0.17 ml), hydroxylamine hydrochloride (0.0242 g, 0.349 mmol, 20 eq), and Et_3N (0.050 ml, 20 eq). The reaction was stirred at rt overnight. The next day the reaction mixture was diluted and extracted with EtOAc. The organic layer was dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (19:1 DCM:methanol) to afford **194** (0.0063 g, 68% yield). ^1H NMR (400 MHz, CDCl_3) δ 9.03 (s, 1H), 6.71 (s, 1H), 6.56 (s, 1H), 6.20 (dd, J = 16.1, 10.7 Hz, 1H), 5.74 (dd, J = 15.7, 11.0 Hz, 1H), 5.63 – 5.22 (m, 4H), 5.01 (s, 1H), 4.90 (s, 1H), 4.66 (d, J = 7.9 Hz, 1H), 4.48 (s, 2H), 4.15 (s, 1H), 4.12 (s, 1H), 3.53 – 3.38 (m, 1H), 2.12 – 1.98 (m, 1H), 1.89 (d, J = 14.7 Hz, 1H), 1.50 (s, 3H), 1.16 (d, J = 6.7 Hz, 3H), 0.97 (s, 9H), 0.20 (s, 3H), 0.16 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.61, 156.24, 155.87, 154.44,

To a 3 ml vial was added alcohol **198** (0.0097 g, 0.0206 mmol), PPh_3 (0.027 g, 0.103 mmol, 5 eq), PhCO_2H (0.0126 g, 0.103 mmol, 5 eq), and THF (0.206 ml). The vial was cooled to $0\text{ }^\circ\text{C}$ and diisopropyl azodicarboxylate (DIAD) (0.0208 g, 0.103 mmol, 5 eq) was added dropwise. The reaction was raised to rt overnight. The reaction was quenched with water. The reaction mixture was extracted three times with Et_2O , and the combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (3:1 hexanes:ethyl acetate) to afford ester **199**. ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 2.2$ Hz, 1H), 7.57 – 7.35 (m, 5H), 6.86 (d, $J = 2.1$ Hz, 1H), 6.25 (d, $J = 6.0$ Hz, 1H), 6.06 (dd, $J = 17.3, 10.6$ Hz, 1H), 5.79 (s, 1H), 5.35 – 5.24 (m, 2H), 4.33 – 4.22 (m, 2H), 4.05 (d, $J = 8.2$ Hz, 1H), 2.75 (dt, $J = 9.4, 6.5$ Hz, 1H), 1.96 (s, 3H), 1.39 – 1.18 (m, 6H), 1.17 – 0.99 (m, 18H).

To a 3 ml vial was added **199** (0.0608 g, 0.106 mmol), MeCN (1.06 ml), and TBAF(^tBuOH)₄ (0.059 g, 0.106 mmol, 1 eq). The reaction was stirred for 1 hour, then quenched with saturated aqueous NH₄Cl. The reaction mixture was extracted three times with Et₂O, and the combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (3:1 hexanes:ethyl acetate) to afford phenol **200** (0.0233 g, 0.0561 mmol, 53%). ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 2.1 Hz, 1H), 7.51 – 7.37 (m, 5H), 7.24 (d, *J* = 2.0 Hz, 1H), 6.32 (d, *J* = 6.1 Hz, 1H), 6.10 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.81 (s, 1H), 5.43 – 5.31 (m, 2H), 4.45 (d, *J* = 8.7 Hz, 1H), 4.27 (d, *J* = 8.2 Hz, 1H), 4.10 (d, *J* = 8.2 Hz, 1H), 2.84 (dt, *J* = 9.3, 6.8 Hz, 1H), 1.99 (s, 3H), 1.31 (d, *J* = 6.8 Hz, 3H).

To a 3 ml vial was added ester **199** (0.0421 g, 0.0734 mmol), MeOH (0.734 ml), and K₂CO₃ (0.020 g 0.145 mmol, 2 eq). The reaction was stirred at room temperature overnight. The reaction was quenched with saturated aqueous NH₄Cl solution. The reaction mixture was extracted three times with Et₂O, and the combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (9:1

hexanes:ethyl acetate to 3:1 hexanes:ethyl acetate) to afford alcohol **201** (0.0297 g, 0.0632 mmol, 86%). ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 2.2$ Hz, 1H), 6.72 (d, $J = 2.2$ Hz, 1H), 6.01 (dd, $J = 17.3, 10.6$ Hz, 1H), 5.76 (s, 1H), 5.33 – 5.21 (m, 2H), 4.78 (t, $J = 5.5$ Hz, 1H), 4.24 (d, $J = 8.1$ Hz, 1H), 4.12 (d, $J = 7.4$ Hz, 1H), 4.03 (d, $J = 8.1$ Hz, 1H), 2.51 – 3.40 (m, 1H), 1.93 (s, 3H), 1.40 – 1.19 (m, 6H), 1.15 – 1.06 (m, 18H).

To a 3 ml vial was added alcohol **201** (0.0297 g, 0.0632 mmol), DMAP (0.0077 g, 0.0632 mmol, 1 eq), and CH_2Cl_2 (0.632 ml). The vial was cooled to 0 °C. Then, PhNCO was added dropwise (0.0076 ml, 0.0695 mmol, 1.1 eq) and the reaction stirred overnight. The reaction was quenched with water. The reaction mixture was extracted three times with Et_2O , and the combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (3:1 hexanes:ethyl acetate) to afford carbamate **202** (0.034 g, 0.0557 mmol, 88% yield).

To a 3 ml vial was added carbamate **202** (0.034 g, 0.0557 mmol), THF (0.577 ml), and TBAF($t\text{BuOH}$) $_4$ (0.0322 g, 0.0577 mmol, 1 eq). The reaction mixture was stirred for 1 hour. The reaction was quenched with saturated aqueous NH_4Cl solution. The reaction mixture was extracted three times with Et_2O , and the combined organic extracts were

washed with brine, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (1:1 hexanes:ethyl acetate) to afford phenol **203** (0.016 g, 0.0370 mmol, 64% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 2.2$ Hz, 1H), 7.40 – 7.26 (m, 5H), 7.07 – 7.00 (m, 1H), 6.85 (d, $J = 1.7$ Hz, 1H), 6.59 (s, 1H), 6.15 – 5.97 (m, 2H), 5.76 (s, 1H), 5.39 – 5.29 (m, 2H), 4.26 (d, $J = 8.3$ Hz, 1H), 4.17 (d, $J = 9.4$ Hz, 1H), 4.07 (d, $J = 8.3$ Hz, 1H), 2.75 – 2.63 (m, 1H), 1.94 (s, 3H), 1.24 (d, $J = 2.5$ Hz, 3H).

To a 3 ml vial was at 0°C was added **186** (0.0694 g, 0.107 mmol), CH_2Cl_2 (1.13 ml), and TBAF (0.107 ml, 1M in THF, 1 eq). The reaction was stirred for 1 hour, then quenched with saturated aqueous NH_4Cl . The reaction mixture was extracted three times with Et_2O , and the combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford phenol **205** (0.0286 g, 0.0584 mmol, 55%). ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 1.8$ Hz, 1H), 7.61 (s, 1H), 6.75 (s, 1H), 5.67 (s, 1H), 4.54 (d, $J = 8.4$ Hz, 1H), 3.83 (d, $J = 10.4$ Hz, 1H), 2.51 – 2.28 (m, 2H), 2.23 – 2.14 (m, 1H), 1.92 (s, 3H), 1.81 (s, 3H), 1.36 (d, $J = 6.3$ Hz, 3H),

0.97 (s, 9H), 0.75 (t, $J = 7.2$ Hz, 3H), 0.23 (s, 3H), 0.17 (s, 3H). HRMS (ESI): Calculated for $C_{26}H_{37}NO_4SiCl$ ($[M+H]^+$): m/z 490.2180, found: 490.2177.

To a 3 ml vial was added phenol **205** (0.0146 g, 0.0298 mmol), MeCN (0.3 ml), THF (0.3 ml), and H_2O (0.15 ml). The vial was cooled to 0 °C and PIFA (0.0154 g, 0.0358 mmol, 1.2 eq) was added in one portion. The reaction was stirred at 0 °C for 15 minutes. The reaction was quenched with saturated aqueous $NaHCO_3$. The reaction mixture was extracted three times with EtOAc, and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (3:1 hexanes:ethyl acetate) to afford epoxide **206** (0.009g, 0.0172 mmol 58%). 1H NMR (500 MHz, CD_2Cl_2) δ 6.97 (d, $J = 2.2$ Hz, 1H), 6.88 (d, $J = 2.2$ Hz, 1H), 6.51 (s, 1H), 4.66 (s, 1H), 4.34 (s, 1H), 3.22 (s, 1H), 2.45 (q, $J = 6.8$ Hz, 1H), 2.03 – 1.91 (m, 1H), 1.78 (s, 3H), 1.62 (s, 3H), 1.36 – 1.29 (m, 1H), 0.91 (s, 9H), 0.87 (d, $J = 6.8$ Hz, 3H), 0.64 (t, $J = 7.3$ Hz, 3H), 0.24 (s, 3H), 0.19 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 205.07, 169.13, 157.91, 147.63, 131.83, 130.93, 115.01, 114.86, 86.67, 80.66, 75.53, 68.81, 63.10, 56.58, 53.68, 26.01, 23.34, 21.19, 20.66, 18.37, 15.28, 8.53, -4.24, -4.49.

To a 3 ml vial was added phenol **205** (0.0072 g, 0.0147 mmol), wet THF (0.59 ml), and Bengal rose (0.044 g, 30 mg/mmol). Oxygen was bubbled through the solution while vial was irradiated for 15 minutes with visible light in a photoreactor. The reaction was then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (3:1 hexanes:ethyl acetate) to afford epoxide **206** (0.0019g, 0.0036 mmol, 25%). ^1H NMR (500 MHz, CDCl_3) δ 7.02 (s, 1H), 6.84 (s, 1H), 5.76 (s, 1H), 4.62 (s, 1H), 4.33 (s, 1H), 3.26 (s, 1H), 2.49 – 2.42 (m, 1H), 2.01 – 1.92 (m, 1H), 1.79 (s, 3H), 1.66 (s, 3H), 1.37 – 1.28 (m, 1H), 0.97 – 0.79 (m, 12H), 0.65 (t, $J = 7.1$ Hz, 3H), 0.23 (s, 3H), 0.18 (s, 3H).

To a 3 ml vial was at 0 °C was added **206** (0.008 g, 0.0153 mmol), THF (0.169 ml), and TBAF (0.045 ml, 1M in THF, 3 eq). The reaction was stirred for 1 hour, then quenched with saturated aqueous NH₄Cl. The reaction mixture was extracted three times with Et₂O, and the combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (1:1 hexanes:ethyl acetate) to afford phenol **207** (0.0033 g, 0.0081 mmol, 53%). ¹H NMR (500 MHz, CD₃CN) δ 7.38 (s, 1H), 6.94 (d, *J* = 2.2 Hz, 1H), 6.87 (d, *J* = 2.2 Hz, 1H), 4.44 (d, *J* = 9.2 Hz, 1H), 4.35 (s, 1H), 3.85 (d, *J* = 9.2 Hz, 1H), 3.36 (s, 1H), 2.45 (q, *J* = 6.8 Hz, 1H), 1.99 – 1.91 (under solvent peak) (m, 1H), 1.77 (s, 3H), 1.56 (s, 3H), 1.43 – 1.23 (m, 1H), 0.84 (d, *J* = 6.8 Hz, 3H), 0.64 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (126 MHz, CD₃CN) δ 205.23, 167.51, 158.02, 148.98, 130.58, 130.02, 114.01, 113.53, 86.37, 79.28, 74.67, 69.87, 63.19, 56.39, 51.99, 22.66, 20.56, 19.51, 14.17, 7.41.

To a 10 ml round-bottom flask under argon was added tetracycle **189** (0.1 g, 0.16 mmol) and THF (1.6 ml). TBAF(*t*BuOH)₄ (0.1 g, 0.179 mmol, 1.1 eq) dissolved in THF (1.6 ml) was added to the reaction mixture dropwise. The reaction was stirred at RT for 15

To a 3 ml vial was added Pd/C (5%, 0.004 g, 0.2 eq), phenol **208** (0.010 g, 0.0213 mmol), and EtOAc (0.426 ml). The vial was sparged with H₂ for 15 minutes then stirred at room temperature overnight. The reaction was filtered over a plug of celite. The reaction mixture was concentrated under reduced pressure to afford **210** as a 7:1 mixture of

To a 3 ml vial under argon was added **210** (0.0063 g, 0.0134 mmol) and deoxygenated 4:1 MeCN:H₂O solution (0.27 ml). The vial was cooled to 0 °C. In a separate vial, PIFA (0.0085 g, 0.0198 mmol, 1.5 eq) was dissolved in deoxygenated 4:1 MeCN:H₂O solution (0.27 ml), and this PIFA solution was added dropwise over 10 minutes to the vial containing **210**. The reaction was then quenched with saturated aqueous NaHCO₃ solution. The reaction mixture was extracted three times with EtOAc, and the combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (1:1 hexanes:ethyl acetate) to afford **211** (0.0017 g, 0.0035 mmol, 26% yield). ¹H NMR (500 MHz, CDCl₃) δ 9.12 (s, 1H), 6.72 (d, *J* = 1.5 Hz, 1H), 6.44 (s, 1H), 4.15 (s, 1H), 4.10 (s, 3H), 2.50 (s, 1H), 2.36 (q, *J* = 7.7 Hz, 1H), 2.25 – 2.18 (m, 1H),

To a 20 ml scintillation vial under argon was added phenol **208** (0.059 g, 0.126 mmol), DCE (2.52 ml), and Rh₂(cap)₄ (0.8 mg, 1.26 μmol, 0.01 eq). The vial was heated to 60 °C to dissolve the Rh₂(cap)₄ fully. The vial was cooled to 0 °C and *t*BuOOH (70% in H₂O, 0.162 g, 10 eq) was added dropwise. The reaction was stirred at 0 °C for 4 hours. The reaction mixture was concentrated under reduced pressure and purified by preparatory TLC (3:1 hexanes:ethyl acetate). The bands containing products were scraped from the preparatory TLC plate, filtered with EtOAc, and concentrated under reduced pressure to afford **212** (0.033 g, 0.059 mmol, 47% yield) and its C15 epimer (0.026 g, 0.047 mmol, 37% yield). ¹H NMR (400 MHz, CDCl₃) δ 6.95 (s, 1H), 6.10 (s, 1H), 5.64 (s, 1H), 4.56 (d, *J* = 8.2 Hz, 1H), 4.13 (s, 3H), 2.96 (d, *J* = 8.9 Hz, 1H), 2.76 (dq, *J* = 14.0, 7.0 Hz, 1H), 2.03 (s, 3H), 1.97 – 1.87 (m, 1H), 1.83 (dq, *J* = 14.0, 7.0 Hz, 1H), 1.76 (s, 3H), 1.24 (d, *J* = 6.5 Hz, 3H), 1.15 (s, 9H), 0.95 (s, 9H), 0.73 (t, *J* = 7.0 Hz, 3H), 0.12 (d, *J* = 2.2 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 187.96, 174.23, 171.41, 162.38, 149.31, 138.35,

124.99, 119.54, 118.90, 102.96, 82.65, 80.01, 67.36, 59.21, 51.37, 42.54, 26.79, 25.94, 25.69, 22.47, 19.98, 18.28, 8.36, 8.30, -4.16, -4.64.

To a 3 ml vial was added peroxide **212** (0.033 g, 0.060 mmol), THF (1.19 ml), Aq. 1M NH₄OAc solution (1.19 ml), and 10% Cd/Pb Couple (prepared according to the literature)⁸ (0.29 g, 2.39 mmol, 40 eq). The reaction mixture was stirred rapidly and monitored by TLC for the complete consumption of starting material. Extra 10% Cd/Pb couple was added whenever the reaction progress appeared to stall by TLC. Upon complete consumption of starting material, the reaction mixture was filtered through a plug of celite and diluted with EtOAc and water. The reaction mixture was extracted three times with EtOAc, and the combined organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated under rotary evaporation. The crude residue was purified by flash column chromatography (3:1 hexanes:ethyl acetate to 2.85:1 hexanes:ethyl acetate) to afford **192** (0.022 g, 0.045 mmol, 75% yield). ¹H NMR (500 MHz, CDCl₃) δ 6.75 (d, *J* = 1.3 Hz, 1H), 5.98 (s, 1H), 5.62 (s, 1H), 4.69 (dd, *J* = 9.7, 1.3 Hz, 1H), 4.12 (s, 3H), 3.91 (s, 1H), 3.25 (d, *J* = 9.2 Hz, 1H), 3.10 (dq, *J* = 14.1, 7.2 Hz, 1H), 1.96 (s, 3H), 1.88 – 1.81 (m, 1H), 1.75 (s, 3H), 1.71 (dq, *J* = 14.1, 7.2 Hz, 2H), 1.27

(d, $J = 6.4$ Hz, 3H), 0.96 (s, 9H), 0.72 (t, $J = 7.2$ Hz, 3H), 0.15 (s, 3H), 0.12 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 187.18, 174.69, 171.86, 165.69, 151.07, 139.66, 124.60, 116.05, 102.96, 73.04, 67.98, 59.37, 53.92, 42.53, 26.00, 24.39, 22.15, 19.91, 18.35, 8.20, 7.18, -4.41, -4.71. IR (neat, cm^{-1}): 3320 (s), 2970 (s), 2920 (s), 2840 (s), 1800 (w), 1655 (s), 1620 (s), 1580 (w), 1460 (w), 1389 (m), 1350 (w), 1316 (s), 1300 (s), 1242 (s), 1157 (w), 1096 (w), 1070 (w), 1007 (w), 876 (s), 833 (s), 752 (s), 667 (w). HRMS (ESI): Calculated for $\text{C}_{27}\text{H}_{40}\text{NO}_5\text{Si}$ ($[\text{M}+\text{H}]^+$): m/z 486.2676, found: 486.2674.

To a 1.5 ml Eppendorf tube was added *para*-quinol **192** (0.0138 g, 0.0284 mmol) and THF (0.568 ml). HF•pyridine (0.14 ml) was added dropwise and the reaction mixture was stirred at room temperature for 2 hours. The reaction was then quenched with saturated aqueous NaHCO_3 solution. The reaction mixture was extracted three times with EtOAc, dried over MgSO_4 , filtered, and concentrated under rotary evaporation. The crude residue was purified by preparatory TLC (49:1 dichloromethane:methanol). The product band was scraped from the preparatory TLC plate, filtered with 9:1 dichloromethane:methanol solution, and concentrated under reduced pressure. This residue was further purified by flash column chromatography (19:1 dichloromethane:methanol) to afford **11** (0.0063 g, 0.0170 mmol, 60% yield). ^1H NMR (500 MHz, CD_3OD) δ 6.83 (d, $J = 1.9$ Hz, 1H), 6.01

(t, $J = 1.9$ Hz, 1H), 5.71 (s, 1H), 4.61 (dd, $J = 9.9, 1.9$ Hz, 1H), 4.22 (s, 3H), 3.28 (d, $J = 9.8$ Hz, 1H), 3.17 (dq, $J = 14.0, 7.1$ Hz, 1H), 2.05 (s, 3H), 1.93 – 1.83 (m, 1H), 1.80 – 1.74 (m, 1H), 1.79 (s, 3H), 1.33 (d, $J = 6.4$ Hz, 3H), 0.71 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CD_3OD) δ 190.13, 176.78, 174.05, 169.61, 155.39, 141.10, 125.63, 115.87, 115.29, 103.83, 76.85, 73.85, 69.22, 60.23, 55.79, 43.55, 25.06, 22.15, 20.11, 8.01, 7.37. . IR (neat, cm^{-1}): 3306 (s), 2943 (s), 2832 (s), 1659 (m), 1609 (m), 1447 (w), 1393 (w), 1300 (m), 1096 (m), 1022 (s), 949 (w), 910 (w), 876 (w), 826 (w), 746 (w), 679 (w), 644 (w), 613 (w). HRMS (ESI): Calculated for $\text{C}_{21}\text{H}_{26}\text{NO}_5$ ($[\text{M}+\text{H}]^+$): m/z 372.1811, found: 372.1800.

6.5. Experimental Procedures from Chapter 5

Glycal **220** was synthesized according to the literature.⁹ To a 3ml vial was added glycal **220** (0.012 g, 0.076 mmol), *rac*-**114** (0.1 g, 0.228 mmol, 3 eq), $\text{Pd(PPh}_3)_4$ (0.009 g, 0.0076 mmol, 0.1 eq), and THF (0.76 ml). The reaction mixture was heated to 40°C . The reaction mixture was cooled to room temperature when TLC analysis indicated the complete consumption of **220** (about 6 hours). The solvent was removed under reduced pressure and the crude material purified by flash column chromatography (19:1 hexanes:ethyl acetate to 9:1 hexanes:ethyl acetate) to furnish unreacted *rac*-**114** and **221a/b** (0.017 g, 0.030 mmol, 40% yield) Diastereomer 1: ^1H NMR (500 MHz, CDCl_3) δ 7.08 (s, 1H), 6.96 (d, $J = 1.9$ Hz, 1H), 6.18 (dd, $J = 9.9, 5.2$ Hz, 1H), 5.89 (d, $J = 9.9$ Hz, 1H), 5.24 (s, 1H), 4.88 (s, 1H), 4.85 (s, 1H), 4.72 (d, $J = 6.5$ Hz, 1H), 3.77 (dd, $J = 8.7, 4.1$ Hz, 1H), 3.72 – 3.56 (m, 1H), 3.22 (d, $J = 7.2$ Hz, 1H), 2.21 (dd, $J = 13.8, 6.9$ Hz, 1H), 1.63 (s, 3H), 1.52 (d, $J = 11.4$ Hz, 1H), 1.35 (d, $J = 6.4$ Hz, 3H), 1.29 – 1.23 (m, 3H), 1.22 (d, $J = 6.9$ Hz, 3H), 1.10 (dd, $J = 7.4, 2.6$ Hz, 18H). Diastereomer 2: ^1H NMR (500 MHz, CDCl_3) δ 7.00 (d, $J = 1.9$ Hz, 1H), 6.88 (s, 1H), 6.17 (dd, $J = 9.6, 4.8$ Hz, 1H), 5.82 (d, $J = 9.6$ Hz, 1H), 5.24 (s, 1H), 4.85 (s, 1H), 4.72 (d, $J = 4.9$ Hz, 1H), 4.71 (s,

1H), 3.76 (d, $J = 6.5$ Hz, 1H), 3.68 (d, $J = 10.9$ Hz, 1H), 3.22 (d, $J = 5.4$ Hz, 1H), 2.28 (dd, $J = 11.9, 5.2$ Hz, 1H), 1.66 (s, 3H), 1.35 (d, $J = 6.5$ Hz, 3H), 1.26 (s, 3H), 1.20 (d, $J = 7.1$ Hz, 3H), 1.10 (d, $J = 7.2$ Hz, 18H).

To a flame-dried 250 ml round-bottom flask cooled to -40 °C was added EtMgBr (3M in THF, 3.67 ml, 11 mmol, 1.1 eq) followed by dropwise addition of 2-methyl-1-butene-3-yne (1.9 ml, 20 mmol, 2 eq). The reaction mixture was stirred for 1 h. Then, 50 ml dry toluene was added to the round-bottom flask. Commercially available (–)-menthyl (S)-p-toluenesulfinate (2.94 g, 10 mmol) was dissolved in 50 ml toluene and added dropwise to the round-bottom flask while maintaining the temperature at -40 °C. The reaction mixture was stirred for 3 h then quenched with a saturated aqueous solution of NH_4Cl . The mixture was diluted and extracted with ether, dried over MgSO_4 , filtered, then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford **225** (1.36 g, 67%) and unreacted (–)-menthyl (S)-p-toluenesulfinate (0.55 g, 19%). ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 5.52 (s, 1H), 5.47 (s, 1H), 2.43 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.58, 140.92, 130.36, 127.16, 125.38, 124.62, 103.32, 85.20, 22.37, 21.63.

To a flame-dried 250 ml round-bottom flask was added **225** (1.36 g, 6.66 mmol), toluene (66 ml), and Pd(PPh₃)₄ (0.154 g, 0.133 mmol, 0.02 eq). The flask was cooled to -78 °C. Bu₃SnH (1.97 ml, 7.33 mmol, 1.1 eq) was added dropwise after which the flask was raised to 0 °C and stirred for 1 h. The reaction was concentrated under reduced pressure and purified by column chromatography (19:1 hexanes:ethyl acetate) to afford **226** (2.17 g, 66%) ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.85 – 6.51 (m, 1H), 5.21 (s, 1H), 5.13 (s, 1H), 2.37 (s, 3H), 2.02 (s, 3H), 1.50 – 1.12 (m, 12H), 0.96 – 0.74 (m, 15H). ¹³C NMR (101 MHz, CDCl₃) δ 158.19, 146.78, 142.59, 142.04, 140.07, 129.68, 125.01, 121.99, 28.85, 27.37, 23.03, 21.33, 13.74, 11.96.

To a flame-dried 250 ml round-bottom flask was added **S1** and dry THF (6.3 ml). The flask was cooled to -78 °C. *n*-BuLi (2.1 M in hexanes, 2.1 ml, 1 eq) was added dropwise and the reaction stirred for 15 minutes. Then, freshly crushed solid CO₂ (20 g) was added in one portion. The reaction was stirred for 15 minutes at -78 °C, then allowed to warm to rt. The mixture was diluted and extracted with EtOAc, dried over MgSO₄, filtered, then

concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate, then 9:1 hexanes:ethyl acetate, then 3:1 hexanes:ethyl acetate) to afford **S17** as a white solid (1.17 g, 71%). ^1H NMR (400 MHz, CDCl_3) δ 7.87 – 7.79 (m, 1H), 7.52 (dd, J = 2.2, 1.3 Hz, 1H), 7.32 – 7.25 (m, 1H), 1.37 – 1.22 (m, 3H), 1.11 (d, J = 7.3 Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.87, 157.13, 131.87, 128.63, 125.98, 122.74, 120.23, 17.99, 12.72. IR (neat, cm^{-1}): 2965 (w), 2947 (m), 2928 (w), 2891 (w), 2866 (m), 1690 (s), 1593 (s), 1568 (s), 1452 (s), 1429 (s), 1410 (m), 1385 (w), 1308 (m), 1288 (s), 1267 (m), 1117 (m), 1067 (m), 1001 (m), 982 (s), 920 (m), 878 (s), 868 (m), 849 (s), 770 (s), 748 (s), 700 (s). HRMS (ESI): Calculated for $\text{C}_{16}\text{H}_{24}\text{O}_3\text{SiBr}$ ($[\text{M}-\text{H}]^+$): m/z 371.0678, found: 371.0678.

To a 3 ml vial was added **S8** (0.045 g, 0.12 mmol), DCM (1.2 ml), and DMF (1 drop). The vial was cooled to 0 °C. $(\text{COCl})_2$ (0.021 ml, 0.24 mmol, 2 eq) was added dropwise. The vial was raised to rt over 1 hour. The reaction mixture was concentrated under reduced pressure, and the crude residue was dissolved in hexanes and filtered through a short plug of silica gel. The hexanes solution was concentrated under reduced pressure to afford **227** which was immediately taken to the cross-coupling step without further purification.

To a flame-dried 3-ml vial under argon was added $\text{Pd(PPh}_3)_4$ (0.012 g, 0.01 mmol, 0.1 eq) and dry DCM (0.5 ml). **226** (0.05 g, 0.1 mmol) was dissolved in 0.25 ml dry DCM and added to the vial. Freshly prepared **227** (presumably 0.12 mmol, 1.2 eq) was dissolved in 0.25 ml dry DCM and added to the vial. CuTc (0.0038 g, 0.02 mmol, 0.2 eq) was added to the vial and the reaction was stirred overnight. TLC analysis revealed complete consumption of **226** the next day. The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford **228** (0.0158 g, 28%). ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 7.8$ Hz, 1H), 7.19 – 7.08 (m, 5H), 7.02 (s, 1H), 5.30 (s, 1H), 5.18 (s, 1H), 2.30 (s, 3H), 1.61 (s, 3H), 1.28 – 1.14 (m, 3H), 1.06 (d, $J = 7.3$ Hz, 18H).

231 was prepared according to the literature.¹⁰ To a 10 ml round-bottom flask were added **231** (0.050 g, 0.291 mmol), DCM (1.45 ml), commercially available (S)-4-

phenyloxazolidin-2-one (0.237 g, 1.45 mmol, 5 eq), 1,2-dimethylimidazole (0.0103 ml, 0.4 eq), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.0074 g, 0.15 eq), and oven-dried 4Å MS (0.2 g). The reaction was stirred vigorously under 1 atm O_2 at rt for 48 hours. The reaction mixture was filtered over celite and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (3:1 hexanes:ethyl acetate) to afford **232** (0.050 g, 75%). ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.25 (m, 5H), 5.14 – 5.00 (m, 3H), 4.74 (t, J = 8.8 Hz, 1H), 4.33 – 4.12 (m, 1H), 1.73 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.56, 136.12, 129.51, 129.31, 126.94, 125.63, 120.86, 74.30, 70.72, 62.16, 23.38.

To a flame-dried 25 ml round-bottom flask was added **232** (0.181 g, 0.796 mmol), DCM (8 ml), and $\text{Pd(PPh}_3)_4$ (0.092 g, 0.1 eq). The flask was cooled to 0 °C. Bu_3SnH (0.43 ml, 1.59 mmol, 2 eq) was added dropwise after which the flask was raised to rt and stirred for 30 min. The reaction was concentrated under reduced pressure and purified by column chromatography (19:1 hexanes:ethyl acetate) to afford **233** (0.314 g, 76%). ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.28 (m, 3H), 7.12 (d, J = 6.8 Hz, 2H), 5.60 (dd, J = 8.6, 5.7 Hz, 1H), 5.34 – 5.16 (m, 1H), 5.14 (s, 1H), 4.78 (s, 1H), 4.62 (t, J = 8.6 Hz, 1H), 4.18 (dd, J = 8.6, 5.7 Hz, 1H), 1.49 – 1.39 (m, 6H), 1.39 (s, 3H), 1.35 – 1.20 (m, 6H), 1.02 – 0.80 (m, 15H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.96, 143.00, 138.96, 138.45, 130.08, 128.83, 128.50, 127.27, 115.47, 70.35, 58.91, 29.02, 27.46, 23.14, 13.86, 12.14.

To a flame-dried 3-ml vial under argon was added $\text{Pd(PPh}_3)_4$ (0.014 g, 0.1 eq) and dry DCM (0.5 ml). **233** (0.065 g, 0.125 mmol) was dissolved in 0.5 ml dry DCM and added to the vial. Freshly prepared **227** (0.138 mmol, 1.1 eq) was dissolved in 0.25 ml dry DCM and added to the vial. CuTc (0.0048 g, 0.2 eq) was added to the vial and the reaction was stirred overnight. TLC analysis revealed complete consumption of **233** the next day. The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (9:1 hexanes:ethyl acetate) to afford **234** (0.032 g, 44%). ^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.31 (m, 5H), 7.20 (s, 1H), 7.17 (d, J = 2.0 Hz, 1H), 6.86 (s, 1H), 6.47 (s, 1H), 5.37 – 5.30 (m, 2H), 5.24 (s, 1H), 4.76 (t, J = 8.7 Hz, 1H), 4.42 (t, J = 9.2 Hz, 1H), 1.81 (s, 3H), 1.23 – 1.15 (m, 3H), 1.05 (dd, J = 7.4, 2.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 191.18, 156.78, 156.64, 139.92, 139.09, 135.61, 130.92, 129.59, 129.52, 129.14, 128.45, 127.16, 125.88, 124.98, 124.11, 122.79, 119.50, 70.32, 59.90, 21.13, 17.93, 12.61.

231 (0.050 g, 0.29 mmol) is converted to **235** (0.0293 g, 52%) with the procedure used to synthesize **232**. Commercially available (S)-4-isopropylloxazolidin-2-one is used instead of (S)-4-phenylloxazolidin-2-one. ^1H NMR (500 MHz, CDCl_3) δ 5.22 (s, 1H), 5.15 (s, 1H), 4.36 (t, J = 8.9 Hz, 1H), 4.12 (dd, J = 8.9, 5.8 Hz, 1H), 3.95 (dd, J = 8.9, 5.8 Hz, 1H), 2.23 – 2.13 (m, 1H), 1.88 (s, 3H), 1.00 – 0.89 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 156.02, 125.86, 120.70, 77.82, 73.68, 64.91, 62.01, 29.32, 23.51, 17.19, 15.27. IR (neat, cm^{-1}): 2970 (m), 2884 (w), 2239 (m), 1746 (s), 1715 (w), 1449 (m), 1418 (s), 1393 (s), 1290 (s), 1222 (s), 1194 (m), 1140 (w), 1107 (s), 1042 (s), 1009 (s), 984 (s), 881 (s), 756 (m), 743 (m), 718 (s). HRMS (ESI): Calculated for $\text{C}_{11}\text{H}_{16}\text{NO}_2$ ($[\text{M}+\text{H}]^+$): m/z 194.1181, found: 194.1180.

235 (0.182 g, 0.945 mmol) is converted to **236** (0.286 g, 84%) with the procedure used to synthesize **233**. ^1H NMR (400 MHz, CDCl_3) δ 5.53 – 5.31 (m, 1H), 5.10 (s, 1H), 4.73 (s, 1H), 4.53 (dt, J = 8.4, 3.7 Hz, 1H), 4.19 (t, J = 8.4 Hz, 1H), 4.11 (dd, J = 8.4, 3.7 Hz, 1H), 1.95 – 1.88 (m, 1H), 1.78 (s, 3H), 1.60 – 1.41 (m, 6H), 1.39 – 1.22 (m, 6H), 1.07 – 0.90 (m, 6H), 0.87 (t, J = 7.3 Hz, 9H), 0.78 (d, J = 7.1 Hz, 3H), 0.75 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.91, 142.20, 138.96, 128.84, 115.23, 62.88, 58.94, 29.05, 27.44, 26.08, 23.05, 17.85, 14.06, 13.80, 12.33. IR (neat, cm^{-1}): 2959 (m), 2918 (m), 2870 (w), 2853 (w), 1783 (s), 1456 (w), 1402 (s), 1393 (w), 1373 (m), 1231 (s),

1080 (m), 1055 (w), 1011 (w), 899 (m). HRMS (ESI): Calculated for $C_{23}H_{44}NO_2^{120}Sn$ ($[M+H]^+$): m/z 486.2394, found: 486.2397.

To a flame-dried 250 ml round-bottom flask under argon was added $\text{Pd(PPh}_3)_4$ (0.618 g, 0.05 eq) and dry THF (32 ml). **236** (5.18 g, 10.7 mmol) was dissolved in 16 ml dry THF and added to the flask. Freshly prepared **227** (14.18 mmol, 1.32 eq) was dissolved in 16 ml dry THF and added to the flask. CuCl (1.59 g, 1.5 eq) was added to the flask and the reaction was stirred for 6 hours. TLC analysis revealed complete consumption of **236**. The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (neat hexanes, then 19:1 hexanes:ethyl acetate, then 9:1 hexanes:ethyl acetate) to afford **237** (5.52 g, 10.0 mmol, 93%). ^1H NMR (500 MHz, CDCl_3) δ 7.42 (s, 1H), 7.23 (s, 1H), 7.13 (s, 1H), 6.81 (s, 1H), 5.41 (s, 1H), 5.36 (s, 1H), 4.47 (t, $J = 8.7$ Hz, 1H), 4.16 (t, $J = 8.1$ Hz, 1H), 3.95 (dd, $J = 13.4, 7.6$ Hz, 1H), 2.06 (s, 3H), 1.87 (dq, $J = 13.4, 6.7$ Hz, 1H), 1.33 – 1.19 (m, 3H), 1.09 (d, $J = 7.4$ Hz, 18H), 0.97 (d, $J = 6.8$ Hz, 3H), 0.94 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 191.09, 158.01, 156.93, 144.63, 139.97, 139.33, 132.57, 127.35, 126.09, 125.01, 122.96, 119.49, 66.26, 61.32, 31.44, 20.82, 19.52, 17.96, 17.21, 12.71. IR (neat, cm^{-1}): 2945 (m), 2866 (m), 1759 (s), 1659 (m), 1589 (s), 1562 (s), 1462 (w), 1435 (w), 1410 (w), 1393 (w), 1369 (w), 1287 (s), 1207 (s), 1117 (m), 1061 (m), 1015 (w), 995 (m), 972 (s), 945 (w),

918 (w), 881 (s), 886 (w), 752 (s), 729 (s). HRMS (ESI): Calculated for $C_{27}H_{41}NO_4BrSi$ ($[M+H]^+$): m/z 550.1988, found: 550.1991.

To a flame-dried 100 ml flask was added AlCl_3 (0.105 g, 0.784 mmol, 1.1 eq). Dry DCM was added (7 ml) and the flask was cooled to $-78\text{ }^\circ\text{C}$. **237** (0.366 g, 0.713 mmol) dissolved in DCM (7 ml) was added dropwise, and the flask was raised slowly to rt and then heated at $35\text{ }^\circ\text{C}$. Extra AlCl_3 (0.1 eq) was added every hour. When TLC analysis showed complete consumption of starting material, the reaction was quenched by the addition of a saturated solution of sodium potassium tartrate. The mixture was diluted and extracted with Et_2O , dried over MgSO_4 , filtered, then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate, then 9:1 hexanes:ethyl acetate) to afford **238** as a 9:1 mixture of diastereomers (0.163 g, 45% yield). **238** can be isolated as a single diastereomer from recrystallization with 3:1 hexanes:ether. ^1H NMR (400 MHz, CDCl_3) δ 7.35 (s, 1H), 7.15 (s, 1H), 5.09 (s, 1H), 5.08 (s, 1H), 4.41 (t, $J = 8.9\text{ Hz}$, 1H), 4.36 (d, $J = 4.8\text{ Hz}$, 1H), 4.23 – 4.09 (m, 1H), 4.06 – 3.91 (m, 1H), 3.78 (d, $J = 4.8\text{ Hz}$, 1H), 1.92 – 1.74 (m, 1H), 1.63 (s, 3H), 1.36 – 1.18 (m, 3H), 1.09 (d, $J = 7.3\text{ Hz}$, 18H), 0.96 (d, $J = 6.7\text{ Hz}$, 3H), 0.89 (d, $J = 6.9\text{ Hz}$, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 200.74, 158.41, 157.15, 143.78, 142.32, 137.85, 132.33, 122.35, 116.86, 112.78, 64.63, 63.78, 62.28, 51.07, 29.17, 18.77, 18.25,

17.98, 14.68, 12.71. IR (neat, cm^{-1}): 2940 (m), 2870 (m), 1760 (m), 1722 (s), 1600 (m), 1460 (s), 1308 (m), 1263 (w), 1100 (m), 966 (s), 887 (m), 873 (m), 762 (s). HRMS (ESI): Calculated for $\text{C}_{27}\text{H}_{41}\text{NO}_4\text{BrSi}$ ($[\text{M}+\text{H}]^+$): m/z 550.1988, found: 550.1996.

To a flame-dried 3 ml vial was added **238** (0.021 g, 0.038 mmol) and THF (0.38 ml). The vial was cooled to $-78\text{ }^\circ\text{C}$. 0.1 M LiNap solution (prepared by taking equimolar freshly cut lithium metal and naphthalene and dissolving into the appropriate volume of THF, followed by sonication) (0.74 ml, 1.95 eq) was added dropwise. The reaction was quenched with concentrated aqueous NH_4Cl solution, diluted and extracted with Et_2O , dried over MgSO_4 , filtered, then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (neat hexanes, then 19:1 hexanes:ethyl acetate, then 9:1 hexanes:ethyl acetate, then 3:1 hexanes:ethyl acetate) to afford **(S)-113** (0.0031 g, 19%) and recovered **238** (0.0119 g, 57%). ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, $J = 2.2$ Hz, 1H), 7.14 (d, $J = 2.2$ Hz, 1H), 4.86 (s, 1H), 4.68 (s, 1H), 3.98 (dd, $J = 8.1$, 1.9 Hz, 1H), 2.99 (dd, $J = 19.1$, 8.1 Hz, 1H), 2.50 (dd, $J = 19.1$, 1.9 Hz, 1H), 1.57 (s, 3H), 1.32 – 1.21 (m, 3H), 1.09 (d, $J = 7.4$ Hz, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 204.98, 157.12, 147.65, 144.79, 140.05, 131.02, 122.49, 113.13, 112.34, 46.05, 44.80, 19.91, 17.97, 12.69. IR (neat, cm^{-1}): 2947 (s), 2866 (s), 1717 (s), 1601 (s), 1559 (w), 1458 (s), 1385 (w), 1288 (s), 1261 (w), 1211 (w), 1119 (w), 1049 (m), 961 (s), 910 (m), 880 (s),

864 (m), 826 (m), 756 (w), 733 (s), 687 (s), 648 (w); HRMS (ESI): Calculated for $C_{21}H_{32}BrO_2Si$ ($[M+H]^+$): m/z 423.1355, found: 423.1353.

To a flame-dried 3 ml vial was added **238** (0.0122 g, 0.0222 mmol) and THF (0.15 ml). 0.0846 M SmI_2 solution (prepared by adding 0.095 g I_2 dissolved in 3.74 ml THF to 0.112 g Sm powder and heating overnight at 60 °C, followed by iodometric titration) (0.47 ml, 1.8 eq) was added dropwise. The reaction was quenched with 10% Rochelle's salt solution, diluted and extracted with Et_2O , dried over MgSO_4 , filtered, then concentrated under reduced pressure. The crude residue was purified by flash column chromatography (neat hexanes, then 19:1 hexanes:ethyl acetate, then 9:1 hexanes:ethyl acetate, then 3:1 hexanes:ethyl acetate) to afford **(S)-113** (0.0057 g, 54%) and recovered **238** (0.0055 g, 45%) .

6.6. NMR Data Comparison to Literature Values for 11

Position	11 (Reference 11)	11 (this work)
	^1H NMR (δ)	^1H NMR (δ)
1	-	-
2	-	-
3	-	-
4	-	-
5	5.70 (br. s)	5.71 (s)
6	-	-
7	3.27 (br. d, $J = \text{ca. } 8.0 \text{ Hz}$)	3.28 (d, $J = 9.8 \text{ Hz}$)
8	ca. 1.8 (m)	1.93 – 1.83 (m)
9	4.61 (dd, $J = 9.6, 2.0 \text{ Hz}$)	4.61 (dd, $J = 9.9, 1.9 \text{ Hz}$)
10	-	-
11	6.00 (t, $J = 2.0 \text{ Hz}$)	6.01 (t, $J = 1.9 \text{ Hz}$)
12	-	-
13	6.83 (d, $J = 2.0 \text{ Hz}$)	6.83 (d, $J = 1.9 \text{ Hz}$)
14	-	-
15	-	-
16	2.05 (s)	2.05 (s)
17	ca. 1.8 (m) and 3.16 (m)	1.80 – 1.74 (m) and 3.17 (dq, $J = 14.0, 7.1 \text{ Hz}$)
18	0.71 (t, $J = 7.2 \text{ Hz}$)	0.71 (t, $J = 7.1 \text{ Hz}$)
19	1.79 (s)	1.79 (s)
20	1.32 (d, $J = 6.4 \text{ Hz}$)	1.33 (d, $J = 6.4 \text{ Hz}$)
OCH ₃	4.21 (s)	4.22 (s)

11 (this work) was referenced to CD₃OD (3.31 ppm)

Carbon numbering by Hirota *et al.*¹¹

6.7. References

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Appendix A: NMR Spectroscopic Data

¹H NMR Spectrum of Compound **S1**

^{13}C NMR Spectrum of Compound **S1**

¹H NMR Spectrum of Compound **103**

¹H NMR Spectrum of Compound **104**

^{13}C NMR Spectrum of Compound **91**

¹H NMR Spectrum of Compound S3

¹H NMR Spectrum of Compound **94**

^1H NMR Spectrum of Compound **98**

¹H NMR Spectrum of Compound **101**

^{13}C NMR Spectrum of Compound **101**

¹H NMR Spectrum of Compound **92**

^{13}C NMR Spectrum of Compound S4

¹H NMR Spectrum of Compound **95**

¹H NMR Spectrum of Compound **99**

^{13}C NMR Spectrum of Compound **99**

^1H NMR Spectrum of Compound **102**

^{13}C NMR Spectrum of Compound **102**

^1H NMR Spectrum of Compound **S5**

^{13}C NMR Spectrum of Compound **S5**

¹H NMR Spectrum of Compound **96**

^{13}C NMR Spectrum of Compound **96**

¹H NMR Spectrum of Compound **100**

¹³C NMR Spectrum of Compound **110**

¹H NMR Spectrum of Compound **S6**

¹H NMR Spectrum of Compound **S7**

¹H NMR Spectrum of Compound **93**

¹H NMR Spectrum of Compound **S8**

^1H NMR Spectrum of Compound **97**

¹³C NMR Spectrum of Compound **97**

¹H NMR Spectrum of Compound **106**

¹H NMR Spectrum of Compound **108**

^{13}C NMR Spectrum of Compound **108**

^1H NMR Spectrum of Compound **109**

^1H NMR Spectrum of Compound **110**

¹H NMR Spectrum of Compound **112**

¹H NMR Spectrum of Compound **113**

¹³C NMR Spectrum of Compound **113**

¹H NMR Spectrum of Compound **114**

¹³C NMR Spectrum of Compound **114**

¹H NMR Spectrum of Compound **115**

^{13}C NMR Spectrum of Compound **115**

¹H NMR Spectrum of Compound **116**

^{13}C NMR Spectrum of Compound **116**

^1H NMR Spectrum of Compound **120**

^1H NMR Spectrum of Compound **121**

¹H NMR Spectrum of Compound **122**

^{13}C NMR Spectrum of Compound **122**

¹H NMR Spectrum of Compound **123**

^{13}C NMR Spectrum of Compound **123**

^1H NMR Spectrum of Compound **S9**

^1H NMR Spectrum of Compound **124**

^{13}C NMR Spectrum of Compound **124**

^1H NMR Spectrum of Compound **S9**

¹³C NMR Spectrum of Compound **S9**

¹H NMR Spectrum of Compound **S10**

¹H NMR Spectrum of Compound **125**

^{13}C NMR Spectrum of Compound **125**

^1H NMR Spectrum of Compound **131**

^{13}C NMR Spectrum of Compound **131**

¹H NMR Spectrum of Compound **132**

¹H NMR Spectrum of Compound **133**

¹H NMR Spectrum of Compound **134**

^{13}C NMR Spectrum of Compound **134**

¹H NMR Spectrum of Compound **S11**

¹H NMR Spectrum of Compound **140**

^{13}C NMR Spectrum of Compound **140**

¹H NMR Spectrum of Compound **S12**

^{13}C NMR Spectrum of Compound **S12**

¹H NMR Spectrum of Compound **139**

¹³C NMR Spectrum of Compound **139**

^1H NMR Spectrum of Compound **S13**

¹H NMR Spectrum of Compound **143**

¹³C NMR Spectrum of Compound **143**

¹H NMR Spectrum of Compound **S14**

^{13}C NMR Spectrum of Compound **S14**

¹H NMR Spectrum of Compound **S15**

^{13}C NMR Spectrum of Compound **S15**

¹H NMR Spectrum of Compound **144**

¹³C NMR Spectrum of Compound **144**

¹H NMR Spectrum of Compound **145**

^1H NMR Spectrum of Compound **146**

^{13}C NMR Spectrum of Compound **146**

¹H NMR Spectrum of Compound **S16**

¹H NMR Spectrum of Compound **148**

¹H NMR Spectrum of Compound **149**

^1H NMR Spectrum of Compound **152**

^1H NMR Spectrum of Compound **153a**

^{13}C NMR Spectrum of Compound **153a**

^1H NMR Spectrum of Compound **163**

^1H NMR Spectrum of Compound **164**

^{13}C NMR Spectrum of Compound **166**

^1H NMR Spectrum of Compound **169**

^{13}C NMR Spectrum of Compound **169**

¹H NMR Spectrum of Compound **167**

¹H NMR Spectrum of Compound **171**

¹³C NMR Spectrum of Compound **171**

¹H NMR Spectrum of Compound **172**

¹H NMR Spectrum of Compound **174**

¹H NMR Spectrum of Compound **176**

¹H NMR Spectrum of Compound **177**

¹H NMR Spectrum of Compound **179**

¹³C NMR Spectrum of Compound **180**

^1H NMR Spectrum of Compound **181**

^1H - ^1H COSY NMR Spectrum of Compound **181**

^{13}C NMR Spectrum of Compound **181**

¹H NMR Spectrum of Compound **182**

^{13}C NMR Spectrum of Compound **182**

¹H NMR Spectrum of Compound **183**

^{13}C NMR Spectrum of Compound **183**

¹H NMR Spectrum of Compound **185** (Set 1)

¹H NMR Spectrum of Compound **185** (Set 2)

¹H NMR Spectrum of Compound **187**

^{13}C NMR Spectrum of Compound **187**

^1H - ^1H COSY NMR Spectrum of Compound **186**

¹H NMR Spectrum of Compound **193**

^{13}C NMR Spectrum of Compound **194**

¹H NMR Spectrum of Compound **198**

¹H NMR Spectrum of Compound **199**

¹H NMR Spectrum of Compound **200**

¹H NMR Spectrum of Compound **201**

¹H NMR Spectrum of Compound **203**

^1H NMR Spectrum of Compound **205**

^{13}C NMR Spectrum of Compound **206** (from PIFA oxidation)

¹H NMR Spectrum of Compound **206** (from photooxidation)

¹H NMR Spectrum of Compound **207**

^1H - ^1H COSY NMR Spectrum of Compound **207**

^{13}C NMR Spectrum of Compound **207**

¹H NMR Spectrum of Compound **208**

^{13}C NMR Spectrum of Compound **208**

^1H NMR Spectrum of Compound **209**

^1H NMR Spectrum of Compound **210**

^1H NMR Spectrum of Compound **211**

¹H NMR Spectrum of Compound **212**

^{13}C NMR Spectrum of Compound **212**

¹H NMR Spectrum of Compound **192**

^{13}C NMR Spectrum of Compound **192**

^1H NMR Spectrum of Compound **11**

^1H - ^1H COSY NMR Spectrum of Compound **11**

^{13}C NMR Spectrum of Compound **11**

^1H NMR Spectrum of Compound **221a**

^1H NMR Spectrum of Compound **221b**

¹H NMR Spectrum of Compound **225**

^{13}C NMR Spectrum of Compound **225**

¹H NMR Spectrum of Compound **226**

^{13}C NMR Spectrum of Compound **226**

¹H NMR Spectrum of Compound **S17**

^{13}C NMR Spectrum of Compound **S17**

¹H NMR Spectrum of Compound **228**

¹H NMR Spectrum of Compound **232**

¹³C NMR Spectrum of Compound **232**

^1H NMR Spectrum of Compound **130**

^{13}C NMR Spectrum of Compound **233**

^1H NMR Spectrum of Compound **234**

^{13}C NMR Spectrum of Compound **234**

^1H NMR Spectrum of Compound **235**

^{13}C NMR Spectrum of Compound **235**

¹H NMR Spectrum of Compound **236**

^{13}C NMR Spectrum of Compound **236**

^1H NMR Spectrum of Compound **237**

^{13}C NMR Spectrum of Compound **237**

^1H NMR Spectrum of Compound **238**

^{13}C NMR Spectrum of Compound **238**

Appendix B: IR Spectroscopic Data

For Compound **S1**

C:\Program Files\Shimadzu\IRsolution\data\default101.smf

No. of Scans; 30

Resolution; 8 [1/cm]

Date & Time; 3/31/2012 9:30:41 AM

For Compound **91**

University of Rochester

C:\Program Files\IRsolution\Data\0608144924.smf

Date & Time: 6/8/2013 2:49:23 PM

Resolution;

No. of Scans;

For Compound **S5**

University of Rochester

342 793 collect

C:\Program Files\IRsolution\Data\0608145114.smf

No. of Scans;

Resolution;

Date & Time; 6/8/2013 2:51:14 PM

For Compound **96**

University of Rochester

Transmittance (%)

Wavenumber (1/cm)

C:\Program Files\IRsolution\Data\0608145445.smf

No. of Scans;

Resolution;

Date & Time; 6/8/2013 2:54:45 PM

For Compound **100**

University of Rochester

C:\Program Files\IRsolution\Data\0608143137.smf

No. of Scans;

Resolution;

Date & Time: 6/8/2013 2:31:36 PM

For Compound **113**

University of Rochester

C:\Program Files\IRsolution\Data\0608143538.smf

No. of Scans;

Resolution;

Date & Time; 6/8/2013 2:35:38 PM

For Compound **114**

University of Rochester

C:\Program Files\IRsolution\Data\0608143930.smf

No. of Scans;

Resolution;

Date & Time; 6/8/2013 2:39:30 PM

For Compound **115**

University of Rochester

C:\Program Files\IRsolution\Data\0608144218.smf

No. of Scans;

Resolution;

Date & Time; 6/8/2013 2:42:17 PM

For Compound **116**

University of Rochester

C:\Program Files\IRResolution\Data\0608145845.smf

No. of Scans;

Resolution;

Date & Time; 6/8/2013 2:58:45 PM

For Compound **140**

University of Rochester

C:\Program Files\IRsolution\Data\0608150228.smf

Date & Time; 6/8/2013 3:02:28 PM

Resolution;

No. of Scans;

For Compound **141**

University of Rochester

C:\Program Files\IRsolution\Data\0608150552.smf

No. of Scans;

Resolution;

Date & Time: 6/8/2013 3:05:51 PM

For Compound **S12**

University of Rochester

13
KOH
20705

C:\Program Files\IRsolution\Data\0608144458.smf

No. of Scans;

Resolution;

Date & Time; 6/8/2013 2:44:58 PM

For Compound **139**

University of Rochester

H₂O

C:\Program Files\IRsolution\Data\0608142449.smf

No. of Scans;

Resolution;

Date & Time; 6/8/2013 2:24:49 PM

For Compound **153a**

University of Rochester

C:\Program Files\IRsolution\Data\0608150910.smf

Date & Time: 6/8/2013 3:09:10 PM

Resolution;

No. of Scans;

For Compound **166**

University of Rochester

C:\Program Files\IRsolution\Data\0608151622.smf

No. of Scans;

Resolution;

Date & Time; 6/8/2013 3:16:21 PM

For Compound **181**

University of Rochester

C:\Program Files\IRsolution\Data\0608152731.smf

No. of Scans;

Resolution;

Date & Time; 6/8/2013 3:27:30 PM

For Compound **182**

University of Rochester

E:\117006

C:\Program Files\IRsolution\Data\0608153113.smf

No. of Scans;

Resolution;

Date & Time: 6/8/2013 3:31:13 PM

For Compound **187**

University of Rochester

C:\Program Files\IRsolution\Data\0608153526.smf

No. of Scans;

Resolution;

Date & Time: 6/8/2013 3:35:26 PM

For Compound **186**

University of Rochester

C:\Program Files\IRsolution\Data\0330145153.smf

No. of Scans;

Resolution;

Date & Time: 3/30/2014 2:51:53 PM

For Compound **189**

University of Rochester

C:\Program Files\IRsolution\Data\0330133219.smf

No. of Scans;

Resolution;

Date & Time; 3/30/2014 1:32:19 PM

For Compound **208**

University of Rochester

Program Files\IRsolution\Data\0330143424.smf

Date & Time; 3/30/2014 2:34:24 PM

Resolution;

No. of Scans;

For Compound **192**

University of Rochester

752.26
833.28
875.71
1006.88
1095.60
1157.33
1242.2
1300.07
1315.5
1350.22
1386.79
1620.26
1654.98

C:\Program Files\IRsolution\Data\0330133915.smf

Date & Time: 3/30/2014 1:39:15 PM

Resolution:

No. of Scans:

For Compound **11**

University of Rochester

C:\Program Files\IRsolution\Data\0330142021.smf

No. of Scans;

Resolution;

Date & Time; 3/30/2014 2:20:20 PM

For Compound **S17**

SHIMADZU

mmment;

For Compound **235**

SHIMADZU

Comment:

For Compound **236**

SHIMADZU

Comment:

IR Spectrum
of Compound 236

For Compound **237**

SHIMADZU

omment;

For Compound **238**

SHIMADZU

omment;

Appendix C: HRMS Data

For Compound S1

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

402 formula(e) evaluated with 6 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-250 H: 0-250 N: 0-4 O: 0-5 Br: 0-1 I: 1-1 Si: 1-2

Peter Carlsen, PNC-1 University of Illinois, SCS, Mass Spectrometry Lab
Qtof_43275A 46 (3.293) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (41:46)

Q-tof UE521
1: TOF MS ES+
1.88e+002

Minimum: -1.5
Maximum: 5.0 10.0 600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
454.9897	454.9897	0.0	0.0	14.5	81.4	C19 H16 N2 I Si2
454.9903	454.9903	-0.6	-1.3	3.5	1.0	C15 H25 O Br I Si
454.9924	454.9924	-2.7	-5.9	10.5	83.8	C16 H16 N2 O4 I Si
454.9863	454.9863	3.4	7.5	-0.5	1.0	C10 H25 N2 O3 Br I Si
454.9934	454.9934	-3.7	-8.1	-1.5	0.8	C11 H29 O2 Br I Si2
454.9857	454.9857	4.0	8.8	10.5	79.7	C14 H16 N4 O2 I Si2

For Compound **91**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

682 formula(e) evaluated with 7 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-250 H: 0-250 N: 0-4 O: 0-7 Si: 1-2 Br: 0-1

Minimum:

Maximum:

5.0

10.0

-1.5

600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
411.0990	411.0991	-0.1	-0.2	6.5	0.6	C19 H28 O3 Si Br
	411.0985	0.5	1.2	17.5	465.1	C23 H19 N2 O2 Si2
	411.1012	-2.2	-5.4	13.5	488.3	C20 H19 N2 O6 Si
	411.1023	-3.3	-8.0	1.5	1.5	C15 H32 O4 Si2 Br
	411.1025	-3.5	-8.5	21.5	476.4	C28 H19 Si2
	411.0954	3.6	8.8	22.5	497.4	C27 H15 N2 O Si
	411.0951	3.9	9.5	2.5	2.5	C14 H28 N2 O5 Si Br

For Compound S5

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1009 formula(e) evaluated with 8 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-250 H: 0-250 N: 0-4 O: 0-7 Si: 1-2 Br: 0-1

Minimum:

Maximum:

5.0

10.0

-1.5

600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
582.2064	582.2060	0.4	0.7	19.5	444.7	C32 H32 N3 O6 Si
	582.2071	-0.7	-1.2	7.5	5.7	C27 H45 N O4 Si2 Br
	582.2073	-0.9	-1.5	27.5	419.3	C40 H32 N Si2
	582.2039	2.5	4.3	12.5	4.2	C31 H41 N O3 Si Br
	582.2092	-2.8	-4.8	14.5	410.2	C28 H36 N3 O7 Si2
	582.2033	3.1	5.3	23.5	415.3	C35 H32 N3 O2 Si2
	582.2030	3.4	5.8	3.5	2.9	C22 H45 N3 O6 Si2 Br
	582.2101	-3.7	-6.4	23.5	444.0	C37 H32 N O4 Si

For Compound **96**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

171 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-250 H: 0-250 O: 0-6 Si: 1-2 Br: 0-1

Minimum:

Maximum: 5.0 10.0 -1.5 600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
553.1814	553.1808	0.6	1.1	27.5	234.1	C39 H29 Si2
	553.1805	0.9	1.6	7.5	1.5	C26 H42 O4 Si2 Br
	553.1835	-2.1	-3.8	23.5	251.8	C36 H29 O4 Si
	553.1774	4.0	7.2	12.5	0.8	C30 H38 O3 Si Br
	553.1867	-5.3	-9.6	18.5	232.6	C32 H33 O5 Si2

For Compound **100**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

147 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-250 H: 0-250 O: 0-6 Si: 1-2 Br: 0-1

Minimum:

Maximum: 5.0 10.0 -1.5 600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
481.1402	481.1410	-0.8	-1.7	7.5	2.8	C23 H34 O4 Si Br
	481.1413	-1.1	-2.3	27.5	648.1	C36 H21 Si
	481.1382	2.0	4.2	11.5	24.1	C26 H34 Si2 Br
	481.1441	-3.9	-8.1	2.5	5.5	C19 H38 O5 Si2 Br
	481.1444	-4.2	-8.7	22.5	608.5	C32 H25 O Si2

For Compound **113**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

133 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-250 H: 0-250 O: 0-6 Si: 1-2 Br: 0-1

Minimum: -1.5
 Maximum: 600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
423.1353	423.1355	-0.2	-0.5	6.5	0.4	C21 H32 O2 Si Br
	423.1386	-3.3	-7.8	1.5	1.2	C17 H36 O3 Si2 Br

For Compound **114**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

404 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-120 H: 0-250 N: 0-5 O: 0-7 Br: 1-1 Na: 0-1 Si: 1-1

Minimum:				-1.5									
Maximum:		5.0	10.0	600.0									
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula							
461.1492	461.1487	0.5	1.1	5.5	24.7	C22	H35	O2	Br	Na	Si		
	461.1511	-1.9	-4.1	8.5	39.3	C24	H34	O2	Br	Si			
	461.1471	2.1	4.6	4.5	14.2	C19	H34	N2	O4	Br	Si		
	461.1447	4.5	9.8	1.5	13.1	C17	H35	N2	O4	Br	Na	Si	

For Compound **115**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

223 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-250 H: 0-250 N: 0-4 O: 0-7 Si: 2-2

Minimum: -1.5
 Maximum: 600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
490.3531	490.3537	-0.6	-1.2	5.5	2.3	C28 H52 N O2 Si2
	490.3496	3.5	7.1	1.5	0.5	C23 H52 N3 O4 Si2

For Compound **140**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

380 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-120 H: 0-250 N: 0-5 O: 0-7 Si: 2-2

Peter Carlsen, PNC-11

University of Illinois, SCS, Mass Spectrometry Lab

Q-tof UE521

Qtof_44398 31 (2.221) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (29:31)

1: TOF MS ES+

2.63e+003

Minimum:

Maximum:

5.0 10.0 -1.5 600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
688.4063	688.4065	-0.2	-0.3	9.5	14.6	C37 H62 N O7 Si2
	688.4078	-1.5	-2.2	14.5	22.6	C38 H58 N5 O3 Si2
	688.4118	-5.5	-8.0	18.5	43.7	C43 H58 N3 O Si2
	688.4006	5.7	8.3	18.5	46.2	C44 H58 N O2 Si2

For Compound **141**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

571 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-250 H: 0-250 N: 0-4 O: 0-7 Si: 1-2

Peter Carlsen, PNC-12

University of Illinois, SCS, Mass Spectrometry Lab

Q-tof UE521

Qtof_43278 27 (1.935) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (26:27)

1: TOF MS ES+

8.85e+002

Minimum:

Maximum:

5.0

10.0

-1.5

600.0

Mass

Calc. Mass

mDa

PPM

DBE

i-FIT

Formula

612.3903

612.3904

-0.1

-0.2

9.5

4.1

C35 H58 N O4 Si2

612.3873

3.0

4.9

14.5

4.2

C39 H54 N O3 Si

612.3864

3.9

6.4

5.5

0.8

C30 H58 N3 O6 Si2

For Compound **S12**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

344 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-250 H: 0-250 N: 0-4 O: 0-5 Na: 0-1 Si: 1-2

Peter Carlsen, PNC-15_NaCl

University of Illinois, SCS, Mass Spectrometry Lab

Q-tof UE521

Qtof_43281A 32 (2.293) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (32:33)

1: TOF MS ES+

1.75e+003

Minimum:

Maximum:

5.0 10.0 -1.5

600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
251.1447	251.1443	0.4	1.6	1.5	3.6	C12 H24 O2 Na Si
	251.1467	-2.0	-8.0	4.5	5.2	C14 H23 O2 Si
	251.1427	2.0	8.0	0.5	5.6	C9 H23 N2 O4 Si

For Compound **139**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

151 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-250 H: 0-250 N: 0-4 O: 0-5 Na: 0-1

Peter Carlsen, PNC-16_NaCl

University of Illinois, SCS, Mass Spectrometry Lab

Q-tof UE521

Qtof_43282B 27 (1.935) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (26:27)

1: TOF MS ES+
9.56e+002

Minimum:

Maximum:

5.0 10.0 -1.5 600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
195.0643	195.0647	-0.4	-2.1	7.5	2.6	C9 H8 N4 Na
	195.0633	1.0	5.1	2.5	0.7	C8 H12 O4 Na
	195.0657	-1.4	-7.2	5.5	0.7	C10 H11 O4

For Compound **153a**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

544 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-250 H: 0-250 N: 0-4 O: 0-7 Si: 1-2

Peter Carlsen, PNC-13

University of Illinois, SCS, Mass Spectrometry Lab

Q-tof UE521

Qtof_43279 51 (3.650) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (51:52)

1: TOF MS ES+

1.06e+003

Minimum:

Maximum:

5.0 10.0 -1.5

600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
584.3588	584.3591	-0.3	-0.5	9.5	7.1	C33 H54 N O4 Si2
	584.3560	2.8	4.8	14.5	19.6	C37 H50 N O3 Si
	584.3551	3.7	6.3	5.5	13.5	C28 H54 N3 O6 Si2

For Compound **166**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

304 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-120 H: 0-250 N: 0-5 O: 0-7 Si: 2-2

Peter Carlsen, PNC-17

University of Illinois, SCS, Mass Spectrometry Lab

Q-tof UE521

Qtof_44399 47 (3.364) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (47)

1: TOF MS ES+

1.96e+003

Minimum:

Maximum:

5.0 10.0 600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
558.3790	558.3799	-0.9	-1.6	7.5	61.2	C32 H56 N O3 Si2
	558.3759	3.1	5.6	3.5	59.8	C27 H56 N3 O5 Si2

For Compound **171**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

368 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-120 H: 0-250 N: 0-5 O: 0-7 Si: 3-3

Peter Carlsen, PNC-18

University of Illinois, SCS, Mass Spectrometry Lab

Q-tof UE521

Qtof_44400 41 (2.936) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (40:41)

1: TOF MS ES+

6.61e+003

Minimum:

Maximum:

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
672.4655	672.4664	-0.9	-1.3	7.5	58.5	C38 H70 N O3 Si3
	672.4623	3.2	4.8	3.5	27.1	C33 H70 N3 O5 Si3

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
672.4655	672.4664	-0.9	-1.3	7.5	58.5	C38 H70 N O3 Si3
	672.4623	3.2	4.8	3.5	27.1	C33 H70 N3 O5 Si3

For Compound **181**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

327 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-120 H: 0-250 N: 0-5 O: 0-6 Si: 3-3

Peter Carlsen, PNC-20

University of Illinois, SCS, Mass Spectrometry Lab

Q-tof UE521

Qtof_45070 39 (2.793) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x5.00); Cm (32:39)

1: TOF MS ES+

2.56e+003

Minimum:

Maximum:

5.0 10.0 -1.5 600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
674.4828	674.4820	0.8	1.2	6.5	1.2	C38 H72 N O3 Si3
	674.4780	4.8	7.1	2.5	2.1	C33 H72 N3 O5 Si3
	674.4892	-6.4	-9.5	2.5	2.9	C32 H72 N5 O4 Si3

For Compound **182**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

298 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-120 H: 0-250 N: 0-5 O: 0-6 Si: 2-2

Peter Carlsen, PNC-21

University of Illinois, SCS, Mass Spectrometry Lab

Qtof_45071 41 (2.936) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x5.00); Cm (41:43)

Q-tof UE521

1: TOF MS ES+

2.22e+003

Minimum:

Maximum:

5.0

10.0

-1.5

600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
614.4069	614.4074	-0.5	-0.8	13.5	7.3	C36 H56 N5 Si2
	614.4061	0.8	1.3	8.5	3.4	C35 H60 N O4 Si2
	614.4021	4.8	7.8	4.5	0.9	C30 H60 N3 O6 Si2

For Compound **183**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

297 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-120 H: 0-250 N: 0-5 O: 0-6 Si: 2-2

Peter Carlsen, PNC - 22

University of Illinois, SCS, Mass Spectrometry Lab

Qtof_45067 32 (2.293) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x5.00); Cm (28:32)

Q-tof UE521

1: TOF MS ES+

1.60e+003

Minimum:

Maximum:

5.0

10.0

-1.5

600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
612.3898	612.3904	-0.6	-1.0	9.5	2.2	C35 H58 N O4 Si2
	612.3918	-2.0	-3.3	14.5	4.0	C36 H54 N5 Si2
	612.3864	3.4	5.6	5.5	4.5	C30 H58 N3 O6 Si2

For Compound **187**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

800 formula(e) evaluated with 6 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-120 H: 0-200 N: 0-6 O: 0-7 Si: 2-2 Cl: 0-1

Peter CarlsenPNC-26

University of Illinois, SCS, Mass Spectrometry Lab

Qtof_47172 50 (3.737) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x5.00); Cm (50:52)

Q-tof UE521

1: TOF MS ES+

9.79e+002

Minimum:

Maximum:

5.0

10.0

-1.5

600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
646.3524	646.3528	-0.4	-0.6	14.5	0.6	C36 H53 N5 Si2 Cl
	646.3515	0.9	1.4	9.5	0.1	C35 H57 N O4 Si2 Cl
	646.3537	-1.3	-2.0	18.5	79.4	C41 H52 N O2 Si2
	646.3496	2.8	4.3	14.5	84.7	C36 H52 N3 O4 Si2
	646.3474	5.0	7.7	5.5	1.6	C30 H57 N3 O6 Si2 Cl
	646.3587	-6.3	-9.7	5.5	1.9	C29 H57 N5 O5 Si2 Cl

For Compound **186**

Elemental Composition Report

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Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

352 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-120 H: 0-200 N: 0-3 O: 0-5 Si: 1-2

Peter CarlsenPNC-28

University of Illinois, SCS, Mass Spectrometry Lab

Q-tof UE521

Qtof_47174 44 (3.290) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x5.00); Cm (44:46)

1: TOF MS ES+

1.72e+003

Minimum:

Maximum:

5.0

10.0

-1.5

600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
612.3904	612.3904	0.0	0.0	9.5	1.8	C35 H58 N O4 Si2
	612.3873	3.1	5.1	14.5	6.5	C39 H54 N O3 Si

For Compound **189**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

206 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-125 H: 0-250 N: 0-3 O: 0-6 Si: 2-2

Peter Carlsen, PNC-29

University of Illinois, SCS, Mass Spectrometry Lab

Q-tof UE521

Qtof_51746 29 (2.171) AM (Cen,3, 80.00, Ar,15000.0,558.36,0.70,LS 3); Sm (SG, 2x5.00); Cm (29)

1: TOF MS ES+

1.39e+003

Minimum:

Maximum:

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
626.4055	626.4061	-0.6	-1.0	9.5	16.1	C36 H60 N O4 Si2
	626.4021	3.4	5.4	5.5	27.2	C31 H60 N3 O6 Si2

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
626.4055	626.4061	-0.6	-1.0	9.5	16.1	C36 H60 N O4 Si2
	626.4021	3.4	5.4	5.5	27.2	C31 H60 N3 O6 Si2

For Compound **205**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

278 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-120 H: 0-200 N: 0-3 O: 0-5 Si: 1-1 Cl: 0-1

Peter CarlsenPNC-27

University of Illinois, SCS, Mass Spectrometry Lab

Qtof_47173 29 (2.170) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x5.00); Cm (29:30)

Q-tof UE521

1: TOF MS ES+

7.96e+002

Minimum:

Maximum:

5.0

10.0

-1.5

600.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
490.2177	490.2180	-0.3	-0.6	9.5	1.2	C26 H37 N O4 Si Cl
	490.2162	1.5	3.1	14.5	107.4	C27 H32 N3 O4 Si
	490.2202	-2.5	-5.1	18.5	105.6	C32 H32 N O2 Si

For Compound **208**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

158 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-125 H: 0-250 N: 0-3 O: 0-6 Si: 1-1

Peter Carlsen, PNC-31

University of Illinois, SCS, Mass Spectrometry Lab

Q-tof UE521

Qtof_51747 24 (1.797) AM (Cen,3, 80.00, Ar,15000.0,558.36,0.70,LS 3); Sm (SG, 2x5.00); Cm (24)

1: TOF MS ES+

1.11e+003

Minimum:

Maximum:

5.0

10.0

-1.5

600.0

Mass

Calc. Mass

mDa

PPM

DBE

i-FIT

Formula

470.2722

470.2727

-0.5

-1.1

9.5

1.9

C27 H40 N O4 Si

470.2686

3.6

7.7

5.5

9.7

C22 H40 N3 O6 Si

For Compound **192**

Elemental Composition Report

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Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

164 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-125 H: 0-250 N: 0-3 O: 0-6 Si: 1-1

Peter Carlsen, PNC-32

University of Illinois, SCS, Mass Spectrometry Lab

Q-tof UE521

Qtof_51748 20 (1.499) AM (Cen,3, 80.00, Ar,15000.0,558.36,0.70,LS 3); Sm (SG, 2x5.00); Cm (20:21)

1: TOF MS ES+

1.22e+003

Minimum:

Maximum:

5.0

10.0

-1.5

600.0

Mass

Calc. Mass

mDa

PPM

DBE

i-FIT

Formula

486.2674

486.2676

-0.2

-0.4

9.5

1.4

C27 H40 N O5 Si

For Compound 11

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

131 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-125 H: 0-250 N: 0-3 O: 0-6

Peter Carlsen, PNC-34

University of Illinois, SCS, Mass Spectrometry Lab

Q-tof UE521

Qtof_51750 18 (1.351) AM (Cen,3, 80.00, Ar,15000.0,558.36,0.70,LS 3); Sm (SG, 2x5.00)

1: TOF MS ES+
1.57e+003

Minimum:

Maximum:

5.0

10.0

-1.5

600.0

Mass

Calc. Mass

mDa

PPM

DBE

i-FIT

Formula

372.1800

372.1811

-1.1

-3.0

9.5

3.0

C21 H26 N O5

For Compound **S17**

Peter Carlsen; PNC-37
Synapt_1055n 56 (0.543)

Mass Spectrometry Center, SCS, University of Illinois

1: TOF MS ES-
4.33e5

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 200.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

53 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-120 H: 0-200 O: 0-6 Si: 0-1 Br: 1-1

Minimum:				-1.5					
Maximum:	5.0	10.0	200.0						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula	
371.0678	371.0678	0.0	0.0	5.5	1543.0	0.008	99.19	C16 H24 O3 Si Br	
	371.0647	3.1	8.4	10.5	1547.8	4.819	0.81	C20 H20 O2 Br	

For Compound **235**

Peter Carlsen; PNC-35
Synapt_1053 30 (0.603) Cm (30-10x2.000)

Mass Spectrometry Center, SCS, University of Illinois

1: TOF MS ES+
1.04e6

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 200.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

38 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-120 H: 0-200 N: 0-1 O: 0-6

Minimum:				-1.5					
Maximum:		5.0	10.0	200.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula	
194.1180	194.1181	-0.1	-0.5	4.5	295.6	n/a	n/a	C11 H16 N O2	

For Compound **236**

Peter Carlsen; PNC-36

Mass Spectrometry Center, SCS, University of Illinois

Synapt_1054 33 (0.674) Cm (33-12x2.000)

1: TOF MS ES+
3.08e6

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 200.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

154 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-120 H: 0-200 N: 0-1 O: 0-6 120Sn: 0-1

Minimum: -1.5
Maximum: 5.0 10.0 200.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
486.2397	486.2394	0.3	0.6	3.5	374.2	0.453	63.59	C23 H44 N O2 120Sn
	486.2433	-3.6	-7.4	19.5	374.8	1.010	36.41	C34 H32 N O2

For Compound **237**

Peter Carlsen; PNC-38

Mass Spectrometry Center, SCS, University of Illinois

Synapt_1056 32 (0.637) Cm (32-14x2.000)

1: TOF MS ES+
5.00e5

Elemental Composition Report

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Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 200.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

165 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-120 H: 0-200 N: 0-1 O: 0-6 Br: 1-1 Si: 0-1

Minimum: -1.5
Maximum: 5.0 10.0 200.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
550.1991	550.1988	0.3	0.5	8.5	208.3	0.037	96.37	C27 H41 N O4 Br Si
	550.1957	3.4	6.2	13.5	211.6	3.316	3.63	C31 H37 N O3 Br

For Compound **238**

Peter Carlsen; PNC-39
 Synapt_1057 33 (0.674) Cm (33-12x2.000)

Mass Spectrometry Center, SCS, University of Illinois

1: TOF MS ES+
 5.44e6

Elemental Composition Report

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Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 200.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

165 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-120 H: 0-200 N: 0-1 O: 0-6 Si: 0-1 Br: 1-1

Minimum: -1.5
 Maximum: 5.0 10.0 200.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
550.1996	550.1988	0.8	1.5	8.5	548.4	0.008	99.19	C27 H41 N O4 Si Br
	550.1957	3.9	7.1	13.5	553.2	4.814	0.81	C31 H37 N O3 Br

Appendix D: Crystal Structure Reports

For Compound **114**

REFERENCE NUMBER: fropc10

CRYSTAL STRUCTURE REPORT

$C_{22}H_{35}BrO_2Si$

Report prepared for:
P. Carlsen, Prof. A. Frontier

June 01, 2014

William W. Brennessel
X-ray Crystallographic Facility
Department of Chemistry, University of Rochester
120 Trustee Road
Rochester, NY 14627

Data collection

A crystal (0.22 x 0.14 x 0.06 mm³) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD platform diffractometer for a data collection at 100.0(5) K.¹ A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK α radiation (graphite monochromator) with a frame time of 90 seconds and a detector distance of 4.04 cm. A randomly oriented region of reciprocal space was surveyed: five major sections of frames were collected with 0.50° steps in ω at five different ϕ settings and a detector position of -38° in 2θ . The intensity data were corrected for absorption.² Final cell constants were calculated from the xyz centroids of 2986 strong reflections from the actual data collection after integration.³ See Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR2011⁴ and refined using SHELXL-2014.⁵ The space group *P*-1 was determined based on intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydroxide hydrogen atoms were found from the difference Fourier map, and their positional parameters were refined freely and their isotropic displacement parameters were refined relative to those of their respective bonded oxygen atoms: $U_{\text{iso}}[\text{H}] = 1.5 * U_{\text{eq}}[\text{O}]$. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0696$ (F^2 , $I > 2\sigma(I)$) and $wR2 = 0.1750$ (F^2 , all data). *Although the intensity data were very weak, the structure is unambiguous and may be used to show connectivity and relative configuration.*

Structure description

The structure is the one suggested. The asymmetric unit contains two molecules on general positions. The molecules are arranged in square patterns via hydrogen bonding (see diagram and Table 7). Two isopropyl groups are modeled together as disordered over two positions (51:49).

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic

Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

¹ *APEX2*, version 2014.1-1; Bruker AXS: Madison, WI, 2014.

² Sheldrick, G. M. *SADABS*, version 2012/1; University of Göttingen: Göttingen, Germany, 2012.

³ *SAINT*, version 8.34A; Bruker AXS: Madison, WI, 2013.

⁴ Burla, M. C.; Caliendo, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; Spagna, R. *SIR2011: a new package for crystal structure determination and refinement*, version 1.0; Istituto di Cristallografia: Bari, Italy, 2012.

⁵ Sheldrick, G. M. *SHELXL-2014/3*; University of Göttingen: Göttingen, Germany, 2014.

Some equations of interest:

$$R_{\text{int}} = \Sigma |F_o^2 - \langle F_o^2 \rangle| / \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$$

where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] / (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

Table 1. Crystal data and structure refinement for fropec10.

Identification code	fropec10	
Empirical formula	C ₂₂ H ₃₅ Br O ₂ Si	
Formula weight	439.50	
Temperature	100.0(5) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	<i>a</i> = 12.629(3) Å	α = 89.867(4)°
	<i>b</i> = 12.744(3) Å	β = 83.926(4)°
	<i>c</i> = 14.431(3) Å	γ = 83.825(4)°
Volume	2296.1(10) Å ³	
<i>Z</i>	4	
Density (calculated)	1.271 Mg/m ³	
Absorption coefficient	1.855 mm ⁻¹	
<i>F</i> (000)	928	
Crystal color, morphology	colorless, plate	
Crystal size	0.22 x 0.14 x 0.06 mm ³	
Theta range for data collection	1.419 to 25.090°	
Index ranges	$-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-17 \leq l \leq 17$	
Reflections collected	30216	
Independent reflections	8132 [<i>R</i> (int) = 0.1956]	
Observed reflections	3670	
Completeness to theta = 25.028°	100.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7452 and 0.5217	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	8132 / 13 / 508	
Goodness-of-fit on <i>F</i> ²	0.971	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0696, <i>wR</i> 2 = 0.1282	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1863, <i>wR</i> 2 = 0.1750	
Largest diff. peak and hole	0.431 and -0.572 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc10. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Br1	-1188(1)	7003(1)	1515(1)	50(1)
Si1	2708(2)	4387(2)	3818(2)	50(1)
O1	3616(4)	5265(4)	-140(4)	40(2)
O2	1786(4)	5251(5)	3391(4)	51(2)
C1	1891(5)	5483(5)	861(5)	31(2)
C2	2477(5)	5234(6)	-81(5)	38(2)
C3	1975(6)	6073(6)	-709(5)	40(2)
C4	793(5)	6246(6)	-285(5)	37(2)
C5	898(5)	6059(5)	749(5)	32(2)
C6	222(5)	6288(6)	1560(6)	42(2)
C7	538(6)	6020(6)	2435(6)	38(2)
C8	1530(6)	5484(6)	2510(6)	40(2)
C9	2212(6)	5189(6)	1719(6)	39(2)
C10	2154(6)	5865(7)	-1761(5)	52(2)
C11	226(5)	7268(6)	-576(6)	38(2)
C12	-453(6)	7275(7)	-1233(6)	50(2)
C13	508(5)	8265(6)	-177(6)	42(2)
C14	2430(7)	3011(7)	3587(6)	59(3)
C15	2848(7)	2558(8)	2634(7)	69(3)
C16	1229(7)	2872(8)	3808(7)	76(3)
C17	4096(6)	4615(8)	3302(6)	58(3)
C18	4277(6)	5770(8)	3250(6)	67(3)
C19	4949(7)	3967(8)	3824(6)	75(3)
C20	2512(6)	4705(8)	5105(6)	55(3)
C21	2906(8)	3819(8)	5721(6)	73(3)
C22	1362(7)	5141(8)	5475(6)	69(3)
Br2	7569(1)	-743(1)	-331(1)	53(1)
Si2	7646(2)	444(2)	3603(2)	54(1)
O3	4718(4)	3682(4)	790(4)	41(1)

O4	7296(5)	1337(4)	2816(4)	65(2)
C23	5715(5)	1908(6)	861(6)	38(2)
C24	4829(6)	2614(6)	484(5)	37(2)
C25	5088(5)	2447(6)	-572(6)	41(2)
C26	5634(6)	1312(6)	-687(6)	41(2)
C27	6166(5)	1142(6)	209(6)	37(2)
C28	6952(6)	375(6)	469(6)	42(2)
C29	7306(6)	444(7)	1337(7)	47(2)
C30	6889(6)	1236(7)	1982(7)	51(2)
C31	6078(6)	1970(6)	1738(6)	47(2)
C32	4192(6)	2713(7)	-1167(6)	57(3)
C33	6357(6)	1115(6)	-1589(7)	48(2)
C34	6108(7)	461(7)	-2241(7)	62(3)
C35	7329(6)	1687(7)	-1725(6)	60(3)
C36	6520(30)	-380(40)	4020(20)	50(6)
C37	6480(30)	-1260(40)	3310(30)	50(6)
C38	6494(13)	-869(15)	4984(11)	60(4)
C39	8106(17)	1230(20)	4560(17)	61(5)
C40	7560(20)	2365(16)	4543(15)	92(6)
C41	7856(16)	681(16)	5458(13)	74(4)
C36'	6440(30)	-330(30)	3820(30)	50(6)
C37'	6330(30)	-1200(40)	3150(30)	50(6)
C38'	5470(12)	475(14)	3939(12)	60(4)
C39'	7688(14)	1310(20)	4669(17)	61(5)
C40'	6641(16)	1918(17)	5119(15)	92(6)
C41'	8564(15)	2034(16)	4532(13)	74(4)
C42	8876(6)	-414(7)	3154(6)	58(3)
C43	9760(7)	195(9)	2627(7)	87(4)
C44	9331(8)	-1142(8)	3885(7)	89(4)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for fropc10.

Br(1)-C(6)	1.918(7)	C(13)-H(13A)	0.9800
Si(1)-O(2)	1.680(6)	C(13)-H(13B)	0.9800
Si(1)-C(14)	1.862(9)	C(13)-H(13C)	0.9800
Si(1)-C(17)	1.883(8)	C(14)-C(15)	1.512(11)
Si(1)-C(20)	1.886(9)	C(14)-C(16)	1.546(11)
O(1)-C(2)	1.436(8)	C(14)-H(14A)	1.0000
O(1)-H(1)	0.82(8)	C(15)-H(15A)	0.9800
O(2)-C(8)	1.369(9)	C(15)-H(15B)	0.9800
C(1)-C(9)	1.382(10)	C(15)-H(15C)	0.9800
C(1)-C(5)	1.408(9)	C(16)-H(16A)	0.9800
C(1)-C(2)	1.494(10)	C(16)-H(16B)	0.9800
C(2)-C(3)	1.530(10)	C(16)-H(16C)	0.9800
C(2)-H(2A)	1.0000	C(17)-C(18)	1.513(12)
C(3)-C(10)	1.531(10)	C(17)-C(19)	1.545(11)
C(3)-C(4)	1.545(9)	C(17)-H(17A)	1.0000
C(3)-H(3A)	1.0000	C(18)-H(18A)	0.9800
C(4)-C(11)	1.499(10)	C(18)-H(18B)	0.9800
C(4)-C(5)	1.528(10)	C(18)-H(18C)	0.9800
C(4)-H(4A)	1.0000	C(19)-H(19A)	0.9800
C(5)-C(6)	1.385(10)	C(19)-H(19B)	0.9800
C(6)-C(7)	1.395(10)	C(19)-H(19C)	0.9800
C(7)-C(8)	1.376(10)	C(20)-C(21)	1.510(11)
C(7)-H(7A)	0.9500	C(20)-C(22)	1.539(11)
C(8)-C(9)	1.382(10)	C(20)-H(20A)	1.0000
C(9)-H(9A)	0.9500	C(21)-H(21A)	0.9800
C(10)-H(10A)	0.9800	C(21)-H(21B)	0.9800
C(10)-H(10B)	0.9800	C(21)-H(21C)	0.9800
C(10)-H(10C)	0.9800	C(22)-H(22A)	0.9800
C(11)-C(12)	1.343(10)	C(22)-H(22B)	0.9800
C(11)-C(13)	1.489(10)	C(22)-H(22C)	0.9800
C(12)-H(12A)	0.9500	Br(2)-C(28)	1.883(8)
C(12)-H(12B)	0.9500	Si(2)-O(4)	1.665(6)

Si(2)-C(42)	1.858(9)	C(35)-H(35C)	0.9800
Si(2)-C(39)	1.885(13)	C(36)-C(38)	1.52(5)
Si(2)-C(36')	1.893(13)	C(36)-C(37)	1.522(15)
Si(2)-C(39')	1.901(13)	C(36)-H(36A)	1.0000
Si(2)-C(36)	1.911(13)	C(37)-H(37A)	0.9800
O(3)-C(24)	1.421(9)	C(37)-H(37B)	0.9800
O(3)-H(3)	0.88(8)	C(37)-H(37C)	0.9800
O(4)-C(30)	1.369(9)	C(38)-H(38A)	0.9800
C(23)-C(27)	1.391(10)	C(38)-H(38B)	0.9800
C(23)-C(31)	1.396(10)	C(38)-H(38C)	0.9800
C(23)-C(24)	1.506(10)	C(39)-C(41)	1.49(3)
C(24)-C(25)	1.535(10)	C(39)-C(40)	1.53(2)
C(24)-H(24A)	1.0000	C(39)-H(39A)	1.0000
C(25)-C(32)	1.501(10)	C(40)-H(40A)	0.9800
C(25)-C(26)	1.535(10)	C(40)-H(40B)	0.9800
C(25)-H(25A)	1.0000	C(40)-H(40C)	0.9800
C(26)-C(33)	1.514(11)	C(41)-H(41A)	0.9800
C(26)-C(27)	1.524(10)	C(41)-H(41B)	0.9800
C(26)-H(26A)	1.0000	C(41)-H(41C)	0.9800
C(27)-C(28)	1.397(10)	C(36')-C(37')	1.507(15)
C(28)-C(29)	1.380(11)	C(36')-C(38')	1.51(5)
C(29)-C(30)	1.396(11)	C(36')-H(36B)	1.0000
C(29)-H(29A)	0.9500	C(37')-H(37D)	0.9800
C(30)-C(31)	1.384(10)	C(37')-H(37E)	0.9800
C(31)-H(31A)	0.9500	C(37')-H(37F)	0.9800
C(32)-H(32A)	0.9800	C(38')-H(38D)	0.9800
C(32)-H(32B)	0.9800	C(38')-H(38E)	0.9800
C(32)-H(32C)	0.9800	C(38')-H(38F)	0.9800
C(33)-C(34)	1.343(11)	C(39')-C(41')	1.52(3)
C(33)-C(35)	1.489(11)	C(39')-C(40')	1.54(2)
C(34)-H(34A)	0.9500	C(39')-H(39B)	1.0000
C(34)-H(34B)	0.9500	C(40')-H(40D)	0.9800
C(35)-H(35A)	0.9800	C(40')-H(40E)	0.9800
C(35)-H(35B)	0.9800	C(40')-H(40F)	0.9800

C(41')-H(41D)	0.9800	C(4)-C(3)-H(3A)	106.6
C(41')-H(41E)	0.9800	C(11)-C(4)-C(5)	119.0(6)
C(41')-H(41F)	0.9800	C(11)-C(4)-C(3)	112.7(6)
C(42)-C(44)	1.521(11)	C(5)-C(4)-C(3)	101.7(5)
C(42)-C(43)	1.559(12)	C(11)-C(4)-H(4A)	107.6
C(42)-H(42A)	1.0000	C(5)-C(4)-H(4A)	107.6
C(43)-H(43A)	0.9800	C(3)-C(4)-H(4A)	107.6
C(43)-H(43B)	0.9800	C(6)-C(5)-C(1)	115.8(7)
C(43)-H(43C)	0.9800	C(6)-C(5)-C(4)	134.1(6)
C(44)-H(44A)	0.9800	C(1)-C(5)-C(4)	110.0(6)
C(44)-H(44B)	0.9800	C(5)-C(6)-C(7)	121.8(7)
C(44)-H(44C)	0.9800	C(5)-C(6)-Br(1)	120.7(6)
O(2)-Si(1)-C(14)	110.1(3)	C(7)-C(6)-Br(1)	117.5(6)
O(2)-Si(1)-C(17)	110.6(3)	C(8)-C(7)-C(6)	120.1(7)
C(14)-Si(1)-C(17)	110.9(4)	C(8)-C(7)-H(7A)	119.9
O(2)-Si(1)-C(20)	102.7(4)	C(6)-C(7)-H(7A)	119.9
C(14)-Si(1)-C(20)	111.4(4)	O(2)-C(8)-C(7)	116.9(7)
C(17)-Si(1)-C(20)	110.9(4)	O(2)-C(8)-C(9)	122.8(7)
C(2)-O(1)-H(1)	105(6)	C(7)-C(8)-C(9)	120.3(7)
C(8)-O(2)-Si(1)	133.6(5)	C(8)-C(9)-C(1)	118.5(7)
C(9)-C(1)-C(5)	123.4(7)	C(8)-C(9)-H(9A)	120.8
C(9)-C(1)-C(2)	127.9(7)	C(1)-C(9)-H(9A)	120.8
C(5)-C(1)-C(2)	108.7(6)	C(3)-C(10)-H(10A)	109.5
O(1)-C(2)-C(1)	115.1(6)	C(3)-C(10)-H(10B)	109.5
O(1)-C(2)-C(3)	110.3(6)	H(10A)-C(10)-H(10B)	109.5
C(1)-C(2)-C(3)	103.9(6)	C(3)-C(10)-H(10C)	109.5
O(1)-C(2)-H(2A)	109.1	H(10A)-C(10)-H(10C)	109.5
C(1)-C(2)-H(2A)	109.1	H(10B)-C(10)-H(10C)	109.5
C(3)-C(2)-H(2A)	109.1	C(12)-C(11)-C(13)	121.6(7)
C(2)-C(3)-C(10)	117.2(7)	C(12)-C(11)-C(4)	120.1(7)
C(2)-C(3)-C(4)	103.3(6)	C(13)-C(11)-C(4)	118.1(6)
C(10)-C(3)-C(4)	115.6(6)	C(11)-C(12)-H(12A)	120.0
C(2)-C(3)-H(3A)	106.6	C(11)-C(12)-H(12B)	120.0
C(10)-C(3)-H(3A)	106.6	H(12A)-C(12)-H(12B)	120.0

C(11)-C(13)-H(13A)	109.5	H(18A)-C(18)-H(18C)	109.5
C(11)-C(13)-H(13B)	109.5	H(18B)-C(18)-H(18C)	109.5
H(13A)-C(13)-H(13B)	109.5	C(17)-C(19)-H(19A)	109.5
C(11)-C(13)-H(13C)	109.5	C(17)-C(19)-H(19B)	109.5
H(13A)-C(13)-H(13C)	109.5	H(19A)-C(19)-H(19B)	109.5
H(13B)-C(13)-H(13C)	109.5	C(17)-C(19)-H(19C)	109.5
C(15)-C(14)-C(16)	110.3(7)	H(19A)-C(19)-H(19C)	109.5
C(15)-C(14)-Si(1)	116.3(6)	H(19B)-C(19)-H(19C)	109.5
C(16)-C(14)-Si(1)	111.8(7)	C(21)-C(20)-C(22)	109.6(7)
C(15)-C(14)-H(14A)	105.9	C(21)-C(20)-Si(1)	114.7(7)
C(16)-C(14)-H(14A)	105.9	C(22)-C(20)-Si(1)	114.4(5)
Si(1)-C(14)-H(14A)	105.9	C(21)-C(20)-H(20A)	105.7
C(14)-C(15)-H(15A)	109.5	C(22)-C(20)-H(20A)	105.7
C(14)-C(15)-H(15B)	109.5	Si(1)-C(20)-H(20A)	105.7
H(15A)-C(15)-H(15B)	109.5	C(20)-C(21)-H(21A)	109.5
C(14)-C(15)-H(15C)	109.5	C(20)-C(21)-H(21B)	109.5
H(15A)-C(15)-H(15C)	109.5	H(21A)-C(21)-H(21B)	109.5
H(15B)-C(15)-H(15C)	109.5	C(20)-C(21)-H(21C)	109.5
C(14)-C(16)-H(16A)	109.5	H(21A)-C(21)-H(21C)	109.5
C(14)-C(16)-H(16B)	109.5	H(21B)-C(21)-H(21C)	109.5
H(16A)-C(16)-H(16B)	109.5	C(20)-C(22)-H(22A)	109.5
C(14)-C(16)-H(16C)	109.5	C(20)-C(22)-H(22B)	109.5
H(16A)-C(16)-H(16C)	109.5	H(22A)-C(22)-H(22B)	109.5
H(16B)-C(16)-H(16C)	109.5	C(20)-C(22)-H(22C)	109.5
C(18)-C(17)-C(19)	111.7(7)	H(22A)-C(22)-H(22C)	109.5
C(18)-C(17)-Si(1)	113.5(6)	H(22B)-C(22)-H(22C)	109.5
C(19)-C(17)-Si(1)	110.5(6)	O(4)-Si(2)-C(42)	111.0(4)
C(18)-C(17)-H(17A)	106.9	O(4)-Si(2)-C(39)	104.6(9)
C(19)-C(17)-H(17A)	106.9	C(42)-Si(2)-C(39)	103.3(7)
Si(1)-C(17)-H(17A)	106.9	O(4)-Si(2)-C(36')	104.1(18)
C(17)-C(18)-H(18A)	109.5	C(42)-Si(2)-C(36')	112.0(14)
C(17)-C(18)-H(18B)	109.5	O(4)-Si(2)-C(39')	101.7(10)
H(18A)-C(18)-H(18B)	109.5	C(42)-Si(2)-C(39')	118.7(6)
C(17)-C(18)-H(18C)	109.5	C(36')-Si(2)-C(39')	108.0(11)

O(4)-Si(2)-C(36)	112.7(19)	C(30)-C(29)-H(29A)	118.6
C(42)-Si(2)-C(36)	110.9(16)	O(4)-C(30)-C(31)	119.7(9)
C(39)-Si(2)-C(36)	113.8(13)	O(4)-C(30)-C(29)	122.1(8)
C(24)-O(3)-H(3)	108(5)	C(31)-C(30)-C(29)	118.2(8)
C(30)-O(4)-Si(2)	131.4(5)	C(30)-C(31)-C(23)	119.6(8)
C(27)-C(23)-C(31)	121.8(7)	C(30)-C(31)-H(31A)	120.2
C(27)-C(23)-C(24)	111.0(7)	C(23)-C(31)-H(31A)	120.2
C(31)-C(23)-C(24)	127.2(7)	C(25)-C(32)-H(32A)	109.5
O(3)-C(24)-C(23)	115.4(6)	C(25)-C(32)-H(32B)	109.5
O(3)-C(24)-C(25)	115.1(6)	H(32A)-C(32)-H(32B)	109.5
C(23)-C(24)-C(25)	102.2(6)	C(25)-C(32)-H(32C)	109.5
O(3)-C(24)-H(24A)	107.9	H(32A)-C(32)-H(32C)	109.5
C(23)-C(24)-H(24A)	107.9	H(32B)-C(32)-H(32C)	109.5
C(25)-C(24)-H(24A)	107.9	C(34)-C(33)-C(35)	122.0(9)
C(32)-C(25)-C(24)	117.2(6)	C(34)-C(33)-C(26)	120.4(8)
C(32)-C(25)-C(26)	114.8(6)	C(35)-C(33)-C(26)	117.6(8)
C(24)-C(25)-C(26)	105.0(6)	C(33)-C(34)-H(34A)	120.0
C(32)-C(25)-H(25A)	106.4	C(33)-C(34)-H(34B)	120.0
C(24)-C(25)-H(25A)	106.4	H(34A)-C(34)-H(34B)	120.0
C(26)-C(25)-H(25A)	106.4	C(33)-C(35)-H(35A)	109.5
C(33)-C(26)-C(27)	116.3(6)	C(33)-C(35)-H(35B)	109.5
C(33)-C(26)-C(25)	113.9(7)	H(35A)-C(35)-H(35B)	109.5
C(27)-C(26)-C(25)	102.8(6)	C(33)-C(35)-H(35C)	109.5
C(33)-C(26)-H(26A)	107.8	H(35A)-C(35)-H(35C)	109.5
C(27)-C(26)-H(26A)	107.8	H(35B)-C(35)-H(35C)	109.5
C(25)-C(26)-H(26A)	107.8	C(38)-C(36)-C(37)	108.5(17)
C(23)-C(27)-C(28)	118.5(7)	C(38)-C(36)-Si(2)	119(2)
C(23)-C(27)-C(26)	109.3(6)	C(37)-C(36)-Si(2)	109.0(19)
C(28)-C(27)-C(26)	132.2(8)	C(38)-C(36)-H(36A)	106.6
C(29)-C(28)-C(27)	119.1(8)	C(37)-C(36)-H(36A)	106.6
C(29)-C(28)-Br(2)	118.5(6)	Si(2)-C(36)-H(36A)	106.6
C(27)-C(28)-Br(2)	122.4(6)	C(36)-C(37)-H(37A)	109.5
C(28)-C(29)-C(30)	122.7(8)	C(36)-C(37)-H(37B)	109.5
C(28)-C(29)-H(29A)	118.6	H(37A)-C(37)-H(37B)	109.5

C(36)-C(37)-H(37C)	109.5	C(36')-C(37')-H(37E)	109.5
H(37A)-C(37)-H(37C)	109.5	H(37D)-C(37')-H(37E)	109.5
H(37B)-C(37)-H(37C)	109.5	C(36')-C(37')-H(37F)	109.5
C(36)-C(38)-H(38A)	109.5	H(37D)-C(37')-H(37F)	109.5
C(36)-C(38)-H(38B)	109.5	H(37E)-C(37')-H(37F)	109.5
H(38A)-C(38)-H(38B)	109.5	C(36')-C(38')-H(38D)	109.5
C(36)-C(38)-H(38C)	109.5	C(36')-C(38')-H(38E)	109.5
H(38A)-C(38)-H(38C)	109.5	H(38D)-C(38')-H(38E)	109.5
H(38B)-C(38)-H(38C)	109.5	C(36')-C(38')-H(38F)	109.5
C(41)-C(39)-C(40)	113.5(18)	H(38D)-C(38')-H(38F)	109.5
C(41)-C(39)-Si(2)	107.8(16)	H(38E)-C(38')-H(38F)	109.5
C(40)-C(39)-Si(2)	108.9(15)	C(41')-C(39')-C(40')	110.1(17)
C(41)-C(39)-H(39A)	108.8	C(41')-C(39')-Si(2)	112.3(16)
C(40)-C(39)-H(39A)	108.8	C(40')-C(39')-Si(2)	119.2(11)
Si(2)-C(39)-H(39A)	108.8	C(41')-C(39')-H(39B)	104.6
C(39)-C(40)-H(40A)	109.5	C(40')-C(39')-H(39B)	104.6
C(39)-C(40)-H(40B)	109.5	Si(2)-C(39')-H(39B)	104.6
H(40A)-C(40)-H(40B)	109.5	C(39')-C(40')-H(40D)	109.5
C(39)-C(40)-H(40C)	109.5	C(39')-C(40')-H(40E)	109.5
H(40A)-C(40)-H(40C)	109.5	H(40D)-C(40')-H(40E)	109.5
H(40B)-C(40)-H(40C)	109.5	C(39')-C(40')-H(40F)	109.5
C(39)-C(41)-H(41A)	109.5	H(40D)-C(40')-H(40F)	109.5
C(39)-C(41)-H(41B)	109.5	H(40E)-C(40')-H(40F)	109.5
H(41A)-C(41)-H(41B)	109.5	C(39')-C(41')-H(41D)	109.5
C(39)-C(41)-H(41C)	109.5	C(39')-C(41')-H(41E)	109.5
H(41A)-C(41)-H(41C)	109.5	H(41D)-C(41')-H(41E)	109.5
H(41B)-C(41)-H(41C)	109.5	C(39')-C(41')-H(41F)	109.5
C(37')-C(36')-C(38')	112.9(17)	H(41D)-C(41')-H(41F)	109.5
C(37')-C(36')-Si(2)	118.4(17)	H(41E)-C(41')-H(41F)	109.5
C(38')-C(36')-Si(2)	107(2)	C(44)-C(42)-C(43)	111.3(7)
C(37')-C(36')-H(36B)	106.0	C(44)-C(42)-Si(2)	113.6(7)
C(38')-C(36')-H(36B)	106.1	C(43)-C(42)-Si(2)	113.9(7)
Si(2)-C(36')-H(36B)	106.1	C(44)-C(42)-H(42A)	105.7
C(36')-C(37')-H(37D)	109.5	C(43)-C(42)-H(42A)	105.7

Si(2)-C(42)-H(42A)	105.7	C(42)-C(44)-H(44A)	109.5
C(42)-C(43)-H(43A)	109.5	C(42)-C(44)-H(44B)	109.5
C(42)-C(43)-H(43B)	109.5	H(44A)-C(44)-H(44B)	109.5
H(43A)-C(43)-H(43B)	109.5	C(42)-C(44)-H(44C)	109.5
C(42)-C(43)-H(43C)	109.5	H(44A)-C(44)-H(44C)	109.5
H(43A)-C(43)-H(43C)	109.5	H(44B)-C(44)-H(44C)	109.5
H(43B)-C(43)-H(43C)	109.5		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc10. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	28(1)	57(1)	65(1)	0(1)	-5(1)	-8(1)
Si1	41(1)	72(2)	44(2)	11(1)	-16(1)	-24(1)
O1	27(3)	44(4)	51(4)	13(3)	-12(3)	-5(2)
O2	42(3)	81(5)	34(4)	8(3)	-7(3)	-17(3)
C1	34(4)	24(4)	36(5)	-2(4)	-7(4)	-11(3)
C2	29(4)	41(5)	47(6)	-3(4)	-13(4)	-4(3)
C3	39(4)	44(5)	39(5)	15(4)	-13(4)	-8(4)
C4	27(4)	41(5)	45(5)	6(4)	-12(4)	-12(3)
C5	23(4)	28(4)	45(5)	1(4)	-2(4)	-10(3)
C6	25(4)	45(5)	57(6)	-3(5)	-12(4)	-6(4)
C7	36(4)	42(5)	40(5)	-8(4)	-7(4)	-11(4)
C8	36(4)	55(6)	34(5)	3(4)	-10(4)	-16(4)
C9	36(4)	38(5)	45(6)	11(4)	-17(4)	-10(4)
C10	54(5)	61(6)	42(6)	10(5)	-9(4)	-12(4)
C11	27(4)	38(5)	54(6)	2(4)	-11(4)	-13(3)
C12	36(4)	53(6)	61(6)	-4(5)	-12(4)	-3(4)
C13	30(4)	36(5)	61(6)	0(4)	-11(4)	-4(3)
C14	60(6)	78(7)	45(6)	7(5)	-18(5)	-24(5)
C15	67(6)	78(8)	69(8)	1(6)	-22(6)	-18(5)
C16	76(7)	83(8)	74(8)	-2(6)	-3(6)	-42(6)
C17	45(5)	81(7)	57(6)	17(5)	-25(5)	-23(5)
C18	43(5)	104(9)	60(7)	15(6)	-8(5)	-39(5)
C19	47(5)	116(9)	65(7)	0(6)	-24(5)	-12(6)
C20	49(5)	84(7)	39(6)	14(5)	-17(4)	-38(5)
C21	86(7)	95(8)	51(6)	27(6)	-36(6)	-43(6)
C22	60(6)	109(9)	45(6)	4(6)	-15(5)	-33(6)
Br2	37(1)	40(1)	84(1)	6(1)	-16(1)	-2(1)
Si2	51(1)	48(2)	71(2)	12(1)	-34(1)	-14(1)
O3	34(3)	34(3)	58(4)	6(3)	-15(3)	-6(2)

O4	82(4)	46(4)	78(5)	11(3)	-53(4)	-13(3)
C23	31(4)	31(5)	55(6)	7(4)	-16(4)	-11(3)
C24	34(4)	35(5)	46(6)	5(4)	-13(4)	-10(4)
C25	32(4)	29(5)	65(6)	8(4)	-24(4)	-2(3)
C26	33(4)	35(5)	60(6)	6(4)	-21(4)	-12(4)
C27	28(4)	29(5)	59(6)	6(4)	-15(4)	-12(3)
C28	31(4)	40(5)	61(6)	7(4)	-16(4)	-15(4)
C29	37(4)	33(5)	75(7)	22(5)	-21(5)	-13(4)
C30	50(5)	38(6)	74(7)	19(5)	-32(5)	-18(4)
C31	56(5)	20(5)	69(7)	11(4)	-21(5)	-11(4)
C32	48(5)	46(6)	79(7)	-3(5)	-18(5)	0(4)
C33	47(5)	35(5)	66(7)	11(5)	-24(5)	2(4)
C34	55(6)	60(7)	72(7)	-9(6)	-24(5)	-1(5)
C35	41(5)	66(7)	72(7)	9(5)	-4(5)	1(5)
C36	46(6)	56(5)	54(12)	9(8)	-25(8)	-15(5)
C37	46(6)	56(5)	54(12)	9(8)	-25(8)	-15(5)
C38	46(7)	92(11)	41(8)	11(8)	-4(6)	-10(7)
C39	31(13)	54(8)	102(11)	1(7)	-37(11)	2(9)
C40	112(15)	79(13)	85(15)	-32(11)	-35(11)	22(11)
C41	89(10)	77(11)	70(11)	9(9)	-41(9)	-34(8)
C36'	46(6)	56(5)	54(12)	9(8)	-25(8)	-15(5)
C37'	46(6)	56(5)	54(12)	9(8)	-25(8)	-15(5)
C38'	46(7)	92(11)	41(8)	11(8)	-4(6)	-10(7)
C39'	31(13)	54(8)	102(11)	1(7)	-37(11)	2(9)
C40'	112(15)	79(13)	85(15)	-32(11)	-35(11)	22(11)
C41'	89(10)	77(11)	70(11)	9(9)	-41(9)	-34(8)
C42	38(5)	64(6)	79(7)	16(5)	-30(5)	-16(4)
C43	55(6)	131(10)	83(8)	23(7)	-20(6)	-36(6)
C44	66(7)	82(8)	117(10)	37(7)	-34(7)	21(6)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc10.

	x	y	z	U(eq)
H1	3840(60)	4770(70)	180(60)	60
H2A	2325	4522	-286	46
H3A	2296	6739	-595	48
H4A	418	5662	-516	44
H7A	66	6209	2981	46
H9A	2886	4793	1764	46
H10A	2923	5710	-1954	77
H10B	1870	6490	-2090	77
H10C	1784	5261	-1914	77
H12A	-766	7927	-1454	60
H12B	-621	6628	-1477	60
H13A	140	8870	-477	63
H13B	1284	8290	-287	63
H13C	286	8292	494	63
H14A	2811	2560	4043	71
H15A	2676	1829	2594	104
H15B	3626	2570	2536	104
H15C	2511	2982	2156	104
H16A	1113	2142	3673	114
H16B	807	3353	3423	114
H16C	1005	3033	4468	114
H17A	4184	4339	2647	70
H18A	4997	5837	2945	100
H18B	4208	6069	3881	100
H18C	3744	6150	2891	100
H19A	5660	4004	3487	112
H19B	4795	3229	3860	112
H19C	4933	4255	4454	112

H20A	2964	5288	5193	66
H21A	2839	4070	6368	109
H21B	3659	3583	5517	109
H21C	2476	3229	5678	109
H22A	1335	5327	6136	104
H22B	877	4603	5400	104
H22C	1140	5771	5123	104
H3	5350(60)	3920(60)	690(50)	62
H24A	4139	2316	677	45
H25A	5650	2919	-776	49
H26A	5060	828	-679	49
H29A	7856	-69	1503	56
H31A	5771	2512	2166	56
H32A	3932	3464	-1092	86
H32B	3606	2288	-975	86
H32C	4454	2561	-1822	86
H34A	6558	351	-2810	74
H34B	5482	108	-2133	74
H35A	7732	1484	-2327	90
H35B	7781	1505	-1224	90
H35C	7115	2450	-1713	90
H36A	5831	90	4014	60
H37A	5916	-1697	3528	75
H37B	7174	-1693	3236	75
H37C	6334	-945	2710	75
H38A	5885	-1287	5088	89
H38B	6421	-307	5457	89
H38C	7161	-1327	5030	89
H39A	8899	1244	4442	73
H40A	7698	2746	5100	139
H40B	6790	2353	4533	139
H40C	7854	2721	3985	139
H41A	8155	1032	5959	112
H41B	8171	-56	5404	112

H41C	7077	706	5602	112
H36B	6496	-666	4441	60
H37D	5652	-1493	3316	75
H37E	6926	-1762	3180	75
H37F	6353	-926	2514	75
H38D	4843	125	4175	89
H38E	5352	798	3336	89
H38F	5583	1022	4383	89
H39B	7918	802	5160	73
H40D	6768	2225	5715	139
H40E	6088	1435	5228	139
H40F	6403	2483	4702	139
H41D	8541	2478	5089	112
H41E	8454	2482	3990	112
H41F	9262	1612	4429	112
H42A	8649	-888	2678	69
H43A	10335	-311	2331	130
H43B	10052	639	3070	130
H43C	9448	641	2149	130
H44A	9988	-1553	3610	134
H44B	8805	-1622	4108	134
H44C	9492	-720	4409	134

Table 6. Torsion angles [°] for fropec10.

C14-Si1-O2-C8	-64.9(7)	C6-C7-C8-C9	-1.2(11)
C17-Si1-O2-C8	57.9(8)	O2-C8-C9-C1	-178.5(7)
C20-Si1-O2-C8	176.4(7)	C7-C8-C9-C1	2.6(11)
C9-C1-C2-O1	-38.7(11)	C5-C1-C9-C8	-0.7(11)
C5-C1-C2-O1	143.3(6)	C2-C1-C9-C8	-178.4(7)
C9-C1-C2-C3	-159.4(7)	C5-C4-C11-C12	-138.2(7)
C5-C1-C2-C3	22.6(7)	C3-C4-C11-C12	103.0(8)
O1-C2-C3-C10	73.5(8)	C5-C4-C11-C13	46.9(9)
C1-C2-C3-C10	-162.7(6)	C3-C4-C11-C13	-72.0(9)
O1-C2-C3-C4	-158.0(6)	O2-Si1-C14-C15	83.2(7)
C1-C2-C3-C4	-34.2(7)	C17-Si1-C14-C15	-39.5(8)
C2-C3-C4-C11	161.0(6)	C20-Si1-C14-C15	-163.5(6)
C10-C3-C4-C11	-69.6(9)	O2-Si1-C14-C16	-44.7(7)
C2-C3-C4-C5	32.5(7)	C17-Si1-C14-C16	-167.4(6)
C10-C3-C4-C5	161.9(6)	C20-Si1-C14-C16	68.6(7)
C9-C1-C5-C6	-2.4(10)	O2-Si1-C17-C18	43.2(7)
C2-C1-C5-C6	175.7(6)	C14-Si1-C17-C18	165.6(6)
C9-C1-C5-C4	-179.6(6)	C20-Si1-C17-C18	-70.2(7)
C2-C1-C5-C4	-1.6(8)	O2-Si1-C17-C19	169.5(6)
C11-C4-C5-C6	39.3(11)	C14-Si1-C17-C19	-68.1(7)
C3-C4-C5-C6	163.7(8)	C20-Si1-C17-C19	56.2(8)
C11-C4-C5-C1	-144.2(6)	O2-Si1-C20-C21	157.4(6)
C3-C4-C5-C1	-19.8(7)	C14-Si1-C20-C21	39.6(7)
C1-C5-C6-C7	3.8(11)	C17-Si1-C20-C21	-84.4(7)
C4-C5-C6-C7	-179.8(7)	O2-Si1-C20-C22	29.5(7)
C1-C5-C6-Br1	-176.7(5)	C14-Si1-C20-C22	-88.3(7)
C4-C5-C6-Br1	-0.4(12)	C17-Si1-C20-C22	147.7(7)
C5-C6-C7-C8	-2.1(11)	C42-Si2-O4-C30	70.1(8)
Br1-C6-C7-C8	178.4(6)	C39-Si2-O4-C30	-179.0(10)
Si1-O2-C8-C7	161.7(5)	C36'-Si2-O4-C30	-50.5(11)
Si1-O2-C8-C9	-17.3(11)	C39'-Si2-O4-C30	-162.7(10)
C6-C7-C8-O2	179.7(7)	C36-Si2-O4-C30	-54.9(13)

C27-C23-C24-O3	-146.3(7)	C27-C26-C33-C34	127.1(8)
C31-C23-C24-O3	33.6(11)	C25-C26-C33-C34	-113.6(8)
C27-C23-C24-C25	-20.7(8)	C27-C26-C33-C35	-54.0(9)
C31-C23-C24-C25	159.3(7)	C25-C26-C33-C35	65.2(9)
O3-C24-C25-C32	-75.1(8)	O4-Si2-C39-C41	148.9(12)
C23-C24-C25-C32	159.1(6)	C42-Si2-C39-C41	-94.9(13)
O3-C24-C25-C26	156.2(6)	C36'-Si2-C39-C41	32(3)
C23-C24-C25-C26	30.3(7)	C39'-Si2-C39-C41	67(6)
C32-C25-C26-C33	74.0(9)	C36-Si2-C39-C41	25(3)
C24-C25-C26-C33	-155.8(6)	O4-Si2-C39-C40	25(2)
C32-C25-C26-C27	-159.3(7)	C42-Si2-C39-C40	141.6(17)
C24-C25-C26-C27	-29.1(7)	C36'-Si2-C39-C40	-92(3)
C31-C23-C27-C28	4.4(11)	C39'-Si2-C39-C40	-56(5)
C24-C23-C27-C28	-175.6(6)	C36-Si2-C39-C40	-98(3)
C31-C23-C27-C26	-177.5(7)	O4-Si2-C36'-C37'	82.5(19)
C24-C23-C27-C26	2.4(8)	C42-Si2-C36'-C37'	-37(2)
C33-C26-C27-C23	142.0(7)	C39-Si2-C36'-C37'	-160.1(15)
C25-C26-C27-C23	16.9(8)	C39'-Si2-C36'-C37'	-169.9(16)
C33-C26-C27-C28	-40.3(11)	C36-Si2-C36'-C37'	-123(17)
C25-C26-C27-C28	-165.4(8)	O4-Si2-C36'-C38'	-46(2)
C23-C27-C28-C29	-4.4(10)	C42-Si2-C36'-C38'	-165.9(15)
C26-C27-C28-C29	178.1(7)	C39-Si2-C36'-C38'	71(3)
C23-C27-C28-Br2	176.7(5)	C39'-Si2-C36'-C38'	62(3)
C26-C27-C28-Br2	-0.8(11)	C36-Si2-C36'-C38'	108(14)
C27-C28-C29-C30	1.8(11)	O4-Si2-C42-C44	171.7(6)
Br2-C28-C29-C30	-179.3(6)	C39-Si2-C42-C44	60.0(12)
Si2-O4-C30-C31	138.7(7)	C36'-Si2-C42-C44	-72.5(18)
Si2-O4-C30-C29	-44.9(12)	C39'-Si2-C42-C44	54.5(14)
C28-C29-C30-O4	-175.6(7)	C36-Si2-C42-C44	-62.2(16)
C28-C29-C30-C31	0.9(12)	O4-Si2-C42-C43	42.7(7)
O4-C30-C31-C23	175.6(7)	C39-Si2-C42-C43	-68.9(12)
C29-C30-C31-C23	-1.0(11)	C36'-Si2-C42-C43	158.6(17)
C27-C23-C31-C30	-1.7(11)	C39'-Si2-C42-C43	-74.5(13)
C24-C23-C31-C30	178.3(7)	C36-Si2-C42-C43	168.8(16)

Table 7. Hydrogen bonds and close contacts for fropec10 [$\text{\AA}$ and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1...O3	0.82(8)	1.95(8)	2.754(7)	166(8)
O3-H3...O1#1	0.88(8)	1.87(8)	2.700(7)	157(7)

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y+1, -z$

For compound **164**

REFERENCE NUMBER: froc02

CRYSTAL STRUCTURE REPORT

$C_{24}H_{35}NO_4Si$

Report prepared for:
P. Carlsen, Prof. A. Frontier

February 09, 2012

William W. Brennessel
X-ray Crystallographic Facility
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Data collection

A crystal ($0.26 \times 0.10 \times 0.05 \text{ mm}^3$) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(5) K.¹ A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK α radiation (graphite monochromator) with a frame time of 90 seconds and a detector distance of 4.01 cm. A randomly oriented region of reciprocal space was surveyed: four major sections of frames were collected with 0.50° steps in ω at four different ϕ settings and a detector position of -38° in 2θ . The intensity data were corrected for absorption.² Final cell constants were calculated from the xyz centroids of 2956 strong reflections from the actual data collection after integration.³ See Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR97⁴ and refined using SHELXL-97.⁵ The space group $P2_1/c$ was determined based on systematic absences. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydroxide hydrogen atom was found from the difference Fourier map. Its positional and isotropic displacement parameters were refined independently from those of its bonded oxygen atom. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0497$ (F^2 , $I > 2\sigma(I)$) and $wR2 = 0.1133$ (F^2 , all data).

Structure description

The structure is the one suggested, with all atoms in general positions. Hydrogen bonding links molecules pairwise throughout the crystal (see diagram and Table 7).

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of

Rochester.

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- ¹ *APEX2*, version 2011.4-1; Bruker AXS: Madison, WI, 2011.
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- ³ *SAINT*, version 7.68A; Bruker AXS: Madison, WI, 2009.
- ⁴ Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97: A new program for solving and refining crystal structures*; Istituto di Cristallografia, CNR: Bari, Italy, 1999.
- ⁵ Sheldrick, G. M. *Acta. Cryst.* **2008**, *A64*, 112-122.

Some equations of interest:

$$R_{\text{int}} = \Sigma |F_o^2 - \langle F_o^2 \rangle| / \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$$

where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] / (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

Table 1. Crystal data and structure refinement for fropc02.

Identification code	fropc02	
Empirical formula	C ₂₄ H ₃₅ N O ₄ Si	
Formula weight	429.62	
Temperature	100.0(5) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> ₂ ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 10.756(3) Å	$\alpha = 90^\circ$
	<i>b</i> = 16.063(4) Å	$\beta = 97.997(5)^\circ$
	<i>c</i> = 13.492(4) Å	$\gamma = 90^\circ$
Volume	2308.4(10) Å ³	
<i>Z</i>	4	
Density (calculated)	1.236 Mg/m ³	
Absorption coefficient	0.131 mm ⁻¹	
<i>F</i> (000)	928	
Crystal color, morphology	colorless, plate	
Crystal size	0.26 x 0.10 x 0.05 mm ³	
Theta range for data collection	1.91 to 25.03°	
Index ranges	-12 ≤ <i>h</i> ≤ 12, -19 ≤ <i>k</i> ≤ 19, -16 ≤ <i>l</i> ≤ 16	
Reflections collected	19840	
Independent reflections	4060 [<i>R</i> (int) = 0.1083]	
Observed reflections	2636	
Completeness to theta = 25.03°	100.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9935 and 0.9667	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	4060 / 0 / 283	
Goodness-of-fit on <i>F</i> ²	1.002	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0497, <i>wR</i> 2 = 0.0973	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0953, <i>wR</i> 2 = 0.1133	
Largest diff. peak and hole	0.307 and -0.290 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc02. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Si1	-1130(1)	1944(1)	10477(1)	24(1)
O1	3727(2)	558(1)	5368(1)	29(1)
O2	1634(2)	674(1)	5034(1)	29(1)
O3	-1665(2)	-283(1)	6914(2)	31(1)
O4	-276(2)	2056(1)	9564(1)	24(1)
N1	2633(2)	446(1)	6640(2)	22(1)
C1	2557(3)	566(2)	5635(2)	25(1)
C2	4607(3)	331(2)	6230(2)	28(1)
C3	3945(2)	558(2)	7124(2)	24(1)
C4	4149(2)	1473(2)	7389(2)	23(1)
C5	3526(2)	1918(2)	7997(2)	22(1)
C6	2639(2)	1501(2)	8617(2)	20(1)
C7	1912(2)	2057(2)	9273(2)	22(1)
C8	750(2)	1540(2)	9413(2)	22(1)
C9	514(2)	1024(2)	8476(2)	21(1)
C10	-575(2)	613(2)	8107(2)	24(1)
C11	-583(3)	136(2)	7251(2)	25(1)
C12	481(2)	82(2)	6780(2)	23(1)
C13	1564(2)	520(2)	7155(2)	21(1)
C14	1591(2)	990(2)	8020(2)	20(1)
C15	4289(2)	-62(2)	7969(2)	25(1)
C16	5651(3)	0(2)	8434(2)	41(1)
C17	3675(3)	2849(2)	8055(2)	28(1)
C18	2650(3)	2316(2)	10265(2)	27(1)
C19	-1688(3)	857(2)	10528(2)	33(1)
C20	-201(3)	2207(2)	11696(2)	37(1)
C21	-2478(3)	2681(2)	10113(2)	30(1)
C22	-2075(3)	3567(2)	10350(3)	60(1)
C23	-3572(3)	2462(2)	10679(3)	54(1)

C24	-2928(3)	2606(2)	8994(2)	50(1)
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Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for fropec02.

Si(1)-O(4)	1.6456(19)	C(10)-C(11)	1.385(4)
Si(1)-C(20)	1.851(3)	C(10)-H(10A)	0.9500
Si(1)-C(19)	1.851(3)	C(11)-C(12)	1.386(4)
Si(1)-C(21)	1.882(3)	C(12)-C(13)	1.395(4)
O(1)-C(1)	1.356(3)	C(12)-H(12A)	0.9500
O(1)-C(2)	1.441(3)	C(13)-C(14)	1.388(4)
O(2)-C(1)	1.204(3)	C(15)-C(16)	1.515(4)
O(3)-C(11)	1.366(3)	C(15)-H(15A)	0.9900
O(3)-H(3)	0.86(3)	C(15)-H(15B)	0.9900
O(4)-C(8)	1.417(3)	C(16)-H(16A)	0.9800
N(1)-C(1)	1.361(3)	C(16)-H(16B)	0.9800
N(1)-C(13)	1.428(3)	C(16)-H(16C)	0.9800
N(1)-C(3)	1.481(3)	C(17)-H(17A)	0.9800
C(2)-C(3)	1.527(4)	C(17)-H(17B)	0.9800
C(2)-H(2A)	0.9900	C(17)-H(17C)	0.9800
C(2)-H(2B)	0.9900	C(18)-H(18A)	0.9800
C(3)-C(15)	1.521(4)	C(18)-H(18B)	0.9800
C(3)-C(4)	1.522(4)	C(18)-H(18C)	0.9800
C(4)-C(5)	1.335(4)	C(19)-H(19A)	0.9800
C(4)-H(4A)	0.9500	C(19)-H(19B)	0.9800
C(5)-C(17)	1.505(4)	C(19)-H(19C)	0.9800
C(5)-C(6)	1.510(4)	C(20)-H(20A)	0.9800
C(6)-C(14)	1.530(3)	C(20)-H(20B)	0.9800
C(6)-C(7)	1.544(4)	C(20)-H(20C)	0.9800
C(6)-H(6A)	1.0000	C(21)-C(22)	1.510(4)
C(7)-C(18)	1.517(4)	C(21)-C(24)	1.525(4)
C(7)-C(8)	1.534(4)	C(21)-C(23)	1.530(4)
C(7)-H(7A)	1.0000	C(22)-H(22A)	0.9800
C(8)-C(9)	1.504(4)	C(22)-H(22B)	0.9800
C(8)-H(8A)	1.0000	C(22)-H(22C)	0.9800
C(9)-C(10)	1.376(4)	C(23)-H(23A)	0.9800
C(9)-C(14)	1.385(4)	C(23)-H(23B)	0.9800

C(23)-H(23C)	0.9800	C(4)-C(5)-C(17)	120.3(2)
C(24)-H(24A)	0.9800	C(4)-C(5)-C(6)	120.8(2)
C(24)-H(24B)	0.9800	C(17)-C(5)-C(6)	118.9(2)
C(24)-H(24C)	0.9800	C(5)-C(6)-C(14)	115.0(2)
O(4)-Si(1)-C(20)	110.54(12)	C(5)-C(6)-C(7)	118.1(2)
O(4)-Si(1)-C(19)	110.39(12)	C(14)-C(6)-C(7)	102.5(2)
C(20)-Si(1)-C(19)	108.63(14)	C(5)-C(6)-H(6A)	106.9
O(4)-Si(1)-C(21)	103.11(11)	C(14)-C(6)-H(6A)	106.9
C(20)-Si(1)-C(21)	112.93(14)	C(7)-C(6)-H(6A)	106.9
C(19)-Si(1)-C(21)	111.18(13)	C(18)-C(7)-C(8)	112.0(2)
C(1)-O(1)-C(2)	108.4(2)	C(18)-C(7)-C(6)	114.8(2)
C(11)-O(3)-H(3)	108(2)	C(8)-C(7)-C(6)	104.1(2)
C(8)-O(4)-Si(1)	124.81(16)	C(18)-C(7)-H(7A)	108.5
C(1)-N(1)-C(13)	122.1(2)	C(8)-C(7)-H(7A)	108.5
C(1)-N(1)-C(3)	110.1(2)	C(6)-C(7)-H(7A)	108.5
C(13)-N(1)-C(3)	123.9(2)	O(4)-C(8)-C(9)	113.5(2)
O(2)-C(1)-O(1)	122.0(3)	O(4)-C(8)-C(7)	111.4(2)
O(2)-C(1)-N(1)	128.4(3)	C(9)-C(8)-C(7)	103.8(2)
O(1)-C(1)-N(1)	109.6(2)	O(4)-C(8)-H(8A)	109.3
O(1)-C(2)-C(3)	104.6(2)	C(9)-C(8)-H(8A)	109.3
O(1)-C(2)-H(2A)	110.8	C(7)-C(8)-H(8A)	109.3
C(3)-C(2)-H(2A)	110.8	C(10)-C(9)-C(14)	122.8(3)
O(1)-C(2)-H(2B)	110.8	C(10)-C(9)-C(8)	127.2(2)
C(3)-C(2)-H(2B)	110.8	C(14)-C(9)-C(8)	110.0(2)
H(2A)-C(2)-H(2B)	108.9	C(9)-C(10)-C(11)	118.3(3)
N(1)-C(3)-C(15)	111.6(2)	C(9)-C(10)-H(10A)	120.9
N(1)-C(3)-C(4)	108.5(2)	C(11)-C(10)-H(10A)	120.9
C(15)-C(3)-C(4)	116.4(2)	O(3)-C(11)-C(10)	117.1(2)
N(1)-C(3)-C(2)	98.2(2)	O(3)-C(11)-C(12)	122.4(3)
C(15)-C(3)-C(2)	110.2(2)	C(10)-C(11)-C(12)	120.4(2)
C(4)-C(3)-C(2)	110.4(2)	C(11)-C(12)-C(13)	120.3(3)
C(5)-C(4)-C(3)	126.4(3)	C(11)-C(12)-H(12A)	119.9
C(5)-C(4)-H(4A)	116.8	C(13)-C(12)-H(12A)	119.9
C(3)-C(4)-H(4A)	116.8	C(14)-C(13)-C(12)	119.9(2)

C(14)-C(13)-N(1)	122.0(2)	H(19A)-C(19)-H(19C)	109.5
C(12)-C(13)-N(1)	118.1(2)	H(19B)-C(19)-H(19C)	109.5
C(9)-C(14)-C(13)	118.3(2)	Si(1)-C(20)-H(20A)	109.5
C(9)-C(14)-C(6)	110.2(2)	Si(1)-C(20)-H(20B)	109.5
C(13)-C(14)-C(6)	131.4(2)	H(20A)-C(20)-H(20B)	109.5
C(16)-C(15)-C(3)	112.8(2)	Si(1)-C(20)-H(20C)	109.5
C(16)-C(15)-H(15A)	109.0	H(20A)-C(20)-H(20C)	109.5
C(3)-C(15)-H(15A)	109.0	H(20B)-C(20)-H(20C)	109.5
C(16)-C(15)-H(15B)	109.0	C(22)-C(21)-C(24)	109.0(3)
C(3)-C(15)-H(15B)	109.0	C(22)-C(21)-C(23)	109.2(3)
H(15A)-C(15)-H(15B)	107.8	C(24)-C(21)-C(23)	108.4(3)
C(15)-C(16)-H(16A)	109.5	C(22)-C(21)-Si(1)	110.5(2)
C(15)-C(16)-H(16B)	109.5	C(24)-C(21)-Si(1)	109.6(2)
H(16A)-C(16)-H(16B)	109.5	C(23)-C(21)-Si(1)	110.1(2)
C(15)-C(16)-H(16C)	109.5	C(21)-C(22)-H(22A)	109.5
H(16A)-C(16)-H(16C)	109.5	C(21)-C(22)-H(22B)	109.5
H(16B)-C(16)-H(16C)	109.5	H(22A)-C(22)-H(22B)	109.5
C(5)-C(17)-H(17A)	109.5	C(21)-C(22)-H(22C)	109.5
C(5)-C(17)-H(17B)	109.5	H(22A)-C(22)-H(22C)	109.5
H(17A)-C(17)-H(17B)	109.5	H(22B)-C(22)-H(22C)	109.5
C(5)-C(17)-H(17C)	109.5	C(21)-C(23)-H(23A)	109.5
H(17A)-C(17)-H(17C)	109.5	C(21)-C(23)-H(23B)	109.5
H(17B)-C(17)-H(17C)	109.5	H(23A)-C(23)-H(23B)	109.5
C(7)-C(18)-H(18A)	109.5	C(21)-C(23)-H(23C)	109.5
C(7)-C(18)-H(18B)	109.5	H(23A)-C(23)-H(23C)	109.5
H(18A)-C(18)-H(18B)	109.5	H(23B)-C(23)-H(23C)	109.5
C(7)-C(18)-H(18C)	109.5	C(21)-C(24)-H(24A)	109.5
H(18A)-C(18)-H(18C)	109.5	C(21)-C(24)-H(24B)	109.5
H(18B)-C(18)-H(18C)	109.5	H(24A)-C(24)-H(24B)	109.5
Si(1)-C(19)-H(19A)	109.5	C(21)-C(24)-H(24C)	109.5
Si(1)-C(19)-H(19B)	109.5	H(24A)-C(24)-H(24C)	109.5
H(19A)-C(19)-H(19B)	109.5	H(24B)-C(24)-H(24C)	109.5
Si(1)-C(19)-H(19C)	109.5		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc02. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	22(1)	27(1)	22(1)	-1(1)	8(1)	0(1)
O1	27(1)	38(1)	24(1)	-5(1)	11(1)	-4(1)
O2	30(1)	37(1)	21(1)	-3(1)	5(1)	-5(1)
O3	25(1)	47(1)	23(1)	-9(1)	8(1)	-14(1)
O4	20(1)	29(1)	26(1)	-1(1)	9(1)	4(1)
N1	20(1)	29(1)	20(1)	-4(1)	8(1)	-2(1)
C1	26(2)	25(2)	26(2)	-5(1)	8(1)	-5(1)
C2	27(2)	31(2)	30(2)	-3(1)	12(1)	-2(1)
C3	19(2)	29(2)	24(2)	-1(1)	7(1)	-1(1)
C4	17(2)	28(2)	23(2)	3(1)	5(1)	-3(1)
C5	18(1)	27(2)	21(2)	1(1)	1(1)	-2(1)
C6	18(2)	24(2)	20(2)	0(1)	4(1)	2(1)
C7	20(2)	24(2)	23(2)	-2(1)	6(1)	2(1)
C8	20(2)	24(2)	23(2)	1(1)	4(1)	3(1)
C9	22(2)	23(2)	18(2)	1(1)	4(1)	3(1)
C10	19(2)	31(2)	23(2)	0(1)	8(1)	1(1)
C11	20(2)	34(2)	21(2)	1(1)	4(1)	-5(1)
C12	27(2)	27(2)	16(2)	-5(1)	5(1)	-3(1)
C13	21(2)	23(2)	20(2)	3(1)	7(1)	0(1)
C14	21(2)	21(1)	19(2)	2(1)	4(1)	1(1)
C15	25(2)	24(2)	29(2)	-1(1)	8(1)	2(1)
C16	30(2)	42(2)	49(2)	9(2)	-1(2)	3(2)
C17	26(2)	30(2)	28(2)	0(1)	9(1)	-1(1)
C18	24(2)	35(2)	23(2)	-6(1)	4(1)	-1(1)
C19	32(2)	37(2)	30(2)	6(1)	9(1)	0(1)
C20	35(2)	51(2)	26(2)	-5(2)	8(1)	-2(2)
C21	31(2)	29(2)	33(2)	-5(1)	12(1)	1(1)
C22	57(3)	30(2)	90(3)	0(2)	2(2)	9(2)
C23	35(2)	69(3)	64(3)	7(2)	24(2)	13(2)

C24	34(2)	69(3)	46(2)	4(2)	1(2)	21(2)
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Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc02.

	x	y	z	U(eq)
H3	-1630(30)	-440(20)	6310(20)	47(11)
H2A	5400	646	6246	34
H2B	4795	-272	6226	34
H4A	4781	1756	7094	27
H6A	3153	1106	9078	24
H7A	1630	2570	8885	26
H8A	957	1164	10004	26
H10A	-1302	656	8430	29
H12A	471	-255	6200	28
H15A	3747	35	8493	30
H15B	4121	-633	7707	30
H16A	5821	-409	8975	61
H16B	5820	561	8704	61
H16C	6194	-113	7923	61
H17A	4295	3026	7629	41
H17B	3961	3013	8749	41
H17C	2867	3115	7823	41
H18A	2107	2640	10647	41
H18B	3369	2657	10143	41
H18C	2951	1819	10646	41
H19A	-990	474	10475	49
H19B	-2361	758	9973	49
H19C	-2007	763	11165	49
H20A	462	1790	11862	55
H20B	-751	2211	12217	55
H20C	180	2758	11654	55
H22A	-2782	3943	10146	90
H22B	-1377	3711	9986	90

H22C	-1805	3623	11071	90
H23A	-4264	2853	10492	82
H23B	-3294	2498	11401	82
H23C	-3858	1894	10507	82
H24A	-3633	2988	8808	75
H24B	-3202	2034	8837	75
H24C	-2240	2749	8620	75

Table 6. Torsion angles [°] for fropec02.

C20-Si1-O4-C8	69.1(2)	Si1-O4-C8-C9	113.1(2)
C19-Si1-O4-C8	-51.1(2)	Si1-O4-C8-C7	-130.13(19)
C21-Si1-O4-C8	-170.0(2)	C18-C7-C8-O4	83.2(3)
C2-O1-C1-O2	-174.1(3)	C6-C7-C8-O4	-152.1(2)
C2-O1-C1-N1	6.5(3)	C18-C7-C8-C9	-154.2(2)
C13-N1-C1-O2	-6.7(4)	C6-C7-C8-C9	-29.6(3)
C3-N1-C1-O2	-165.3(3)	O4-C8-C9-C10	-41.3(4)
C13-N1-C1-O1	172.6(2)	C7-C8-C9-C10	-162.4(3)
C3-N1-C1-O1	13.9(3)	O4-C8-C9-C14	140.6(2)
C1-O1-C2-C3	-23.3(3)	C7-C8-C9-C14	19.5(3)
C1-N1-C3-C15	-142.0(2)	C14-C9-C10-C11	1.0(4)
C13-N1-C3-C15	59.8(3)	C8-C9-C10-C11	-176.9(3)
C1-N1-C3-C4	88.5(3)	C9-C10-C11-O3	178.4(2)
C13-N1-C3-C4	-69.7(3)	C9-C10-C11-C12	-0.5(4)
C1-N1-C3-C2	-26.4(3)	O3-C11-C12-C13	-179.9(2)
C13-N1-C3-C2	175.4(2)	C10-C11-C12-C13	-1.0(4)
O1-C2-C3-N1	28.8(2)	C11-C12-C13-C14	2.1(4)
O1-C2-C3-C15	145.5(2)	C11-C12-C13-N1	-179.7(2)
O1-C2-C3-C4	-84.6(3)	C1-N1-C13-C14	-131.0(3)
N1-C3-C4-C5	60.0(3)	C3-N1-C13-C14	24.7(4)
C15-C3-C4-C5	-66.9(4)	C1-N1-C13-C12	50.8(3)
C2-C3-C4-C5	166.6(3)	C3-N1-C13-C12	-153.5(2)
C3-C4-C5-C17	-169.7(2)	C10-C9-C14-C13	0.0(4)
C3-C4-C5-C6	8.9(4)	C8-C9-C14-C13	178.2(2)
C4-C5-C6-C14	-56.5(3)	C10-C9-C14-C6	-179.3(2)
C17-C5-C6-C14	122.1(3)	C8-C9-C14-C6	-1.1(3)
C4-C5-C6-C7	-177.7(2)	C12-C13-C14-C9	-1.5(4)
C17-C5-C6-C7	0.8(3)	N1-C13-C14-C9	-179.6(2)
C5-C6-C7-C18	-81.1(3)	C12-C13-C14-C6	177.6(3)
C14-C6-C7-C18	151.4(2)	N1-C13-C14-C6	-0.6(4)
C5-C6-C7-C8	156.0(2)	C5-C6-C14-C9	-147.0(2)
C14-C6-C7-C8	28.5(3)	C7-C6-C14-C9	-17.6(3)

C5-C6-C14-C13	33.9(4)	C19-Si1-C21-C22	164.2(2)
C7-C6-C14-C13	163.3(3)	O4-Si1-C21-C24	42.7(2)
N1-C3-C15-C16	176.3(2)	C20-Si1-C21-C24	162.0(2)
C4-C3-C15-C16	-58.4(3)	C19-Si1-C21-C24	-75.6(2)
C2-C3-C15-C16	68.2(3)	O4-Si1-C21-C23	161.8(2)
O4-Si1-C21-C22	-77.5(3)	C20-Si1-C21-C23	-78.9(3)
C20-Si1-C21-C22	41.8(3)	C19-Si1-C21-C23	43.5(3)

Table 7. Hydrogen bonds and close contacts for fropec02 [$\text{\AA}$ and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O3-H3...O2#1	0.86(3)	1.85(3)	2.706(3)	174(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+1

For Compound **182**

REFERENCE NUMBER: fropc04

CRYSTAL STRUCTURE REPORT

$C_{35} H_{59} N O_4 Si_2$

Report prepared for:

P. Carlsen, Prof. A. Frontier

June 19, 2013

William W. Brennessel

X-ray Crystallographic Facility

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Data collection

A crystal ($0.50 \times 0.14 \times 0.08 \text{ mm}^3$) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD platform diffractometer for a data collection at 100.0(5) K.¹ A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK α radiation (graphite monochromator) with a frame time of 120 seconds and a detector distance of 4.96 cm. A randomly oriented region of reciprocal space was surveyed: six major sections of frames were collected with 0.50° steps in ω at six different ϕ settings and a detector position of -33° in 2θ . The intensity data were corrected for absorption.² Final cell constants were calculated from the xyz centroids of 4037 strong reflections from the actual data collection after integration.³ See Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR97⁴ and refined using SHELXL-2013.⁵ The space group $P2_1$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. Only silicon and oxygen atoms were refined with anisotropic displacement parameters; carbon and nitrogen atoms were refined with isotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The structure refined as an inversion twin (84:16). The final full matrix least squares refinement converged to $R1 = 0.2018$ (F^2 , $I > 2\sigma(I)$) and $wR2 = 0.5040$ (F^2 , all data).

The structure suffers from unknown problems. At the time of this writing efforts are underway to obtain a better crystallization. However, the relative stereochemistry, which was the goal of the experiment, is unambiguous. Also, since the crystals formed from a racemic mixture, the refined 84:16 mass ratio of inversion twinning components is not an issue. Due to the poor quality of the data and refinement, only the connectivity and relative stereochemistry are reliable; bond lengths and angles are for advice only.

Structure description

The structure is the one suggested.

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

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- ¹ *APEX2*, version 2013.2-0; Bruker AXS: Madison, WI, 2013.
- ² Sheldrick, G. M. *SADABS*, version 2012/1; University of Göttingen: Göttingen, Germany, 2012.
- ³ *SAINT*, version 8.27B; Bruker AXS: Madison, WI, 2013.
- ⁴ Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97: A new program for solving and refining crystal structures*; Istituto di Cristallografia, CNR: Bari, Italy, 1999.
- ⁵ Sheldrick, G. M. *SHELXL-2013/2* University of Göttingen: Göttingen, Germany, 2013.

Some equations of interest:

$$R_{\text{int}} = \Sigma |F_o^2 - \langle F_o^2 \rangle| / \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$$

where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] / (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

Table 1. Crystal data and structure refinement for fropc04.

Identification code	fropc04	
Empirical formula	C ₃₅ H ₅₉ N O ₄ Si ₂	
Formula weight	614.01	
Temperature	100.0(5) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>P</i> 2 ₁	
Unit cell dimensions	<i>a</i> = 13.331(3) Å	$\alpha = 90^\circ$
	<i>b</i> = 7.6227(16) Å	$\beta = 98.754(5)^\circ$
	<i>c</i> = 17.875(4) Å	$\gamma = 90^\circ$
Volume	1795.2(7) Å ³	
<i>Z</i>	2	
Density (calculated)	1.136 Mg/m ³	
Absorption coefficient	0.135 mm ⁻¹	
<i>F</i> (000)	672	
Crystal color, morphology	colorless, needle	
Crystal size	0.50 x 0.14 x 0.08 mm ³	
Theta range for data collection	1.153 to 25.201°	
Index ranges	-15 ≤ <i>h</i> ≤ 15, -9 ≤ <i>k</i> ≤ 9, -21 ≤ <i>l</i> ≤ 21	
Reflections collected	25016	
Independent reflections	6370 [<i>R</i> (int) = 0.1041]	
Observed reflections	4954	
Completeness to theta = 25.030°	100.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7452 and 0.5323	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	6370 / 52 / 224	
Goodness-of-fit on <i>F</i> ²	2.023	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.2018, <i>wR</i> 2 = 0.4872	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.2243, <i>wR</i> 2 = 0.5040	
Absolute structure parameter	0.2(8)	
Largest diff. peak and hole	2.747 and -0.836 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc04. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Si1	406(3)	9219(7)	8223(2)	21(1)
O1	1300(11)	5449(19)	4157(7)	42(3)
O2	2222(9)	12116(17)	4576(6)	29(3)
O3	697(9)	7823(17)	7559(6)	28(3)
N1	1836(9)	9551(16)	5221(7)	17(3)
C1	3001(11)	8350(20)	6238(8)	19(3)
C2	2008(11)	8920(20)	5972(9)	23(3)
C3	1253(15)	8670(30)	6408(11)	35(4)
C4	1486(13)	8070(20)	7116(10)	28(4)
C5	2459(13)	7480(20)	7423(10)	31(4)
C6	3227(12)	7610(20)	6969(9)	27(4)
C7	4322(13)	7310(20)	7168(10)	31(4)
C8	4758(13)	7410(30)	6393(10)	33(4)
C9	3938(12)	8540(20)	5875(9)	24(4)
C10	3831(11)	8050(20)	5027(8)	19(3)
C11	2988(12)	7990(20)	4526(9)	23(3)
C12	1893(11)	8380(20)	4582(9)	20(3)
C13	5834(17)	8080(30)	6515(13)	49(5)
C14	4844(14)	7760(30)	4753(10)	33(4)
C15	1326(13)	6700(20)	4746(10)	27(4)
C16	1386(10)	9130(20)	3815(8)	19(3)
C17	324(15)	9850(30)	3774(12)	40(5)
C18	2031(13)	11340(20)	5172(9)	26(4)
C19	2141(13)	12410(20)	5904(10)	29(4)
C20	2738(14)	13670(20)	6042(11)	33(4)
C21	436(17)	11580(30)	7844(13)	46(5)
C22	1511(17)	12280(30)	7899(13)	49(5)
C23	-220(20)	12870(40)	8227(16)	69(7)
C24	-856(19)	8470(40)	8334(14)	59(6)

C25	-1626(18)	8730(30)	7572(14)	55(6)
C26	-1336(19)	9220(40)	9009(14)	59(6)
C27	1362(16)	8950(30)	9071(12)	47(5)
C28	1360(20)	10160(40)	9715(17)	72(7)
C29	1443(18)	6980(30)	9337(13)	51(6)
O4	4550(40)	5560(20)	7460(20)	34(5)
Si2	5505(7)	5074(13)	8130(5)	32(2)
C30	6570(20)	4060(50)	7720(20)	49(7)
C31	5950(30)	6990(40)	8740(20)	38(7)
C32	4944(16)	3230(20)	8568(12)	28(4)
C33	5870(20)	2140(40)	9048(17)	28(4)
C34	4380(20)	1860(40)	7955(19)	45(8)
C35	4140(30)	3590(60)	9140(20)	73(11)
O4'	4490(50)	5630(30)	7546(19)	34(5)
Si2'	5014(8)	5235(15)	8428(6)	32(2)
C30'	4110(30)	5730(60)	9100(20)	49(7)
C31'	6180(20)	6550(50)	8700(30)	38(7)
C32'	5230(20)	2870(20)	8481(15)	28(4)
C33'	4250(30)	1610(60)	8400(20)	45(8)
C34'	5820(20)	2640(50)	9326(16)	28(4)
C35'	5950(30)	2140(80)	7910(20)	73(11)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for fropc04.

Si(1)-O(3)	1.682(12)	C(11)-C(12)	1.51(2)
Si(1)-C(24)	1.82(3)	C(11)-H(11)	0.9500
Si(1)-C(27)	1.84(2)	C(12)-C(15)	1.54(2)
Si(1)-C(21)	1.92(2)	C(12)-C(16)	1.54(2)
O(1)-C(15)	1.42(2)	C(13)-H(13A)	0.9800
O(1)-H(1)	0.8400	C(13)-H(13B)	0.9800
O(2)-C(18)	1.28(2)	C(13)-H(13C)	0.9800
O(3)-C(4)	1.42(2)	C(14)-H(14A)	0.9800
N(1)-C(18)	1.39(2)	C(14)-H(14B)	0.9800
N(1)-C(2)	1.409(19)	C(14)-H(14C)	0.9800
N(1)-C(12)	1.464(19)	C(15)-H(15A)	0.9900
C(1)-C(2)	1.41(2)	C(15)-H(15B)	0.9900
C(1)-C(6)	1.41(2)	C(16)-C(17)	1.51(2)
C(1)-C(9)	1.50(2)	C(16)-H(16A)	0.9900
C(2)-C(3)	1.38(2)	C(16)-H(16B)	0.9900
C(3)-C(4)	1.34(3)	C(17)-H(17A)	0.9800
C(3)-H(3)	0.9500	C(17)-H(17B)	0.9800
C(4)-C(5)	1.40(2)	C(17)-H(17C)	0.9800
C(5)-C(6)	1.40(2)	C(18)-C(19)	1.53(2)
C(5)-H(5)	0.9500	C(19)-C(20)	1.25(3)
C(6)-C(7)	1.47(2)	C(19)-H(19)	0.9500
C(7)-O(4')	1.45(2)	C(20)-H(20A)	0.9500
C(7)-O(4)	1.45(2)	C(20)-H(20B)	0.9500
C(7)-C(8)	1.58(2)	C(21)-C(22)	1.52(3)
C(7)-H(7)	1.0000	C(21)-C(23)	1.55(4)
C(8)-C(13)	1.51(3)	C(21)-H(21)	1.0000
C(8)-C(9)	1.57(2)	C(22)-H(22A)	0.9800
C(8)-H(8)	1.0000	C(22)-H(22B)	0.9800
C(9)-C(10)	1.55(2)	C(22)-H(22C)	0.9800
C(9)-H(9)	1.0000	C(23)-H(23A)	0.9800
C(10)-C(11)	1.33(2)	C(23)-H(23B)	0.9800
C(10)-C(14)	1.52(2)	C(23)-H(23C)	0.9800

C(24)-C(26)	1.56(3)	C(34)-H(34A)	0.9800
C(24)-C(25)	1.59(3)	C(34)-H(34B)	0.9800
C(24)-H(24)	1.0000	C(34)-H(34C)	0.9800
C(25)-H(25A)	0.9800	C(35)-H(35A)	0.9800
C(25)-H(25B)	0.9800	C(35)-H(35B)	0.9800
C(25)-H(25C)	0.9800	C(35)-H(35C)	0.9800
C(26)-H(26A)	0.9800	O(4')-Si(2')	1.650(14)
C(26)-H(26B)	0.9800	Si(2')-C(32')	1.823(13)
C(26)-H(26C)	0.9800	Si(2')-C(31')	1.856(14)
C(27)-C(28)	1.48(4)	Si(2')-C(30')	1.868(14)
C(27)-C(29)	1.57(3)	C(30')-H(30D)	0.9800
C(27)-H(27)	1.0000	C(30')-H(30E)	0.9800
C(28)-H(28A)	0.9800	C(30')-H(30F)	0.9800
C(28)-H(28B)	0.9800	C(31')-H(31D)	0.9800
C(28)-H(28C)	0.9800	C(31')-H(31E)	0.9800
C(29)-H(29A)	0.9800	C(31')-H(31F)	0.9800
C(29)-H(29B)	0.9800	C(32')-C(33')	1.60(2)
C(29)-H(29C)	0.9800	C(32')-C(34')	1.61(2)
O(4)-Si(2)	1.650(14)	C(32')-C(35')	1.61(2)
Si(2)-C(32)	1.826(13)	C(33')-H(33D)	0.9800
Si(2)-C(30)	1.861(13)	C(33')-H(33E)	0.9800
Si(2)-C(31)	1.864(13)	C(33')-H(33F)	0.9800
C(30)-H(30A)	0.9800	C(34')-H(34D)	0.9800
C(30)-H(30B)	0.9800	C(34')-H(34E)	0.9800
C(30)-H(30C)	0.9800	C(34')-H(34F)	0.9800
C(31)-H(31A)	0.9800	C(35')-H(35D)	0.9800
C(31)-H(31B)	0.9800	C(35')-H(35E)	0.9800
C(31)-H(31C)	0.9800	C(35')-H(35F)	0.9800
C(32)-C(34)	1.61(2)	O(3)-Si(1)-C(24)	101.2(9)
C(32)-C(35)	1.61(2)	O(3)-Si(1)-C(27)	107.8(8)
C(32)-C(33)	1.617(19)	C(24)-Si(1)-C(27)	114.3(11)
C(33)-H(33A)	0.9800	O(3)-Si(1)-C(21)	108.9(8)
C(33)-H(33B)	0.9800	C(24)-Si(1)-C(21)	113.7(11)
C(33)-H(33C)	0.9800	C(27)-Si(1)-C(21)	110.3(10)

C(15)-O(1)-H(1)	109.5	C(13)-C(8)-H(8)	108.3
C(4)-O(3)-Si(1)	125.5(11)	C(9)-C(8)-H(8)	108.3
C(18)-N(1)-C(2)	112.8(13)	C(7)-C(8)-H(8)	108.3
C(18)-N(1)-C(12)	121.2(12)	C(1)-C(9)-C(10)	116.3(13)
C(2)-N(1)-C(12)	121.0(12)	C(1)-C(9)-C(8)	104.1(13)
C(2)-C(1)-C(6)	119.6(14)	C(10)-C(9)-C(8)	113.5(14)
C(2)-C(1)-C(9)	128.8(14)	C(1)-C(9)-H(9)	107.5
C(6)-C(1)-C(9)	111.3(13)	C(10)-C(9)-H(9)	107.5
C(3)-C(2)-C(1)	119.7(15)	C(8)-C(9)-H(9)	107.5
C(3)-C(2)-N(1)	124.0(14)	C(11)-C(10)-C(14)	118.6(14)
C(1)-C(2)-N(1)	115.9(13)	C(11)-C(10)-C(9)	127.8(14)
C(4)-C(3)-C(2)	119.9(17)	C(14)-C(10)-C(9)	113.4(13)
C(4)-C(3)-H(3)	120.0	C(10)-C(11)-C(12)	132.7(15)
C(2)-C(3)-H(3)	120.0	C(10)-C(11)-H(11)	113.7
C(3)-C(4)-C(5)	123.3(17)	C(12)-C(11)-H(11)	113.7
C(3)-C(4)-O(3)	119.1(16)	N(1)-C(12)-C(11)	109.6(12)
C(5)-C(4)-O(3)	117.3(15)	N(1)-C(12)-C(15)	105.9(12)
C(6)-C(5)-C(4)	117.6(16)	C(11)-C(12)-C(15)	111.2(13)
C(6)-C(5)-H(5)	121.2	N(1)-C(12)-C(16)	113.5(12)
C(4)-C(5)-H(5)	121.2	C(11)-C(12)-C(16)	108.1(12)
C(5)-C(6)-C(1)	119.4(15)	C(15)-C(12)-C(16)	108.5(13)
C(5)-C(6)-C(7)	129.5(16)	C(8)-C(13)-H(13A)	109.5
C(1)-C(6)-C(7)	110.5(14)	C(8)-C(13)-H(13B)	109.5
O(4')-C(7)-C(6)	109(3)	H(13A)-C(13)-H(13B)	109.5
O(4)-C(7)-C(6)	112(2)	C(8)-C(13)-H(13C)	109.5
O(4')-C(7)-C(8)	113(3)	H(13A)-C(13)-H(13C)	109.5
O(4)-C(7)-C(8)	106(3)	H(13B)-C(13)-H(13C)	109.5
C(6)-C(7)-C(8)	105.4(14)	C(10)-C(14)-H(14A)	109.5
O(4)-C(7)-H(7)	111.0	C(10)-C(14)-H(14B)	109.5
C(6)-C(7)-H(7)	111.0	H(14A)-C(14)-H(14B)	109.5
C(8)-C(7)-H(7)	111.0	C(10)-C(14)-H(14C)	109.5
C(13)-C(8)-C(9)	117.5(16)	H(14A)-C(14)-H(14C)	109.5
C(13)-C(8)-C(7)	111.1(16)	H(14B)-C(14)-H(14C)	109.5
C(9)-C(8)-C(7)	103.1(13)	O(1)-C(15)-C(12)	112.0(14)

O(1)-C(15)-H(15A)	109.2	H(22A)-C(22)-H(22B)	109.5
C(12)-C(15)-H(15A)	109.2	C(21)-C(22)-H(22C)	109.5
O(1)-C(15)-H(15B)	109.2	H(22A)-C(22)-H(22C)	109.5
C(12)-C(15)-H(15B)	109.2	H(22B)-C(22)-H(22C)	109.5
H(15A)-C(15)-H(15B)	107.9	C(21)-C(23)-H(23A)	109.5
C(17)-C(16)-C(12)	117.3(13)	C(21)-C(23)-H(23B)	109.5
C(17)-C(16)-H(16A)	108.0	H(23A)-C(23)-H(23B)	109.5
C(12)-C(16)-H(16A)	108.0	C(21)-C(23)-H(23C)	109.5
C(17)-C(16)-H(16B)	108.0	H(23A)-C(23)-H(23C)	109.5
C(12)-C(16)-H(16B)	108.0	H(23B)-C(23)-H(23C)	109.5
H(16A)-C(16)-H(16B)	107.2	C(26)-C(24)-C(25)	109(2)
C(16)-C(17)-H(17A)	109.5	C(26)-C(24)-Si(1)	117.6(18)
C(16)-C(17)-H(17B)	109.5	C(25)-C(24)-Si(1)	110.7(17)
H(17A)-C(17)-H(17B)	109.5	C(26)-C(24)-H(24)	106.2
C(16)-C(17)-H(17C)	109.5	C(25)-C(24)-H(24)	106.2
H(17A)-C(17)-H(17C)	109.5	Si(1)-C(24)-H(24)	106.2
H(17B)-C(17)-H(17C)	109.5	C(24)-C(25)-H(25A)	109.5
O(2)-C(18)-N(1)	124.6(15)	C(24)-C(25)-H(25B)	109.5
O(2)-C(18)-C(19)	117.5(15)	H(25A)-C(25)-H(25B)	109.5
N(1)-C(18)-C(19)	117.5(14)	C(24)-C(25)-H(25C)	109.5
C(20)-C(19)-C(18)	123.7(17)	H(25A)-C(25)-H(25C)	109.5
C(20)-C(19)-H(19)	118.1	H(25B)-C(25)-H(25C)	109.5
C(18)-C(19)-H(19)	118.1	C(24)-C(26)-H(26A)	109.5
C(19)-C(20)-H(20A)	120.0	C(24)-C(26)-H(26B)	109.5
C(19)-C(20)-H(20B)	120.0	H(26A)-C(26)-H(26B)	109.5
H(20A)-C(20)-H(20B)	120.0	C(24)-C(26)-H(26C)	109.5
C(22)-C(21)-C(23)	110(2)	H(26A)-C(26)-H(26C)	109.5
C(22)-C(21)-Si(1)	112.1(16)	H(26B)-C(26)-H(26C)	109.5
C(23)-C(21)-Si(1)	113.4(17)	C(28)-C(27)-C(29)	112(2)
C(22)-C(21)-H(21)	107.0	C(28)-C(27)-Si(1)	119.4(18)
C(23)-C(21)-H(21)	107.0	C(29)-C(27)-Si(1)	111.4(15)
Si(1)-C(21)-H(21)	107.0	C(28)-C(27)-H(27)	104.2
C(21)-C(22)-H(22A)	109.5	C(29)-C(27)-H(27)	104.2
C(21)-C(22)-H(22B)	109.5	Si(1)-C(27)-H(27)	104.2

C(27)-C(28)-H(28A)	109.5	C(34)-C(32)-Si(2)	112.6(19)
C(27)-C(28)-H(28B)	109.5	C(35)-C(32)-Si(2)	119(2)
H(28A)-C(28)-H(28B)	109.5	C(33)-C(32)-Si(2)	107.1(16)
C(27)-C(28)-H(28C)	109.5	C(32)-C(33)-H(33A)	109.5
H(28A)-C(28)-H(28C)	109.5	C(32)-C(33)-H(33B)	109.5
H(28B)-C(28)-H(28C)	109.5	H(33A)-C(33)-H(33B)	109.5
C(27)-C(29)-H(29A)	109.5	C(32)-C(33)-H(33C)	109.5
C(27)-C(29)-H(29B)	109.5	H(33A)-C(33)-H(33C)	109.5
H(29A)-C(29)-H(29B)	109.5	H(33B)-C(33)-H(33C)	109.5
C(27)-C(29)-H(29C)	109.5	C(32)-C(34)-H(34A)	109.5
H(29A)-C(29)-H(29C)	109.5	C(32)-C(34)-H(34B)	109.5
H(29B)-C(29)-H(29C)	109.5	H(34A)-C(34)-H(34B)	109.5
C(7)-O(4)-Si(2)	124.3(16)	C(32)-C(34)-H(34C)	109.5
O(4)-Si(2)-C(32)	99.3(17)	H(34A)-C(34)-H(34C)	109.5
O(4)-Si(2)-C(30)	111(3)	H(34B)-C(34)-H(34C)	109.5
C(32)-Si(2)-C(30)	103.5(16)	C(32)-C(35)-H(35A)	109.5
O(4)-Si(2)-C(31)	112.9(17)	C(32)-C(35)-H(35B)	109.5
C(32)-Si(2)-C(31)	118.0(16)	H(35A)-C(35)-H(35B)	109.5
C(30)-Si(2)-C(31)	111.4(19)	C(32)-C(35)-H(35C)	109.5
Si(2)-C(30)-H(30A)	109.5	H(35A)-C(35)-H(35C)	109.5
Si(2)-C(30)-H(30B)	109.5	H(35B)-C(35)-H(35C)	109.5
H(30A)-C(30)-H(30B)	109.5	C(7)-O(4')-Si(2')	128.2(18)
Si(2)-C(30)-H(30C)	109.5	O(4')-Si(2')-C(32')	105.6(14)
H(30A)-C(30)-H(30C)	109.5	O(4')-Si(2')-C(31')	112(2)
H(30B)-C(30)-H(30C)	109.5	C(32')-Si(2')-C(31')	113.7(18)
Si(2)-C(31)-H(31A)	109.5	O(4')-Si(2')-C(30')	111(3)
Si(2)-C(31)-H(31B)	109.5	C(32')-Si(2')-C(30')	106.1(19)
H(31A)-C(31)-H(31B)	109.5	C(31')-Si(2')-C(30')	109(2)
Si(2)-C(31)-H(31C)	109.5	Si(2')-C(30')-H(30D)	109.5
H(31A)-C(31)-H(31C)	109.5	Si(2')-C(30')-H(30E)	109.5
H(31B)-C(31)-H(31C)	109.5	H(30D)-C(30')-H(30E)	109.5
C(34)-C(32)-C(35)	105.2(14)	Si(2')-C(30')-H(30F)	109.5
C(34)-C(32)-C(33)	105.3(13)	H(30D)-C(30')-H(30F)	109.5
C(35)-C(32)-C(33)	106.2(14)	H(30E)-C(30')-H(30F)	109.5

Si(2')-C(31')-H(31D)	109.5	C(32')-C(33')-H(33F)	109.5
Si(2')-C(31')-H(31E)	109.5	H(33D)-C(33')-H(33F)	109.5
H(31D)-C(31')-H(31E)	109.5	H(33E)-C(33')-H(33F)	109.5
Si(2')-C(31')-H(31F)	109.5	C(32')-C(34')-H(34D)	109.5
H(31D)-C(31')-H(31F)	109.5	C(32')-C(34')-H(34E)	109.5
H(31E)-C(31')-H(31F)	109.5	H(34D)-C(34')-H(34E)	109.5
C(33')-C(32')-C(34')	107.5(14)	C(32')-C(34')-H(34F)	109.5
C(33')-C(32')-C(35')	106.8(14)	H(34D)-C(34')-H(34F)	109.5
C(34')-C(32')-C(35')	107.5(15)	H(34E)-C(34')-H(34F)	109.5
C(33')-C(32')-Si(2')	118(2)	C(32')-C(35')-H(35D)	109.5
C(34')-C(32')-Si(2')	102.0(19)	C(32')-C(35')-H(35E)	109.5
C(35')-C(32')-Si(2')	114(3)	H(35D)-C(35')-H(35E)	109.5
C(32')-C(33')-H(33D)	109.5	C(32')-C(35')-H(35F)	109.5
C(32')-C(33')-H(33E)	109.5	H(35D)-C(35')-H(35F)	109.5
H(33D)-C(33')-H(33E)	109.5	H(35E)-C(35')-H(35F)	109.5

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropec04. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	8(2)	48(3)	7(2)	-2(2)	2(1)	-2(2)
O1	46(8)	52(9)	21(6)	-11(6)	-13(5)	2(7)
O2	32(6)	45(7)	9(5)	10(5)	4(4)	1(6)
O3	30(5)	38(5)	16(4)	2(4)	9(4)	-2(4)
O4	31(8)	38(7)	28(9)	-11(6)	-15(8)	4(6)
Si2	21(4)	57(5)	19(4)	8(3)	3(2)	7(3)
O4'	31(8)	38(7)	28(9)	-11(6)	-15(8)	4(6)
Si2'	21(4)	57(5)	19(4)	8(3)	3(2)	7(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc04.

	x	y	z	U(eq)
H1	1583	4519	4331	63
H3	568	8932	6208	42
H5	2593	7007	7920	37
H7	4640	8221	7532	37
H8	4756	6203	6177	39
H9	4156	9792	5926	28
H11	3097	7638	4035	27
H13A	6090	8116	6029	73
H13B	6261	7297	6863	73
H13C	5852	9263	6731	73
H14A	4726	7471	4212	50
H14B	5203	6784	5036	50
H14C	5256	8825	4834	50
H15A	1663	6178	5226	33
H15B	622	7007	4810	33
H16A	1824	10078	3670	23
H16B	1371	8190	3430	23
H17A	87	10278	3261	60
H17B	325	10811	4136	60
H17C	-130	8914	3898	60
H19	1733	12092	6275	35
H20A	3155	14018	5682	40
H20B	2774	14289	6507	40
H21	147	11538	7294	55
H22A	1493	13465	7689	74
H22B	1905	11511	7612	74
H22C	1828	12302	8431	74
H23A	-191	14040	8001	104

H23B	34	12939	8770	104
H23C	-928	12465	8153	104
H24	-800	7172	8418	71
H25A	-2302	8323	7644	82
H25B	-1393	8058	7164	82
H25C	-1660	9979	7437	82
H26A	-2013	8719	9003	88
H26B	-1389	10500	8963	88
H26C	-906	8919	9487	88
H27	2023	9181	8889	56
H28A	1921	9853	10117	107
H28B	716	10062	9909	107
H28C	1452	11364	9547	107
H29A	1975	6874	9777	77
H29B	1612	6246	8925	77
H29C	792	6608	9474	77
H30A	6304	3107	7376	73
H30B	7068	3583	8128	73
H30C	6890	4945	7440	73
H31A	5372	7499	8946	57
H31B	6235	7878	8435	57
H31C	6467	6610	9154	57
H33A	5594	1133	9293	42
H33B	6241	2902	9434	42
H33C	6325	1719	8706	42
H34A	4084	909	8216	68
H34B	4881	1368	7660	68
H34C	3850	2467	7614	68
H35A	3943	2480	9348	110
H35B	3539	4175	8865	110
H35C	4454	4353	9553	110
H30D	3514	4968	8991	73
H30E	3895	6962	9043	73
H30F	4444	5531	9620	73

H31D	6672	6284	8360	57
H31E	6484	6258	9223	57
H31F	6015	7801	8671	57
H33D	4473	387	8435	68
H33E	3832	1814	7907	68
H33F	3855	1871	8804	68
H34D	5980	1399	9423	42
H34E	5399	3070	9689	42
H34F	6456	3318	9381	42
H35D	6026	869	7971	110
H35E	6615	2704	8018	110
H35F	5644	2404	7386	110

Table 6. Torsion angles [°] for fropec04.

C24-Si1-O3-C4	163.3(15)	O4-C7-C8-C13	-91(2)
C27-Si1-O3-C4	-76.4(15)	C6-C7-C8-C13	149.9(17)
C21-Si1-O3-C4	43.2(15)	O4'-C7-C8-C9	143(2)
C6-C1-C2-C3	-3(2)	O4-C7-C8-C9	142.2(17)
C9-C1-C2-C3	-177.8(17)	C6-C7-C8-C9	23.2(18)
C6-C1-C2-N1	-176.4(14)	C2-C1-C9-C10	-47(2)
C9-C1-C2-N1	9(2)	C6-C1-C9-C10	138.4(15)
C18-N1-C2-C3	98.6(19)	C2-C1-C9-C8	-172.5(16)
C12-N1-C2-C3	-106.2(18)	C6-C1-C9-C8	12.7(18)
C18-N1-C2-C1	-88.8(16)	C13-C8-C9-C1	-143.8(16)
C12-N1-C2-C1	66.5(18)	C7-C8-C9-C1	-21.4(17)
C1-C2-C3-C4	7(3)	C13-C8-C9-C10	89(2)
N1-C2-C3-C4	179.7(17)	C7-C8-C9-C10	-148.9(14)
C2-C3-C4-C5	-7(3)	C1-C9-C10-C11	22(2)
C2-C3-C4-O3	179.7(16)	C8-C9-C10-C11	142.5(17)
Si1-O3-C4-C3	-99.7(18)	C1-C9-C10-C14	-163.3(14)
Si1-O3-C4-C5	86.7(18)	C8-C9-C10-C14	-42.5(19)
C3-C4-C5-C6	3(3)	C14-C10-C11-C12	-173.6(17)
O3-C4-C5-C6	176.0(15)	C9-C10-C11-C12	1(3)
C4-C5-C6-C1	1(2)	C18-N1-C12-C11	77.1(16)
C4-C5-C6-C7	171.6(18)	C2-N1-C12-C11	-76.0(17)
C2-C1-C6-C5	-1(2)	C18-N1-C12-C15	-162.8(14)
C9-C1-C6-C5	174.5(15)	C2-N1-C12-C15	44.1(17)
C2-C1-C6-C7	-172.9(15)	C18-N1-C12-C16	-43.9(18)
C9-C1-C6-C7	2(2)	C2-N1-C12-C16	163.0(13)
C5-C6-C7-O4'	50(3)	C10-C11-C12-N1	23(2)
C1-C6-C7-O4'	-139(2)	C10-C11-C12-C15	-94(2)
C5-C6-C7-O4	58(3)	C10-C11-C12-C16	147.2(18)
C1-C6-C7-O4	-131(3)	N1-C12-C15-O1	178.6(12)
C5-C6-C7-C8	172.5(18)	C11-C12-C15-O1	-62.3(17)
C1-C6-C7-C8	-16.5(19)	C16-C12-C15-O1	56.5(17)
O4'-C7-C8-C13	-91(3)	N1-C12-C16-C17	-49.8(19)

C11-C12-C16-C17	-171.6(15)	C7-O4-Si2-C31	23(6)
C15-C12-C16-C17	67.6(18)	O4-Si2-C32-C34	46(2)
C2-N1-C18-O2	158.6(15)	C30-Si2-C32-C34	-69(2)
C12-N1-C18-O2	3(2)	C31-Si2-C32-C34	167.8(19)
C2-N1-C18-C19	-14.1(19)	O4-Si2-C32-C35	-78(3)
C12-N1-C18-C19	-169.3(13)	C30-Si2-C32-C35	167(2)
O2-C18-C19-C20	-28(3)	C31-Si2-C32-C35	44(2)
N1-C18-C19-C20	145.1(18)	O4-Si2-C32-C33	161(2)
O3-Si1-C24-C26	169.6(18)	C30-Si2-C32-C33	47(2)
C27-Si1-C24-C26	54(2)	C31-Si2-C32-C33	-77(2)
C21-Si1-C24-C26	-74(2)	O4-C7-O4'-Si2'	131(28)
O3-Si1-C24-C25	-63.8(18)	C6-C7-O4'-Si2'	-115(5)
C27-Si1-C24-C25	-179.3(16)	C8-C7-O4'-Si2'	128(5)
C21-Si1-C24-C25	53(2)	C7-O4'-Si2'-C32'	-169(5)
O3-Si1-C27-C28	172.9(19)	C7-O4'-Si2'-C31'	-45(7)
C24-Si1-C27-C28	-75(2)	C7-O4'-Si2'-C30'	77(6)
C21-Si1-C27-C28	54(2)	O4'-Si2'-C32'-C33'	-68(3)
O3-Si1-C27-C29	-54.6(17)	C31'-Si2'-C32'-C33'	169(2)
C24-Si1-C27-C29	57.0(19)	C30'-Si2'-C32'-C33'	50(3)
C21-Si1-C27-C29	-173.3(15)	O4'-Si2'-C32'-C34'	175(3)
O4'-C7-O4-Si2	-77(18)	C31'-Si2'-C32'-C34'	52(2)
C6-C7-O4-Si2	-145(4)	C30'-Si2'-C32'-C34'	-67(2)
C8-C7-O4-Si2	100(5)	O4'-Si2'-C32'-C35'	59(3)
C7-O4-Si2-C32	149(5)	C31'-Si2'-C32'-C35'	-64(3)
C7-O4-Si2-C30	-103(5)	C30'-Si2'-C32'-C35'	177(2)

For Compound **207**

REFERENCE NUMBER: 13170cw

CRYSTAL STRUCTURE REPORT

$C_{40} H_{44.47} Cl_2 N_2 O_{12.23}$

Report prepared for:
P. Carlsen, Prof. A. Frontier

December 12, 2014

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Data collection

A crystal (approximate dimensions 0.22 x 0.17 x 0.03 mm³) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker-AXS D8 Venture diffractometer for a data collection at 173(2) K.¹ A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 2690 reflections. The data collection was carried out using CuK α radiation (parabolic mirrors) with a frame time of 10 seconds and a detector distance of 4.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.83 Å. All major sections of frames were collected with 0.80° steps in ω or ϕ at different detector positions in 2θ . The intensity data were corrected for absorption and decay (SADABS).² Final cell constants were calculated from 2690 strong reflections from the actual data collection after integration (SAINT).³ Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2013⁴ and refined using SHELXL-2014/7.⁵ The space group *P*-1 was determined based on intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters except for cocrystallized water atom O7, which had partial occupancy (see below).

Hydrogen atoms on hydroxyl groups O6A, O4B, O5B, and O6B were located in the difference Fourier map. Those on O4A and O5A could not be located unambiguously, likely as a result of disorder. When the cocrystallized water molecule is present (partial occupancy, see below), an ordered hydrogen bonding scheme could be laid out logically. When the water molecule is not present, the hydrogen atoms appear to be involved in a disorder across a crystallographic inversion center. The disorder is such that one of the pair of hydrogen atoms forms an intramolecular hydrogen bond while the other forms an intermolecular interaction,⁶ and vice versa, in a 1:1 ratio across the inversion center. In all cases for the disordered hydrogen atoms, they were either found from the difference

Fourier map from weak data at low resolution or placed logically to fit the proposed hydrogen bonding schemes. Once placed, all hydroxyl group and water hydrogen atoms were refined as riding atoms with fixed O—H distances of 0.85 Å and isotropic displacement parameters of 1.5 times the equivalent isotropic parameters of their bonded oxygen atoms. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

The data were very weak because the only suitable crystal available was very small. The final full matrix least squares refinement converged to $R1 = 0.0739$ and $wR2 = 0.1614$ (F^2 , obs. data).

Structure description

The structure is the one suggested. The asymmetric unit contains two independent organic molecules of interest and a cocrystallized water molecule with a partial occupancy of 0.23(2). All species are linked via hydrogen bonding; because the hydrogen bonding is different between the two organic molecules, the formula unit is based on both plus the water (see Table 7 and diagrams).

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1224900) and the University of Minnesota.

¹ *APEX2*, version 2014.7-1; Bruker AXS: Madison, WI, 2014.

² Sheldrick, G. M. *SADABS*, version 2014/3; University of Göttingen: Göttingen, Germany, 2014.

³ *SAINT*, version 8.32B; Bruker AXS: Madison, WI, 2013.

⁴ Sheldrick, G. M. *SHELXT-2013*; University of Göttingen: Göttingen, Germany, 2013.

⁵ Sheldrick, G. M. *SHELXL-2014/7*; University of Göttingen: Göttingen, Germany, 2014.

⁶ The nearest intermolecular acceptors for the O4A/O5A pair, which lie across an inversion center, are just outside the van der Waals radii of the donor and acceptor atoms, and therefore are not true hydrogen bonds. However, they may have played a role in the initial crystal formation and/or simply reoriented themselves due to lack or loss of cocrystallized water.

Some equations of interest:

$$R_{\text{int}} = \Sigma |F_o^2 - \langle F_o^2 \rangle| / \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$$

where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] / (m - n)]^{1/2}$$

where m = number of reflections and n = number of parameters

Figure: Hydrogen bonding scheme incorporating the cocrystallized water molecule.

Figure: Proposed alternating hydrogen bonding scheme due to a crystallographic inversion center when water molecule is not present.

Table 1. Crystal data and structure refinement for 13170cw.

Identification code	13170cw	
Empirical formula	C ₄₀ H _{44.47} Cl ₂ N ₂ O _{12.23}	
Formula weight	819.90	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	<i>a</i> = 12.3557(6) Å	$\alpha = 82.957(4)^\circ$
	<i>b</i> = 12.4260(6) Å	$\beta = 87.930(4)^\circ$
	<i>c</i> = 12.7972(8) Å	$\gamma = 74.504(4)^\circ$
Volume	1879.06(18) Å ³	
<i>Z</i>	2	
Density (calculated)	1.449 Mg/m ³	
Absorption coefficient	2.147 mm ⁻¹	
<i>F</i> (000)	861	
Crystal color, morphology	colorless, plate	
Crystal size	0.22 x 0.17 x 0.03 mm ³	
Theta range for data collection	3.480 to 50.588°	
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-11 \leq l \leq 12$	
Reflections collected	8543	
Independent reflections	3867 [<i>R</i> (int) = 0.0852]	
Observed reflections	2316	
Completeness to theta = 50.588°	97.6%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9285 and 0.7290	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	3867 / 0 / 518	
Goodness-of-fit on <i>F</i> ²	1.048	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0739, <i>wR</i> 2 = 0.1614	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1346, <i>wR</i> 2 = 0.1962	
Largest diff. peak and hole	0.477 and -0.392 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 13170cw. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cl1A	4520(2)	1713(2)	617(2)	70(1)
O1A	3620(4)	1277(5)	2995(4)	40(1)
O2A	2994(5)	4303(5)	288(5)	54(2)
O3A	1827(5)	1833(5)	65(5)	65(2)
O4A	547(5)	437(5)	960(6)	78(2)
O5A	-1275(6)	133(6)	2209(6)	80(2)
O6A	638(4)	1470(5)	5485(5)	57(2)
N1A	2068(5)	2382(5)	2078(5)	38(2)
C1A	3187(7)	2003(7)	2298(7)	38(2)
C2A	3814(7)	2660(7)	1526(7)	43(2)
C3A	4618(7)	3151(7)	2048(7)	51(2)
C4A	2880(7)	3530(8)	917(7)	46(2)
C5A	1746(6)	3306(7)	1218(6)	37(2)
C6A	902(7)	4343(7)	1543(7)	44(2)
C7A	1272(7)	4809(7)	2462(7)	54(3)
C8A	1338(7)	2950(8)	244(7)	50(2)
C9A	557(7)	2251(7)	175(7)	44(2)
C10A	-13(7)	2335(8)	-870(7)	59(3)
C11A	82(7)	1670(7)	1106(8)	54(3)
C12A	-1207(7)	1865(7)	1156(8)	53(3)
C13A	-1793(8)	3133(8)	1102(8)	66(3)
C14A	-1402(8)	1311(7)	2241(8)	56(3)
C15A	-480(7)	1482(7)	2888(8)	44(2)
C16A	-411(7)	1372(7)	3970(8)	48(2)
C17A	496(6)	1579(7)	4435(8)	44(2)
C18A	1307(6)	1914(6)	3792(7)	39(2)
C19A	1229(6)	2002(6)	2701(7)	37(2)
C20A	354(7)	1762(6)	2237(7)	37(2)
Cl1B	2850(2)	6314(2)	6092(2)	63(1)

O1B	3717(5)	4490(5)	4432(5)	54(2)
O2B	1809(4)	4513(5)	7670(4)	48(2)
O3B	4920(4)	4526(4)	7529(4)	43(2)
O4B	7098(4)	3496(4)	6894(4)	42(2)
O5B	8702(4)	1670(5)	6489(4)	52(2)
O6B	5771(4)	599(4)	3798(4)	48(2)
N1B	4073(5)	3454(5)	6047(5)	34(2)
C1B	3502(6)	4308(7)	5373(8)	42(2)
C2B	2508(6)	5022(7)	5936(7)	42(2)
C3B	1417(7)	5272(8)	5387(7)	63(3)
C4B	2538(7)	4351(7)	7009(7)	40(2)
C5B	3618(6)	3404(6)	7138(6)	31(2)
C12B	7214(6)	1688(6)	7811(6)	36(2)
C13B	6631(7)	872(7)	8439(7)	48(2)
C14B	7822(6)	1163(7)	6850(6)	40(2)
C15B	6869(6)	1403(7)	6056(7)	36(2)
C16B	6796(6)	851(6)	5213(6)	34(2)
C17B	5816(6)	1174(6)	4626(7)	36(2)
C18B	4927(6)	2046(7)	4904(6)	36(2)
C19B	5022(6)	2614(6)	5758(6)	34(2)
C20B	5997(6)	2306(6)	6335(6)	34(2)
C11B	6386(6)	2755(6)	7282(6)	35(2)
C8B	4325(6)	3723(6)	7920(7)	40(2)
C9B	5555(6)	3427(6)	8018(6)	34(2)
C10B	6047(7)	3542(7)	9045(6)	44(2)
C6B	3386(7)	2277(7)	7517(7)	46(2)
C7B	2597(7)	1950(7)	6828(8)	59(3)
O7	-2980(30)	60(30)	1030(30)	114(17)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for 13170cw.

C11A-C2A	1.793(8)	C7A-H7AC	0.9800
O1A-C1A	1.215(9)	C8A-C9A	1.472(12)
O2A-C4A	1.211(9)	C8A-H8AA	1.0000
O3A-C8A	1.401(10)	C9A-C11A	1.500(12)
O3A-C9A	1.523(10)	C9A-C10A	1.513(12)
O4A-C11A	1.518(10)	C10A-H10A	0.9800
O4A-H4A	0.8499	C10A-H10B	0.9800
O4A-H4A'	0.8500	C10A-H10C	0.9800
O4A-H4A''	0.8500	C11A-C20A	1.521(12)
O5A-C14A	1.436(10)	C11A-C12A	1.546(12)
O5A-H5A	0.8500	C12A-C14A	1.514(12)
O5A-H5A'	0.8500	C12A-C13A	1.542(12)
O5A-H5A''	0.8500	C12A-H12A	1.0000
O6A-C17A	1.347(10)	C13A-H13A	0.9800
O6A-H6A	0.8501	C13A-H13B	0.9800
N1A-C1A	1.364(10)	C13A-H13C	0.9800
N1A-C19A	1.429(10)	C14A-C15A	1.505(12)
N1A-C5A	1.471(10)	C14A-H14A	1.0000
C1A-C2A	1.525(11)	C15A-C16A	1.378(12)
C2A-C3A	1.509(11)	C15A-C20A	1.391(11)
C2A-C4A	1.516(12)	C16A-C17A	1.384(12)
C3A-H3AA	0.9800	C16A-H16A	0.9500
C3A-H3AB	0.9800	C17A-C18A	1.390(11)
C3A-H3AC	0.9800	C18A-C19A	1.392(11)
C4A-C5A	1.527(11)	C18A-H18A	0.9500
C5A-C6A	1.518(11)	C19A-C20A	1.369(11)
C5A-C8A	1.518(12)	C11B-C2B	1.801(8)
C6A-C7A	1.508(11)	O1B-C1B	1.231(10)
C6A-H6AA	0.9900	O2B-C4B	1.207(9)
C6A-H6AB	0.9900	O3B-C8B	1.426(9)
C7A-H7AA	0.9800	O3B-C9B	1.458(9)
C7A-H7AB	0.9800	O4B-C11B	1.469(8)

O4B-H4B	0.8501	C20B-C11B	1.537(11)
O5B-C14B	1.432(9)	C11B-C9B	1.517(11)
O5B-H5B	0.8500	C8B-C9B	1.472(11)
O6B-C17B	1.359(9)	C8B-H8BA	1.0000
O6B-H6B	0.8500	C9B-C10B	1.506(11)
N1B-C1B	1.337(10)	C10B-H10D	0.9800
N1B-C19B	1.418(9)	C10B-H10E	0.9800
N1B-C5B	1.488(9)	C10B-H10F	0.9800
C1B-C2B	1.524(11)	C6B-C7B	1.502(11)
C2B-C3B	1.482(11)	C6B-H6BB	0.9900
C2B-C4B	1.513(11)	C6B-H6BC	0.9900
C3B-H3BA	0.9800	C7B-H7BA	0.9800
C3B-H3BB	0.9800	C7B-H7BB	0.9800
C3B-H3BC	0.9800	C7B-H7BC	0.9800
C4B-C5B	1.523(11)	O7-H7A	0.8500
C5B-C8B	1.505(11)	O7-H7B	0.8500
C5B-C6B	1.521(10)	C8A-O3A-C9A	60.3(5)
C12B-C13B	1.529(10)	C11A-O4A-H4A	116.0
C12B-C11B	1.538(10)	C11A-O4A-H4A'	109.6
C12B-C14B	1.540(11)	C11A-O4A-H4A"	109.6
C12B-H12B	1.0000	C14A-O5A-H5A	109.9
C13B-H13D	0.9800	C14A-O5A-H5A'	115.0
C13B-H13E	0.9800	C14A-O5A-H5A"	104.9
C13B-H13F	0.9800	C17A-O6A-H6A	111.1
C14B-C15B	1.528(11)	C1A-N1A-C19A	123.1(7)
C14B-H14B	1.0000	C1A-N1A-C5A	116.1(7)
C15B-C16B	1.365(11)	C19A-N1A-C5A	120.6(6)
C15B-C20B	1.404(10)	O1A-C1A-N1A	126.3(8)
C16B-C17B	1.387(10)	O1A-C1A-C2A	125.3(8)
C16B-H16B	0.9500	N1A-C1A-C2A	108.4(8)
C17B-C18B	1.392(10)	C3A-C2A-C4A	114.1(7)
C18B-C19B	1.396(11)	C3A-C2A-C1A	113.7(7)
C18B-H18B	0.9500	C4A-C2A-C1A	103.5(7)
C19B-C20B	1.375(10)	C3A-C2A-C11A	111.8(6)

C4A-C2A-C11A	106.6(6)	C5A-C8A-H8AA	113.0
C1A-C2A-C11A	106.4(5)	C8A-C9A-C11A	124.5(8)
C2A-C3A-H3AA	109.5	C8A-C9A-C10A	117.6(8)
C2A-C3A-H3AB	109.5	C11A-C9A-C10A	116.3(7)
H3AA-C3A-H3AB	109.5	C8A-C9A-O3A	55.8(5)
C2A-C3A-H3AC	109.5	C11A-C9A-O3A	113.9(7)
H3AA-C3A-H3AC	109.5	C10A-C9A-O3A	110.8(7)
H3AB-C3A-H3AC	109.5	C9A-C10A-H10A	109.5
O2A-C4A-C2A	126.0(8)	C9A-C10A-H10B	109.5
O2A-C4A-C5A	123.9(8)	H10A-C10A-H10B	109.5
C2A-C4A-C5A	110.1(7)	C9A-C10A-H10C	109.5
N1A-C5A-C6A	113.8(6)	H10A-C10A-H10C	109.5
N1A-C5A-C8A	113.2(7)	H10B-C10A-H10C	109.5
C6A-C5A-C8A	110.2(7)	C9A-C11A-O4A	102.6(7)
N1A-C5A-C4A	101.4(6)	C9A-C11A-C20A	122.8(7)
C6A-C5A-C4A	112.0(7)	O4A-C11A-C20A	105.6(7)
C8A-C5A-C4A	105.8(7)	C9A-C11A-C12A	117.3(8)
C7A-C6A-C5A	114.1(7)	O4A-C11A-C12A	105.1(6)
C7A-C6A-H6AA	108.7	C20A-C11A-C12A	101.8(7)
C5A-C6A-H6AA	108.7	C14A-C12A-C13A	108.4(7)
C7A-C6A-H6AB	108.7	C14A-C12A-C11A	103.3(7)
C5A-C6A-H6AB	108.7	C13A-C12A-C11A	110.2(7)
H6AA-C6A-H6AB	107.6	C14A-C12A-H12A	111.6
C6A-C7A-H7AA	109.5	C13A-C12A-H12A	111.6
C6A-C7A-H7AB	109.5	C11A-C12A-H12A	111.6
H7AA-C7A-H7AB	109.5	C12A-C13A-H13A	109.5
C6A-C7A-H7AC	109.5	C12A-C13A-H13B	109.5
H7AA-C7A-H7AC	109.5	H13A-C13A-H13B	109.5
H7AB-C7A-H7AC	109.5	C12A-C13A-H13C	109.5
O3A-C8A-C9A	64.0(5)	H13A-C13A-H13C	109.5
O3A-C8A-C5A	115.4(7)	H13B-C13A-H13C	109.5
C9A-C8A-C5A	128.6(8)	O5A-C14A-C15A	110.3(7)
O3A-C8A-H8AA	113.0	O5A-C14A-C12A	109.9(8)
C9A-C8A-H8AA	113.0	C15A-C14A-C12A	103.3(8)

O5A-C14A-H14A	111.0	C3B-C2B-C11B	109.8(6)
C15A-C14A-H14A	111.0	C4B-C2B-C11B	108.3(6)
C12A-C14A-H14A	111.0	C1B-C2B-C11B	106.7(6)
C16A-C15A-C20A	122.1(8)	C2B-C3B-H3BA	109.5
C16A-C15A-C14A	127.4(8)	C2B-C3B-H3BB	109.5
C20A-C15A-C14A	110.5(8)	H3BA-C3B-H3BB	109.5
C15A-C16A-C17A	119.6(8)	C2B-C3B-H3BC	109.5
C15A-C16A-H16A	120.2	H3BA-C3B-H3BC	109.5
C17A-C16A-H16A	120.2	H3BB-C3B-H3BC	109.5
O6A-C17A-C16A	123.3(8)	O2B-C4B-C2B	125.8(7)
O6A-C17A-C18A	117.9(8)	O2B-C4B-C5B	123.9(7)
C16A-C17A-C18A	118.8(9)	C2B-C4B-C5B	110.3(7)
C17A-C18A-C19A	120.6(8)	N1B-C5B-C8B	113.5(6)
C17A-C18A-H18A	119.7	N1B-C5B-C6B	112.7(6)
C19A-C18A-H18A	119.7	C8B-C5B-C6B	111.0(7)
C20A-C19A-C18A	120.8(7)	N1B-C5B-C4B	100.9(6)
C20A-C19A-N1A	120.9(8)	C8B-C5B-C4B	106.5(6)
C18A-C19A-N1A	118.3(7)	C6B-C5B-C4B	111.8(6)
C19A-C20A-C15A	117.9(8)	C13B-C12B-C11B	113.2(6)
C19A-C20A-C11A	133.8(8)	C13B-C12B-C14B	110.0(6)
C15A-C20A-C11A	108.3(8)	C11B-C12B-C14B	101.6(6)
C8B-O3B-C9B	61.4(5)	C13B-C12B-H12B	110.6
C11B-O4B-H4B	122.8	C11B-C12B-H12B	110.6
C14B-O5B-H5B	109.7	C14B-C12B-H12B	110.6
C17B-O6B-H6B	108.7	C12B-C13B-H13D	109.5
C1B-N1B-C19B	123.8(6)	C12B-C13B-H13E	109.5
C1B-N1B-C5B	115.3(6)	H13D-C13B-H13E	109.5
C19B-N1B-C5B	120.9(6)	C12B-C13B-H13F	109.5
O1B-C1B-N1B	125.9(7)	H13D-C13B-H13F	109.5
O1B-C1B-C2B	124.3(8)	H13E-C13B-H13F	109.5
N1B-C1B-C2B	109.8(8)	O5B-C14B-C15B	112.9(6)
C3B-C2B-C4B	114.0(7)	O5B-C14B-C12B	111.1(6)
C3B-C2B-C1B	114.9(7)	C15B-C14B-C12B	102.2(6)
C4B-C2B-C1B	102.6(7)	O5B-C14B-H14B	110.1

C15B-C14B-H14B	110.1	O3B-C8B-H8BA	113.1
C12B-C14B-H14B	110.1	C9B-C8B-H8BA	113.1
C16B-C15B-C20B	122.4(8)	C5B-C8B-H8BA	113.1
C16B-C15B-C14B	128.6(7)	O3B-C9B-C8B	58.2(5)
C20B-C15B-C14B	109.0(7)	O3B-C9B-C10B	110.1(6)
C15B-C16B-C17B	118.9(7)	C8B-C9B-C10B	118.4(7)
C15B-C16B-H16B	120.5	O3B-C9B-C11B	113.9(6)
C17B-C16B-H16B	120.5	C8B-C9B-C11B	125.4(7)
O6B-C17B-C16B	117.3(7)	C10B-C9B-C11B	114.6(6)
O6B-C17B-C18B	122.8(7)	C9B-C10B-H10D	109.5
C16B-C17B-C18B	119.8(8)	C9B-C10B-H10E	109.5
C17B-C18B-C19B	120.5(8)	H10D-C10B-H10E	109.5
C17B-C18B-H18B	119.8	C9B-C10B-H10F	109.5
C19B-C18B-H18B	119.8	H10D-C10B-H10F	109.5
C20B-C19B-C18B	119.9(7)	H10E-C10B-H10F	109.5
C20B-C19B-N1B	121.6(7)	C7B-C6B-C5B	114.2(7)
C18B-C19B-N1B	118.4(7)	C7B-C6B-H6BB	108.7
C19B-C20B-C15B	118.4(8)	C5B-C6B-H6BB	108.7
C19B-C20B-C11B	133.3(7)	C7B-C6B-H6BC	108.7
C15B-C20B-C11B	108.2(7)	C5B-C6B-H6BC	108.7
O4B-C11B-C9B	104.4(6)	H6BB-C6B-H6BC	107.6
O4B-C11B-C20B	108.5(6)	C6B-C7B-H7BA	109.5
C9B-C11B-C20B	121.8(6)	C6B-C7B-H7BB	109.5
O4B-C11B-C12B	104.3(6)	H7BA-C7B-H7BB	109.5
C9B-C11B-C12B	115.4(6)	C6B-C7B-H7BC	109.5
C20B-C11B-C12B	101.2(6)	H7BA-C7B-H7BC	109.5
O3B-C8B-C9B	60.4(5)	H7BB-C7B-H7BC	109.5
O3B-C8B-C5B	116.5(7)	H7A-O7-H7B	115.7
C9B-C8B-C5B	129.3(7)		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 13170cw. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1A	73(2)	63(2)	73(2)	-18(1)	35(1)	-20(1)
O1A	32(3)	41(4)	46(4)	-1(3)	-1(3)	-9(3)
O2A	54(4)	59(4)	51(4)	7(4)	0(3)	-26(3)
O3A	76(5)	58(5)	64(4)	-15(4)	3(4)	-21(4)
O4A	79(5)	50(4)	105(6)	-16(4)	-1(4)	-13(4)
O5A	84(5)	70(5)	96(6)	2(4)	-4(4)	-40(4)
O6A	41(4)	85(5)	42(4)	5(3)	6(3)	-17(3)
N1A	30(4)	36(4)	47(5)	-6(4)	-3(3)	-6(3)
C1A	36(6)	40(6)	41(6)	-16(5)	5(5)	-11(5)
C2A	40(5)	42(5)	49(6)	-9(5)	16(5)	-14(4)
C3A	45(5)	52(6)	63(6)	-1(5)	1(5)	-28(5)
C4A	52(6)	46(6)	41(6)	-13(5)	4(5)	-15(5)
C5A	34(5)	41(5)	39(6)	6(5)	-5(4)	-20(4)
C6A	43(5)	40(5)	50(6)	-8(5)	-9(4)	-8(4)
C7A	47(6)	45(6)	69(7)	-2(5)	-2(5)	-12(4)
C8A	53(6)	46(6)	54(7)	-9(5)	2(5)	-15(5)
C9A	33(5)	44(6)	57(7)	-12(5)	3(5)	-11(4)
C10A	58(6)	66(7)	54(7)	-19(5)	-19(5)	-11(5)
C11A	38(6)	39(6)	85(8)	-14(5)	-9(5)	-6(4)
C12A	47(6)	41(6)	69(7)	-11(5)	-10(5)	-6(5)
C13A	54(6)	81(8)	58(7)	-5(6)	-7(5)	-11(5)
C14A	50(6)	35(6)	84(8)	-9(5)	-8(5)	-12(4)
C15A	33(5)	34(5)	66(7)	-2(5)	-8(5)	-10(4)
C16A	32(5)	51(6)	59(7)	7(5)	3(5)	-13(4)
C17A	21(5)	53(6)	53(7)	5(5)	0(5)	-6(4)
C18A	26(5)	39(5)	47(6)	-3(4)	4(4)	-2(4)
C19A	22(5)	35(5)	53(7)	-3(4)	5(4)	-9(4)
C20A	32(5)	34(5)	46(6)	-1(4)	1(5)	-11(4)
Cl1B	74(2)	42(1)	68(2)	-7(1)	11(1)	-9(1)

O1B	55(4)	48(4)	45(4)	6(3)	5(3)	6(3)
O2B	32(3)	58(4)	52(4)	-14(3)	9(3)	-5(3)
O3B	41(3)	39(3)	52(4)	-6(3)	9(3)	-17(3)
O4B	44(3)	39(3)	44(4)	6(3)	-2(3)	-17(3)
O5B	34(3)	62(4)	61(4)	2(3)	7(3)	-17(3)
O6B	36(3)	50(4)	53(4)	-21(3)	-2(3)	3(3)
N1B	25(4)	35(4)	36(4)	-4(4)	4(3)	2(3)
C1B	27(5)	38(6)	56(7)	-3(5)	-3(5)	-1(4)
C2B	36(5)	37(5)	49(6)	0(5)	0(4)	-5(4)
C3B	33(6)	83(7)	56(7)	5(6)	0(5)	9(5)
C4B	29(5)	41(5)	49(6)	-5(5)	-3(5)	-8(4)
C5B	24(4)	36(5)	34(5)	-4(4)	4(4)	-12(4)
C12B	25(4)	37(5)	52(6)	-6(4)	-7(4)	-15(4)
C13B	57(6)	40(5)	46(6)	13(4)	1(5)	-17(5)
C14B	29(5)	36(5)	53(6)	3(4)	0(4)	-9(4)
C15B	25(5)	36(5)	42(6)	14(5)	2(4)	-7(4)
C16B	29(5)	34(5)	39(6)	-8(4)	10(4)	-7(4)
C17B	30(5)	31(5)	42(6)	8(5)	2(4)	-4(4)
C18B	28(5)	44(5)	33(5)	1(4)	-6(4)	-7(4)
C19B	26(5)	37(5)	37(6)	4(4)	-2(4)	-9(4)
C20B	33(5)	35(5)	39(6)	2(4)	1(4)	-17(4)
C11B	32(5)	36(5)	42(5)	4(4)	0(4)	-18(4)
C8B	34(5)	39(5)	44(6)	-3(4)	7(4)	-8(4)
C9B	33(5)	33(5)	36(5)	8(4)	-7(4)	-16(4)
C10B	46(5)	46(6)	43(6)	-5(4)	-8(4)	-18(4)
C6B	40(5)	48(6)	51(6)	-14(5)	12(5)	-13(4)
C7B	56(6)	53(6)	79(7)	-16(5)	16(6)	-31(5)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 13170cw.

	x	y	z	U(eq)
H4A	262	210	462	117
H4A'	134	58	1288	117
H4A''	134	58	1288	117
H5A	-706	-137	1838	121
H5A'	-1112	-276	2795	121
H5A''	-1818	104	1834	121
H6A	15	1533	5808	86
H3AA	4215	3612	2582	76
H3AB	4936	3619	1518	76
H3AC	5224	2541	2385	76
H6AA	759	4935	934	53
H6AB	185	4154	1729	53
H7AA	673	5451	2649	81
H7AB	1951	5055	2268	81
H7AC	1434	4225	3066	81
H8AA	1330	3498	-398	60
H10A	-761	2861	-862	88
H10B	-83	1592	-987	88
H10C	437	2606	-1437	88
H12A	-1481	1514	591	63
H13A	-2608	3245	1144	99
H13B	-1599	3519	436	99
H13C	-1543	3440	1691	99
H14A	-2158	1683	2520	67
H16A	-982	1157	4394	58
H18A	1920	2086	4101	47
H4B	6855	4103	6490	63
H5B	8479	2377	6503	79

H6B	5109	813	3549	72
H3BA	1213	4570	5343	95
H3BB	1481	5645	4676	95
H3BC	837	5768	5780	95
H12B	7754	1889	8266	43
H13D	6134	1260	8968	73
H13E	7198	233	8790	73
H13F	6189	600	7961	73
H14B	8133	334	7030	48
H16B	7406	255	5032	41
H18B	4251	2257	4509	43
H8BA	3924	3888	8599	48
H10D	5501	4095	9414	66
H10E	6733	3791	8906	66
H10F	6229	2813	9483	66
H6BB	4107	1687	7558	55
H6BC	3067	2305	8237	55
H7BA	2511	1207	7106	89
H7BB	2901	1927	6110	89
H7BC	1863	2504	6817	89
H7A	-2713	-491	687	171
H7B	-3648	439	885	171

Table 6. Torsion angles [°] for 13170cw.

C19A-N1A-C1A-O1A	3.6(12)	N1A-C5A-C8A-O3A	-31.3(9)
C5A-N1A-C1A-O1A	177.4(8)	C6A-C5A-C8A-O3A	-160.0(7)
C19A-N1A-C1A-C2A	-175.4(7)	C4A-C5A-C8A-O3A	78.9(9)
C5A-N1A-C1A-C2A	-1.6(9)	N1A-C5A-C8A-C9A	44.6(11)
O1A-C1A-C2A-C3A	-49.5(11)	C6A-C5A-C8A-C9A	-84.0(10)
N1A-C1A-C2A-C3A	129.5(7)	C4A-C5A-C8A-C9A	154.8(8)
O1A-C1A-C2A-C4A	-173.9(8)	O3A-C8A-C9A-C11A	97.3(8)
N1A-C1A-C2A-C4A	5.2(8)	C5A-C8A-C9A-C11A	-5.4(13)
O1A-C1A-C2A-C11A	73.9(9)	O3A-C8A-C9A-C10A	-97.4(8)
N1A-C1A-C2A-C11A	-107.0(6)	C5A-C8A-C9A-C10A	159.9(8)
C3A-C2A-C4A-O2A	48.3(11)	C5A-C8A-C9A-O3A	-102.7(10)
C1A-C2A-C4A-O2A	172.5(8)	C8A-O3A-C9A-C11A	-116.6(9)
C11A-C2A-C4A-O2A	-75.5(10)	C8A-O3A-C9A-C10A	110.0(8)
C3A-C2A-C4A-C5A	-131.0(7)	C8A-C9A-C11A-O4A	-117.2(8)
C1A-C2A-C4A-C5A	-6.9(8)	C10A-C9A-C11A-O4A	77.4(8)
C11A-C2A-C4A-C5A	105.1(6)	O3A-C9A-C11A-O4A	-53.4(9)
C1A-N1A-C5A-C6A	-123.0(7)	C8A-C9A-C11A-C20A	0.9(12)
C19A-N1A-C5A-C6A	50.9(9)	C10A-C9A-C11A-C20A	-164.5(7)
C1A-N1A-C5A-C8A	110.2(7)	O3A-C9A-C11A-C20A	64.7(10)
C19A-N1A-C5A-C8A	-75.9(9)	C8A-C9A-C11A-C12A	128.2(9)
C1A-N1A-C5A-C4A	-2.7(9)	C10A-C9A-C11A-C12A	-37.2(10)
C19A-N1A-C5A-C4A	171.3(7)	O3A-C9A-C11A-C12A	-168.0(7)
O2A-C4A-C5A-N1A	-173.5(8)	C9A-C11A-C12A-C14A	-172.2(7)
C2A-C4A-C5A-N1A	5.9(8)	O4A-C11A-C12A-C14A	74.6(8)
O2A-C4A-C5A-C6A	-51.8(11)	C20A-C11A-C12A-C14A	-35.2(8)
C2A-C4A-C5A-C6A	127.6(7)	C9A-C11A-C12A-C13A	-56.6(11)
O2A-C4A-C5A-C8A	68.2(10)	O4A-C11A-C12A-C13A	-169.8(7)
C2A-C4A-C5A-C8A	-112.4(7)	C20A-C11A-C12A-C13A	80.3(9)
N1A-C5A-C6A-C7A	55.7(9)	C13A-C12A-C14A-O5A	157.5(7)
C8A-C5A-C6A-C7A	-176.0(7)	C11A-C12A-C14A-O5A	-85.6(8)
C4A-C5A-C6A-C7A	-58.6(10)	C13A-C12A-C14A-C15A	-84.8(8)
C9A-O3A-C8A-C5A	122.5(8)	C11A-C12A-C14A-C15A	32.1(8)

O5A-C14A-C15A-C16A	-78.5(11)	O1B-C1B-C2B-C3B	48.0(12)
C12A-C14A-C15A-C16A	164.0(8)	N1B-C1B-C2B-C3B	-130.5(8)
O5A-C14A-C15A-C20A	100.5(8)	O1B-C1B-C2B-C4B	172.3(8)
C12A-C14A-C15A-C20A	-16.9(9)	N1B-C1B-C2B-C4B	-6.2(9)
C20A-C15A-C16A-C17A	2.0(12)	O1B-C1B-C2B-C11B	-74.0(10)
C14A-C15A-C16A-C17A	-179.0(8)	N1B-C1B-C2B-C11B	107.5(7)
C15A-C16A-C17A-O6A	-178.7(7)	C3B-C2B-C4B-O2B	-43.8(12)
C15A-C16A-C17A-C18A	1.2(12)	C1B-C2B-C4B-O2B	-168.7(8)
O6A-C17A-C18A-C19A	177.6(7)	C11B-C2B-C4B-O2B	78.8(9)
C16A-C17A-C18A-C19A	-2.3(12)	C3B-C2B-C4B-C5B	134.7(7)
C17A-C18A-C19A-C20A	0.1(11)	C1B-C2B-C4B-C5B	9.9(9)
C17A-C18A-C19A-N1A	178.2(7)	C11B-C2B-C4B-C5B	-102.7(6)
C1A-N1A-C19A-C20A	-137.5(8)	C1B-N1B-C5B-C8B	-107.7(8)
C5A-N1A-C19A-C20A	49.0(10)	C19B-N1B-C5B-C8B	74.7(9)
C1A-N1A-C19A-C18A	44.5(10)	C1B-N1B-C5B-C6B	125.1(7)
C5A-N1A-C19A-C18A	-129.0(8)	C19B-N1B-C5B-C6B	-52.5(9)
C18A-C19A-C20A-C15A	3.0(11)	C1B-N1B-C5B-C4B	5.8(8)
N1A-C19A-C20A-C15A	-175.0(7)	C19B-N1B-C5B-C4B	-171.8(7)
C18A-C19A-C20A-C11A	-173.4(8)	O2B-C4B-C5B-N1B	169.0(7)
N1A-C19A-C20A-C11A	8.6(13)	C2B-C4B-C5B-N1B	-9.6(8)
C16A-C15A-C20A-C19A	-4.1(12)	O2B-C4B-C5B-C8B	-72.3(10)
C14A-C15A-C20A-C19A	176.8(7)	C2B-C4B-C5B-C8B	109.1(7)
C16A-C15A-C20A-C11A	173.2(7)	O2B-C4B-C5B-C6B	49.0(11)
C14A-C15A-C20A-C11A	-5.9(9)	C2B-C4B-C5B-C6B	-129.6(7)
C9A-C11A-C20A-C19A	-23.8(13)	C13B-C12B-C14B-O5B	-157.6(6)
O4A-C11A-C20A-C19A	92.8(10)	C11B-C12B-C14B-O5B	82.3(7)
C12A-C11A-C20A-C19A	-157.6(9)	C13B-C12B-C14B-C15B	81.8(7)
C9A-C11A-C20A-C15A	159.5(7)	C11B-C12B-C14B-C15B	-38.4(7)
O4A-C11A-C20A-C15A	-83.8(8)	O5B-C14B-C15B-C16B	84.2(10)
C12A-C11A-C20A-C15A	25.7(8)	C12B-C14B-C15B-C16B	-156.4(7)
C19B-N1B-C1B-O1B	-0.7(13)	O5B-C14B-C15B-C20B	-97.7(7)
C5B-N1B-C1B-O1B	-178.2(8)	C12B-C14B-C15B-C20B	21.7(8)
C19B-N1B-C1B-C2B	177.7(7)	C20B-C15B-C16B-C17B	-1.6(11)
C5B-N1B-C1B-C2B	0.3(9)	C14B-C15B-C16B-C17B	176.3(7)

C15B-C16B-C17B-O6B	-179.5(7)	C13B-C12B-C11B-C20B	-77.2(7)
C15B-C16B-C17B-C18B	-0.2(11)	C14B-C12B-C11B-C20B	40.6(7)
O6B-C17B-C18B-C19B	-179.5(7)	C9B-O3B-C8B-C5B	-122.0(7)
C16B-C17B-C18B-C19B	1.2(11)	N1B-C5B-C8B-O3B	31.0(9)
C17B-C18B-C19B-C20B	-0.4(11)	C6B-C5B-C8B-O3B	159.0(6)
C17B-C18B-C19B-N1B	-176.6(7)	C4B-C5B-C8B-O3B	-79.1(8)
C1B-N1B-C19B-C20B	131.6(8)	N1B-C5B-C8B-C9B	-41.2(11)
C5B-N1B-C19B-C20B	-51.1(10)	C6B-C5B-C8B-C9B	86.8(9)
C1B-N1B-C19B-C18B	-52.4(11)	C4B-C5B-C8B-C9B	-151.3(8)
C5B-N1B-C19B-C18B	125.0(8)	C8B-O3B-C9B-C10B	-111.6(7)
C18B-C19B-C20B-C15B	-1.4(11)	C8B-O3B-C9B-C11B	118.0(8)
N1B-C19B-C20B-C15B	174.7(7)	C5B-C8B-C9B-O3B	101.4(9)
C18B-C19B-C20B-C11B	178.5(7)	O3B-C8B-C9B-C10B	97.2(7)
N1B-C19B-C20B-C11B	-5.5(13)	C5B-C8B-C9B-C10B	-161.4(8)
C16B-C15B-C20B-C19B	2.4(11)	O3B-C8B-C9B-C11B	-98.4(8)
C14B-C15B-C20B-C19B	-175.9(7)	C5B-C8B-C9B-C11B	3.0(13)
C16B-C15B-C20B-C11B	-177.5(7)	O4B-C11B-C9B-O3B	55.9(8)
C14B-C15B-C20B-C11B	4.3(8)	C20B-C11B-C9B-O3B	-67.0(9)
C19B-C20B-C11B-O4B	-99.0(9)	C12B-C11B-C9B-O3B	169.7(6)
C15B-C20B-C11B-O4B	80.9(7)	O4B-C11B-C9B-C8B	122.9(8)
C19B-C20B-C11B-C9B	22.0(12)	C20B-C11B-C9B-C8B	-0.1(11)
C15B-C20B-C11B-C9B	-158.1(7)	C12B-C11B-C9B-C8B	-123.3(8)
C19B-C20B-C11B-C12B	151.7(8)	O4B-C11B-C9B-C10B	-72.2(8)
C15B-C20B-C11B-C12B	-28.5(7)	C20B-C11B-C9B-C10B	164.9(7)
C13B-C12B-C11B-O4B	170.2(6)	C12B-C11B-C9B-C10B	41.6(9)
C14B-C12B-C11B-O4B	-72.0(7)	N1B-C5B-C6B-C7B	-56.9(8)
C13B-C12B-C11B-C9B	56.3(9)	C8B-C5B-C6B-C7B	174.6(6)
C14B-C12B-C11B-C9B	174.1(6)	C4B-C5B-C6B-C7B	56.0(9)

Table 7. Hydrogen bonds and close contacts for 13170cw [$\text{\AA}$ and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O4A-H4A"...O5A	0.85	2.06	2.795(9)	145.1
O4A-H4A...O4A#1	0.85	2.42	3.274(14)	179.9
O5A-H5A...O4A	0.85	2.11	2.795(9)	137.9
O5A-H5A"...O7	0.85	1.81	2.66(4)	179.2
O5A-H5A'...O6A#2	0.85	2.49	3.344(9)	179.8
O6A-H6A...O5B#3	0.85	1.79	2.640(7)	179.8
O4B-H4B...O1B#4	0.85	1.96	2.809(8)	179.4
O5B-H5B...O4B	0.85	1.98	2.675(7)	137.8
O6B-H6B...O1A	0.85	1.91	2.760(8)	179.4
O7-H7A...O3A#1	0.85	2.06	2.90(4)	170.9
O7-H7B...Cl1A#3	0.85	2.40	3.24(4)	171.2

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 -x,-y,-z+1 #3 x-1,y,z #4 -x+1,-y+1,-z+1

For Compound **209**

REFERENCE NUMBER: fropc06

CRYSTAL STRUCTURE REPORT

$C_{27}H_{39}NO_4Si$

Report prepared for:

P. Carlsen, Prof. A. Frontier

November 12, 2013

William W. Brennessel

X-ray Crystallographic Facility

Department of Chemistry, University of Rochester

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Data collection

A crystal (0.20 x 0.16 x 0.12 mm³) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD platform diffractometer for a data collection at 100.0(5) K.¹ A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK α radiation (graphite monochromator) with a frame time of 60 seconds and a detector distance of 4.01 cm. A randomly oriented region of reciprocal space was surveyed: four major sections of frames were collected with 0.50° steps in ω at four different ϕ settings and a detector position of -38° in 2θ . The intensity data were corrected for absorption.² Final cell constants were calculated from the xyz centroids of 4021 strong reflections from the actual data collection after integration.³ See Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR2011⁴ and refined using SHELXL-2013.⁵ The space group $P2_1/c$ was determined based on systematic absences. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydroxide hydrogen atom H3 was found from the difference Fourier map and refined freely. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0548$ (F^2 , $I > 2\sigma(I)$) and $wR2 = 0.1493$ (F^2 , all data).

Structure description

The structure is the one suggested. There is one molecule in the asymmetric unit in a general position. Pairs of molecules are linked via hydrogen bonding (see diagram and Table 7).

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

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- ¹ *APEX2*, version 2013.2-0; Bruker AXS: Madison, WI, 2013.
- ² Sheldrick, G. M. *SADABS*, version 2012/1; University of Göttingen: Göttingen, Germany, 2012.
- ³ *SAINT*, version 8.27B; Bruker AXS: Madison, WI, 2013.
- ⁴ Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Casciaro, G. L.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; Spagna, R. *SIR2011: a new package for crystal structure determination and refinement*, version 1.0; Istituto di Cristallografia: Bari, Italy, 2012.
- ⁵ Sheldrick, G. M. *SHELXL-2013/4*; University of Göttingen: Göttingen, Germany, 2013.

Some equations of interest:

$$R_{\text{int}} = \Sigma |F_o^2 - \langle F_o^2 \rangle| / \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$$

where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] / (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

Table 1. Crystal data and structure refinement for fropc06.

Identification code	fropc06	
Empirical formula	C ₂₇ H ₃₉ N O ₄ Si	
Formula weight	469.6	
Temperature	100.0(5) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>P</i> ₂ ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 10.5328(12) Å	$\alpha = 90^\circ$
	<i>b</i> = 16.1589(19) Å	$\beta = 96.854(3)^\circ$
	<i>c</i> = 14.9460(17) Å	$\gamma = 90^\circ$
Volume	2525.6(5) Å ³	
<i>Z</i>	4	
Density (calculated)	1.235 Mg/m ³	
Absorption coefficient	0.126 mm ⁻¹	
<i>F</i> (000)	1016	
Crystal color, morphology	colorless, block	
Crystal size	0.20 x 0.16 x 0.12 mm ³	
Theta range for data collection	1.863 to 35.015°	
Index ranges	$-16 \leq h \leq 16, -25 \leq k \leq 26, -24 \leq l \leq 24$	
Reflections collected	53186	
Independent reflections	11059 [<i>R</i> (int) = 0.0778]	
Observed reflections	7161	
Completeness to theta = 34.970°	99.7%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7469 and 0.6502	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	11059 / 0 / 312	
Goodness-of-fit on <i>F</i> ²	1.016	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0548, <i>wR</i> 2 = 0.1280	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0950, <i>wR</i> 2 = 0.1493	
Largest diff. peak and hole	0.541 and -0.343 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc06. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Si1	4509(1)	1990(1)	-220(1)	18(1)
O1	-665(1)	-1646(1)	3631(1)	24(1)
O2	2964(1)	-136(1)	4946(1)	20(1)
O3	6409(1)	560(1)	3307(1)	23(1)
O4	3510(1)	1803(1)	534(1)	17(1)
N1	2107(1)	-430(1)	3476(1)	16(1)
C1	2158(1)	-481(1)	4400(1)	17(1)
C2	1084(1)	-994(1)	4625(1)	20(1)
C3	413(1)	-1204(1)	3840(1)	19(1)
C4	959(1)	-848(1)	3033(1)	17(1)
C5	-7(1)	-228(1)	2609(1)	19(1)
C6	165(1)	326(1)	1974(1)	19(1)
C7	1378(1)	351(1)	1520(1)	16(1)
C8	1582(1)	1107(1)	914(1)	17(1)
C9	3004(1)	1038(1)	798(1)	16(1)
C10	3580(1)	728(1)	1707(1)	15(1)
C11	4830(1)	817(1)	2094(1)	16(1)
C12	5166(1)	471(1)	2942(1)	17(1)
C13	4272(1)	56(1)	3388(1)	16(1)
C14	2998(1)	-12(1)	2995(1)	15(1)
C15	2649(1)	322(1)	2134(1)	15(1)
C16	913(2)	-1211(1)	5579(1)	32(1)
C17	-1612(2)	-1617(1)	4246(1)	26(1)
C18	1290(1)	-1543(1)	2396(1)	20(1)
C19	2263(2)	-2152(1)	2841(1)	26(1)
C20	-908(2)	912(1)	1680(1)	31(1)
C21	734(1)	1150(1)	16(1)	24(1)
C22	5896(2)	1263(1)	-58(1)	33(1)
C23	5040(2)	3069(1)	33(1)	29(1)

C24	3724(1)	1907(1)	-1420(1)	20(1)
C25	3160(2)	1042(1)	-1630(1)	26(1)
C26	2677(2)	2566(1)	-1620(1)	25(1)
C27	4760(2)	2054(1)	-2048(1)	29(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for fropec06.

Si(1)-O(4)	1.6584(10)	C(10)-C(15)	1.3960(17)
Si(1)-C(23)	1.8556(16)	C(11)-C(12)	1.3918(17)
Si(1)-C(22)	1.8685(16)	C(11)-H(11)	0.9500
Si(1)-C(24)	1.8880(14)	C(12)-C(13)	1.3888(18)
O(1)-C(3)	1.3457(16)	C(13)-C(14)	1.4035(18)
O(1)-C(17)	1.4354(17)	C(13)-H(13)	0.9500
O(2)-C(1)	1.2376(15)	C(14)-C(15)	1.4037(17)
O(3)-C(12)	1.3644(16)	C(16)-H(16A)	0.9800
O(3)-H(3)	0.87(2)	C(16)-H(16B)	0.9800
O(4)-C(9)	1.4203(15)	C(16)-H(16C)	0.9800
N(1)-C(1)	1.3776(16)	C(17)-H(17A)	0.9800
N(1)-C(14)	1.4196(16)	C(17)-H(17B)	0.9800
N(1)-C(4)	1.4721(16)	C(17)-H(17C)	0.9800
C(1)-C(2)	1.4738(19)	C(18)-C(19)	1.516(2)
C(2)-C(3)	1.3392(18)	C(18)-H(18A)	0.9900
C(2)-C(16)	1.4998(19)	C(18)-H(18B)	0.9900
C(3)-C(4)	1.5104(18)	C(19)-H(19A)	0.9800
C(4)-C(5)	1.5122(19)	C(19)-H(19B)	0.9800
C(4)-C(18)	1.5386(18)	C(19)-H(19C)	0.9800
C(5)-C(6)	1.3328(19)	C(20)-H(20A)	0.9800
C(5)-H(5)	0.9500	C(20)-H(20B)	0.9800
C(6)-C(20)	1.500(2)	C(20)-H(20C)	0.9800
C(6)-C(7)	1.5181(18)	C(21)-H(21A)	0.9800
C(7)-C(15)	1.5303(17)	C(21)-H(21B)	0.9800
C(7)-C(8)	1.5506(18)	C(21)-H(21C)	0.9800
C(7)-H(7)	1.0000	C(22)-H(22A)	0.9800
C(8)-C(21)	1.5220(18)	C(22)-H(22B)	0.9800
C(8)-C(9)	1.5332(18)	C(22)-H(22C)	0.9800
C(8)-H(8)	1.0000	C(23)-H(23A)	0.9800
C(9)-C(10)	1.5066(17)	C(23)-H(23B)	0.9800
C(9)-H(9)	1.0000	C(23)-H(23C)	0.9800
C(10)-C(11)	1.3810(18)	C(24)-C(26)	1.536(2)

C(24)-C(25)	1.537(2)	C(3)-C(4)-C(5)	106.62(11)
C(24)-C(27)	1.541(2)	N(1)-C(4)-C(18)	112.26(11)
C(25)-H(25A)	0.9800	C(3)-C(4)-C(18)	110.59(11)
C(25)-H(25B)	0.9800	C(5)-C(4)-C(18)	114.52(11)
C(25)-H(25C)	0.9800	C(6)-C(5)-C(4)	127.03(12)
C(26)-H(26A)	0.9800	C(6)-C(5)-H(5)	116.5
C(26)-H(26B)	0.9800	C(4)-C(5)-H(5)	116.5
C(26)-H(26C)	0.9800	C(5)-C(6)-C(20)	118.15(13)
C(27)-H(27A)	0.9800	C(5)-C(6)-C(7)	121.96(12)
C(27)-H(27B)	0.9800	C(20)-C(6)-C(7)	119.83(12)
C(27)-H(27C)	0.9800	C(6)-C(7)-C(15)	116.96(10)
O(4)-Si(1)-C(23)	103.51(6)	C(6)-C(7)-C(8)	117.66(11)
O(4)-Si(1)-C(22)	110.30(6)	C(15)-C(7)-C(8)	101.70(10)
C(23)-Si(1)-C(22)	110.66(9)	C(6)-C(7)-H(7)	106.6
O(4)-Si(1)-C(24)	113.01(6)	C(15)-C(7)-H(7)	106.6
C(23)-Si(1)-C(24)	110.33(7)	C(8)-C(7)-H(7)	106.6
C(22)-Si(1)-C(24)	108.95(7)	C(21)-C(8)-C(9)	112.42(11)
C(3)-O(1)-C(17)	117.74(11)	C(21)-C(8)-C(7)	116.30(11)
C(12)-O(3)-H(3)	110.2(14)	C(9)-C(8)-C(7)	102.32(10)
C(9)-O(4)-Si(1)	129.55(8)	C(21)-C(8)-H(8)	108.5
C(1)-N(1)-C(14)	125.98(11)	C(9)-C(8)-H(8)	108.5
C(1)-N(1)-C(4)	110.79(10)	C(7)-C(8)-H(8)	108.5
C(14)-N(1)-C(4)	123.20(10)	O(4)-C(9)-C(10)	114.56(10)
O(2)-C(1)-N(1)	125.18(12)	O(4)-C(9)-C(8)	111.84(10)
O(2)-C(1)-C(2)	125.97(11)	C(10)-C(9)-C(8)	102.46(10)
N(1)-C(1)-C(2)	108.84(11)	O(4)-C(9)-H(9)	109.2
C(3)-C(2)-C(1)	106.41(11)	C(10)-C(9)-H(9)	109.2
C(3)-C(2)-C(16)	131.52(13)	C(8)-C(9)-H(9)	109.2
C(1)-C(2)-C(16)	122.05(12)	C(11)-C(10)-C(15)	122.98(11)
C(2)-C(3)-O(1)	132.87(12)	C(11)-C(10)-C(9)	127.19(11)
C(2)-C(3)-C(4)	113.02(12)	C(15)-C(10)-C(9)	109.83(11)
O(1)-C(3)-C(4)	114.07(11)	C(10)-C(11)-C(12)	117.78(12)
N(1)-C(4)-C(3)	100.76(10)	C(10)-C(11)-H(11)	121.1
N(1)-C(4)-C(5)	111.07(11)	C(12)-C(11)-H(11)	121.1

O(3)-C(12)-C(13)	122.18(11)	H(19A)-C(19)-H(19C)	109.5
O(3)-C(12)-C(11)	116.71(11)	H(19B)-C(19)-H(19C)	109.5
C(13)-C(12)-C(11)	121.12(12)	C(6)-C(20)-H(20A)	109.5
C(12)-C(13)-C(14)	120.45(11)	C(6)-C(20)-H(20B)	109.5
C(12)-C(13)-H(13)	119.8	H(20A)-C(20)-H(20B)	109.5
C(14)-C(13)-H(13)	119.8	C(6)-C(20)-H(20C)	109.5
C(13)-C(14)-C(15)	119.10(11)	H(20A)-C(20)-H(20C)	109.5
C(13)-C(14)-N(1)	118.85(11)	H(20B)-C(20)-H(20C)	109.5
C(15)-C(14)-N(1)	122.05(11)	C(8)-C(21)-H(21A)	109.5
C(10)-C(15)-C(14)	118.54(11)	C(8)-C(21)-H(21B)	109.5
C(10)-C(15)-C(7)	108.86(10)	H(21A)-C(21)-H(21B)	109.5
C(14)-C(15)-C(7)	132.59(11)	C(8)-C(21)-H(21C)	109.5
C(2)-C(16)-H(16A)	109.5	H(21A)-C(21)-H(21C)	109.5
C(2)-C(16)-H(16B)	109.5	H(21B)-C(21)-H(21C)	109.5
H(16A)-C(16)-H(16B)	109.5	Si(1)-C(22)-H(22A)	109.5
C(2)-C(16)-H(16C)	109.5	Si(1)-C(22)-H(22B)	109.5
H(16A)-C(16)-H(16C)	109.5	H(22A)-C(22)-H(22B)	109.5
H(16B)-C(16)-H(16C)	109.5	Si(1)-C(22)-H(22C)	109.5
O(1)-C(17)-H(17A)	109.5	H(22A)-C(22)-H(22C)	109.5
O(1)-C(17)-H(17B)	109.5	H(22B)-C(22)-H(22C)	109.5
H(17A)-C(17)-H(17B)	109.5	Si(1)-C(23)-H(23A)	109.5
O(1)-C(17)-H(17C)	109.5	Si(1)-C(23)-H(23B)	109.5
H(17A)-C(17)-H(17C)	109.5	H(23A)-C(23)-H(23B)	109.5
H(17B)-C(17)-H(17C)	109.5	Si(1)-C(23)-H(23C)	109.5
C(19)-C(18)-C(4)	113.21(11)	H(23A)-C(23)-H(23C)	109.5
C(19)-C(18)-H(18A)	108.9	H(23B)-C(23)-H(23C)	109.5
C(4)-C(18)-H(18A)	108.9	C(26)-C(24)-C(25)	109.79(12)
C(19)-C(18)-H(18B)	108.9	C(26)-C(24)-C(27)	108.59(12)
C(4)-C(18)-H(18B)	108.9	C(25)-C(24)-C(27)	107.48(12)
H(18A)-C(18)-H(18B)	107.7	C(26)-C(24)-Si(1)	111.03(9)
C(18)-C(19)-H(19A)	109.5	C(25)-C(24)-Si(1)	111.97(10)
C(18)-C(19)-H(19B)	109.5	C(27)-C(24)-Si(1)	107.85(10)
H(19A)-C(19)-H(19B)	109.5	C(24)-C(25)-H(25A)	109.5
C(18)-C(19)-H(19C)	109.5	C(24)-C(25)-H(25B)	109.5

H(25A)-C(25)-H(25B)	109.5	H(26A)-C(26)-H(26C)	109.5
C(24)-C(25)-H(25C)	109.5	H(26B)-C(26)-H(26C)	109.5
H(25A)-C(25)-H(25C)	109.5	C(24)-C(27)-H(27A)	109.5
H(25B)-C(25)-H(25C)	109.5	C(24)-C(27)-H(27B)	109.5
C(24)-C(26)-H(26A)	109.5	H(27A)-C(27)-H(27B)	109.5
C(24)-C(26)-H(26B)	109.5	C(24)-C(27)-H(27C)	109.5
H(26A)-C(26)-H(26B)	109.5	H(27A)-C(27)-H(27C)	109.5
C(24)-C(26)-H(26C)	109.5	H(27B)-C(27)-H(27C)	109.5

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc06. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	17(1)	21(1)	15(1)	3(1)	1(1)	-1(1)
O1	21(1)	33(1)	20(1)	-5(1)	5(1)	-12(1)
O2	20(1)	25(1)	13(1)	-1(1)	-2(1)	-3(1)
O3	16(1)	36(1)	15(1)	4(1)	-3(1)	-5(1)
O4	20(1)	18(1)	15(1)	2(1)	2(1)	0(1)
N1	16(1)	21(1)	11(1)	1(1)	0(1)	-4(1)
C1	17(1)	20(1)	13(1)	0(1)	1(1)	-1(1)
C2	21(1)	26(1)	14(1)	1(1)	3(1)	-5(1)
C3	18(1)	24(1)	16(1)	0(1)	3(1)	-4(1)
C4	16(1)	22(1)	12(1)	-1(1)	0(1)	-5(1)
C5	14(1)	27(1)	15(1)	-1(1)	0(1)	-2(1)
C6	16(1)	25(1)	15(1)	-1(1)	-1(1)	0(1)
C7	15(1)	20(1)	13(1)	1(1)	-1(1)	-1(1)
C8	16(1)	21(1)	13(1)	1(1)	-1(1)	0(1)
C9	17(1)	17(1)	12(1)	0(1)	0(1)	-1(1)
C10	16(1)	16(1)	12(1)	0(1)	0(1)	0(1)
C11	16(1)	20(1)	12(1)	1(1)	1(1)	-2(1)
C12	14(1)	22(1)	14(1)	-1(1)	-2(1)	-1(1)
C13	18(1)	18(1)	12(1)	1(1)	-1(1)	-1(1)
C14	17(1)	16(1)	13(1)	0(1)	2(1)	-2(1)
C15	14(1)	17(1)	12(1)	-1(1)	-1(1)	-1(1)
C16	30(1)	51(1)	15(1)	2(1)	2(1)	-13(1)
C17	22(1)	33(1)	24(1)	-2(1)	7(1)	-7(1)
C18	22(1)	22(1)	16(1)	-3(1)	2(1)	-5(1)
C19	29(1)	22(1)	27(1)	1(1)	7(1)	-1(1)
C20	21(1)	40(1)	33(1)	10(1)	8(1)	8(1)
C21	19(1)	34(1)	17(1)	7(1)	-3(1)	-2(1)
C22	26(1)	45(1)	30(1)	11(1)	7(1)	12(1)
C23	34(1)	29(1)	23(1)	1(1)	-1(1)	-12(1)

C24	21(1)	24(1)	15(1)	0(1)	2(1)	-1(1)
C25	30(1)	27(1)	22(1)	-6(1)	2(1)	-3(1)
C26	27(1)	28(1)	19(1)	5(1)	-1(1)	3(1)
C27	31(1)	37(1)	19(1)	3(1)	8(1)	-1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropec06.

	x	y	z	U(eq)
H3	6510(20)	376(13)	3859(15)	36(5)
H5	-824	-234	2818	23
H7	1359	-149	1123	19
H8	1450	1623	1261	20
H9	3118	609	331	19
H11	5440	1104	1792	19
H13	4525	-183	3962	20
H16A	643	-1790	5608	47
H16B	260	-851	5788	47
H16C	1725	-1134	5964	47
H17A	-2419	-1844	3953	39
H17B	-1742	-1042	4422	39
H17C	-1320	-1945	4783	39
H18A	498	-1846	2174	24
H18B	1630	-1292	1869	24
H19A	2382	-2603	2420	39
H19B	1957	-2379	3384	39
H19C	3080	-1868	3005	39
H20A	-1571	862	2084	46
H20B	-1274	778	1063	46
H20C	-582	1481	1700	46
H21A	1051	1582	-360	36
H21B	-145	1279	121	36
H21C	750	615	-292	36
H22A	6403	1374	522	50
H22B	6431	1340	-545	50
H22C	5582	691	-67	50
H23A	5396	3111	668	43

H23B	4309	3444	-85	43
H23C	5697	3221	-350	43
H25A	2873	999	-2277	39
H25B	2432	954	-1290	39
H25C	3815	622	-1459	39
H26A	2266	2498	-2240	38
H26B	3059	3118	-1548	38
H26C	2037	2500	-1200	38
H27A	4357	2103	-2671	43
H27B	5359	1588	-2000	43
H27C	5224	2566	-1872	43

Table 6. Torsion angles [°] for fropec06.

C23-Si1-O4-C9	-165.65(11)	C4-C5-C6-C20	-177.07(13)
C22-Si1-O4-C9	-47.24(13)	C4-C5-C6-C7	5.7(2)
C24-Si1-O4-C9	74.99(12)	C5-C6-C7-C15	-48.13(18)
C14-N1-C1-O2	3.4(2)	C20-C6-C7-C15	134.72(14)
C4-N1-C1-O2	-174.63(13)	C5-C6-C7-C8	-169.69(12)
C14-N1-C1-C2	-177.84(12)	C20-C6-C7-C8	13.15(18)
C4-N1-C1-C2	4.16(15)	C6-C7-C8-C21	-71.93(15)
O2-C1-C2-C3	176.62(14)	C15-C7-C8-C21	158.93(11)
N1-C1-C2-C3	-2.15(16)	C6-C7-C8-C9	165.16(11)
O2-C1-C2-C16	-4.8(2)	C15-C7-C8-C9	36.02(12)
N1-C1-C2-C16	176.40(14)	Si1-O4-C9-C10	105.64(12)
C1-C2-C3-O1	-178.25(15)	Si1-O4-C9-C8	-138.33(10)
C16-C2-C3-O1	3.4(3)	C21-C8-C9-O4	74.77(14)
C1-C2-C3-C4	-0.64(17)	C7-C8-C9-O4	-159.74(9)
C16-C2-C3-C4	-179.00(16)	C21-C8-C9-C10	-162.06(11)
C17-O1-C3-C2	31.7(2)	C7-C8-C9-C10	-36.57(12)
C17-O1-C3-C4	-145.87(13)	O4-C9-C10-C11	-34.61(18)
C1-N1-C4-C3	-4.21(14)	C8-C9-C10-C11	-155.93(13)
C14-N1-C4-C3	177.71(11)	O4-C9-C10-C15	145.10(11)
C1-N1-C4-C5	108.44(12)	C8-C9-C10-C15	23.78(13)
C14-N1-C4-C5	-69.63(15)	C15-C10-C11-C12	1.11(19)
C1-N1-C4-C18	-121.90(12)	C9-C10-C11-C12	-179.21(12)
C14-N1-C4-C18	60.03(15)	C10-C11-C12-O3	179.39(12)
C2-C3-C4-N1	2.92(15)	C10-C11-C12-C13	-0.54(19)
O1-C3-C4-N1	-179.00(11)	O3-C12-C13-C14	179.09(12)
C2-C3-C4-C5	-113.10(13)	C11-C12-C13-C14	-1.0(2)
O1-C3-C4-C5	64.99(15)	C12-C13-C14-C15	1.94(19)
C2-C3-C4-C18	121.82(13)	C12-C13-C14-N1	-179.05(11)
O1-C3-C4-C18	-60.10(15)	C1-N1-C14-C13	29.20(19)
N1-C4-C5-C6	59.45(17)	C4-N1-C14-C13	-153.03(12)
C3-C4-C5-C6	168.34(13)	C1-N1-C14-C15	-151.82(13)
C18-C4-C5-C6	-69.00(18)	C4-N1-C14-C15	25.95(18)

C11-C10-C15-C14	-0.15(19)	N1-C4-C18-C19	51.97(15)
C9-C10-C15-C14	-179.88(11)	C3-C4-C18-C19	-59.71(15)
C11-C10-C15-C7	179.18(12)	C5-C4-C18-C19	179.82(11)
C9-C10-C15-C7	-0.55(14)	O4-Si1-C24-C26	63.71(11)
C13-C14-C15-C10	-1.38(18)	C23-Si1-C24-C26	-51.63(12)
N1-C14-C15-C10	179.64(11)	C22-Si1-C24-C26	-173.31(10)
C13-C14-C15-C7	179.48(13)	O4-Si1-C24-C25	-59.40(11)
N1-C14-C15-C7	0.5(2)	C23-Si1-C24-C25	-174.74(11)
C6-C7-C15-C10	-152.15(11)	C22-Si1-C24-C25	63.58(12)
C8-C7-C15-C10	-22.57(13)	O4-Si1-C24-C27	-177.44(9)
C6-C7-C15-C14	27.1(2)	C23-Si1-C24-C27	67.22(12)
C8-C7-C15-C14	156.64(13)	C22-Si1-C24-C27	-54.46(12)

Table 7. Hydrogen bonds and close contacts for fropec06 [$\text{\AA}$ and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O3-H3...O2#1	0.87(2)	1.85(2)	2.7032(14)	167(2)
C13-H13...O2	0.95	2.33	2.8622(16)	114.5
C17-H17B...O2#2	0.98	2.54	3.4524(19)	154.6

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y, -z+1$ #2 $-x, -y, -z+1$

For Compound **192**

REFERENCE NUMBER: fropc07

CRYSTAL STRUCTURE REPORT

$C_{27}H_{39}NO_5Si$

Report prepared for:

P. Carlsen, Prof. A. Frontier

March 01, 2014

William W. Brennessel

X-ray Crystallographic Facility

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120 Trustee Road

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Data collection

A crystal (0.50 x 0.14 x 0.08 mm³) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD platform diffractometer for a data collection at 100.0(5) K.¹ A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK α radiation (graphite monochromator) with a frame time of 90 seconds and a detector distance of 4.99 cm. A randomly oriented region of reciprocal space was surveyed: five major sections of frames were collected with 0.50° steps in ω at five different ϕ settings and a detector position of -33° in 2θ . The intensity data were corrected for absorption.² Final cell constants were calculated from the xyz centroids of 4058 strong reflections from the actual data collection after integration.³ See Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR2011⁴ and refined using SHELXL-2014.⁵ The space group $P2_1/c$ was determined based on systematic absences. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

The refinement stalled at $R1 = 0.178$, at which point twin modeling was required. After the non-merohedral twin law, $[-1\ 0\ 0 / 0\ -1\ 0 / 0.405\ 0\ 1]$, a 180° rotation about reciprocal lattice $[0\ 0\ 1]$, was determined,⁶ the data were re-integrated,³ and a new absorption correction was applied.⁷ There were 3843 unique reflections solely in the first component, 3806 unique reflections solely in the second component, and 2575 unique overlapping reflections. The mass ratio of the two components refined to 54:46. The final full matrix least squares refinement converged to $R1 = 0.0739$ (F^2 , $I > 2\sigma(I)$) and $wR2 = 0.1740$ (F^2 , all data).

Structure description

The structure is the one suggested. There is one molecule in the asymmetric unit in a general position. Molecules are linked pairwise via hydrogen bonding (see diagram and Table 7).

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

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- ⁷ Sheldrick, G. M. *TWINABS*, version 2012/1; University of Göttingen: Göttingen, Germany, 2012.

Some equations of interest:

$$R_{\text{int}} = \Sigma |F_o^2 - \langle F_o^2 \rangle| / \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$$

where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] / (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

Table 1. Crystal data and structure refinement for fropc07.

Identification code	fropc07	
Empirical formula	C ₂₇ H ₃₉ N O ₅ Si	
Formula weight	485.68	
Temperature	100.0(5) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 7.048(3) Å	$\alpha = 90^\circ$
	<i>b</i> = 30.602(12) Å	$\beta = 96.372(5)^\circ$
	<i>c</i> = 12.897(5) Å	$\gamma = 90^\circ$
Volume	2764.2(18) Å ³	
<i>Z</i>	4	
Density (calculated)	1.167 Mg/m ³	
Absorption coefficient	0.120 mm ⁻¹	
<i>F</i> (000)	1048	
Crystal color, morphology	colorless, needle	
Crystal size	0.50 x 0.14 x 0.08 mm ³	
Theta range for data collection	3.944 to 25.082°	
Index ranges	-8 ≤ <i>h</i> ≤ 8, 0 ≤ <i>k</i> ≤ 36, 0 ≤ <i>l</i> ≤ 15	
Reflections collected	52092	
Independent reflections	4860 [<i>R</i> (int) = 0.1302]	
Observed reflections	3629	
Completeness to theta = 25.028°	99.3%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7452 and 0.5400	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	4860 / 0 / 322	
Goodness-of-fit on <i>F</i> ²	1.098	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0739, <i>wR</i> 2 = 0.1612	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1039, <i>wR</i> 2 = 0.1740	
Largest diff. peak and hole	0.300 and -0.345 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc07. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Si1	6117(2)	3121(1)	912(1)	30(1)
O1	2897(4)	5130(1)	5473(2)	24(1)
O2	376(4)	6037(1)	2652(2)	27(1)
O3	4246(4)	3394(1)	1250(2)	27(1)
O4	3145(4)	3628(1)	5090(2)	29(1)
O5	5571(4)	4667(1)	2517(2)	24(1)
N1	2665(5)	5066(1)	3669(2)	20(1)
C1	2453(6)	5285(1)	4597(3)	21(1)
C2	1622(6)	5718(1)	4364(3)	23(1)
C3	1180(6)	5736(1)	3325(3)	24(1)
C4	1942(6)	5346(1)	2763(3)	23(1)
C5	363(7)	5110(1)	2088(3)	25(1)
C6	569(6)	4751(1)	1522(3)	22(1)
C7	2514(6)	4531(1)	1485(3)	22(1)
C8	2515(6)	4085(1)	914(3)	26(1)
C9	4268(6)	3848(1)	1458(3)	24(1)
C10	4068(6)	3966(1)	2576(3)	23(1)
C11	3867(6)	3697(1)	3352(3)	24(1)
C12	3275(6)	3868(1)	4331(3)	24(1)
C13	2795(6)	4331(1)	4361(3)	22(1)
C14	2968(6)	4613(1)	3571(3)	20(1)
C15	3741(6)	4455(1)	2585(3)	21(1)
C16	1491(6)	6036(1)	5245(3)	26(1)
C17	3520(6)	5536(1)	2138(3)	24(1)
C18	5124(7)	5772(2)	2796(3)	30(1)
C19	-1150(6)	4556(2)	887(3)	30(1)
C20	2565(7)	4118(2)	-262(3)	33(1)
C21	-204(7)	6450(1)	3053(3)	34(1)
C22	6922(8)	3358(2)	-303(3)	41(1)

C23	8140(8)	3161(2)	1980(4)	43(1)
C24	5198(8)	2549(2)	687(3)	36(1)
C25	3344(8)	2557(2)	-62(4)	50(1)
C26	6692(9)	2267(2)	198(4)	53(2)
C27	4805(10)	2335(2)	1722(4)	57(2)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for fropec07.

Si(1)-O(3)	1.660(3)	C(10)-C(11)	1.315(6)
Si(1)-C(22)	1.871(5)	C(10)-C(15)	1.514(6)
Si(1)-C(23)	1.873(5)	C(11)-C(12)	1.471(6)
Si(1)-C(24)	1.877(5)	C(11)-H(11A)	0.9500
O(1)-C(1)	1.233(5)	C(12)-C(13)	1.458(6)
O(2)-C(3)	1.347(5)	C(13)-C(14)	1.352(5)
O(2)-C(21)	1.441(5)	C(13)-H(13A)	0.9500
O(3)-C(9)	1.414(5)	C(14)-C(15)	1.517(6)
O(4)-C(12)	1.235(5)	C(16)-H(16A)	0.9800
O(5)-C(15)	1.455(5)	C(16)-H(16B)	0.9800
O(5)-H(5)	0.80(5)	C(16)-H(16C)	0.9800
N(1)-C(1)	1.396(5)	C(17)-C(18)	1.518(6)
N(1)-C(14)	1.409(5)	C(17)-H(17A)	0.9900
N(1)-C(4)	1.493(5)	C(17)-H(17B)	0.9900
C(1)-C(2)	1.467(6)	C(18)-H(18A)	0.9800
C(2)-C(3)	1.342(6)	C(18)-H(18B)	0.9800
C(2)-C(16)	1.505(6)	C(18)-H(18C)	0.9800
C(3)-C(4)	1.524(6)	C(19)-H(19A)	0.9800
C(4)-C(5)	1.518(6)	C(19)-H(19B)	0.9800
C(4)-C(17)	1.557(6)	C(19)-H(19C)	0.9800
C(5)-C(6)	1.335(6)	C(20)-H(20A)	0.9800
C(5)-H(5A)	0.9500	C(20)-H(20B)	0.9800
C(6)-C(19)	1.509(6)	C(20)-H(20C)	0.9800
C(6)-C(7)	1.533(6)	C(21)-H(21A)	0.9800
C(7)-C(8)	1.550(6)	C(21)-H(21B)	0.9800
C(7)-C(15)	1.594(5)	C(21)-H(21C)	0.9800
C(7)-H(7A)	1.0000	C(22)-H(22A)	0.9800
C(8)-C(20)	1.525(6)	C(22)-H(22B)	0.9800
C(8)-C(9)	1.534(6)	C(22)-H(22C)	0.9800
C(8)-H(8A)	1.0000	C(23)-H(23A)	0.9800
C(9)-C(10)	1.508(5)	C(23)-H(23B)	0.9800
C(9)-H(9A)	1.0000	C(23)-H(23C)	0.9800

C(24)-C(25)	1.536(7)	N(1)-C(4)-C(3)	100.7(3)
C(24)-C(27)	1.539(7)	C(5)-C(4)-C(3)	111.8(4)
C(24)-C(26)	1.549(7)	N(1)-C(4)-C(17)	114.7(3)
C(25)-H(25A)	0.9800	C(5)-C(4)-C(17)	113.6(3)
C(25)-H(25B)	0.9800	C(3)-C(4)-C(17)	105.3(3)
C(25)-H(25D)	0.9800	C(6)-C(5)-C(4)	126.0(4)
C(26)-H(26A)	0.9800	C(6)-C(5)-H(5A)	117.0
C(26)-H(26D)	0.9800	C(4)-C(5)-H(5A)	117.0
C(26)-H(26B)	0.9800	C(5)-C(6)-C(19)	119.6(4)
C(27)-H(27D)	0.9800	C(5)-C(6)-C(7)	122.0(4)
C(27)-H(27A)	0.9800	C(19)-C(6)-C(7)	118.4(3)
C(27)-H(27B)	0.9800	C(6)-C(7)-C(8)	116.7(3)
O(3)-Si(1)-C(22)	110.3(2)	C(6)-C(7)-C(15)	115.8(3)
O(3)-Si(1)-C(23)	109.7(2)	C(8)-C(7)-C(15)	105.4(3)
C(22)-Si(1)-C(23)	108.3(3)	C(6)-C(7)-H(7A)	106.0
O(3)-Si(1)-C(24)	103.9(2)	C(8)-C(7)-H(7A)	106.0
C(22)-Si(1)-C(24)	111.3(2)	C(15)-C(7)-H(7A)	106.0
C(23)-Si(1)-C(24)	113.3(2)	C(20)-C(8)-C(9)	112.3(4)
C(3)-O(2)-C(21)	118.9(3)	C(20)-C(8)-C(7)	114.7(3)
C(9)-O(3)-Si(1)	123.6(3)	C(9)-C(8)-C(7)	104.0(3)
C(15)-O(5)-H(5)	110(4)	C(20)-C(8)-H(8A)	108.5
C(1)-N(1)-C(14)	125.6(3)	C(9)-C(8)-H(8A)	108.5
C(1)-N(1)-C(4)	109.5(3)	C(7)-C(8)-H(8A)	108.5
C(14)-N(1)-C(4)	122.5(3)	O(3)-C(9)-C(10)	114.6(3)
O(1)-C(1)-N(1)	124.1(4)	O(3)-C(9)-C(8)	112.8(3)
O(1)-C(1)-C(2)	126.2(4)	C(10)-C(9)-C(8)	99.7(3)
N(1)-C(1)-C(2)	109.7(3)	O(3)-C(9)-H(9A)	109.8
C(3)-C(2)-C(1)	106.5(4)	C(10)-C(9)-H(9A)	109.8
C(3)-C(2)-C(16)	134.4(4)	C(8)-C(9)-H(9A)	109.8
C(1)-C(2)-C(16)	119.0(3)	C(11)-C(10)-C(9)	127.4(4)
C(2)-C(3)-O(2)	134.9(4)	C(11)-C(10)-C(15)	125.7(4)
C(2)-C(3)-C(4)	112.9(4)	C(9)-C(10)-C(15)	105.9(3)
O(2)-C(3)-C(4)	111.9(3)	C(10)-C(11)-C(12)	119.7(4)
N(1)-C(4)-C(5)	109.9(3)	C(10)-C(11)-H(11A)	120.2

C(12)-C(11)-H(11A)	120.2	C(6)-C(19)-H(19A)	109.5
O(4)-C(12)-C(13)	121.3(4)	C(6)-C(19)-H(19B)	109.5
O(4)-C(12)-C(11)	121.4(4)	H(19A)-C(19)-H(19B)	109.5
C(13)-C(12)-C(11)	117.3(4)	C(6)-C(19)-H(19C)	109.5
C(14)-C(13)-C(12)	124.0(4)	H(19A)-C(19)-H(19C)	109.5
C(14)-C(13)-H(13A)	118.0	H(19B)-C(19)-H(19C)	109.5
C(12)-C(13)-H(13A)	118.0	C(8)-C(20)-H(20A)	109.5
C(13)-C(14)-N(1)	122.2(4)	C(8)-C(20)-H(20B)	109.5
C(13)-C(14)-C(15)	119.9(4)	H(20A)-C(20)-H(20B)	109.5
N(1)-C(14)-C(15)	117.5(3)	C(8)-C(20)-H(20C)	109.5
O(5)-C(15)-C(10)	107.6(3)	H(20A)-C(20)-H(20C)	109.5
O(5)-C(15)-C(14)	108.1(3)	H(20B)-C(20)-H(20C)	109.5
C(10)-C(15)-C(14)	113.0(3)	O(2)-C(21)-H(21A)	109.5
O(5)-C(15)-C(7)	106.2(3)	O(2)-C(21)-H(21B)	109.5
C(10)-C(15)-C(7)	101.9(3)	H(21A)-C(21)-H(21B)	109.5
C(14)-C(15)-C(7)	119.3(3)	O(2)-C(21)-H(21C)	109.5
C(2)-C(16)-H(16A)	109.5	H(21A)-C(21)-H(21C)	109.5
C(2)-C(16)-H(16B)	109.5	H(21B)-C(21)-H(21C)	109.5
H(16A)-C(16)-H(16B)	109.5	Si(1)-C(22)-H(22A)	109.5
C(2)-C(16)-H(16C)	109.5	Si(1)-C(22)-H(22B)	109.5
H(16A)-C(16)-H(16C)	109.5	H(22A)-C(22)-H(22B)	109.5
H(16B)-C(16)-H(16C)	109.5	Si(1)-C(22)-H(22C)	109.5
C(18)-C(17)-C(4)	114.8(3)	H(22A)-C(22)-H(22C)	109.5
C(18)-C(17)-H(17A)	108.6	H(22B)-C(22)-H(22C)	109.5
C(4)-C(17)-H(17A)	108.6	Si(1)-C(23)-H(23A)	109.5
C(18)-C(17)-H(17B)	108.6	Si(1)-C(23)-H(23B)	109.5
C(4)-C(17)-H(17B)	108.6	H(23A)-C(23)-H(23B)	109.5
H(17A)-C(17)-H(17B)	107.5	Si(1)-C(23)-H(23C)	109.5
C(17)-C(18)-H(18A)	109.5	H(23A)-C(23)-H(23C)	109.5
C(17)-C(18)-H(18B)	109.5	H(23B)-C(23)-H(23C)	109.5
H(18A)-C(18)-H(18B)	109.5	C(25)-C(24)-C(27)	109.3(5)
C(17)-C(18)-H(18C)	109.5	C(25)-C(24)-C(26)	108.8(4)
H(18A)-C(18)-H(18C)	109.5	C(27)-C(24)-C(26)	108.2(4)
H(18B)-C(18)-H(18C)	109.5	C(25)-C(24)-Si(1)	109.7(3)

C(27)-C(24)-Si(1)	110.8(3)	H(26A)-C(26)-H(26D)	109.5
C(26)-C(24)-Si(1)	110.1(4)	C(24)-C(26)-H(26B)	109.5
C(24)-C(25)-H(25A)	109.5	H(26A)-C(26)-H(26B)	109.5
C(24)-C(25)-H(25B)	109.5	H(26D)-C(26)-H(26B)	109.5
H(25A)-C(25)-H(25B)	109.5	C(24)-C(27)-H(27D)	109.5
C(24)-C(25)-H(25D)	109.5	C(24)-C(27)-H(27A)	109.5
H(25A)-C(25)-H(25D)	109.5	H(27D)-C(27)-H(27A)	109.5
H(25B)-C(25)-H(25D)	109.5	C(24)-C(27)-H(27B)	109.5
C(24)-C(26)-H(26A)	109.5	H(27D)-C(27)-H(27B)	109.5
C(24)-C(26)-H(26D)	109.5	H(27A)-C(27)-H(27B)	109.5

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropec07. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	32(1)	27(1)	30(1)	-1(1)	3(1)	3(1)
O1	21(2)	30(2)	21(1)	-1(1)	0(1)	-3(1)
O2	31(2)	25(2)	26(2)	0(1)	-2(1)	4(1)
O3	30(2)	23(2)	28(2)	-3(1)	3(1)	-1(1)
O4	27(2)	32(2)	29(2)	6(1)	4(1)	0(2)
O5	16(2)	32(2)	23(2)	0(1)	3(1)	-3(1)
N1	18(2)	22(2)	20(2)	2(1)	-2(2)	1(2)
C1	13(2)	30(2)	20(2)	-2(2)	1(2)	-5(2)
C2	13(2)	27(2)	29(2)	-1(2)	0(2)	-2(2)
C3	19(2)	23(2)	31(2)	3(2)	4(2)	0(2)
C4	26(2)	24(2)	18(2)	1(2)	-2(2)	-1(2)
C5	18(2)	28(2)	29(2)	6(2)	1(2)	-1(2)
C6	18(2)	28(2)	21(2)	3(2)	0(2)	-2(2)
C7	21(2)	28(2)	16(2)	1(2)	0(2)	-1(2)
C8	22(2)	29(2)	24(2)	-2(2)	-4(2)	-1(2)
C9	22(2)	26(2)	24(2)	-2(2)	0(2)	-3(2)
C10	12(2)	30(2)	25(2)	-4(2)	-4(2)	-1(2)
C11	18(2)	23(2)	31(2)	-1(2)	-3(2)	2(2)
C12	16(2)	27(2)	27(2)	1(2)	0(2)	-3(2)
C13	15(2)	29(2)	20(2)	-3(2)	-2(2)	-2(2)
C14	11(2)	25(2)	22(2)	2(2)	-4(2)	0(2)
C15	14(2)	26(2)	23(2)	-1(2)	0(2)	-5(2)
C16	18(2)	28(2)	33(2)	-5(2)	-1(2)	2(2)
C17	20(2)	27(2)	24(2)	3(2)	-1(2)	-4(2)
C18	31(3)	36(3)	23(2)	-4(2)	4(2)	-8(2)
C19	22(2)	39(3)	30(2)	-5(2)	0(2)	0(2)
C20	40(3)	37(3)	22(2)	-4(2)	0(2)	7(2)
C21	39(3)	27(2)	34(2)	0(2)	-1(2)	8(2)
C22	54(3)	36(3)	36(3)	-2(2)	17(3)	3(3)

C23	35(3)	46(3)	45(3)	-1(2)	-5(2)	2(3)
C24	44(3)	31(3)	34(2)	-2(2)	2(2)	4(2)
C25	52(4)	38(3)	57(3)	-12(3)	-4(3)	-4(3)
C26	61(4)	31(3)	67(4)	-7(3)	6(3)	14(3)
C27	83(5)	39(3)	49(3)	2(2)	13(3)	-17(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc07.

	x	y	z	U(eq)
H5	6140(80)	4693(17)	3090(40)	57(19)
H5A	-886	5229	2065	30
H7A	3278	4734	1089	26
H8A	1345	3920	1050	31
H9A	5459	3981	1243	29
H11A	4103	3393	3279	29
H13A	2332	4441	4974	26
H16A	464	6246	5048	40
H16B	2705	6192	5389	40
H16C	1218	5876	5870	40
H17A	4077	5294	1762	28
H17B	2918	5742	1609	28
H18A	6132	5847	2361	45
H18B	5649	5582	3368	45
H18C	4627	6040	3083	45
H19A	-2286	4729	986	45
H19B	-1332	4255	1116	45
H19C	-948	4557	147	45
H20A	2679	3824	-553	50
H20B	3662	4295	-409	50
H20C	1385	4255	-581	50
H21A	-718	6637	2471	51
H21B	901	6593	3439	51
H21C	-1189	6400	3520	51
H22A	7233	3668	-189	62
H22B	5898	3330	-878	62
H22C	8057	3201	-477	62
H23A	8480	3468	2103	64

H23B	9247	3002	1775	64
H23C	7753	3033	2621	64
H25A	2868	2258	-176	75
H25B	3599	2685	-730	75
H25D	2385	2733	241	75
H26A	6256	1963	147	80
H26D	7917	2283	637	80
H26B	6849	2378	-501	80
H27D	4282	2041	1585	85
H27A	3883	2513	2053	85
H27B	5999	2315	2188	85

Table 6. Torsion angles [°] for fropec07.

C22-Si1-O3-C9	-58.2(3)	C4-C5-C6-C19	-179.9(4)
C23-Si1-O3-C9	61.0(3)	C4-C5-C6-C7	-0.6(6)
C24-Si1-O3-C9	-177.6(3)	C5-C6-C7-C8	172.5(4)
C14-N1-C1-O1	15.9(6)	C19-C6-C7-C8	-8.2(5)
C4-N1-C1-O1	178.7(4)	C5-C6-C7-C15	47.6(5)
C14-N1-C1-C2	-163.6(4)	C19-C6-C7-C15	-133.1(4)
C4-N1-C1-C2	-0.9(4)	C6-C7-C8-C20	85.4(5)
O1-C1-C2-C3	-173.7(4)	C15-C7-C8-C20	-144.6(4)
N1-C1-C2-C3	5.8(5)	C6-C7-C8-C9	-151.6(3)
O1-C1-C2-C16	8.1(6)	C15-C7-C8-C9	-21.6(4)
N1-C1-C2-C16	-172.4(4)	Si1-O3-C9-C10	-113.5(3)
C1-C2-C3-O2	179.0(4)	Si1-O3-C9-C8	133.3(3)
C16-C2-C3-O2	-3.1(9)	C20-C8-C9-O3	-71.5(4)
C1-C2-C3-C4	-8.5(5)	C7-C8-C9-O3	164.0(3)
C16-C2-C3-C4	169.3(4)	C20-C8-C9-C10	166.6(4)
C21-O2-C3-C2	0.0(7)	C7-C8-C9-C10	42.0(4)
C21-O2-C3-C4	-172.5(4)	O3-C9-C10-C11	-0.6(6)
C1-N1-C4-C5	-121.8(4)	C8-C9-C10-C11	120.1(5)
C14-N1-C4-C5	41.6(5)	O3-C9-C10-C15	-169.3(3)
C1-N1-C4-C3	-3.7(4)	C8-C9-C10-C15	-48.7(4)
C14-N1-C4-C3	159.6(4)	C9-C10-C11-C12	-166.6(4)
C1-N1-C4-C17	108.7(4)	C15-C10-C11-C12	0.0(6)
C14-N1-C4-C17	-87.9(4)	C10-C11-C12-O4	-177.1(4)
C2-C3-C4-N1	7.8(5)	C10-C11-C12-C13	4.6(6)
O2-C3-C4-N1	-178.0(3)	O4-C12-C13-C14	177.7(4)
C2-C3-C4-C5	124.4(4)	C11-C12-C13-C14	-4.0(6)
O2-C3-C4-C5	-61.4(4)	C12-C13-C14-N1	-173.7(4)
C2-C3-C4-C17	-111.8(4)	C12-C13-C14-C15	-1.3(6)
O2-C3-C4-C17	62.5(4)	C1-N1-C14-C13	10.4(6)
N1-C4-C5-C6	-67.2(5)	C4-N1-C14-C13	-150.2(4)
C3-C4-C5-C6	-178.2(4)	C1-N1-C14-C15	-162.2(4)
C17-C4-C5-C6	62.9(5)	C4-N1-C14-C15	37.2(5)

C11-C10-C15-O5	114.3(4)	C8-C7-C15-C10	-7.4(4)
C9-C10-C15-O5	-76.7(4)	C6-C7-C15-C14	-2.0(5)
C11-C10-C15-C14	-5.0(6)	C8-C7-C15-C14	-132.6(4)
C9-C10-C15-C14	164.0(3)	N1-C4-C17-C18	-52.1(5)
C11-C10-C15-C7	-134.2(4)	C5-C4-C17-C18	-179.7(4)
C9-C10-C15-C7	34.8(4)	C3-C4-C17-C18	57.7(4)
C13-C14-C15-O5	-113.6(4)	O3-Si1-C24-C25	51.5(4)
N1-C14-C15-O5	59.2(4)	C22-Si1-C24-C25	-67.2(4)
C13-C14-C15-C10	5.5(5)	C23-Si1-C24-C25	170.5(3)
N1-C14-C15-C10	178.2(3)	O3-Si1-C24-C27	-69.2(4)
C13-C14-C15-C7	125.2(4)	C22-Si1-C24-C27	172.1(4)
N1-C14-C15-C7	-62.1(5)	C23-Si1-C24-C27	49.8(5)
C6-C7-C15-O5	-124.2(3)	O3-Si1-C24-C26	171.2(3)
C8-C7-C15-O5	105.2(3)	C22-Si1-C24-C26	52.4(4)
C6-C7-C15-C10	123.2(4)	C23-Si1-C24-C26	-69.9(4)

Table 7. Hydrogen bonds and close contacts for fropec07 [$\text{\AA}$ and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O5-H5...O1#1	0.80(5)	1.98(5)	2.765(4)	166(6)
C13-H13A...O1	0.95	2.23	2.832(5)	120.6
C17-H17A...O5	0.99	2.35	3.042(5)	126.3
C21-H21C...O4#2	0.98	2.38	3.345(6)	167.7

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y+1, -z+1$ #2 $-x, -y+1, -z+1$

For Compound **11**

REFERENCE NUMBER: fropc08

CRYSTAL STRUCTURE REPORT

$C_{21}H_{25}NO_5$

Report prepared for:

P. Carlsen, Prof. A. Frontier

April 02, 2014

William W. Brennessel

X-ray Crystallographic Facility

Department of Chemistry, University of Rochester

120 Trustee Road

Rochester, NY 14627

Data collection

A crystal ($0.38 \times 0.22 \times 0.10 \text{ mm}^3$) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD platform diffractometer for a data collection at 100.0(5) K.¹ A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK α radiation (graphite monochromator) with a frame time of 60 seconds and a detector distance of 4.00 cm. A randomly oriented region of reciprocal space was surveyed: four major sections of frames were collected with 0.50° steps in ω at four different ϕ settings and a detector position of -38° in 2θ . The intensity data were corrected for absorption.² Final cell constants were calculated from the xyz centroids of 4020 strong reflections from the actual data collection after integration.³ See Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR2011⁴ and refined using SHELXL-2014.⁵ The space group $P2_1/n$ was determined based on systematic absences. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms involved in O—H...O hydrogen bonding (H3 and H5) were found from the difference Fourier map and refined freely. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0560$ (F^2 , $I > 2\sigma(I)$) and $wR2 = 0.1592$ (F^2 , all data).

Structure description

The structure is the one suggested. The asymmetric unit contains one molecule in a general position. Hydrogen bonding creates a network of molecules (see Table 7).

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

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- ¹ *APEX2*, version 2013.10-0; Bruker AXS: Madison, WI, 2013.
- ² Sheldrick, G. M. *SADABS*, version 2012/1; University of Göttingen: Göttingen, Germany, 2012.
- ³ *SAINT*, version 8.34A; Bruker AXS: Madison, WI, 2013.
- ⁴ Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; Spagna, R. *SIR2011: a new package for crystal structure determination and refinement*, version 1.0; Istituto di Cristallografia: Bari, Italy, 2012.
- ⁵ Sheldrick, G. M. *SHELXL-2014/3*; University of Göttingen: Göttingen, Germany, 2014.

Some equations of interest:

$$R_{\text{int}} = \Sigma |F_o^2 - \langle F_o^2 \rangle| / \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$$

where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] / (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

Table 1. Crystal data and structure refinement for fropc08.

Identification code	fropc08	
Empirical formula	C ₂₁ H ₂₅ N O ₅	
Formula weight	371.42	
Temperature	100.0(5) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>P</i> 2 ₁ / <i>n</i>	
Unit cell dimensions	<i>a</i> = 7.8471(15) Å	$\alpha = 90^\circ$
	<i>b</i> = 10.2749(19) Å	$\beta = 96.030(4)^\circ$
	<i>c</i> = 22.656(4) Å	$\gamma = 90^\circ$
Volume	1816.6(6) Å ³	
<i>Z</i>	4	
Density (calculated)	1.358 Mg/m ³	
Absorption coefficient	0.097 mm ⁻¹	
<i>F</i> (000)	792	
Crystal color, morphology	colorless, plate	
Crystal size	0.38 x 0.22 x 0.10 mm ³	
Theta range for data collection	1.808 to 38.735°	
Index ranges	-13 ≤ <i>h</i> ≤ 13, -17 ≤ <i>k</i> ≤ 18, -38 ≤ <i>l</i> ≤ 39	
Reflections collected	44981	
Independent reflections	10082 [<i>R</i> (int) = 0.0619]	
Observed reflections	6502	
Completeness to theta = 37.785°	100.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7476 and 0.6604	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	10082 / 0 / 257	
Goodness-of-fit on <i>F</i> ²	1.023	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0560, <i>wR</i> 2 = 0.1384	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0979, <i>wR</i> 2 = 0.1592	
Largest diff. peak and hole	0.591 and -0.376 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc08. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O1	3004(1)	5672(1)	-130(1)	16(1)
O2	-144(1)	1779(1)	-545(1)	23(1)
O3	6524(1)	2318(1)	2789(1)	21(1)
O4	5154(1)	6690(1)	1784(1)	21(1)
O5	6108(1)	2329(1)	883(1)	17(1)
N1	3011(1)	3625(1)	320(1)	13(1)
C1	2474(1)	4550(1)	-116(1)	13(1)
C2	1176(1)	3964(1)	-547(1)	15(1)
C3	893(1)	2756(1)	-353(1)	16(1)
C4	2095(1)	2372(1)	186(1)	15(1)
C5	1106(1)	1990(1)	697(1)	16(1)
C6	1795(1)	1720(1)	1250(1)	16(1)
C7	3723(1)	1625(1)	1409(1)	14(1)
C8	4329(2)	1356(1)	2073(1)	17(1)
C9	6061(1)	2064(1)	2182(1)	16(1)
C10	5679(1)	3263(1)	1816(1)	14(1)
C11	5824(1)	4492(1)	2003(1)	16(1)
C12	5030(1)	5527(1)	1628(1)	16(1)
C13	4050(1)	5168(1)	1072(1)	15(1)
C14	3875(1)	3927(1)	874(1)	13(1)
C15	4801(1)	2830(1)	1224(1)	13(1)
C16	491(1)	4740(1)	-1077(1)	18(1)
C17	3251(2)	1275(1)	-26(1)	18(1)
C18	4157(2)	1651(1)	-564(1)	27(1)
C19	607(2)	1489(1)	1721(1)	23(1)
C20	4448(2)	-90(1)	2231(1)	25(1)
C21	-1103(2)	1861(1)	-1119(1)	22(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for fropec08.

O(1)-C(1)	1.2266(13)	C(11)-H(11A)	0.9500
O(2)-C(3)	1.3363(13)	C(12)-C(13)	1.4529(14)
O(2)-C(21)	1.4353(13)	C(13)-C(14)	1.3540(14)
O(3)-C(9)	1.4095(13)	C(13)-H(13A)	0.9500
O(3)-H(3)	0.79(2)	C(14)-C(15)	1.5188(14)
O(4)-C(12)	1.2471(13)	C(16)-H(16A)	0.9800
O(5)-C(15)	1.4430(12)	C(16)-H(16B)	0.9800
O(5)-H(5)	0.86(2)	C(16)-H(16C)	0.9800
N(1)-C(14)	1.3971(12)	C(17)-C(18)	1.5243(17)
N(1)-C(1)	1.4045(13)	C(17)-H(17A)	0.9900
N(1)-C(4)	1.4904(13)	C(17)-H(17B)	0.9900
C(1)-C(2)	1.4649(14)	C(18)-H(18A)	0.9800
C(2)-C(3)	1.3437(15)	C(18)-H(18B)	0.9800
C(2)-C(16)	1.4932(14)	C(18)-H(18C)	0.9800
C(3)-C(4)	1.5139(14)	C(19)-H(19A)	0.9800
C(4)-C(5)	1.5118(15)	C(19)-H(19B)	0.9800
C(4)-C(17)	1.5544(15)	C(19)-H(19C)	0.9800
C(5)-C(6)	1.3393(15)	C(20)-H(20A)	0.9800
C(5)-H(5A)	0.9500	C(20)-H(20B)	0.9800
C(6)-C(19)	1.5085(15)	C(20)-H(20C)	0.9800
C(6)-C(7)	1.5215(15)	C(21)-H(21A)	0.9800
C(7)-C(8)	1.5548(14)	C(21)-H(21C)	0.9800
C(7)-C(15)	1.5803(14)	C(21)-H(21D)	0.9800
C(7)-H(7A)	1.0000	C(3)-O(2)-C(21)	119.64(9)
C(8)-C(20)	1.5288(16)	C(9)-O(3)-H(3)	112.0(15)
C(8)-C(9)	1.5385(16)	C(15)-O(5)-H(5)	110.4(14)
C(8)-H(8A)	1.0000	C(14)-N(1)-C(1)	124.27(8)
C(9)-C(10)	1.4965(14)	C(14)-N(1)-C(4)	123.61(8)
C(9)-H(9A)	1.0000	C(1)-N(1)-C(4)	109.81(8)
C(10)-C(11)	1.3328(15)	O(1)-C(1)-N(1)	125.17(9)
C(10)-C(15)	1.5091(14)	O(1)-C(1)-C(2)	125.74(9)
C(11)-C(12)	1.4592(15)	N(1)-C(1)-C(2)	109.08(9)

C(3)-C(2)-C(1)	106.76(9)	C(10)-C(9)-H(9A)	110.1
C(3)-C(2)-C(16)	134.42(10)	C(8)-C(9)-H(9A)	110.1
C(1)-C(2)-C(16)	118.82(9)	C(11)-C(10)-C(9)	126.78(9)
O(2)-C(3)-C(2)	134.65(10)	C(11)-C(10)-C(15)	125.22(9)
O(2)-C(3)-C(4)	111.94(9)	C(9)-C(10)-C(15)	107.20(8)
C(2)-C(3)-C(4)	113.28(9)	C(10)-C(11)-C(12)	119.27(9)
N(1)-C(4)-C(5)	110.10(8)	C(10)-C(11)-H(11A)	120.4
N(1)-C(4)-C(3)	100.69(8)	C(12)-C(11)-H(11A)	120.4
C(5)-C(4)-C(3)	111.02(9)	O(4)-C(12)-C(13)	120.49(9)
N(1)-C(4)-C(17)	113.88(9)	O(4)-C(12)-C(11)	121.17(9)
C(5)-C(4)-C(17)	114.32(9)	C(13)-C(12)-C(11)	118.32(9)
C(3)-C(4)-C(17)	105.89(8)	C(14)-C(13)-C(12)	123.55(9)
C(6)-C(5)-C(4)	125.49(10)	C(14)-C(13)-H(13A)	118.2
C(6)-C(5)-H(5A)	117.3	C(12)-C(13)-H(13A)	118.2
C(4)-C(5)-H(5A)	117.3	C(13)-C(14)-N(1)	122.03(9)
C(5)-C(6)-C(19)	118.42(10)	C(13)-C(14)-C(15)	119.94(9)
C(5)-C(6)-C(7)	121.89(9)	N(1)-C(14)-C(15)	117.68(8)
C(19)-C(6)-C(7)	119.68(9)	O(5)-C(15)-C(10)	107.28(8)
C(6)-C(7)-C(8)	115.85(8)	O(5)-C(15)-C(14)	108.24(8)
C(6)-C(7)-C(15)	115.69(8)	C(10)-C(15)-C(14)	113.26(8)
C(8)-C(7)-C(15)	106.12(8)	O(5)-C(15)-C(7)	106.97(8)
C(6)-C(7)-H(7A)	106.1	C(10)-C(15)-C(7)	101.70(8)
C(8)-C(7)-H(7A)	106.1	C(14)-C(15)-C(7)	118.69(8)
C(15)-C(7)-H(7A)	106.1	C(2)-C(16)-H(16A)	109.5
C(20)-C(8)-C(9)	113.01(10)	C(2)-C(16)-H(16B)	109.5
C(20)-C(8)-C(7)	113.83(9)	H(16A)-C(16)-H(16B)	109.5
C(9)-C(8)-C(7)	104.23(8)	C(2)-C(16)-H(16C)	109.5
C(20)-C(8)-H(8A)	108.5	H(16A)-C(16)-H(16C)	109.5
C(9)-C(8)-H(8A)	108.5	H(16B)-C(16)-H(16C)	109.5
C(7)-C(8)-H(8A)	108.5	C(18)-C(17)-C(4)	113.57(9)
O(3)-C(9)-C(10)	113.83(9)	C(18)-C(17)-H(17A)	108.9
O(3)-C(9)-C(8)	112.09(9)	C(4)-C(17)-H(17A)	108.9
C(10)-C(9)-C(8)	100.28(8)	C(18)-C(17)-H(17B)	108.9
O(3)-C(9)-H(9A)	110.1	C(4)-C(17)-H(17B)	108.9

H(17A)-C(17)-H(17B)	107.7	C(8)-C(20)-H(20A)	109.5
C(17)-C(18)-H(18A)	109.5	C(8)-C(20)-H(20B)	109.5
C(17)-C(18)-H(18B)	109.5	H(20A)-C(20)-H(20B)	109.5
H(18A)-C(18)-H(18B)	109.5	C(8)-C(20)-H(20C)	109.5
C(17)-C(18)-H(18C)	109.5	H(20A)-C(20)-H(20C)	109.5
H(18A)-C(18)-H(18C)	109.5	H(20B)-C(20)-H(20C)	109.5
H(18B)-C(18)-H(18C)	109.5	O(2)-C(21)-H(21A)	109.5
C(6)-C(19)-H(19A)	109.5	O(2)-C(21)-H(21C)	109.5
C(6)-C(19)-H(19B)	109.5	H(21A)-C(21)-H(21C)	109.5
H(19A)-C(19)-H(19B)	109.5	O(2)-C(21)-H(21D)	109.5
C(6)-C(19)-H(19C)	109.5	H(21A)-C(21)-H(21D)	109.5
H(19A)-C(19)-H(19C)	109.5	H(21C)-C(21)-H(21D)	109.5
H(19B)-C(19)-H(19C)	109.5		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc08. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	20(1)	13(1)	16(1)	2(1)	0(1)	-1(1)
O2	31(1)	19(1)	17(1)	0(1)	-8(1)	-8(1)
O3	23(1)	27(1)	12(1)	2(1)	-4(1)	1(1)
O4	28(1)	14(1)	19(1)	-4(1)	-3(1)	0(1)
O5	20(1)	15(1)	15(1)	2(1)	5(1)	5(1)
N1	17(1)	11(1)	11(1)	0(1)	-1(1)	1(1)
C1	15(1)	13(1)	12(1)	0(1)	1(1)	2(1)
C2	18(1)	14(1)	13(1)	0(1)	-1(1)	2(1)
C3	20(1)	15(1)	14(1)	-1(1)	-2(1)	-1(1)
C4	19(1)	12(1)	13(1)	0(1)	-1(1)	-1(1)
C5	18(1)	15(1)	16(1)	0(1)	0(1)	-1(1)
C6	20(1)	14(1)	14(1)	0(1)	2(1)	-1(1)
C7	19(1)	13(1)	11(1)	1(1)	0(1)	0(1)
C8	24(1)	14(1)	11(1)	2(1)	0(1)	-1(1)
C9	20(1)	16(1)	12(1)	2(1)	-1(1)	2(1)
C10	14(1)	16(1)	12(1)	2(1)	0(1)	1(1)
C11	18(1)	17(1)	12(1)	0(1)	-2(1)	0(1)
C12	18(1)	15(1)	14(1)	-1(1)	0(1)	-1(1)
C13	17(1)	13(1)	13(1)	-1(1)	-2(1)	1(1)
C14	14(1)	13(1)	10(1)	1(1)	0(1)	1(1)
C15	16(1)	12(1)	11(1)	1(1)	1(1)	2(1)
C16	20(1)	17(1)	15(1)	2(1)	-3(1)	2(1)
C17	29(1)	12(1)	13(1)	-1(1)	1(1)	3(1)
C18	41(1)	22(1)	19(1)	2(1)	10(1)	12(1)
C19	23(1)	30(1)	18(1)	3(1)	5(1)	-3(1)
C20	39(1)	16(1)	17(1)	4(1)	-6(1)	-2(1)
C21	25(1)	20(1)	20(1)	-3(1)	-7(1)	-1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc08.

	x	y	z	U(eq)
H3	7520(30)	2210(20)	2880(9)	48(6)
H5	6590(30)	2950(20)	709(9)	46(6)
H5A	-105	1937	620	20
H7A	4111	864	1183	17
H8A	3505	1779	2321	20
H9A	6976	1543	2016	20
H11A	6438	4692	2376	19
H13A	3502	5841	835	18
H16A	-147	4167	-1367	27
H16B	1444	5144	-1257	27
H16C	-275	5420	-955	27
H17A	4123	1039	304	22
H17B	2537	495	-126	22
H18A	4961	961	-647	41
H18B	4786	2466	-482	41
H18C	3308	1767	-909	41
H19A	-581	1480	1538	35
H19B	752	2187	2017	35
H19C	879	651	1915	35
H20A	5015	-192	2635	37
H20B	5112	-542	1951	37
H20C	3293	-461	2209	37
H21A	-1712	1040	-1208	34
H21C	-319	2025	-1420	34
H21D	-1933	2574	-1121	34

Table 6. Torsion angles [°] for fropc08.

C14-N1-C1-O1	17.28(16)	C19-C6-C7-C8	-3.00(14)
C4-N1-C1-O1	-179.55(10)	C5-C6-C7-C15	52.68(13)
C14-N1-C1-C2	-162.30(9)	C19-C6-C7-C15	-128.13(10)
C4-N1-C1-C2	0.87(11)	C6-C7-C8-C20	88.35(12)
O1-C1-C2-C3	-176.43(10)	C15-C7-C8-C20	-141.75(10)
N1-C1-C2-C3	3.15(12)	C6-C7-C8-C9	-148.08(9)
O1-C1-C2-C16	4.29(16)	C15-C7-C8-C9	-18.18(10)
N1-C1-C2-C16	-176.14(9)	C20-C8-C9-O3	-76.51(12)
C21-O2-C3-C2	8.9(2)	C7-C8-C9-O3	159.40(9)
C21-O2-C3-C4	-166.51(10)	C20-C8-C9-C10	162.38(9)
C1-C2-C3-O2	178.63(12)	C7-C8-C9-C10	38.28(10)
C16-C2-C3-O2	-2.2(2)	O3-C9-C10-C11	3.77(16)
C1-C2-C3-C4	-6.01(12)	C8-C9-C10-C11	123.63(11)
C16-C2-C3-C4	173.11(11)	O3-C9-C10-C15	-166.33(9)
C14-N1-C4-C5	42.07(13)	C8-C9-C10-C15	-46.46(10)
C1-N1-C4-C5	-121.24(9)	C9-C10-C11-C12	-165.82(10)
C14-N1-C4-C3	159.31(9)	C15-C10-C11-C12	2.58(16)
C1-N1-C4-C3	-4.00(10)	C10-C11-C12-O4	-179.20(11)
C14-N1-C4-C17	-87.84(11)	C10-C11-C12-C13	2.33(15)
C1-N1-C4-C17	108.85(9)	O4-C12-C13-C14	179.44(10)
O2-C3-C4-N1	-177.27(9)	C11-C12-C13-C14	-2.08(16)
C2-C3-C4-N1	6.29(12)	C12-C13-C14-N1	-175.98(9)
O2-C3-C4-C5	-60.71(12)	C12-C13-C14-C15	-2.96(15)
C2-C3-C4-C5	122.85(10)	C1-N1-C14-C13	9.94(15)
O2-C3-C4-C17	63.91(12)	C4-N1-C14-C13	-150.97(10)
C2-C3-C4-C17	-112.53(10)	C1-N1-C14-C15	-163.23(9)
N1-C4-C5-C6	-62.78(14)	C4-N1-C14-C15	35.86(13)
C3-C4-C5-C6	-173.40(10)	C11-C10-C15-O5	112.24(11)
C17-C4-C5-C6	66.89(14)	C9-C10-C15-O5	-77.47(10)
C4-C5-C6-C19	173.85(10)	C11-C10-C15-C14	-7.13(14)
C4-C5-C6-C7	-6.96(17)	C9-C10-C15-C14	163.16(8)
C5-C6-C7-C8	177.81(10)	C11-C10-C15-C7	-135.64(11)

C9-C10-C15-C7	34.65(10)	C8-C7-C15-O5	103.32(9)
C13-C14-C15-O5	-111.76(10)	C6-C7-C15-C10	120.96(9)
N1-C14-C15-O5	61.56(11)	C8-C7-C15-C10	-9.04(10)
C13-C14-C15-C10	7.06(13)	C6-C7-C15-C14	-4.00(12)
N1-C14-C15-C10	-179.62(8)	C8-C7-C15-C14	-134.00(9)
C13-C14-C15-C7	126.18(10)	N1-C4-C17-C18	-55.57(12)
N1-C14-C15-C7	-60.50(12)	C5-C4-C17-C18	176.66(10)
C6-C7-C15-O5	-126.69(9)	C3-C4-C17-C18	54.12(12)

Table 7. Hydrogen bonds and close contacts for fropc08 [$\text{\AA}$ and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O3-H3...O4#1	0.79(2)	1.98(2)	2.7602(13)	169(2)
O5-H5...O1#2	0.86(2)	1.98(2)	2.8048(11)	161.2(19)
C13-H13A...O1	0.95	2.19	2.8085(13)	122.0
C17-H17A...O5	0.99	2.34	3.0784(15)	130.7
C21-H21C...O3#3	0.98	2.51	3.4868(17)	173.7

Symmetry transformations used to generate equivalent atoms:

#1 $-x+3/2, y-1/2, -z+1/2$ #2 $-x+1, -y+1, -z$ #3 $x-1/2, -y+1/2, z-1/2$

For Compound **238**

REFERENCE NUMBER: fropc11

CRYSTAL STRUCTURE REPORT

$C_{27}H_{40}BrNO_4Si$

Report prepared for:
P. Carlsen, Prof. A. Frontier

October 02, 2014

William W. Brennessel
X-ray Crystallographic Facility
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Data collection

A crystal ($0.36 \times 0.12 \times 0.08 \text{ mm}^3$) was placed onto the tip of a thin glass optical fiber and mounted on a Bruker SMART APEX II CCD platform diffractometer for a data collection at $100.0(5) \text{ K}$.¹ A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using $\text{MoK}\alpha$ radiation (graphite monochromator) with a frame time of 60 seconds and a detector distance of 4.02 cm. A randomly oriented region of reciprocal space was surveyed: four major sections of frames were collected with 0.50° steps in ω at four different ϕ settings and a detector position of -38° in 2θ . The intensity data were corrected for absorption.² Final cell constants were calculated from the xyz centroids of 4088 strong reflections from the actual data collection after integration.³ See Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR2011⁴ and refined using SHELXL-2014/7.⁵ The space group $P2_1$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0493$ (F^2 , $I > 2\sigma(I)$) and $wR2 = 0.0902$ (F^2 , all data).

Structure description

The structure is the one suggested. The asymmetric unit contains one molecule in a general position.

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

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- ¹ *APEX2*, version 2014.7-1; Bruker AXS: Madison, WI, 2014.
- ² Sheldrick, G. M. *SADABS*, version 2014/3; University of Göttingen: Göttingen, Germany, 2014.
- ³ *SAINT*, version 8.32B; Bruker AXS: Madison, WI, 2013.
- ⁴ Burla, M. C.; Caliendo, R.; Camalli, M.; Carrozzini, B.; Casciaro, G. L.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; Spagna, R. *SIR2011: a new package for crystal structure determination and refinement*, version 1.0; Istituto di Cristallografia: Bari, Italy, 2012.
- ⁵ Sheldrick, G. M. *SHELXL-2014/7*; University of Göttingen: Göttingen, Germany, 2014.

Some equations of interest:

$$R_{\text{int}} = \Sigma |F_o^2 - \langle F_o^2 \rangle| / \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$$

where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] / (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

Table 1. Crystal data and structure refinement for fropc11.

Identification code	fropc11	
Empirical formula	C ₂₇ H ₄₀ Br N O ₄ Si	
Formula weight	550.60	
Temperature	100.0(5) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>P</i> 2 ₁	
Unit cell dimensions	<i>a</i> = 10.8422(10) Å	$\alpha = 90^\circ$
	<i>b</i> = 10.0519(10) Å	$\beta = 112.1351(19)^\circ$
	<i>c</i> = 14.1126(13) Å	$\gamma = 90^\circ$
Volume	1424.7(2) Å ³	
<i>Z</i>	2	
Density (calculated)	1.283 Mg/m ³	
Absorption coefficient	1.515 mm ⁻¹	
<i>F</i> (000)	580	
Crystal color, morphology	colorless, needle	
Crystal size	0.36 x 0.12 x 0.08 mm ³	
Theta range for data collection	2.028 to 29.644°	
Index ranges	-15 ≤ <i>h</i> ≤ 15, -13 ≤ <i>k</i> ≤ 13, -19 ≤ <i>l</i> ≤ 19	
Reflections collected	22426	
Independent reflections	8009 [<i>R</i> (int) = 0.0833]	
Observed reflections	6009	
Completeness to theta = 29.575°	100.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7459 and 0.6277	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	8009 / 1 / 316	
Goodness-of-fit on <i>F</i> ²	0.985	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0493, <i>wR</i> 2 = 0.0799	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0795, <i>wR</i> 2 = 0.0902	
Absolute structure parameter	0.019(7)	
Largest diff. peak and hole	0.445 and -0.440 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for *frpc11*. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Br1	9661(1)	6376(1)	10652(1)	24(1)
Si1	8455(1)	3293(1)	6225(1)	17(1)
O1	4682(3)	2550(3)	8646(2)	24(1)
O2	2609(3)	5228(3)	9669(2)	24(1)
O3	4152(3)	5680(3)	8994(2)	23(1)
O4	8852(3)	3431(4)	7479(2)	24(1)
N1	4566(4)	4213(4)	10322(3)	16(1)
C1	6800(4)	3645(4)	9009(3)	15(1)
C2	5619(4)	3200(5)	9205(4)	19(1)
C3	5791(4)	3705(5)	10266(4)	17(1)
C4	6964(4)	4705(5)	10594(3)	16(1)
C5	7540(4)	4511(5)	9774(3)	17(1)
C6	8649(4)	5090(5)	9688(3)	18(1)
C7	9041(4)	4754(5)	8890(3)	18(1)
C8	8309(4)	3819(5)	8160(3)	19(1)
C9	7160(4)	3278(5)	8194(3)	18(1)
C10	3825(4)	5080(5)	9607(3)	16(1)
C11	2550(5)	4418(5)	10489(4)	26(1)
C12	3777(4)	3509(5)	10813(3)	18(1)
C13	4498(4)	3326(5)	11964(3)	18(1)
C14	4821(5)	4632(5)	12561(4)	26(1)
C15	3669(5)	2410(5)	12364(4)	29(1)
C16	7934(4)	4441(5)	11682(3)	19(1)
C17	7941(5)	5233(5)	12436(4)	24(1)
C18	8806(5)	3231(5)	11851(4)	28(1)
C19	7505(5)	4810(5)	5571(4)	23(1)
C20	6064(5)	4822(6)	5504(4)	31(1)
C21	8212(5)	6106(5)	6061(4)	35(1)
C22	7435(5)	1745(5)	5759(4)	24(1)

C23	8050(5)	520(5)	6399(4)	30(1)
C24	7158(5)	1500(7)	4619(4)	32(1)
C25	10126(5)	3151(5)	6114(4)	22(1)
C26	10110(6)	3669(6)	5095(5)	32(1)
C27	11267(5)	3821(6)	7002(4)	34(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for fropc11.

Br(1)-C(6)	1.898(5)	C(12)-H(12A)	1.0000
Si(1)-O(4)	1.662(3)	C(13)-C(14)	1.527(7)
Si(1)-C(19)	1.876(5)	C(13)-C(15)	1.537(6)
Si(1)-C(22)	1.879(5)	C(13)-H(13A)	1.0000
Si(1)-C(25)	1.882(5)	C(14)-H(14A)	0.9800
O(1)-C(2)	1.215(5)	C(14)-H(14B)	0.9800
O(2)-C(10)	1.362(5)	C(14)-H(14C)	0.9800
O(2)-C(11)	1.436(6)	C(15)-H(15A)	0.9800
O(3)-C(10)	1.212(5)	C(15)-H(15B)	0.9800
O(4)-C(8)	1.359(5)	C(15)-H(15C)	0.9800
N(1)-C(10)	1.346(6)	C(16)-C(17)	1.327(6)
N(1)-C(3)	1.452(5)	C(16)-C(18)	1.503(7)
N(1)-C(12)	1.469(6)	C(17)-H(17A)	0.9500
C(1)-C(5)	1.384(6)	C(17)-H(17B)	0.9500
C(1)-C(9)	1.395(6)	C(18)-H(18A)	0.9800
C(1)-C(2)	1.478(6)	C(18)-H(18B)	0.9800
C(2)-C(3)	1.525(6)	C(18)-H(18C)	0.9800
C(3)-C(4)	1.549(6)	C(19)-C(20)	1.529(7)
C(3)-H(3A)	1.0000	C(19)-C(21)	1.537(7)
C(4)-C(5)	1.520(6)	C(19)-H(19A)	1.0000
C(4)-C(16)	1.522(6)	C(20)-H(20A)	0.9800
C(4)-H(4A)	1.0000	C(20)-H(20B)	0.9800
C(5)-C(6)	1.382(6)	C(20)-H(20C)	0.9800
C(6)-C(7)	1.386(6)	C(21)-H(21A)	0.9800
C(7)-C(8)	1.399(6)	C(21)-H(21B)	0.9800
C(7)-H(7A)	0.9500	C(21)-H(21C)	0.9800
C(8)-C(9)	1.378(6)	C(22)-C(23)	1.524(7)
C(9)-H(9A)	0.9500	C(22)-C(24)	1.541(6)
C(11)-C(12)	1.534(7)	C(22)-H(22A)	1.0000
C(11)-H(11A)	0.9900	C(23)-H(23A)	0.9800
C(11)-H(11B)	0.9900	C(23)-H(23B)	0.9800
C(12)-C(13)	1.525(6)	C(23)-H(23C)	0.9800

C(24)-H(24A)	0.9800	C(4)-C(3)-H(3A)	107.1
C(24)-H(24B)	0.9800	C(5)-C(4)-C(16)	114.8(4)
C(24)-H(24C)	0.9800	C(5)-C(4)-C(3)	102.5(4)
C(25)-C(26)	1.524(7)	C(16)-C(4)-C(3)	111.5(4)
C(25)-C(27)	1.544(7)	C(5)-C(4)-H(4A)	109.3
C(25)-H(25A)	1.0000	C(16)-C(4)-H(4A)	109.3
C(26)-H(26A)	0.9800	C(3)-C(4)-H(4A)	109.3
C(26)-H(26B)	0.9800	C(6)-C(5)-C(1)	117.6(4)
C(26)-H(26C)	0.9800	C(6)-C(5)-C(4)	129.3(4)
C(27)-H(27A)	0.9800	C(1)-C(5)-C(4)	113.0(4)
C(27)-H(27B)	0.9800	C(5)-C(6)-C(7)	120.8(4)
C(27)-H(27C)	0.9800	C(5)-C(6)-Br(1)	120.7(3)
O(4)-Si(1)-C(19)	109.3(2)	C(7)-C(6)-Br(1)	118.5(3)
O(4)-Si(1)-C(22)	108.9(2)	C(6)-C(7)-C(8)	120.0(4)
C(19)-Si(1)-C(22)	111.0(2)	C(6)-C(7)-H(7A)	120.0
O(4)-Si(1)-C(25)	102.95(19)	C(8)-C(7)-H(7A)	120.0
C(19)-Si(1)-C(25)	112.9(2)	O(4)-C(8)-C(9)	123.4(4)
C(22)-Si(1)-C(25)	111.5(2)	O(4)-C(8)-C(7)	116.0(4)
C(10)-O(2)-C(11)	109.1(3)	C(9)-C(8)-C(7)	120.5(4)
C(8)-O(4)-Si(1)	140.3(3)	C(8)-C(9)-C(1)	117.5(4)
C(10)-N(1)-C(3)	119.1(4)	C(8)-C(9)-H(9A)	121.2
C(10)-N(1)-C(12)	112.1(4)	C(1)-C(9)-H(9A)	121.2
C(3)-N(1)-C(12)	124.3(4)	O(3)-C(10)-N(1)	127.2(4)
C(5)-C(1)-C(9)	123.3(4)	O(3)-C(10)-O(2)	122.8(4)
C(5)-C(1)-C(2)	109.5(4)	N(1)-C(10)-O(2)	110.0(4)
C(9)-C(1)-C(2)	127.2(4)	O(2)-C(11)-C(12)	106.3(4)
O(1)-C(2)-C(1)	127.8(4)	O(2)-C(11)-H(11A)	110.5
O(1)-C(2)-C(3)	125.4(4)	C(12)-C(11)-H(11A)	110.5
C(1)-C(2)-C(3)	106.8(4)	O(2)-C(11)-H(11B)	110.5
N(1)-C(3)-C(2)	113.2(4)	C(12)-C(11)-H(11B)	110.5
N(1)-C(3)-C(4)	114.9(4)	H(11A)-C(11)-H(11B)	108.7
C(2)-C(3)-C(4)	107.0(4)	N(1)-C(12)-C(13)	113.8(4)
N(1)-C(3)-H(3A)	107.1	N(1)-C(12)-C(11)	99.6(4)
C(2)-C(3)-H(3A)	107.1	C(13)-C(12)-C(11)	115.3(4)

N(1)-C(12)-H(12A)	109.2	C(20)-C(19)-Si(1)	113.3(4)
C(13)-C(12)-H(12A)	109.2	C(21)-C(19)-Si(1)	112.2(3)
C(11)-C(12)-H(12A)	109.2	C(20)-C(19)-H(19A)	106.9
C(12)-C(13)-C(14)	113.8(4)	C(21)-C(19)-H(19A)	106.9
C(12)-C(13)-C(15)	109.1(4)	Si(1)-C(19)-H(19A)	106.9
C(14)-C(13)-C(15)	110.9(4)	C(19)-C(20)-H(20A)	109.5
C(12)-C(13)-H(13A)	107.6	C(19)-C(20)-H(20B)	109.5
C(14)-C(13)-H(13A)	107.6	H(20A)-C(20)-H(20B)	109.5
C(15)-C(13)-H(13A)	107.6	C(19)-C(20)-H(20C)	109.5
C(13)-C(14)-H(14A)	109.5	H(20A)-C(20)-H(20C)	109.5
C(13)-C(14)-H(14B)	109.5	H(20B)-C(20)-H(20C)	109.5
H(14A)-C(14)-H(14B)	109.5	C(19)-C(21)-H(21A)	109.5
C(13)-C(14)-H(14C)	109.5	C(19)-C(21)-H(21B)	109.5
H(14A)-C(14)-H(14C)	109.5	H(21A)-C(21)-H(21B)	109.5
H(14B)-C(14)-H(14C)	109.5	C(19)-C(21)-H(21C)	109.5
C(13)-C(15)-H(15A)	109.5	H(21A)-C(21)-H(21C)	109.5
C(13)-C(15)-H(15B)	109.5	H(21B)-C(21)-H(21C)	109.5
H(15A)-C(15)-H(15B)	109.5	C(23)-C(22)-C(24)	111.0(4)
C(13)-C(15)-H(15C)	109.5	C(23)-C(22)-Si(1)	113.1(3)
H(15A)-C(15)-H(15C)	109.5	C(24)-C(22)-Si(1)	110.8(4)
H(15B)-C(15)-H(15C)	109.5	C(23)-C(22)-H(22A)	107.2
C(17)-C(16)-C(18)	123.0(4)	C(24)-C(22)-H(22A)	107.2
C(17)-C(16)-C(4)	119.8(4)	Si(1)-C(22)-H(22A)	107.2
C(18)-C(16)-C(4)	117.1(4)	C(22)-C(23)-H(23A)	109.5
C(16)-C(17)-H(17A)	120.0	C(22)-C(23)-H(23B)	109.5
C(16)-C(17)-H(17B)	120.0	H(23A)-C(23)-H(23B)	109.5
H(17A)-C(17)-H(17B)	120.0	C(22)-C(23)-H(23C)	109.5
C(16)-C(18)-H(18A)	109.5	H(23A)-C(23)-H(23C)	109.5
C(16)-C(18)-H(18B)	109.5	H(23B)-C(23)-H(23C)	109.5
H(18A)-C(18)-H(18B)	109.5	C(22)-C(24)-H(24A)	109.5
C(16)-C(18)-H(18C)	109.5	C(22)-C(24)-H(24B)	109.5
H(18A)-C(18)-H(18C)	109.5	H(24A)-C(24)-H(24B)	109.5
H(18B)-C(18)-H(18C)	109.5	C(22)-C(24)-H(24C)	109.5
C(20)-C(19)-C(21)	110.3(4)	H(24A)-C(24)-H(24C)	109.5

H(24B)-C(24)-H(24C)	109.5	C(25)-C(26)-H(26C)	109.5
C(26)-C(25)-C(27)	109.7(4)	H(26A)-C(26)-H(26C)	109.5
C(26)-C(25)-Si(1)	112.6(4)	H(26B)-C(26)-H(26C)	109.5
C(27)-C(25)-Si(1)	113.6(3)	C(25)-C(27)-H(27A)	109.5
C(26)-C(25)-H(25A)	106.8	C(25)-C(27)-H(27B)	109.5
C(27)-C(25)-H(25A)	106.8	H(27A)-C(27)-H(27B)	109.5
Si(1)-C(25)-H(25A)	106.8	C(25)-C(27)-H(27C)	109.5
C(25)-C(26)-H(26A)	109.5	H(27A)-C(27)-H(27C)	109.5
C(25)-C(26)-H(26B)	109.5	H(27B)-C(27)-H(27C)	109.5
H(26A)-C(26)-H(26B)	109.5		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc11. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	20(1)	24(1)	27(1)	-7(1)	8(1)	-6(1)
Si1	16(1)	20(1)	16(1)	1(1)	8(1)	2(1)
O1	22(2)	25(2)	24(2)	-7(2)	9(2)	-7(2)
O2	23(2)	26(2)	24(2)	3(2)	9(1)	4(2)
O3	29(2)	19(2)	20(2)	3(1)	10(1)	2(2)
O4	21(2)	31(2)	21(2)	-2(2)	10(1)	5(2)
N1	17(2)	14(2)	16(2)	0(2)	7(2)	0(2)
C1	17(2)	11(2)	16(2)	3(2)	4(2)	-1(2)
C2	20(2)	16(3)	21(2)	1(2)	8(2)	4(2)
C3	16(2)	15(2)	20(2)	-1(2)	8(2)	0(2)
C4	18(2)	15(2)	16(2)	0(2)	6(2)	-2(2)
C5	20(2)	15(2)	14(2)	0(2)	6(2)	-1(2)
C6	19(2)	17(2)	14(2)	0(2)	0(2)	-2(2)
C7	18(2)	16(2)	19(2)	4(2)	7(2)	1(2)
C8	22(2)	18(3)	15(2)	2(2)	7(2)	7(2)
C9	24(2)	13(2)	15(2)	-1(2)	4(2)	0(2)
C10	19(2)	13(2)	16(2)	-4(2)	6(2)	1(2)
C11	24(3)	29(3)	26(3)	4(2)	12(2)	1(2)
C12	17(2)	16(3)	21(2)	-1(2)	7(2)	-3(2)
C13	20(2)	18(2)	17(2)	1(2)	10(2)	0(2)
C14	26(3)	29(3)	25(3)	-3(2)	12(2)	-6(2)
C15	35(3)	27(3)	28(3)	4(2)	15(2)	-5(2)
C16	22(2)	18(3)	15(2)	0(2)	6(2)	-6(2)
C17	26(3)	28(3)	17(2)	0(2)	7(2)	-3(2)
C18	27(3)	28(3)	23(3)	5(2)	4(2)	6(2)
C19	28(3)	27(3)	19(2)	1(2)	13(2)	9(2)
C20	29(3)	39(3)	26(3)	3(2)	12(2)	16(3)
C21	40(3)	25(4)	44(3)	3(3)	19(2)	10(2)
C22	15(2)	28(3)	29(3)	-7(2)	9(2)	-2(2)

C23	28(3)	23(3)	44(3)	1(2)	19(2)	-2(2)
C24	26(2)	36(3)	33(3)	-13(3)	10(2)	-1(3)
C25	22(2)	24(3)	25(3)	3(2)	12(2)	3(2)
C26	31(3)	40(4)	32(3)	0(3)	21(2)	4(3)
C27	23(3)	40(3)	41(3)	-3(3)	15(2)	-1(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for fropc11.

	x	y	z	U(eq)
H3A	6076	2930	10743	20
H4A	6608	5630	10548	20
H7A	9806	5158	8840	21
H9A	6631	2678	7683	22
H11A	1724	3881	10255	31
H11B	2568	4981	11070	31
H12A	3511	2618	10484	21
H13A	5360	2865	12079	21
H14A	5124	5289	12183	39
H14B	5526	4480	13233	39
H14C	4022	4965	12649	39
H15A	3564	1541	12028	44
H15B	2790	2807	12216	44
H15C	4123	2296	13105	44
H17A	8516	5046	13120	29
H17B	7372	5987	12292	29
H18A	9330	3128	12583	41
H18B	9406	3335	11482	41
H18C	8249	2441	11596	41
H19A	7470	4795	4853	28
H20A	5600	5595	5106	47
H20B	6053	4872	6195	47
H20C	5615	4005	5169	47
H21A	7709	6868	5673	53
H21B	9112	6115	6054	53
H21C	8266	6160	6769	53
H22A	6555	1901	5818	28
H23A	7471	-251	6126	45

H23B	8148	673	7109	45
H23C	8927	349	6372	45
H24A	6545	748	4372	49
H24B	7996	1297	4536	49
H24C	6758	2298	4224	49
H25A	10342	2181	6142	27
H26A	10984	3522	5056	48
H26B	9910	4623	5039	48
H26C	9427	3196	4533	48
H27A	12106	3708	6900	51
H27B	11343	3408	7651	51
H27C	11076	4771	7020	51

Table 6. Torsion angles [°] for fropc11.

C19-Si1-O4-C8	42.7(6)	Br1-C6-C7-C8	-179.4(3)
C22-Si1-O4-C8	-78.8(5)	Si1-O4-C8-C9	56.8(7)
C25-Si1-O4-C8	162.8(5)	Si1-O4-C8-C7	-127.7(5)
C5-C1-C2-O1	171.8(5)	C6-C7-C8-O4	-172.3(4)
C9-C1-C2-O1	-8.3(8)	C6-C7-C8-C9	3.4(7)
C5-C1-C2-C3	-8.5(5)	O4-C8-C9-C1	172.1(4)
C9-C1-C2-C3	171.3(4)	C7-C8-C9-C1	-3.3(7)
C10-N1-C3-C2	-48.7(6)	C5-C1-C9-C8	-0.3(7)
C12-N1-C3-C2	105.5(5)	C2-C1-C9-C8	179.9(4)
C10-N1-C3-C4	74.6(6)	C3-N1-C10-O3	-13.2(7)
C12-N1-C3-C4	-131.1(4)	C12-N1-C10-O3	-170.4(4)
O1-C2-C3-N1	-41.3(7)	C3-N1-C10-O2	167.9(4)
C1-C2-C3-N1	139.1(4)	C12-N1-C10-O2	10.7(5)
O1-C2-C3-C4	-168.9(5)	C11-O2-C10-O3	-178.1(4)
C1-C2-C3-C4	11.5(5)	C11-O2-C10-N1	0.8(5)
N1-C3-C4-C5	-136.4(4)	C10-O2-C11-C12	-11.2(5)
C2-C3-C4-C5	-9.8(5)	C10-N1-C12-C13	-139.6(4)
N1-C3-C4-C16	100.3(5)	C3-N1-C12-C13	64.6(6)
C2-C3-C4-C16	-133.1(4)	C10-N1-C12-C11	-16.3(5)
C9-C1-C5-C6	3.7(7)	C3-N1-C12-C11	-172.1(4)
C2-C1-C5-C6	-176.5(4)	O2-C11-C12-N1	15.8(5)
C9-C1-C5-C4	-177.7(4)	O2-C11-C12-C13	138.1(4)
C2-C1-C5-C4	2.1(5)	N1-C12-C13-C14	63.8(5)
C16-C4-C5-C6	-55.6(7)	C11-C12-C13-C14	-50.5(5)
C3-C4-C5-C6	-176.6(5)	N1-C12-C13-C15	-171.7(4)
C16-C4-C5-C1	126.0(4)	C11-C12-C13-C15	74.0(5)
C3-C4-C5-C1	5.0(5)	C5-C4-C16-C17	139.5(4)
C1-C5-C6-C7	-3.5(7)	C3-C4-C16-C17	-104.6(5)
C4-C5-C6-C7	178.1(4)	C5-C4-C16-C18	-43.3(6)
C1-C5-C6-Br1	176.0(3)	C3-C4-C16-C18	72.6(5)
C4-C5-C6-Br1	-2.4(7)	O4-Si1-C19-C20	-75.5(4)
C5-C6-C7-C8	0.1(7)	C22-Si1-C19-C20	44.6(4)

C25-Si1-C19-C20	170.6(3)	C19-Si1-C22-C24	65.2(4)
O4-Si1-C19-C21	50.2(4)	C25-Si1-C22-C24	-61.5(4)
C22-Si1-C19-C21	170.3(3)	O4-Si1-C25-C26	-152.3(4)
C25-Si1-C19-C21	-63.7(4)	C19-Si1-C25-C26	-34.7(5)
O4-Si1-C22-C23	-49.0(4)	C22-Si1-C25-C26	91.1(4)
C19-Si1-C22-C23	-169.3(3)	O4-Si1-C25-C27	-26.8(4)
C25-Si1-C22-C23	63.9(4)	C19-Si1-C25-C27	90.9(4)
O4-Si1-C22-C24	-174.4(3)	C22-Si1-C25-C27	-143.4(4)