FRAGMENT COUPLING APPROACH TO C_{19}- AND C_{20}-DITERPENOID ALKALOIDS: TOTAL SYNTHESIS OF (–)-TALATISAMINE, (–)-LILJESTRANDISINE, AND (–)-LILJESTRANDININE

Thesis by

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ABSTRACT

A unified, convergent fragment coupling approach to the C_{19}- and C_{20}-diterpenoid alkaloid natural products is presented. The highly-caged aconitine, denudatine, and napelline cores are disconnected through the central B-ring cyclohexane to an A/E/F-ring fragment common to the structures all three subfamilies. 1,2-addition of an appropriate organometallic C/D-bicycle to an A/F-ring hydrindane epoxy ketone fragment followed by a Lewis acid-catalyzed semipinacol reaction couples the two fragments together and sets a key all-carbon quaternary center at C11. This strategy is realized in the synthesis of the C_{19}-aconitine core by using a [3.2.1]-bicyclooctene C/D-fragment as the nucleophile in the 1,2-addition. This C/D-fragment is prepared using a *meta*-photocycloaddition; this represents an alternative approach to the commonly employed biomimetic Wagner-Meerwein rearrangement of a [2.2.2]-bicyclooctane.

To complete the aconitine core, a radical cyclization cascade to form the E-ring piperidine and B-ring cyclohexane in a single step is investigated. *N*-centered radicals were evaluated to initiate the cascade via a 6-*exo*-trig cyclization. A neutral aminyl radical gave rise to an unexpected Hoffman-Löffler-Freytag type product resulting from 1,5-hydrogen atom transfer. Employing Lewis-acidic single electron reducing metal catalyst led to formation of the E-ring cyclized product, however the second cyclization to close the B-ring did not occur.

As an alternative approach, the E-ring was closed via an intramolecular aziridination. Treatment of this aziridine with acetyl bromide results in an aziridine-opened alkyl bromide product. This alkyl bromide is used as a functional group handle to form the final ring of the aconitine core. From there, the total syntheses of the C_{19}-

diterpenoid alkaloids (–)-talatisamine, (–)-liljestrandisine, and (–)-liljestrandinine were completed in short order. These synthetic efforts led to revision of the proposed structure of (–)-liljestrandisine.

PUBLISHED CONTENT AND CONTRIBUTIONS

Portions of the work described herein were disclosed in the following publications:

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N. J. F. conducted experiments towards (–)-talatisamine, (–)-liljestrandisine, and (–)-liljestrandinine and contributed to the preparation of the manuscripts and supporting information.

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LIST OF ABBREVIATIONS

$[\alpha]_D$	angle of optical rotation of plane-polarized light
Å	angstrom(s)
ABNO	9-azabicyclo[3.3.1]nonane *N*-oxyl
p-ABSA	para-acetamidobenzenesulfonyl azide
Ac	acetyl
acac	acetylacetonate
AIBN	azobisisobutyronitrile
aq	aqueous
Ar	aryl group
atm	atmosphere(s)
BINOL	1,1'-bi-2,2'-naphthol
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
Bipy/bpy	2,2'-bipyridine
Bn	benzyl
Boc	tert-butoxycarbonyl
bp	boiling point
br	broad
Bu	butyl
i-Bu	*iso*-butyl
n-Bu	butyl or *norm*-butyl
t-Bu	*tert*-butyl

BQ	1,4-benzoquinone
BRSM	yield based on recovered starting material
Bz	benzoyl
c	concentration of sample for measurement of optical rotation
^{13}C	carbon-13 isotope
/C	supported on activated carbon charcoal
°C	degrees Celsius
calc'd	calculated
CAN	ceric ammonium nitrate
cat.	catalyst
Cbz	benzyloxycarbonyl
cf.	consult or compare to (Latin: confer)
cis	(zusammen) on the same side
cm^{-1}	wavenumber(s)
CoA	Coenzyme A
conc.	concentrated
conv.	conversion
Cp	cyclopentadienyl
CSA	camphor sulfonic acid
Cy	cyclohexyl
Δ	heat or difference
δ	chemical shift in ppm
d	doublet

d	deutero or dextrorotatory
D	deuterium
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCE	1,2-dichloroethane
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
de novo	starting from the beginning; anew
DIPEA	*N,N*-diisopropylethylamine
DHQ	dihydroquinine
DHQD	dihydroquinidine
DIAD	diisopropyl azodicarboxylate
DIBAL	diisobutylaluminum hydride
DMAP	4-(dimethylamino)pyridine
DMBA	1,3-dimethylbarbituric acid
DME	1,2-dimethoxyethane
DMEDA	N,N'-dimethylethylenediamine
DMF	*N,N*-dimethylformamide
DMP	Dess-Martin Periodinane
DMPU	1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone
DMSO	dimethylsulfoxide
DTBMP	2,6-di-*tert*-butyl-4-methylpyridine
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene

dr	diastereomeric ratio
ee	enantiomeric excess
E	methyl carboxylate (CO_2CH_3)
E^+	electrophile
E	trans (entgegen) olefin geometry
EDCI	N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride
e.g.	for example (Latin: *exempli gratia*)
EI	electron impact
ent	enantiomer of
epi	epimeric
equiv	equivalent(s)
ESI	electrospray ionization
Et	ethyl
et al.	and others (Latin: *et alii*)
FAB	fast atom bombardment
FTIR	fourier transform infrared spectroscopy
g	gram(s)
h	hour(s)
1H	proton
[H]	reduction
HDA	hetero-Diels–Alder
HFIP	hexafluoroisopropanol
HMBC	heteronuclear multiple-bond correlation spectroscopy

HMDS	hexamethyldisilazide
HMPA	hexamethylphosphoramide
h*v*	irradiation with light
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectrometry
Hz	hertz
IC_{50}	half maximal inhibitory concentration (50%)
i.e.	that is (Latin: *id est*)
iso	isomeric
in situ	in the reaction mixture
J	coupling constant in Hz
k	rate constant
kcal	kilocalorie(s)
kg	kilogram(s)
L	liter or neutral ligand
l	levorotatory
LA	Lewis acid
LC/MS	liquid chromatography–mass spectrometry
LDA	lithium diisopropylamide
m	multiplet or meter(s)
M	molar or molecular ion
m	meta
μ	micro

m-CPBA	meta-chloroperbenzoic acid
Me	methyl
^{MeO}bpy	4,4'-dimethoxy-2,2'-bipyridine
mg	milligram(s)
MHz	megahertz
MIC	minimum inhibitory concentration
min	minute(s)
mL	milliliter(s)
MM	mixed method
mol	mole(s)
MOM	methoxymethyl
Ms	methanesulfonyl (mesyl)
MS	molecular sieves
MTT	3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide
m/z	mass-to-charge ratio
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
nd	not determined
NHC	N-heterocyclic carbene
nm	nanometer(s)
nM	nanomolar
NMI	*N*-methylimidazole
NMO	*N*-methylmorpholine N-oxide

NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
NOESY	nuclear Overhauser enhancement spectroscopy
NPh	naphthyl
Nu	nucleophile
o	ortho
[O]	oxidation
P	peak
p	para
PCC	pyridinium chlorochromate
PDC	pyridinium dichromate
Ph	phenyl
pH	hydrogen ion concentration in aqueous solution
PHAL	1,4-phthalazinediyl diether
PIFA	[bis(trifluoroacetoxy)iodo]benzene
Pin	pinacol
PivOH	pivalic acid
pK_a	acid dissociation constant
pm	picometer(s)
PMB	*para*-methoxybenzyl
ppm	parts per million
PPTS	pyridinium para-toluenesulfonate
Pr	propyl

i-Pr	*iso*propyl
n-Pr	propyl or *norm*-propyl
psi	pounds per square inch
py	pyridine
PYR	2,5-diphenyl-4,6-pyrimidinediyl diether
q	quartet
QD	Quinidine
QN	Quinine
quant.	quantitative
R	generic (alkyl) group
RL	large group
R	rectus
RCM	ring-closing metathesis
recry.	recrystallization
ref	reference
Rf	retention factor
rgt.	reagent
rt	room temperature
s	singlet or seconds
sat.	saturated
t	triplet
TBAF	tetra-*n*-butylammonium fluoride
TBAI	tetra-*n*-butylammonium iodide

TBME	*tert*-butyl methyl ether
TBS	*tert*-butyldimethylsilyl
TC	thiophene-2-carboxylate
TCA	trichloroacetic acid
temp	temperature
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TIPS	tri*iso*propylsilyl
TLC	thin layer chromatography
TMS	trimethylsilyl
TOF	time-of-flight
tol	tolyl
TPAP	tetrapropylammonium perruthenate
trans	on the opposite side
Ts	para-toluenesulfonyl (tosyl)
UV	ultraviolet
vide infra	see below
w/v	weight per volume
X	anionic ligand or halide
xs	excess
Z	*cis* (zusammen) olefin geometry

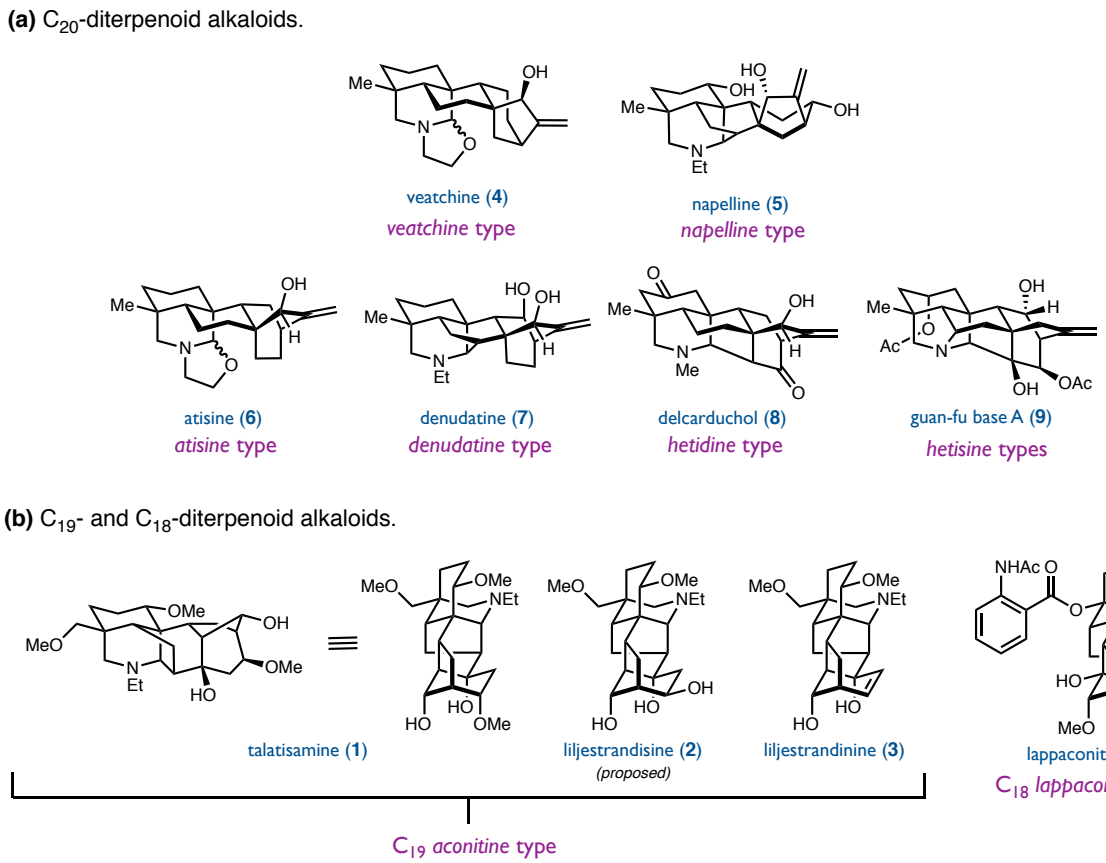
Chapter 1

C_{19}-Diterpenoid Alkaloids: Structure and Synthesis

1.1 INTRODUCTION

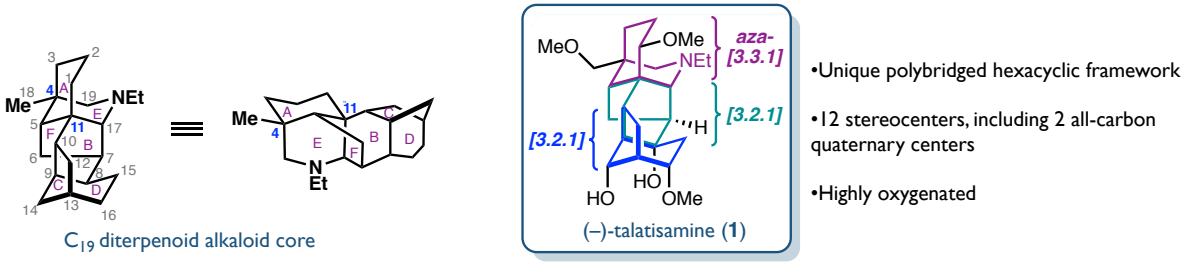
The extracts of the *Aconitum* and *Delphinium* genera of plants have long been used in traditional medicine as local anesthetics and as poisons for hunting and battle.[1] Common names for these flowering plants alluding to their toxicity include "wolf's bane," "the devil's helmet," and "the queen of poisons." Diterpenoid alkaloids are a broad family of natural products associated with the bioactivity of these flowering plants,[2–4] and many of these compounds exhibit analgesic,[5,6] anti-inflamatory, antihypertensive, and antiarrhythmic[7] properties. Talatisamine (**1**) selectively blocks inwardly rectifying K^+ ion channels over Na^+ and Ca^{2+} ion channels in rat neurons.[8] **1** has also been shown to attenuate neurocytotoxicity induced by β-amyloid oligomers.[9] The structural complexity of these highly caged natural products have drawn significant attention from the synthetic community for over 50 years.[10–13]

Figure 1.1 *Varying carbon frameworks of diterpenoid alkaloid subfamilies.*



1.2 STRUCTURAL ANALYSIS AND BIOSYNTHESIS OF C_{19}-DITERPENOID ALKALOIDS

Figure 1.2 *Structural analysis of C_{19}-diterpenoid alkaloid (–)-talatisamine (**1**).*



Diterpenoid alkaloids are a broad class of natural products with a variety of carbon skeletons with over 1200 natural products isolated to date.[3,14] They are classified by the

number of carbons in their backbones (C_{18}, C_{19}, and C_{20}). The highly-caged polycyclic core of these compounds, such as (–)-talatisamine (**1**, Figure 1.2), present a significant synthetic challenge. The C_{19}-aconitine core is comprised of an array of bridged bicycles, including a synthetically challenging [3.2.1]-bicyclooctane. Biosynthetically, diterpenoid alkaloids are derived from the structurally similar kaurane and atisane diterpenoid families by incorporation of serine as a source of nitrogen.[15] These complex skeletons are believed to arise from a series of cationic polyene cyclizations and skeletal rearrangements (Figure 1.3).[16] It is believed that C_{19}-diterpenoid alkaloids are derived from Wagner-Meerwein rearrangement of the C_{20}-denudatine core, wherein the [2.2.2]-bicyclooctane is converted to a [3.2.1]-bicyclooctane (Figure 1.4). The cationic rearrangements of the carbon skeletons which are crucial the biosynthesis of these natural products have also played an important role in many of the total syntheses of C_{18}- and C_{19}-diterpenoid alkaloids.

Figure 1.3 *Biosynthesis of diterpenoid alkaloid cores.*

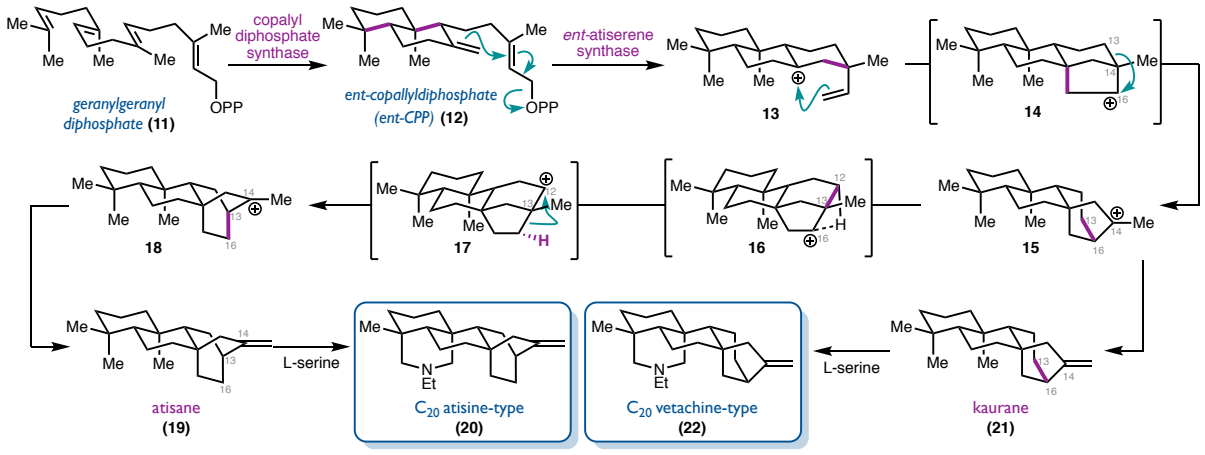
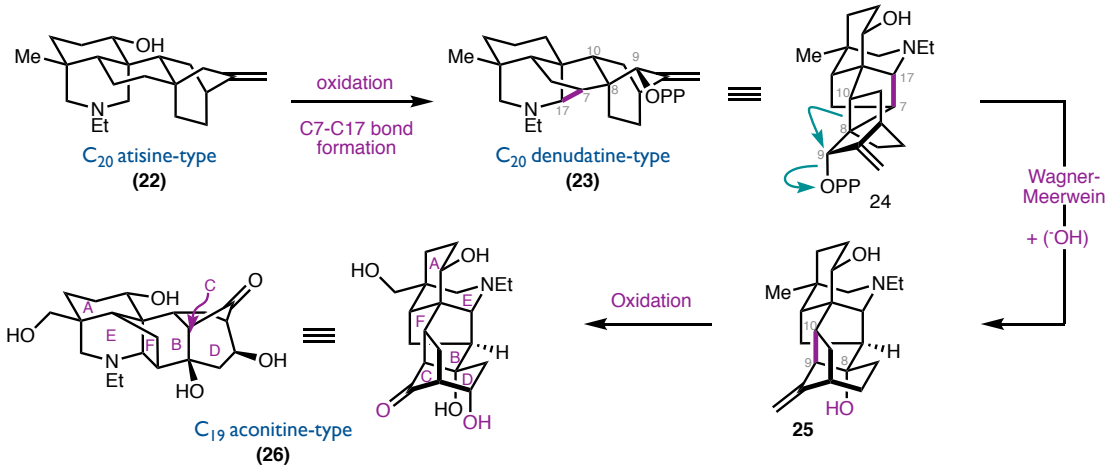


Figure 1.4 *Wagner-Meerwein rearrangement of denudatine core to aconitine core.*

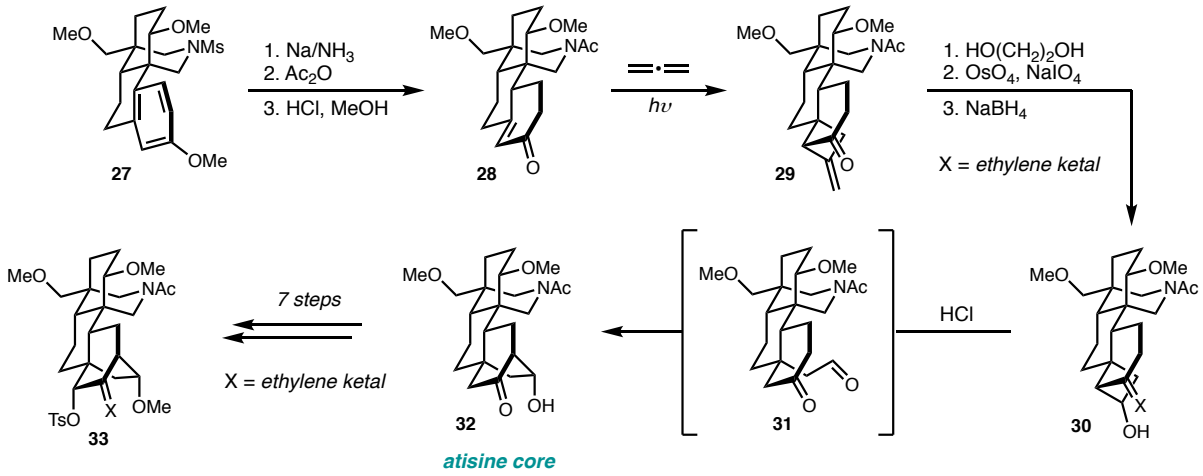


1.3 TOTAL SYNTHESES OF C_{19}-DITERPENOID ALKALOIDS

1.3.1 Biomimetic Wagner-Meerwein Approaches to Aconitine Core

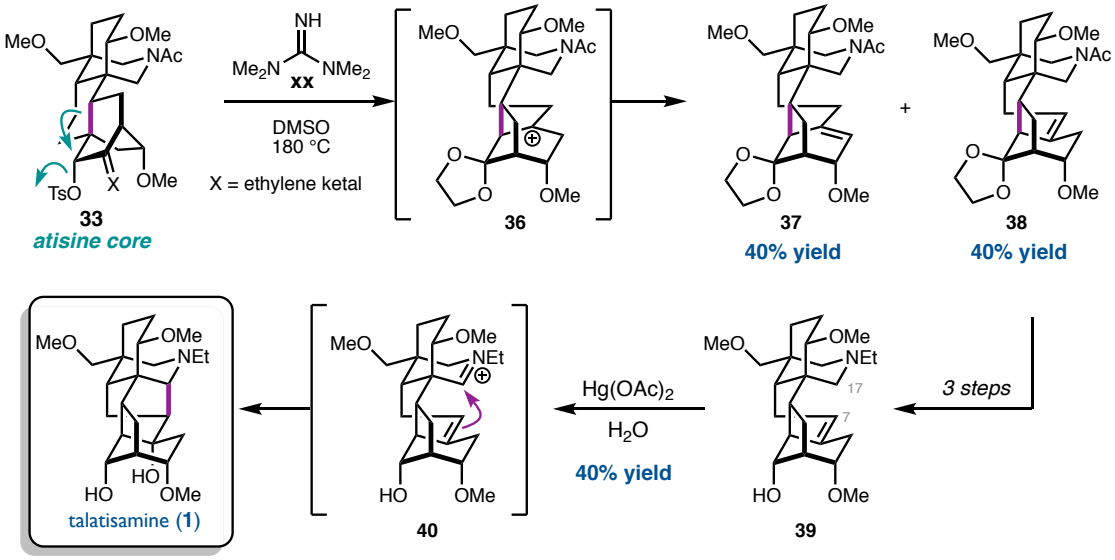
The Wagner-Meerwein rearrangement of a [2.2.2]-bicyclooctane which comprises the C and D rings of the C_{20} atisine and denudatine scaffolds to the [3.2.1]-bicyclooctane characteristic of the C_{18}- and C_{19}-diterpenoid alkaloids has inspired biomimetic approaches in many of the total syntheses reported to date. Targeting a [2.2.2]-bicyclooctane as an intermediate in the synthesis of C_{18}- and C_{19}-diterpenoid alkaloids has two main strategic advantages. Firstly, it allows for the divergent synthesis of two families of natural products via a late stage diversification of the carbon skeleton. Secondly, the [2.2.2]-bicyclooctane structural motif is a classic keying element for retrosynthetic disconnection via a Diels-Alder cycloaddition, one of the most well studied transformations in organic chemistry. Wiesner's synthesis of talatisamine (**1**) employing such an approach represents the first total synthesis of a C_{19}-diterpenoid alkaloid.

Scheme 1.1 *Wiesner's synthesis of the atisine core.*



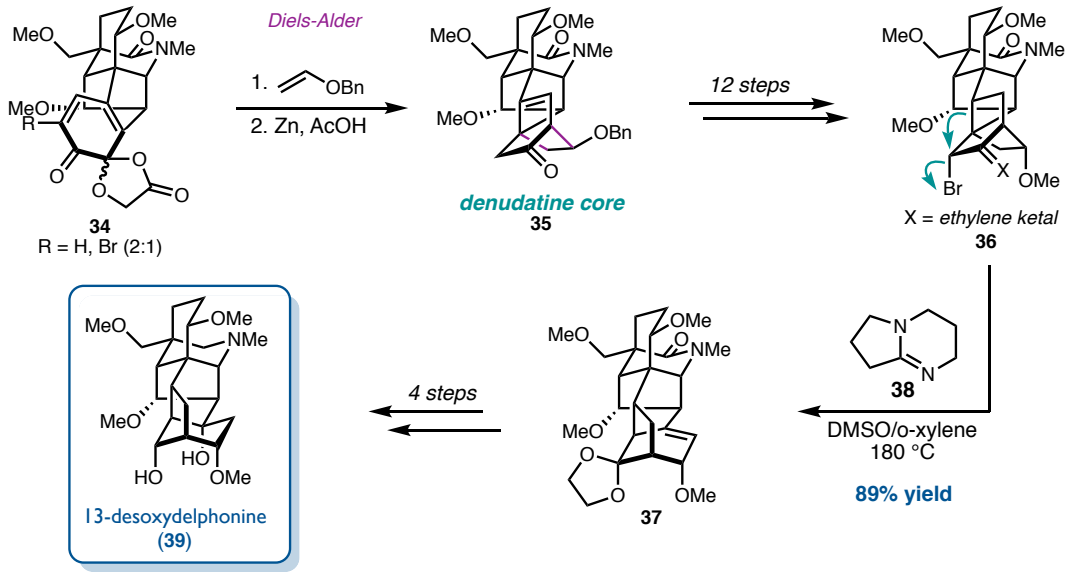
Wiesner's route to talatisamine is summarized here (Schemes 1.1 and 1.2). Beginning from tetracyclic arene **27**, prepared in 21 steps, Birch reduction followed by *N*-acetylation affords enone **28** upon treatment with acid. [2 + 2] photocycloaddition with ketene affords cyclobutane **29**. Ketalization of **29** with ethylene glycol followed by oxidative-cleavage of the cyclobutane *exo*-methylene and subsequent ketone reduction gives cyclobutanol **30**. Treatment with acid effects retro-aldol/aldol cascade to give the less strained cyclohexane isomer **32**, forming the atisine core. In seven further steps, they access a [2.2.2]-bicyclooctane with a tosylate leaving group suitable for the desired rearrangement. Treatment with tetramethylguanidine in DMSO at high temperature forms the rearranged product as a mixture of alkenes after deprotonation of the resulting tertiary carbocation. To complete the core, the C7–C17 bond was formed by an aza-Prins reaction upon oxidation of the amine.

Scheme 1.2 *Wiesner's synthesis of talatisamine (**1**).*



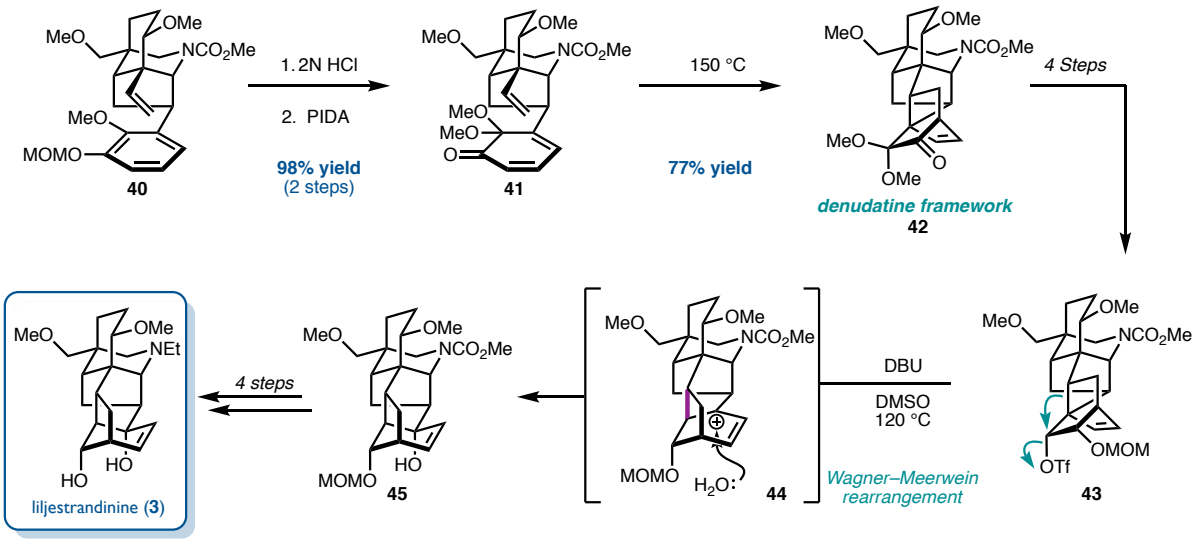
In a later synthesis of the C_{19}-diterpenoid alkaloid 13-desoxydelphonine (**39**), Wiesner and coworkers sought to rearrange the denudatine core, where the C7–C17 bond is already in place (Scheme 1.3).[19] Starting from *ortho*-quinone mono-ketal **34**, Diels-Alder cycloaddition with benzyl vinyl ether followed by global reduction with Zn and acetic acid affords the denudatine core in **35**. This can be elaborated in 12 steps to the substrate for the Wagner-Meerwein rearrangement, which procedes smoothly to deliver the aconitine core in excellent yield. This product can be advanced in 4 steps to 13-desoxydelphonine.

Scheme 1.3 *Wiesner's synthesis of 13-desoxydelphonine (**39**).*



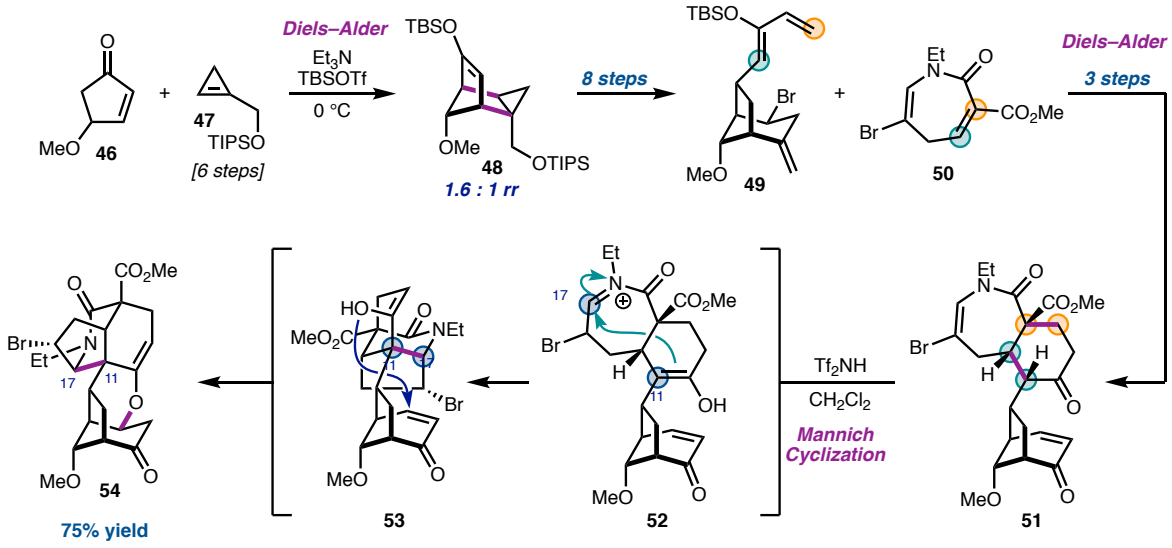
The Sarpong lab has utilized this strategy for the synthesis of a variety of diterpenoid alkaloid carbon skeletons, including the aconitine-type C_{19}-diterpenoid alkaloids (Scheme 1.4).[20,21] In their elegant 2015 synthesis of liljestrandinine (**3**), they employ an intramolecular Diels-Alder cycloaddition of an *ortho*-quinone monoketal with a pendant olefin to build the [2.2.2]-bridged C/D-bicycle **42**. This intramolecular approach also provides an efficient way to form the central B-ring. In short order, they elaborate **42** to an alkyl triflate, which serves as the substrate for the Wagner-Meerwein rearrangement. Similar approaches have been used by the Fukuyama and Inoue labs in their syntheses of C_{19}-diterpenoid alkaloids.[22,23]

Scheme 1.4 *Sarpong's synthesis of liljestrandinine (**3**).*



1.3.2 Gin's Synthesis of Neofinaconitine (60)

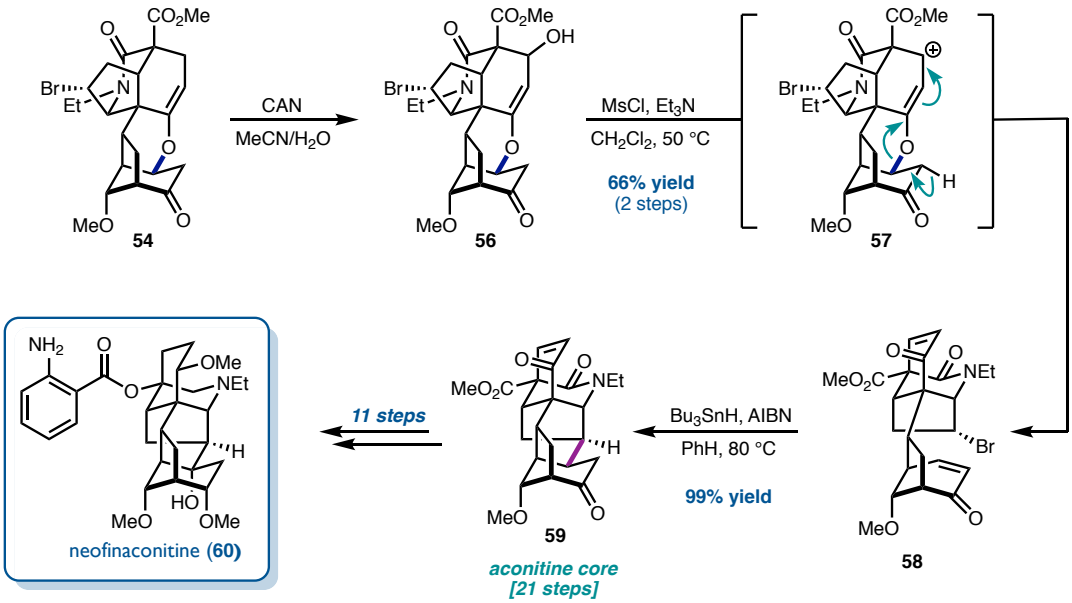
Scheme 1.5 *Gin's approach to aconitine core.*



Gin and coworkers used a different approach to the C/D-bicycle in their synthesis of the C_{18}-diterpenoid alkaloid neofinaconitine (**60**, Schemes 1.5 and 1.6).[24] They assemble the [3.2.1]-bicycle directly via a Diels-Alder reaction between a cyclopentadiene derived from **46** and cyclopropane dienophile (**47**). Prior to the work presented in subsequent chapters, this is

the only example of a total synthesis of a C_{18}- or C_{19}-diterpenoid alkaloid which does not involve a Wagner-Meerwein rearrangement to form the C/D-bicycle. Upon elaboration of **48** to diene **49**, they perform a fragment coupling Diels-Alder with dienophile **50** to form the A-ring of the natural product. Intramolecular Mannich reaction forms the A/E/F-tricycle of the natural product and afforded the unexpected product **54** after intramolecular oxy-Michael.

Scheme 1.6 *Completion of C_{18}-diterpenoid alkaloid neofinaconitine (**60**).*



To break the unnecessary C–O bond of the enol ether **54**, allylic oxidation and mesylate formation enabled elimination to bis-enone **59** (Scheme 1.6). The final bond of the natural product core is forged using a Giese addition of a C7-radical to the D-ring enone to give **59**. This intermediate is elaborated to the C_{18}-diterpenoid alkaloid neofinaconitine (**60**) in 11 further steps.

1.4 CONCLUDING REMARKS

The complex carbon frameworks of the diterpenoid alkaloids have provoked a number of creative synthetic approaches. The early structural elucidation work on diterpenoid alkaloids

provides insight into the probable biosynthetic relationship between different subfamilies of diterpenoid alkaloids. This has informed many of the total synthetic efforts, as multiple groups have reported approaches which convert the carbon framework of one natural product subfamily to another. Despite the success of synthetic chemists in accessing these natural products over the past 50 years, they still remain attractive targets for total synthesis and inspire development of creative synthetic strategies.

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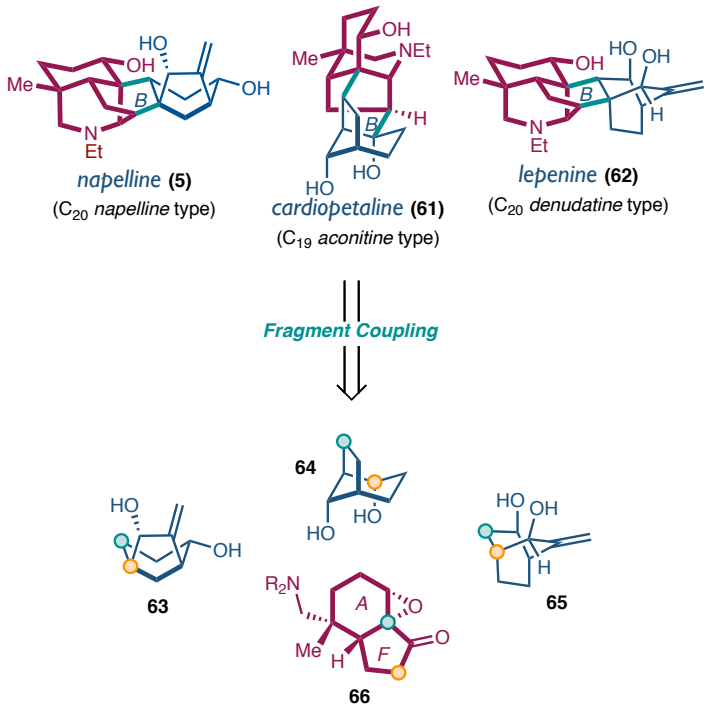
Chapter 2

Convergent Approach to C_{19}-Diterpenoid Alkaloids via 1,2-Addition/Semipinacol Sequence

2.1 INTRODUCTION

This chapter details our fragment coupling approach to the C_{19}-diterpenoid alkaloids as an alternative to the commonly employed biomimetic skeletal rearrangement of the denudatine scaffold. Our retrosynthetic analysis of (–)-talatisamine (**1**) is presented. The asymmetric syntheses of our two coupling partners are described, which includes a direct synthesis of the [3.2.1]-bicyclooctene C/D-ring bicyclic fragment via an arene-alkene *meta*-photocycloaddition. Lastly, our two-step fragment coupling sequence of 1,2-addition of an alkenyl lithium C/D-bicyclic fragment to an epoxy ketone A/F-bicyclic fragment followed by Lewis acid-catalyzed semipinacol rearrangement is presented.

Figure 2.1 *Unified approach to C_{19} and C_{20} diterpenoid alkaloids: disconnection through the central B-ring.*



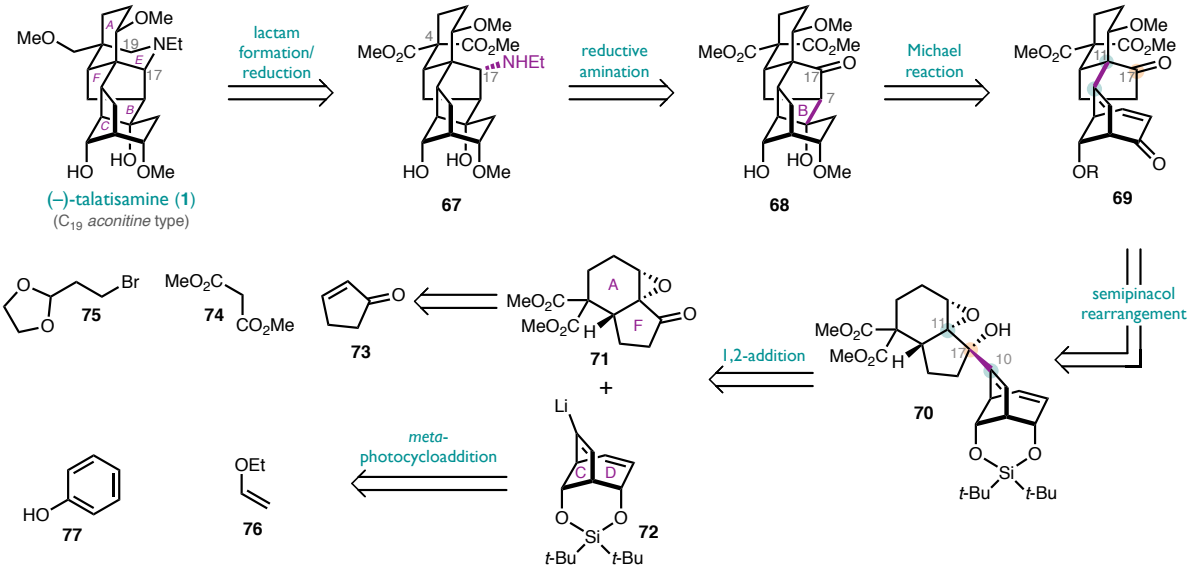
2.2 RETROSYNTHETIC ANALYSIS OF C_{19}-DITERPENOID ALKALOIDS

The structural similarities of various diterpenoid alkaloid subfamilies inspired us to devise a unified approach to access natural products with a variety of carbon skeletons (Figure 2.1). The C_{19}-aconitine, C_{20}-napelline and C_{20}-denudatine type diterpenoid alkaloids share a common A/E/F-tricycle connected by two bonds of the central B-ring to a C/D-bicycle characteristic of each subfamily. As such, we envisioned a retrosynthetic disconnection through the two bonds of the B-ring would allow us to access each subfamily through a fragment coupling of the proper C/D-bicycle with a common A/F-bicycle. We sought to apply this strategy first to the synthesis of C_{19}-diterpenoid alkaloids.

Our retrosynthetic analysis of (–)-talatisamine (**1**) is shown in Figure 2.2. Disconnection of the C19-N bond via lactam formation and reduction gives secondary amine

67, which we envisioned installing through a late stage reductive amination of a C17 ketone (**68**). Disconnection of the C7–C8 bond via enolate functionalization opens the central B-ring. Key to our fragment coupling strategy, we envisioned engaging epoxy-alcohol **70** in a semipinacol rearrangement, using the strain release of the epoxide opening as the enthalpic driving force to form the hindered C11 quaternary center. To form the C10–C17 bond of **70**, we envisioned a 1,2-addition of an organolithium C/D-bicyclic fragment (**72**) to an A/F-epoxy ketone fragment (**71**). The [3.2.1]-bicycle was envisioned to arise from an arene-alkene *meta*-photocycloaddition. Epoxy ketone **71** was disconnected to 2-cyclopenten-1-one (**73**), dimethyl malonate (**74**) and 2-(2-bromoethyl)-1,3-dioxolane (**75**).

Figure 2.2 *Retrosynthetic analysis of (–)-talatisamine (**1**).*

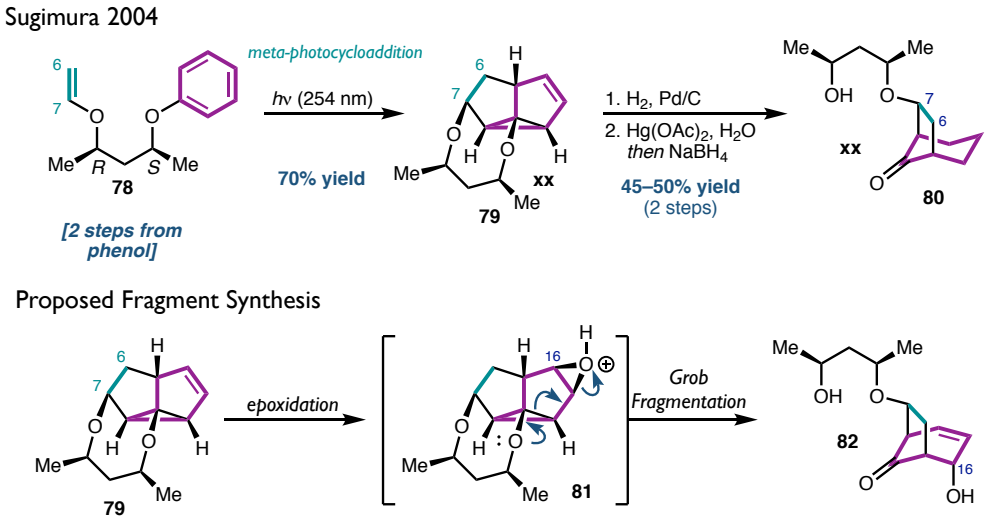


2.3 SYNTHESIS OF FRAGMENT COUPLING PARTNERS

2.3.1 *Synthesis of [3.2.1]-Bicyclooctene C/D-Bicycle 90*

As mentioned above, we envisioned synthesis of the [3.2.1]-bicyclooctane prior to fragment coupling. When considering methods to form these bridged bicycles,[1,2] we were intrigued by a report from Sugimura and coworkers for a diastereoselective intramolecular arene-alkene *meta*-photocycloaddition (Scheme 2.1).[3,4] Following the meta-photocycloaddition, Sugimura and coworkers hydrogenate the olefin; we, however, envision leveraging this alkene to incorporate the oxidation pattern of the natural product. Epoxidation of this olefin, followed by Grob-fragmentation would lead to formation of C/D-bicycle **82** which is oxidized at C16.

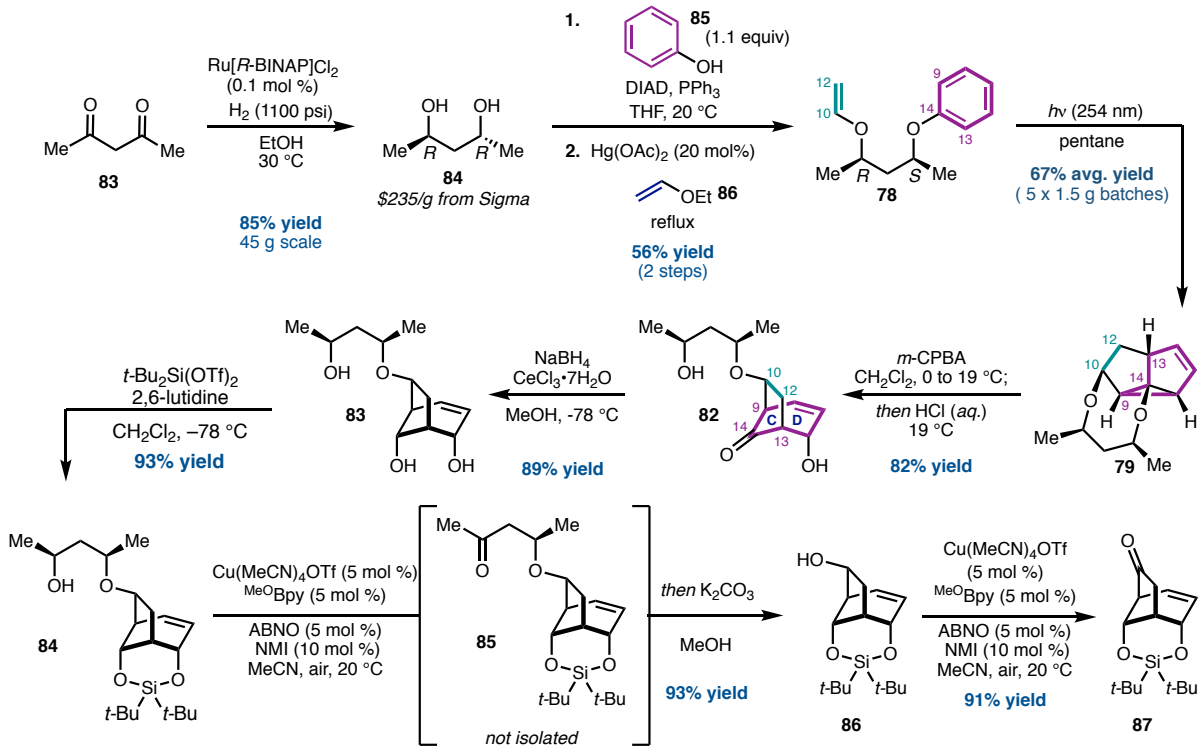
Scheme 2.1 *Sugimura's diastereoselective intramolecular meta-photocycloadition for the synthesis of [3.2.1]-bicyclooctanes.*



To begin, chiral diol **84** was synthesized by Noyori hydrogenation of acetylacetone (**83**, Scheme 2.2).[5] Mitsunobu reaction of **84** with phenol (**85**) followed by transetherfication of ethyl vinyl ether (**86**) affords *meta*-photocycloaddition substrate **78**. Irradiation of **78** with UV

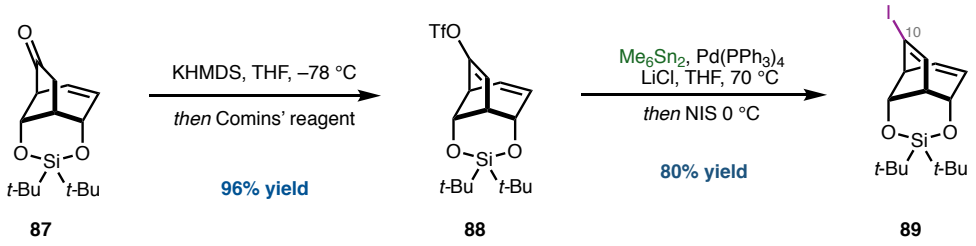
light results in formation of Sugimura's product **79** in yields comparable to those reported in the original communication. These intramolecular photochemical reactions must be run at low concentrations (~0.01 M) to prevent intermolecular reactions, limiting the largest viable scale of this reaction to 1.5 grams per batch. With **79** in hand, we set out to test the proposed epoxidation and Grob-fragmentation to access **82**. Epoxidation with *m*CPBA followed by treatment with aqueous hydrochloric acid furnishes the desired C/D-bicycle **82**. Luche reduction of **82** yields the axial C14 alcohol **83**. The C14/C16-1,3-diol is protected as the siliconide **84**. Having functionalized the D-ring, the chiral auxiliary needed to be removed. Oxidation of alcohol **84** using Stahl's conditions produces β-alkoxyketone **85** which is treated directly with basic methanol to cleave the auxiliary via E1cB elimination to give alcohol **86** as a single enantiomer. This alcohol is then oxidized to give ketone **87**.

Scheme 2.2 *Synthesis of [3.2.1]-bicyclic ketone **87** enabled by Sugimura's meta-photocycloaddition*



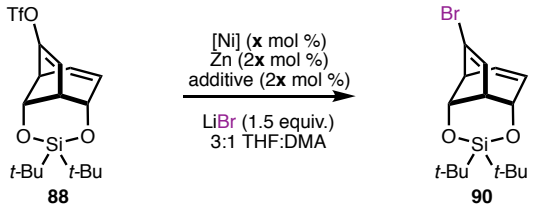
To access a precursor to an organometallic C/D-bicycle fragment, C10-ketone **87** was converted to an alkenyl halide (Scheme 2.3). The ketone was first converted to alkenyl triflate **88** using KHMDS and Comins' reagent. A Stille coupling of **88** and hexamethylditin forms the corresponding alkenyl stannane which is converted to alkenyl iodide **89** upon treatment with *N*-iodosuccinimide. While this sequence was effective, it requires the use of stoichiometric quantities of the expensive and highly toxic reagent hexamethylditin. Recently, our lab reported a convenient nickel-catalyzed method to achieve the same transformation.[6] The conditions were optimized for substrate **88**, screening nickel (II) catalysts, catalyst loading and additives (Table 2.1). 5 mol % loading of $Ni(OAc)_2 \bullet 4H_2O$ with NMI as the additive were the optimal conditions, delivering alkenyl bromide **90** in 87% yield. The main limitation was scalability of the reaction—scaling the reaction past 2.3 mmol (1.0 grams) of substrate results in incomplete conversion. This is likely due to the heterogeneity of the reaction; vigorous stirring was key to achieving complete conversion of starting material. In all, this represents a 10-step synthesis of the C/D-bicycle coupling partner **90**.

Scheme 2.3 *Synthesis alkenyl halide coupling partner **89** via Stille coupling.*



87 **88** **89**

Table 2.1 *Optimization of Ni-catalyzed conversion of enol triflate* ***88*** *to alkenyl bromide* ***90***.



Entry	Scale (mmol)	[Ni]	[Ni] loading (x)	Additive	Temp	yield
1	0.1	$NiBr_2$	10 mol %	DMAP	21 °C	30%[a]
2	0.1	$NiBr_2$•dme	10 mol %	"	21 °C	60%[a]
3	0.1	$Ni(OAc)_2$ •$4H_2O$	2.5 mol %	"	26 °C	3:1 pdt:SM
4	0.1	"	5 mol %	"	26 °C	1.4:1 pdt:SM
5	0.1	"	7.5 mol %	"	21 °C	74%[a]
6	0.1	"	10 mol %	"	26 °C	69%
7	0.1	"	10 mol %	NMI	25 °C	66%
8	0.3	"	7.5 mol %	"	21 °C	78%
9	0.3	"	5 mol %	"	21 °C	81%
10	1.0	"	5 mol %	"	21 °C	87%
11	2.3	$Ni(OAc)_2$ • $4H_2O$	5 mol %	NMI	21 °C	87%

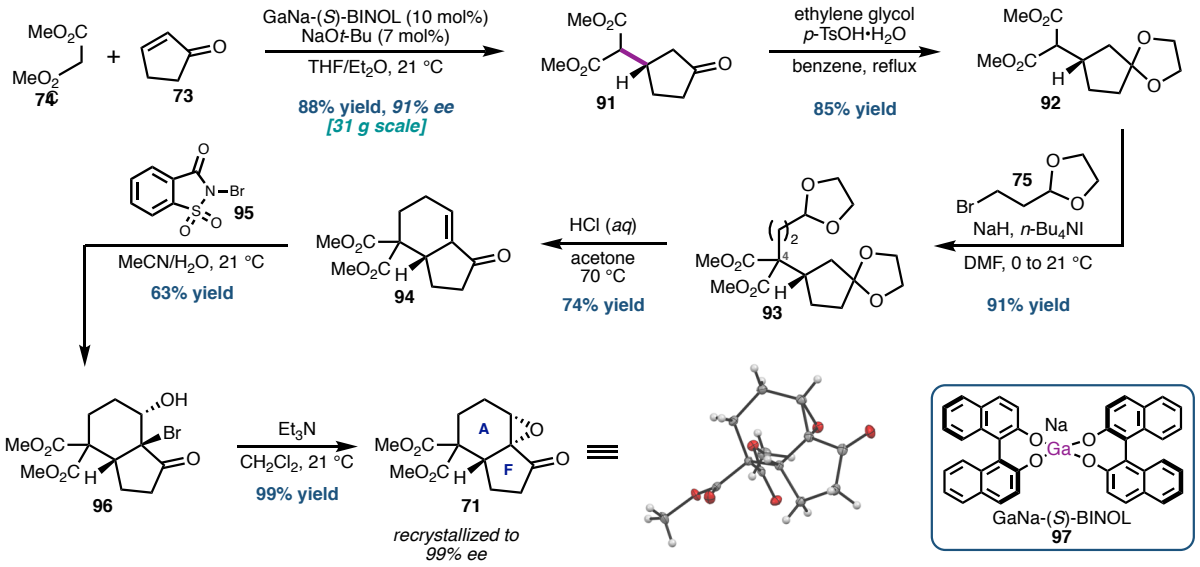
[a]*NMR yield using dimethylfumarate as internal standard*

2.3.2 *Enantioselective Synthesis of A/F-Bicycle Epoxy Ketone 71*

Our synthesis of epoxy ketone fragment **71** began with an asymmetric Michael addition of dimethyl malonate (**74**) to 2-cyclopenten-1-one (**73**) using Shibasaki's heterobimetallic catalyst **97** (Scheme 2.4).[7] We developed a highly scalable protocol for this reaction, providing **91** in 88% yield and 91% enantiomeric excess (ee) on 31 g scale.[8] The ketone of **91** was converted to ketal **92** by treating with ethylene glycol and catalytic acid in benzene at reflux using a Dean-Stark reaction setup. Alkylation of the malonate with three-carbon fragment **75** forms the C4 quaternary center in **93**. Acid-catalyzed double dioxolane deprotection and concomitant aldol condensation closes the A-ring to give enone **94**. A two-step sequence was employed to introduce the epoxide on the concave face: treatment of **94** with the strongly

electrophilic bromonium ion source *N*-bromosacharrin (**95**) and water furnishes bromohydrin **96**, isolated as a single diastereomer in 63% yield. The crude diastereomeric ratio (d.r.) for this reaction was ~3:1. Elimination of HBr to yield the epoxide **71** was easily achieved by treating **96** with triethylamine at ambient temperature. **71** was recrystallized to enantiopurity, giving access to this A/F-fragment in six steps from commercial starting materials.

Scheme 2.4 *Enantioselective synthesis of epoxy ketone **71**.*

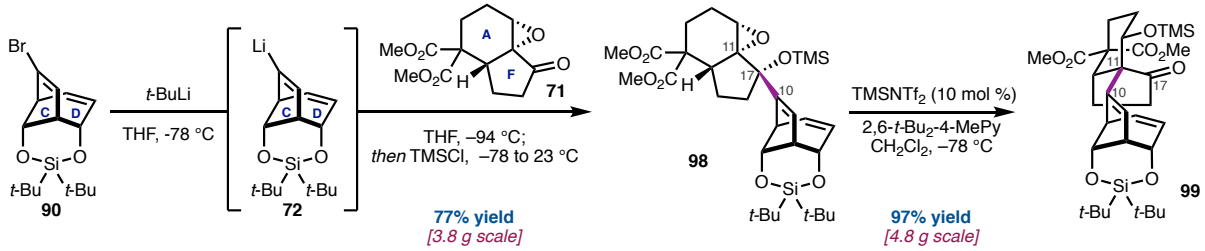


2.4 1,2-ADDITION/SEMIPINACOL REARRANGEMENT FRAGMENT COUPLING SEQUENCE

Having synthesized our key fragments for the synthesis of **1**, we set out to test our fragment coupling sequence (Scheme 2.5). Alkenyl bromide **90** was converted to the alkenyl lithium 72 upon treatment with *tert*-butyllithium at low temperature. This alkenyl lithium was added slowly by cannula to a solution of the epoxy ketone **71** at -94 °C. The 1,2-addition was quenched with TMSCl to give epoxy silyl ether **98** in good yield on 3.8 gram scale. Treatment of the 1,2-addition product **98** with a catalytic amount of the Lewis acid $TMSNTf_2$ and a pyridine base affords semipinacol rearrangement product **99** in near quantitative yield on 4.3

gram scale. This remarkable two-step sequence brings together all of the carbon atoms needed to access the aconitine core and forms the key C11 quaternary center, demonstrating the power of 1,2-addition/semipinacol rearrangement as a fragment coupling tactic.

Scheme 2.5 *1,2-Addition/semipinacol rearrangement fragment coupling to prepare* ***99***.

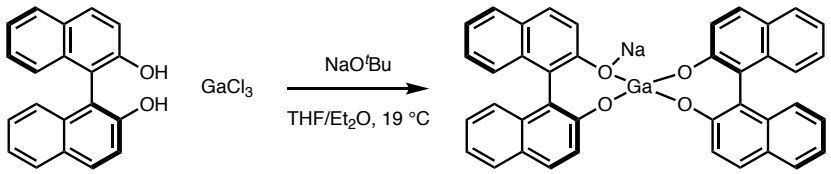


2.5 CONCLUDING REMARKS

A 1,2-addition/semipinacol rearrangement fragment coupling strategy to access C_{19} and C_{20} diterpenoid alkaloids has been described. Retrosynthetic analysis of the C19 diterpenoid alkaloid (–)-talatisamine (**1**) identifies [3.2.1]-bicyclooctene **91** and epoxy ketone **71** as practical coupling partners. Synthesis of a single enantiomer of **91** is achieved through diastereoselective intramolecular *meta*-photocycloaddition of an arene tethered to an alkene by a cleavable chiral auxiliary. An enantioselective Michael addition enables the enantioselective synthesis of epoxy ketone **71**. The aforementioned fragment coupling between **91** and **71** forms the key C11 quaternary center of the natural product in **99**.

2.6 EXPERIMENTAL SECTION

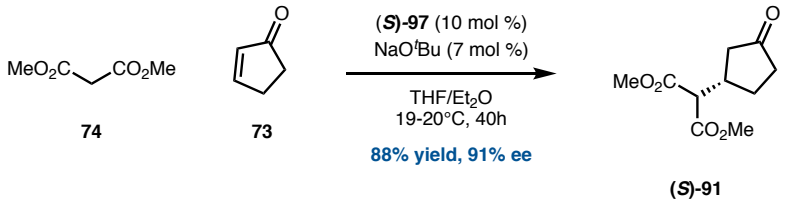
Preparation of GaNa-(*S*)-BINOL solution (0.05 M in 9:1 THF:Et_2O):[1,2]



In a flame-dried 500 mL round-bottom flask, NaO^{t}Bu (10.92 g, 0.114 mol, 4.0 equiv) was dissolved in THF (200 mL) under N_2 atmosphere. In a flame-dried 1 L round-bottom flask, (*S*)-(–)-1,1'-bi(2-naphthol) ((*S*)-BINOL, **(*S*)-100**) (16.26 g, 56.8 mmol, 2.0 equiv) was dissolved in THF (172 mL) under N_2 atmosphere. The solution of NaO^{t}Bu was transferred via cannula to the solution of **(*S*)-100** over ~20 minutes at ambient temperature (19 °C). The mixture was stirred for an additional 30 minutes.

In a flame-dried 1 L round-bottom flask, gallium (III) chloride (5.00 g, 28.4 mmol, 1.0 equiv) was dissolved in a mixture of THF (142 mL) and Et_2O (56 mL) under N_2 atmosphere. The solution of **(*S*)-S1** and NaO^{t}Bu was transferred to the solution of $GaCl_3$ via cannula over ~45 minutes at ambient temperature (19 °C). The mixture was stirred for an additional 2 hours before the heterogeneous mixture was allowed to settle, unperturbed for 18 hours.

Enantioselective synthesis of (*S*)-(–)-14:



A flame-dried 1 L, 3-necked round-bottom flask with 24/40 joints and a 1" Teflon coated egg-shaped magnetic stir bar was charged with NaO^{t}Bu (0.97 g, 10.1 mmol, 0.07 equiv). The flask was fitted with an oven-dried 250 mL graduated addition funnel and two rubber

septa. The flask was evacuated and backfilled with nitrogen three times (5 minutes under vacuum per cycle) before anhydrous THF (22.5 mL) was added by syringe. The supernatant solution of **(*S*)-100** (288 mL, 14.4 mmol, 0.10 equiv) was measured by transferring to the addition funnel via cannula and then added to the suspension of NaO^{t}Bu. Dimethyl malonate (**74**) (16.5 mL, 144 mmol, 1.0 equiv) was then added by syringe, followed by 2-cyclopenten-1-one (**73**) (12.0 mL, 144 mmol, 1.0 equiv). The mixture was stirred at room temperature (19-20 °C) for 40 hours.

The reaction was transferred to a 2L Erlenmeyer flask and 900 mL of 1M HCl (aq.) was added slowly while the mixture stirred. The mixture was transferred to a 4L separatory funnel and extracted with EtOAc (3 x 600 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (400 mL). The aqueous $NaHCO_3$ wash was back-extracted with EtOAc (200 mL). The combined organic phases were washed with brine (400 mL), dried over Na_2SO_4 (~300 g) filtered through cotton and concentrated *in vacuo*. The crude product was transferred to a tared 100 mL round-bottom flask with a 0.25" stir bar and dried on high-vacuum while heating to 75 °C with stirring for 1h. The crude product was obtained as a yellow oil (38.5 g).

The flask of crude product was fitted with a short-path distillation head. The product was purified by distillation under reduced pressure (180 °C oil bath, vacuum line at 210-214 mTorr. Four fractions were collected in the following quantities: 0.48 g (40-108 °C), 19.40 g (108-112 °C), 5.46 g (112-114 °C), 3.05 g (108-120 °C). The first and fourth fractions were combined in a 25 mL round-bottom flask with a 14/20 joint and a 0.25" egg-shaped stir bar and redistilled in the same manor to give 2.16 g (108-112 °C), which was combined with the second and third fractions of the initial distillation to give **(*S*)-91** as a colorless oil (27.0 g, 126

mmol, 88% yield, 91% ee). Enantiomeric excess was measured using chiral supercritical fluid chromatography (SFC) using a Mettler SFC supercritical CO_2 analytical chromatography system (CO_2 = 1450 psi, column temperature = 40 °C) with a Chiralcel AD-H column (4.6 mm x 25 cm) eluting with 5 % isopropanol at a flow rate of 2.5 mL/min over 12 minutes. A racemic standard of **(±)-14** was prepared using previously reported methods.[3]

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.77 (s, 3H), 3.75 (s, 3H), 3.38 (d, J = 9.4 Hz, 1H), 2.90-2.83 (m, 1H), 2.51 (dd, J = 18.4, 7.6 Hz, 1H), 2.34 (dd, J = 17.5, 8.2 Hz, 1H), 2.30 – 2.16 (m, 2H), 2.01 (dd, J = 18.5, 11.0 Hz, 1H), 1.69 – 1.61 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 217.1, 168.6, 168.56, 56.2, 56.2, 52.8, 43.0, 38.3, 36.5, 27.6.

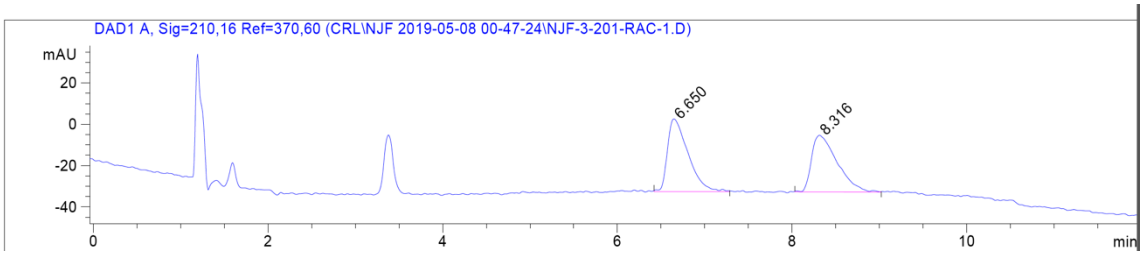
FTIR (NaCl, thin film): 2956, 1738, 1439, 1322, 1236, 1211, 1172, 1154, 1017, 787 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{10}H_{14}O_5$ $[M + H]^+$ 215.0914, found 215.0915 (0.46 ppm difference).

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = –84.8° (*c* = 1.22, $CHCl_3$).

TLC (2:1 Hexanes:EtOAc), R_f: 0.2 (purple in *p*-anisaldehyde)

SFC Data for racemic 91:

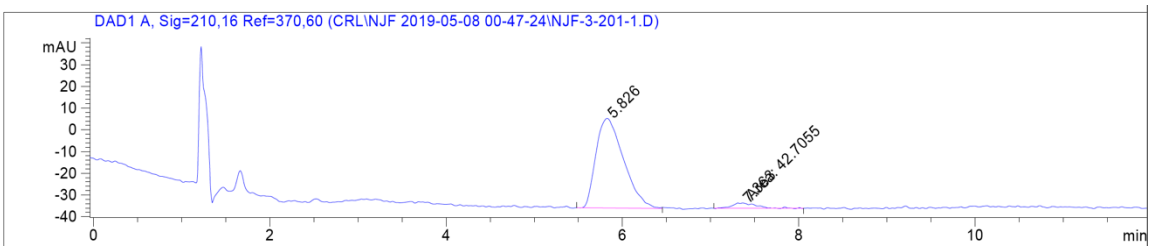


```
Signal 1: DAD1 A, Sig=210,16 Ref=370,60

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.650 BB    0.2416  578.09924   35.20285  50.7730
   2   8.316 BB    0.2859  560.49567   27.48701  49.2270

Totals :                  1138.59491   62.68986
```

SFC Data for enantioenriched (–)-91:

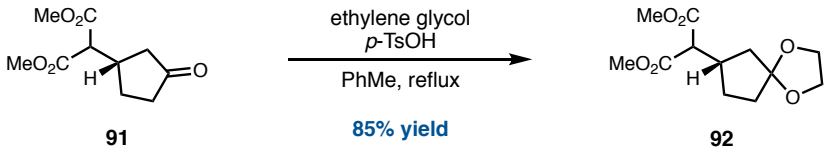



```
Signal 1: DAD1 A, Sig=210,16 Ref=370,60

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.826 BB    0.3083  898.89612   41.24311  95.4646
   2   7.363 MM    0.2972   42.70552    2.39477   4.5354

Totals :                  941.60163   43.63788
```

Preparation of ketal 92:



91 **92**

In a flame dried 1 L, round-bottom flask equipped with a reflux condenser and Dean–Stark trap, ketone **91** (38.6 g, 180 mmol, 1.0 equiv) was dissolved in toluene (600 mL). To this solution was added ethylene glycol (20.2 mL, 360 mmol, 2.0 equiv) and *p*-TsOH•H_2O (3.42 g, 18.0 mmol, 0.10 equiv), and the reaction was heated to reflux for 11 h. The reaction was then

cooled to room temperature and diluted with Et_2O (1200 mL). The solution was washed with saturated aqueous $NaHCO_3$ (2 x 400 mL), and the combined aqueous phase was extracted with Et_2O (750 mL). The combined organic phase was washed with brine (500 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by silica gel chromatography (25% EtOAc in hexanes with 2% NEt_3) provided ketal **92** (39.6 g, 153 mmol, 85% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.93 – 3.84 (m, 4H), 3.72 (m, 6H), 3.31 (d, J = 10.2 Hz, 1H), 2.75 – 2.62 (m, 1H), 2.08 (ddd, J = 13.7, 8.0, 1.2 Hz, 1H), 1.99 – 1.86 (m, 2H), 1.85 – 1.75 (m, 1H), 1.56 (dd, J = 13.6, 9.5 Hz, 1H), 1.48 – 1.36 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.0, 168.9, 117.0, 64.3, 64.2, 56.7, 52.4, 52.4, 40.6, 36.8, 35.5, 28.2.

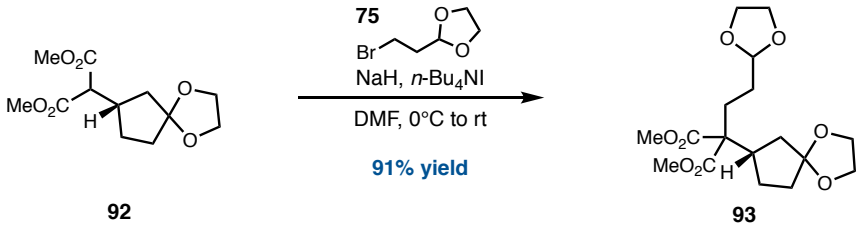
FTIR (NaCl, thin film): 2956, 2885, 1754, 1734, 1435, 1316, 1216, 1151, 1079, 1017, 947 cm^{-1}.

HRMS: (PMM) calc'd for $C_{12}H_{19}O_6$ $[M + H]^+$ 259.1176, found 259.1169.

$[\alpha]_D^{25}$ = +2.2° (c = 1.4, $CHCl_3$).

TLC (2:1 Hexanes:EtOAc), R_f: 0.3 (purple in *p*-anisaldehyde)

Preparation of bis-ketal 93:



A flame dried 1 L round-bottom flask was charged with diester **92** (39.9 g, 155 mmol, 1.0 equiv) and DMF (386 mL). The solution was cooled to 0 °C before NaH (60% dispersion

in mineral oil, 7.42 g, 185 mmol, 1.2 equiv) was added in portions. *n*-Bu_4NI (11.39 g, 30.8 mmol, 0.20 equiv) and 2-(2-bromoethyl)-1,3-dioxolane (**75**, 27.2 mL, 232 mmol, 1.5 equiv) were added sequentially, and the reaction was allowed to warm to room temperature and stirred for 72 hours. The reaction was then quenched by addition of sat. NH_4Cl (600 mL). The mixture was extracted with EtOAc (3 x 1 L), and the combined organic extracts were washed with sat. NH_4Cl (2 x 400 mL) followed by brine (400 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by silica gel chromatography (10 to 50% EtOAc in hexanes) afforded bis-ketal **93** (50.4 g, 141 mmol, 91% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.83 (td, *J* = 4.5, 1.9 Hz, 1H), 3.97 – 3.81 (m, 8H), 3.71 (s, 3H), 3.71 (s, 3H), 2.70 – 2.60 (m, 1H), 2.05 – 1.95 (m, 3H), 1.91 – 1.80 (m, 2H), 1.80 – 1.66 (m, 2H), 1.64 – 1.50 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 171.2, 171.1, 116.6, 103.9, 64.9, 64.9, 64.2, 64.1, 59.8, 52.2, 52.1, 40.4, 38.0, 35.3, 29.0, 27.9, 25.4.

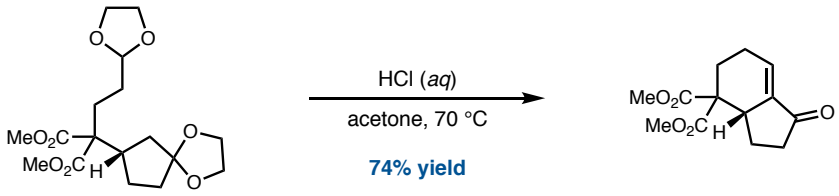
FTIR (NaCl, thin film): 2954, 2915, 2877, 1728, 1434, 1227, 1141, 1024 cm^{-1}.

HRMS: (FAB) calc'd for $C_{17}H_{27}O_8$ $[M + H]^+$ 359.1706, found 359.1716.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = –0.69° (*c* = 0.60, $CHCl_3$).

TLC (1:1 Hexanes:EtOAc), R_f: 0.3 (turquoise in *p*-anisaldehyde)

Preparation of enone 94:



93 **94**

In a 1L, round-bottom flask equipped with a reflux condenser, bis-dioxolane **93** (25.2 g, 70.3 mmol, 1.0 equiv) was dissolved in acetone (280 mL). Aqueous HCl (70 mL, 2 N, 140 mmol, 2.0 equiv) was added, and the reaction was heated to 70 °C with stirring for 16 h. The reaction was cooled to room temperature and quenched with sat. $NaHCO_3$ (300 mL) and partially concentrated *in vacuo* to remove acetone. The resulting mixture was extracted with CH_2Cl_2 (3 x 450 mL), and the combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified by silica gel chromatography (10 to 40% EtOAc in hexanes) to afford enone **94** (13.03 g, 51.6 mmol, 74% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.69 (q, J = 3.8 Hz, 1H), 3.78 (s, 3H), 3.67 (s, 3H), 3.10 (qdd, J = 7.4, 3.5, 2.1 Hz, 1H), 2.53 – 2.37 (m, 4H), 2.32 – 2.22 (m, 2H), 2.11 –1.90 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 204.6, 171.8, 169.5, 137.1, 131.3, 55.0, 52.7, 52.2, 42.8, 37.7, 29.4, 23.9, 23.2.

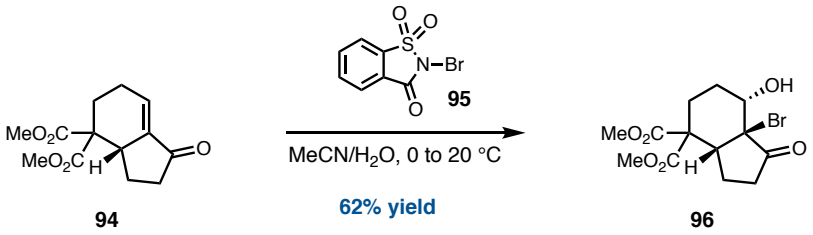
FTIR (NaCl, thin film): 3022, 2956, 2898, 2848, 1732, 1659, 1451, 1434, 1283, 1256, 1214, 1174, 1143, 1064 cm^{-1}.

HRMS: (FAB) calc'd for $C_{13}H_{17}O_5$ $[M + H]^+$ 253.1076, found 253.1076.

$[\alpha]_D^{25}$ = –34° (c = 1.7, $CHCl_3$).

TLC (1:1 Hexanes:EtOAc), R_f: 0.6 (UV, blue in *p*-anisaldehyde)

Preparation bromohydrin 96:



A 250 mL, round-bottom flask was charged with enone **94** (3.91 g, 15.5 mmol, 1.0 equiv), MeCN (64 mL), and H_2O (12 mL), and the mixture was cooled to 0 °C. *N*-bromosaccharin (5.28 g, 20.1 mmol, 1.3 equiv) was added slowly in portions over 30 minutes. The reaction was warmed to 20 °C and stirred for 6.5 h, then quenched by addition of sat. $Na_2S_2O_3$ (150 mL). The mixture was extracted with Et_2O (3 x 250 mL), and the combined organic extracts were washed with sat. $NaHCO_3$ (2 x 150 mL), brine (150 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford a crude white solid. This was dissolved in Et_2O (600 mL) at 35 °C. The solution was concentrated until ca. 300 mL of solvent remained, and then hexanes (300 mL) was added. The solution was concentrated until ca. 300 mL of solvent remained, with white solids suspended within. The solvent was decanted into a Büchner funnel, washing the flask carefully with hexanes. The residual solids in the flask were collected, affording bromohydrin **96** (3.37 g, 9.65 mmol, 62% yield) as a white solid.

Note: An NMR sample of the crude reaction mixture shows ~3:1 mixture of diastereomers.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 4.37 (t, *J* = 2.8 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.10 (ddd, *J* = 12.3, 5.9, 1.6 Hz, 1H), 2.81 (d, *J* = 1.7 Hz, 1H), 2.79 – 2.71 (m, 1H), 2.51 (dd, *J* = 18.0, 7.3 Hz, 1H), 2.41 – 2.32 (m, 2H), 2.30 – 2.17 (m, 2H), 2.07 – 1.98 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 211.6, 171.3, 171.1, 76.5, 55.5, 53.0, 52.5, 47.9, 42.2, 36.2, 28.2, 27.6, 21.3.

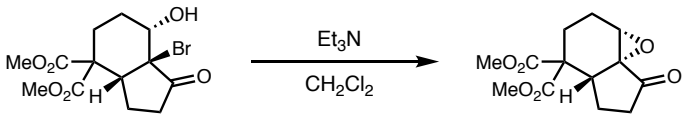
FTIR (NaCl, thin film): 3436, 2998, 2955, 2847, 1748, 1732, 1435, 1403, 1252, 1213, 1152, 1091, 1073, 1056, 980 cm^{-1}.

HRMS: (FAB) calc'd for $C_{13}H_{18}BrO_6$ $[M + H]^+$ 349.0287, found 349.0275.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = –49° (*c* = 0.17, $CHCl_3$).

TLC (1:1 Hexanes:EtOAc), R_f: 0.6 (orange in *p*-anisaldehyde)

Preparation of epoxyketone 71:



96 **71**

In a 250 mL, round-bottom flask, bromohydrin **96** (6.66 g, 19.1 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 191 mL). Et_3N (3.2 mL, 22.9 mmol, 1.2 equiv) was added, and the reaction was stirred at 20 °C for 9 h. The mixture was loaded directly onto a column of silica gel (slurried in hexanes), and purification by chromatography (100% hexanes, then 40% EtOAc in hexanes) afforded epoxyketone **71** (5.10 g, 19.1 mmol, 99% yield) as a white solid. The resulting solid was recrystallized from acetone layered with hexanes to afford epoxyketone **71** in >99% ee.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.76 (s, 1H), 3.76 – 3.73 (m, 4H), 2.93 (dd, *J* = 12.5, 5.8 Hz, 1H), 2.68 (qd, *J* = 11.7, 7.4 Hz, 1H), 2.58 (ddd, *J* = 18.7, 7.6, 1.6 Hz, 1H), 2.48 – 2.28 (m, 4H), 2.12 – 2.01 (m, 1H), 1.72 – 1.61 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 212.0, 171.4, 169.8, 63.0, 56.1, 55.2, 53.1, 52.4, 43.8, 38.4, 29.3, 23.0, 21.7.

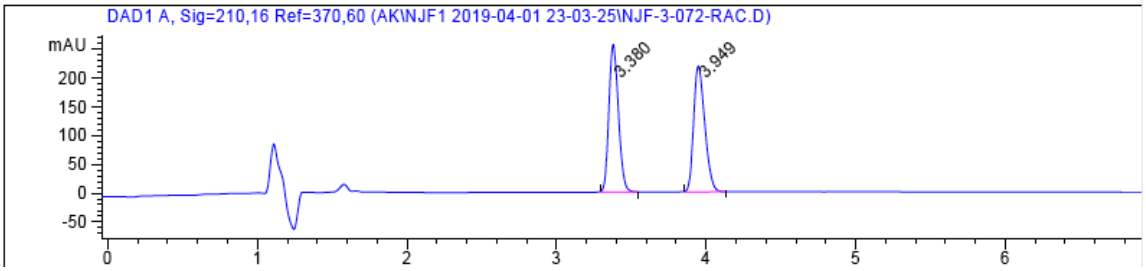
FTIR (NaCl/thin film): 3006, 2956, 2903, 2848, 1755, 1732, 1453, 1434, 1408, 1372, 1306, 1251, 1214, 1176, 1139, 1058, 890 cm^{-1}.

HRMS: (FAB) calc'd for $C_{13}H_{17}O_6$ $[M + H]^+$ 269.1025, found 269.1050.

$[\alpha]_D^{25} = -171°$ (c = 0.60, $CHCl_3$).

TLC (1:1 Hexanes:EtOAc), R_f: 0.6 (yellow/orange in *p*-anisaldehyde)

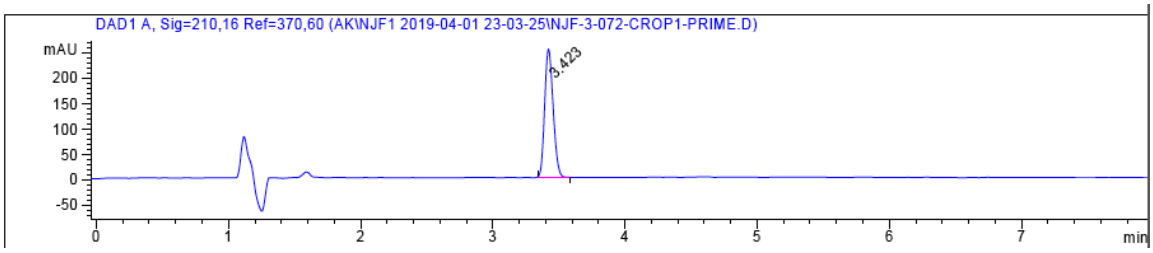
SFC data for racemic epoxyketone 9:



Signal 1: DAD1 A, Sig=210,16 Ref=370,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.380	BB	0.0683	1135.58337	253.08704	50.0585
2	3.949	BB	0.0845	1132.93115	218.41344	49.9415
Totals :				2268.51453	471.50047	

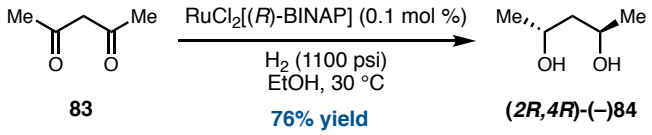
SFC data for enantiopure epoxyketone 9:



Signal 1: DAD1 A, Sig=210,16 Ref=370,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.423	BB	0.0728	1129.82751	249.84152	100.0000
Totals :				1129.82751	249.84152	

Preparation of Diol (2R, 4R)-(–)–84:[4]

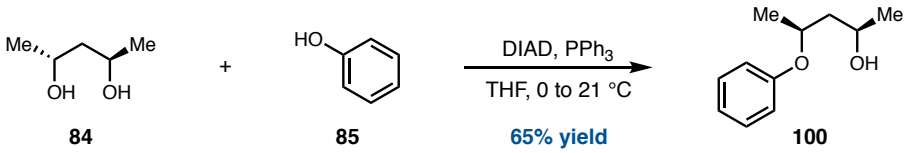


83 **(*2R,4R*)-(–)84**

A flame-dried 100 mL Schlenk flask was charged with acetylacetone (**83**, 32.3 mL, 315 mmol, 1.0 equiv) and 200-proof EtOH (32.3 mL). The solution was sparged with N_2 for 1 hour. A parr bomb, an oven-dried 150 mL glass jar with a stirbar, and the Schlenk flask of acac/EtOH solution were brought into a N_2-filled glovebox. The solution of acac in EtOH was transferred to the glass jar and $RuCl_2$[(*R*)-BINAP] (0.250 g, 0.315 mmol, 0.1 mol %) was added. The jar of reaction mixture was lowered into the bomb, which was then sealed and brought out of the glovebox. The bomb was purged with H_2 by pressurizing to 100 psi then releasing the pressure (3 cycles). The bomb was pressurized with H_2 to 1100 psi, lowered into an oil bath at 30 °C and secured with a chain clamp. After 1 day, the pressure had dropped to ~850 psi, so the vessel was pressurized to 1100 psi. After another 1 day, the pressure had dropped to ~900 psi and was again pressurized to 1100 psi. The reaction was stirred an additional 4 days (6 days total). The pressure was released and the reaction mixture was transferred to a 250 mL round-bottom flask and sparged with N_2 for 1 hour. The mixture was concentrated *in vacuo*. The product was purified by distillation using a short-path distillation head under reduced pressure (120 °C oil bath, 15 torr). (2*R*,4*R*)-2,4-pentanediol (**(*2R,4R*)-(–)-84**) was isolated as a colorless oil which crystallized on standing (b.p. 90-100 °C (15 torr), 24.9 g, 239 mmol, 76% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.18 (q, *J* = 6.0 Hz, 2H), 2.26 (br, 2H), 1.62 (dd, *J* = 6.0, 5.1 Hz, 2H), 1.26 (d, *J* = 6.3 Hz, 6H).

Preparation of aryl ether 100:

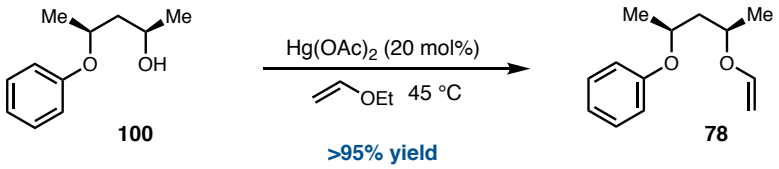


In a flame dried 1 L, round-bottom flask equipped with an addition funnel, (2*R*, 4*R*)-pentanediol (**84**, 10.42 g, 100 mmol, 1.0 equiv), phenol (**85**, 10.35 g, 110 mmol, 1.1 equiv), and PPh_3 (31.47 g, 120 mmol, 1.2 equiv) were dissolved in THF (450 mL) and the mixture was cooled to 0 °C. A solution of DIAD (23.6 mL, 120 mmol, 1.2 equiv) in THF (100 mL) was prepared in another flask, and transferred to the addition funnel. The DIAD solution was added dropwise to the vigorously stirring reaction over 40 min at 0 °C. After complete addition of the DIAD solution, the reaction was allowed to warm to 20 °C and stirred for 11 h before being partially concentrated *in vacuo* to a volume of ~200 mL. The mixture was filtered over celite to remove $(O)PPh_3$, and then further concentrated *in vacuo.* Purification of the crude residue by silica gel chromatography (10 to 45% EtOAc in hexanes) afforded arene **100** (11.7 g, 64.9 mmol, 65% yield). Spectroscopic data matched that reported by Sugimura *et al.*[5]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 2H), 6.99 – 6.91 (m, 3H), 4.61 (dqd, *J* = 8.6, 6.0, 4.4 Hz, 1H), 4.06 (dqt, *J* = 8.9, 6.1, 2.7 Hz, 1H), 2.56 (s, 1H), 1.95 (dt, *J* = 14.4, 8.8 Hz, 1H), 1.70 (ddd, *J* = 14.4, 4.5, 3.1 Hz, 1H), 1.31 (d, J = 6.0 Hz, 3H), 1.23 (d, J = 6.2 Hz, 3H).

TLC (2:1 Hexanes:EtOAc), R_f: 0.4 (UV, purple in *p*-anisaldehyde)

Preparation of arene olefin 78:

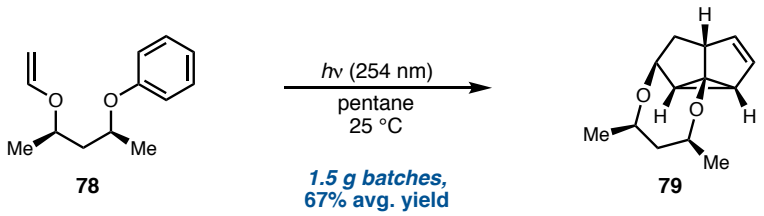


In a 250 mL, round-bottom flask equipped with a reflux condenser, arene **100** (3.90 g, 21.6 mmol, 1.0 equiv) was dissolved in ethyl vinyl ether (108 mL), and $Hg(OAc)_2$ (689 mg, 2.16 mmol, 0.10 equiv) was added. The mixture was heated to reflux and stirred for 18 h, at which point, the reaction was cooled to room temperature, and another portion of $Hg(OAc)_2$ (689 mg, 2.16 mmol, 0.10 equiv) was added, and the reaction was brought back to reflux. After stirring for another 15 h at reflux, the reaction was quenched by addition of sat. $NaHCO_3$ (100 mL). The layers were separated, and the aqueous phase was extracted with Et_2O (3 x 200 mL). The combined organic extracts were washed with brine (200 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by filtering over a short plug of silica (eluting with 10% EtOAc/1% Et_3N in hexanes) to provide arene olefin **78** (4.5 g, 21.8 mmol, 100% yield) as a colorless oil. Spectroscopic data matched that reported by Sugimura *et al.*[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.24 (m, 2H), 6.97 – 6.86 (m, 3H), 6.34 (dd, *J* = 14.2, 6.6 Hz, 1H), 4.52 (h, *J* = 6.2 Hz, 1H), 4.33 (dd, *J* = 14.2, 1.6 Hz, 1H), 4.12 (h, *J* = 6.3 Hz, 1H), 4.03 (dd, *J* = 6.7, 1.6 Hz, 1H), 2.20 (dt, *J* = 13.9, 6.9 Hz, 1H), 1.65 (dt, *J* = 14.0, 6.0 Hz, 1H), 1.33 (d, *J* = 6.1 Hz, 3H), 1.25 (d, *J* = 6.2 Hz, 3H).

TLC (2:1 Hexanes:EtOAc), R_f: 0.7 (UV, purple in *p*-anisaldehyde)

Preparation of 7-substituted *meta*-photoadduct 79:

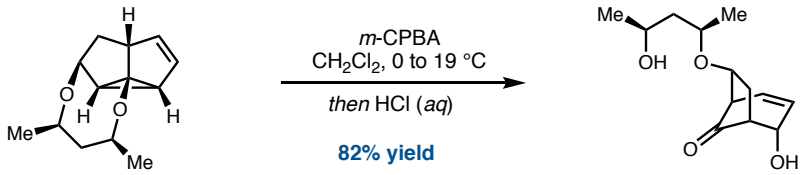


In a 1 L, round-bottom quartz flask, arene olefin **78** (1.5 g, 7.3 mmol, 1.0 equiv) was dissolved in pentane (700 mL). This solution was sparged with Ar for 75 min, then irradiated with stirring using a Honeywell 254 nm lamp for 27 h. The temperature was deliberately maintained at 25 °C using ventilation fans. Upon completion, the reaction was concentrated *in vacuo* to afford a crude residue. *This procedure was repeated for a total of 5 batches*. All 5 crude batches were combined and purified by silica gel chromatography (9% EtOAc in hexanes) to afford 7-substituted photoadduct **79** (5.0 g, 24.2 mmol, 67% average yield over 5 batches) as a white solid. Spectroscopic data matched that reported by Sugimura *et al.*[5]

^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.66 – 5.58 (m, 1H), 5.43 (dd, *J* = 5.6, 1.8 Hz, 1H), 4.48 (dd, *J* = 6.9, 2.5 Hz, 1H), 4.31 (p, *J* = 6.5 Hz, 1H), 4.05 (p, *J* = 6.6 Hz, 1H), 3.25 (dd, *J* = 8.3, 2.6 Hz, 1H), 2.50 – 2.42 (m, 3H), 2.34 (dt, *J* = 17.4, 7.4 Hz, 1H), 2.09 (ddd, *J* = 14.6, 6.9, 1.1 Hz, 1H), 1.59 (d, *J* = 17.4 Hz, 1H), 1.23 (s, 3H), 1.21 (s, 3H).

TLC (3:1 Hexanes:EtOAc), R_f: 0.5 (UV, purple in *p*-anisaldehyde)

Preparation of allylic alcohol 82:



79 **82**

A 2 L, round-bottom flask was charged with photoadduct **79** (11.84 g, 57.4 mmol, 1.0 equiv) and CH_2Cl_2 (575 mL), and cooled to 0 °C. *m*-CPBA (77% by wt., 14.79 g, 66.0 mmol, 1.15 equiv) was added, and the reaction was stirred for 30 min at 0 °C, then warmed to room temperature. After stirring for an additional 5 h at room temperature, 2 N HCl (115 mL, 230 mmol, 4.0 equiv) was added, and the biphasic mixture was stirred vigorously. After 40 min, the reaction was quenched by careful addition of sat. $NaHCO_3$ (330 mL), and stirred until bubbling ceased (ca. 30 min). The layers were separated, and the aqueous phase was extracted with 3:1 $CHCl_3$:*i*-PrOH (3 x 600 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by silica gel chromatography (40 to 45% acetone in hexanes) afforded allylic alcohol **82** (11.34 g, 47.2 mmol, 82% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.97 (dd, *J* = 9.0, 7.2 Hz, 1H), 5.77 (ddd, *J* = 9.0, 3.8, 1.2 Hz, 1H), 4.58 (s, 1H), 4.02 (dd, *J* = 6.1, 2.2 Hz, 1H), 3.90 (dqd, *J* = 9.2, 6.2, 3.0 Hz, 1H), 3.70 (dqd, *J* = 8.8, 6.0, 4.3 Hz, 1H), 2.79 (dd, *J* = 7.2, 1.5 Hz, 1H), 2.67 – 2.53 (m, 2H), 2.29 (br s, 1H), 2.18 – 2.05 (m, 2H), 1.61 (dt, *J* = 14.4, 8.9 Hz, 1H), 1.48 (ddd, *J* = 14.5, 4.4, 3.1 Hz, 1H), 1.16 (d, *J* = 3.8 Hz, 3H), 1.14 (d, *J* = 4.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 213.9, 131.4, 129.6, 81.1, 75.2, 73.9, 67.0, 51.6, 49.5, 45.9, 32.2, 23.6, 20.0.

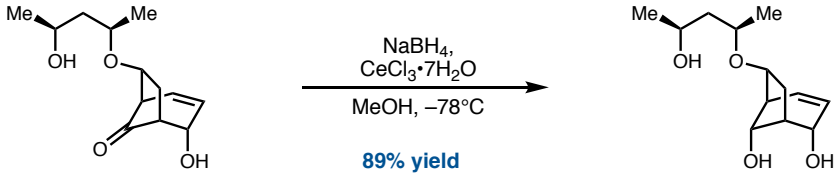
FTIR (NaCl, thin film): 3400, 2969, 2933, 1753, 1458, 1447, 1376, 1329, 1120, 1080, 1048, 926 cm^{-1}.

HRMS: (FAB) calc'd for $C_{13}H_{21}O_4$ $[M + H]^+$ 241.1440, found 241.1421.

$[\alpha]_D^{25}$ = –6.2° (*c* = 1.0, $CHCl_3$).

TLC (1:1 Hexanes:acetone), R_f: 0.3 ($KMnO_4$)

Preparation of triol 83:



82 **83**

In a 1 L, round-bottom flask, ketone **82** (6.7 g, 28 mmol, 1.0 equiv) and $CeCl_3$•$7H_2O$ (15.6 g, 41.8 mmol, 1.5 equiv) were dissolved in MeOH (280 mL). The solution was then cooled to –78 °C, and $NaBH_4$ (1.27 g, 33.5 mmol, 1.2 equiv) was added. After stirring for 2 h at –78 °C, the reaction was quenched with 1 M NaOH (200 mL), and concentrated *in vacuo* to remove MeOH. The aqueous phase was extracted with EtOAc (8 x 250 mL), and the combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Filtration of the crude residue over a short plug of silica (eluting with 50% acetone in hexanes) afforded triol **83** (6.1 g, 25 mmol, 89% yield) as a white solid.

Note: The product is highly water soluble, and thus requires rigorous extraction with a polar solvent such as EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.88 (ddt, *J* = 9.9, 3.7, 1.7 Hz, 1H), 5.74 (dd, *J* = 9.4, 7.0 Hz, 1H), 4.46 (s, 1H), 3.97 (dqd, *J* = 8.9, 6.3, 2.7 Hz, 1H), 3.83 (br s, 1H), 3.77 – 3.67 (m, 3H), 3.56 (br s, 2H), 2.63 – 2.58 (m, 1H), 2.46 (appar s, 1H), 1.77 (td, *J* = 4.7, 4.1, 1.7 Hz, 2H), 1.63 – 1.47 (m, 2H), 1.15 (d, *J* = 6.1 Hz, 3H), 1.12 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 129.7, 126.5, 78.3, 75.4, 72.0, 71.7, 68.1, 45.5, 45.4, 40.8, 33.8, 23.4, 20.1.

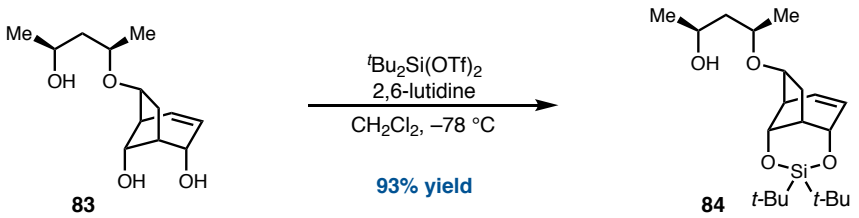
FTIR (NaCl, thin film): 3369, 3032, 2967, 2934, 1757, 1642, 1447, 1420, 1376, 1318, 1180, 1084, 1033, 970, 934 cm^{-1}.

HRMS: (FAB) calc'd for $C_{13}H_{23}O_4$ $[M + H]^+$ 243.1596, found 243.1616.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = –6.2° (*c* = 1.0, $CHCl_3$).

TLC (1:1 Hexanes:acetone), R*f*: 0.4 (UV, blue/green in *p*-anisaldehyde)

Preparation of siliconide 84:



A flame-dried 1 L, round-bottom flask was charged with triol **83** (9.0 g, 37.1 mmol, 1.0 equiv), which was then azeotroped with anhydrous PhMe to remove any trace moisture. CH_2Cl_2 (370 mL) and 2,6-lutidine (10.3 mL, 89.1 mmol, 2.40 equiv) were added, and the mixture was cooled to –78 °C. To this solution was added *t*-$Bu_2Si(OTf)_2$ (15.0 mL, 44.6 mmol, 1.20 equiv), and the reaction was stirred for 1 h. The reaction was quenched with sat. $NaHCO_3$ (150 mL) and H_2O (150 mL), and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 180 mL), and the combined organic extracts were washed with 0.1 M HCl

(300 mL), washed with sat. $NaHCO_3$ (100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified by silica gel chromatography (10 to 25% acetone in hexanes) to afford siliconide **84** (13.27 g, 34.7 mmol, 93% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.83 (ddd, *J* = 9.5, 4.4, 1.6 Hz, 1H), 5.74 (ddd, *J* = 9.6, 6.3, 1.2 Hz, 1H), 4.59 (t, *J* = 4.8 Hz, 1H), 4.04 – 3.91 (m, 2H), 3.80 – 3.70 (m, 2H), 3.39 (s, 1H), 2.78 (dd, *J* = 6.3, 4.1 Hz, 1H), 2.77 – 2.67 (m, 1H), 1.82 (ddd, *J* = 15.2, 7.5, 1.3 Hz, 1H), 1.71 (dd, *J* = 15.0, 7.9 Hz, 1H), 1.59 (dt, *J* = 14.5, 9.2 Hz, 1H), 1.51 (ddd, *J* = 14.5, 4.0, 2.6 Hz, 1H), 1.16 (d, *J* = 6.2 Hz, 3H), 1.12 (d, *J* = 6.0 Hz, 3H), 1.05 (s, 9H), 0.96 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 129.8, 129.1, 76.4, 74.7, 73.7, 71.0, 67.6, 46.4, 45.9, 38.6, 33.0, 28.7, 28.2, 23.6, 21.2, 20.7, 20.0.

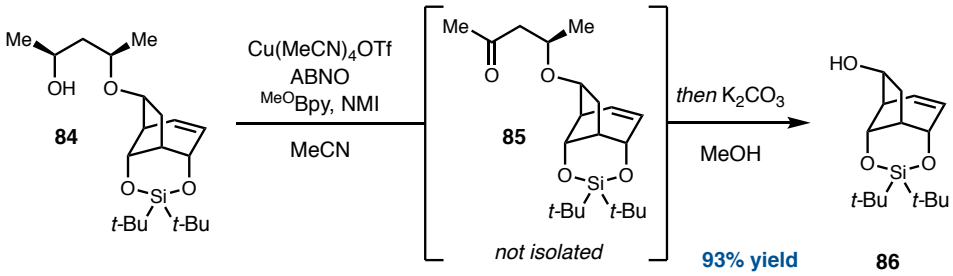
FTIR (NaCl, thin film): 3436, 3032, 2968, 2934, 2900, 2859, 1476, 1388, 1364, 1326, 1196, 1174, 1058, 1036, 1019, 998, 826 cm^{-1}.

HRMS: (FAB) calc'd for $C_{21}H_{39}O_4Si$ $[M + H]^+$ 383.2618, found 383.2630.

$[\alpha]_D^{25}$ = +59° (*c* = 0.90, $CHCl_3$).

TLC (1:1 Hexanes:EtOAc), R_f: 0.7 (green in *p*-anisaldehyde)

Preparation of alcohol 86:[6]



To a 500 mL, round-bottom flask was added alcohol **84** (3.92 g, 10.25 mmol, 1 equiv) and MeCN (102 mL). To this solution was added 4,4-dimethoxy-2,2'-bipyridine (111 mg, 0.513 mmol, 5 mol %), *N*-methylimidazole (82.5 μL, 1.03 mmol, 10 mol %), and ABNO (72

mg, 0.513 mmol, 5 mol %). Finally, $Cu(MeCN)_4OTf$ (193 mg, 0.513 mmol, 5 mol %) was added last, causing the solution to turn red/brown. The reaction was vigorously stirred for 60 minutes at room temperature open to air, during which time the reaction mixture turns blue, indicating its completion. At this time, MeOH (205 mL) was added, followed by powdered K_2CO_3 (powdered with mortar and pestle 7.84 g), causing the solution to turn brown, and the mixture was allowed to stir for 20 hours at room temperature. The mixture was filtered through a plug of silica gel and celite (to remove copper and solid K_2CO_3), flushed with excess ethyl acetate and concentrated *in vacuo*. The crude residue was purified by silica gel chromatography (20% ethyl acetate in hexanes, note: streaky on the column) to afford alcohol **86** (2.82 g, 9.53 mmol, 93% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (ddd, *J* = 9.4, 4.3, 1.6 Hz, 1H), 5.77 (ddd, *J* = 9.5, 6.1, 1.2 Hz, 1H), 4.78 (dd, *J* = 5.5, 4.1 Hz, 1H), 4.06 (dd, *J* = 6.6, 1.6 Hz, 1H), 4.01 (t, *J* = 3.9 Hz, 1H), 2.81 – 2.72 (m, 1H), 2.63 (ddd, *J* = 6.0, 4.3, 1.2 Hz, 1H), 1.82 (dd, *J* = 14.8, 6.8 Hz, 1H), 1.70 (ddt, *J* = 15.0, 7.9, 1.2 Hz, 1H), 1.07 (s, 9H), 0.98 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 129.6, 129.0, 73.6, 71.8, 71.0, 50.4, 38.7, 34.1, 28.7, 28.2, 21.2, 20.7.

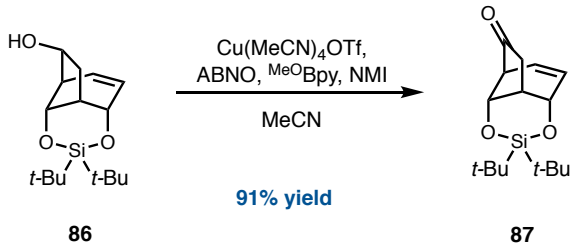
FTIR (NaCl, thin film): 3401, 3033, 2968, 2935, 2896, 2860, 1476, 1442, 1388, 1364, 1321, 1280, 1224, 1175, 1032, 998, 920, 825 cm^{-1}.

HRMS: (FAB) calc'd for $C_{16}H_{27}O_3Si$ $[M + H - H_2]^+$ 295.1747, found 295.1730.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +89° (*c* = 1.3, $CHCl_3$).

TLC (20%EtOAc in Hexanes), R_f: 0.4 (blue in *p*-anisaldehyde)

Preparation of ketone 87:



86 **87**

To a 500 mL, round-bottom flask was added alcohol **86** (2.82 g, 9.53 mmol, 1 equiv) and MeCN (95 mL). To this solution was added 4,4-dimethoxy-2,2'-bipyridine (103 mg, 0.476 mmol, 5 mol %), *N*-methylimidazole (73.6 µL, 0.953 mmol, 10 mol %), and ABNO (66.7 mg, 0.476 mmol, 5 mol %). Finally, $Cu(MeCN)_4OTf$ (179 mg, 0.476 mmol, 5 mol %) was added last, causing the solution to turn red/brown. The reaction was vigorously stirred for 60 minutes at room temperature open to air, during which time the reaction mixture turns blue, indicating its completion. The mixture was then filtered through a plug of silica gel, flushed with excess ethyl acetate, and concentrated *in vacuo*. The crude residue was purified by silica gel chromatography (15% ethyl acetate in hexanes) to afford ketone **87** (2.55 g, 8.67 mmol, 91% yield) as a white crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.08 (ddd, *J* = 9.3, 4.6, 1.6 Hz, 1H), 5.76 (ddd, *J* = 9.2, 6.9, 1.4 Hz, 1H), 4.59 (ddt, *J* = 5.6, 4.1, 1.1 Hz, 1H), 4.27 (ddd, *J* = 4.5, 3.4, 0.9 Hz, 1H), 3.15 (dddd, *J* = 6.8, 4.2, 1.4, 0.7 Hz, 1H), 3.02 (dddq, *J* = 6.8, 5.0, 3.3, 1.6 Hz, 1H), 2.37 – 2.31 (m, 1H), 2.27 (dd, *J* = 19.4, 6.4 Hz, 1H), 1.09 (s, 9H), 0.99 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 206.7, 131.3, 124.8, 71.7, 69.8, 55.1, 38.5, 37.6, 28.6, 28.2, 21.1, 20.8.

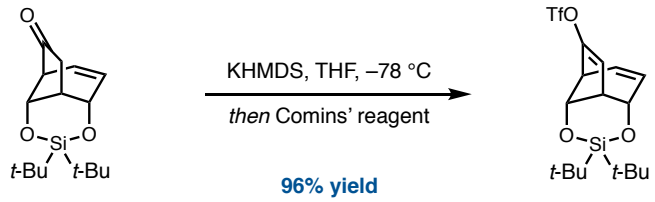
FTIR (NaCl, thin film): 3036, 2968, 2935, 2859, 1743, 1629, 1476, 1404, 1387, 1365, 1298, 1221, 1187, 1145, 1115, 997, 790 cm^{-1}.

HRMS: (FAB) calc'd for $C_{16}H_{27}O_3Si$ $[M + H]^+$ 295.1730, found 295.1731.

$[\alpha]_D^{25}$ = +51° (*c* = 1.1, $CHCl_3$).

TLC (20%EtOAc in Hexanes), R_f: 0.4 ($KMnO_4$) Note: Does not stain in *p*-anisaldehyde.

Preparation of enol triflate 88:



87 **88**

A flame-dried 250 mL, round-bottom flask was charged with ketone **87** (2.00 g, 6.80 mmol, 1.0 equiv), which was azeotroped with anhydrous PhMe to remove trace moisture. THF (58 mL) was added, and the mixture was cooled to –78 °C in a dry ice/acetone bath. KHMDS (16.3 mL, 0.5 M in toluene, 8.15 mmol, 1.2 equiv) was added, causing the solution to turn yellow, and the reaction was stirred for 45 minutes while kept at –78 °C. In a separate flask, a solution of Comins' reagent (2.93 g, 7.47 mmol, 1.1 equiv) in THF (10 mL) was prepared and cannulated into the first reaction flask. The resulting mixture was stirred for an additional hour at –78 °C, and then quenched with sat. $NaHCO_3$ (40 mL), and allowed to warm to room temperature. The biphasic mixture was then transferred to a separatory funnel with Et_2O (75 mL), and the layers were separated. The aqueous layer was extracted with more Et_2O (3 x 75 mL). The combined organic layers were then washed with aq. 0.5 M NaOH solution (4 x 75 mL), followed by brine (1 x 100 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the crude residue by silica gel chromatography (0 to 10% EtOAc in hexanes) afforded vinyl triflate **88** (2.77 g, 6.50 mmol, 96% yield) as a yellow oil which solidified on standing.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.21 (ddd, *J* = 9.6, 6.0, 1.1 Hz, 1H), 5.84 (dddd, *J* = 9.6, 4.5, 2.0, 0.8 Hz, 1H), 5.49 (dd, *J* = 4.1, 0.8 Hz, 1H), 4.69 (tt, *J* = 4.8, 1.0 Hz, 1H), 4.28 (ddd, *J* = 4.0, 2.9, 0.8 Hz, 1H), 3.13 (ddddd, *J* = 4.8, 3.9, 2.8, 1.9, 0.9 Hz, 1H), 2.91 (ddq, J = 5.6, 4.7, 0.9 Hz, 1H), 1.08 (s, 9H), 1.01 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.3, 131.7, 130.8, 118.5 (q, J_{C-F} =321.3 Hz, $SO_2\mathbf{C}F_3$), 113.2, 75.7, 65.0, 45.2, 44.2, 28.8, 28.2, 21.1, 20.7.

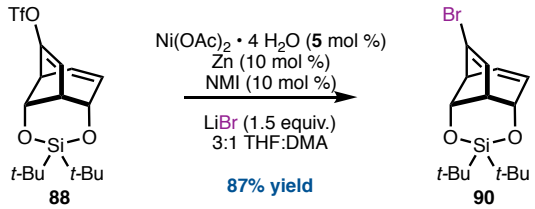
FTIR (NaCl, thin film): 3042, 2976, 2938, 2906, 2852, 1640, 1478, 1429, 1380, 1365, 1258, 1249, 1214, 1141, 1123, 1074, 1001, 926, 901 cm^{-1}.

HRMS: (FAB) calc'd for $C_{17}H_{26}F_3SSiO_5$ $[M + H]^+$ 427.1222, found 427.1205.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +20° (*c* = 1.2, $CHCl_3$).

TLC (4:1 Hexanes:EtOAc), R_f: 0.8 ($KMnO_4$)

Preparation of alkenyl bromide 90:



An oven-dried 20 mL scintillation vial with a cross-shaped star bar was charged with $Ni(OAc)_2$•$4H_2O$ (29.2 mg, 117 μmol, 0.05 equiv), Zn (15.3 mg, 234 μmol, 0.10 equiv), and LiBr (305 mg, 3.52 mmol, 1.50 equiv). The vial was brought into a nitrogen-filled glovebox, and 1-methylimidazole (18.7 uL, 234 μmol), DMA (1.34 mL) and THF (5.0 mL) were added. After stirring for 15 minutes, the enol triflate **88** (1.00 g, 2.34 mmol, 1.0 equiv) was added as a solid, and the vial of **88** was rinsed with a 3:1 mixture of THF:DMA (4 mL). The vial was brought out of the glovebox. The reaction was stirred (1500 rpm) at 21 °C

for 16 hours. Water (20 mL) was added, and the mixture was filtered through cotton. The mixture was extracted with Et_2O (4 x 30 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the crude product as a yellow solid. The product was purified by column chromatography (SiO_2, 1-2-3-4% Et_2O in hexanes) to afford alkenyl bromide **90** (0.730 g, 2.04 mmol, 87% yield) as a waxy white solid.

Note: The reaction is quite sensitive to stirring, presumably due to the heterogeneous reductant. The above procedure represents the largest scale we achieved without a significant reduction in yield (due primarily to incomplete conversion). To improve material throughput, 10 reactions on the scale presented above (10.156 g **10** total, 23.8 mmol) were run in parallel and combined for workup and purification. In this instance, we obtained an 81% yield (6.93 g, 19.3 mmol).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.24 (ddd, *J* = 9.6, 6.0, 1.1 Hz, 1H), 5.86 (d, *J* = 3.9 Hz, 1H), 5.80 (dddd, *J* = 9.5, 4.4, 2.0, 0.8 Hz, 1H), 4.64 (tt, *J* = 4.7, 1.0 Hz, 1H), 4.23 (ddd, *J* = 4.2, 3.0, 0.9 Hz, 1H), 3.06 – 3.03 (m, 1H), 2.83 (ddd, *J* = 6.1, 4.5, 0.8 Hz, 1H), 1.07 (s, 9H), 1.01 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 132.9, 130.4, 128.2, 76.6, 65.1, 51.6, 47.3, 28.8, 28.2, 21.2, 20.7.

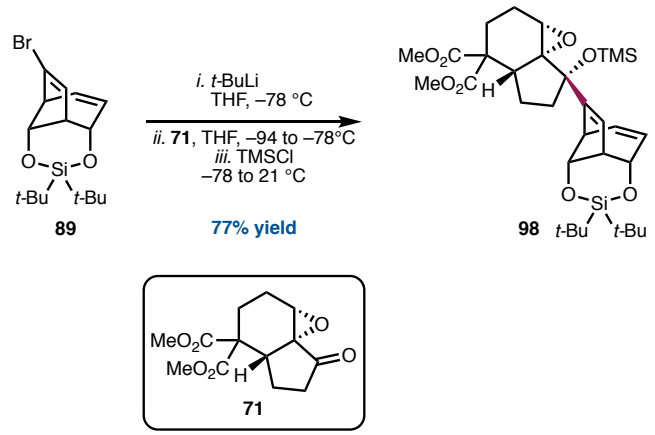
FTIR (NaCl, thin film): 3424, 2970, 2935, 2860, 2709, 1733, 1632, 1476, 1386, 1364, 1315, 1301, 1288, 1250, 1204, 1118, 1085, 1057, 1028, 994, 973, 938, 914, 849, 826, 809, 797, 780, 761, 726, 761, 701, 692, 682, 645, 613 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{16}H_{26}BrO_2Si$ $[M + H]^+$ 357.0880, found 357.0873.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{22}}$ = +14.7° (*c* = 0.52, $CHCl_3$).

TLC (5% Et_2O in Hexanes), R_f: 0.4 ($KMnO_4$)

Preparation of silyl ether 98:



In a 250 mL, round-bottom flask, alkenyl bromide **90** (2.18 g, 6.10 mmol, 1.0 equiv) was dissolved in THF (61 mL) and cooled to –78 °C. To this solution was added *t*-BuLi (7.2 mL, 1.7 M in pentane, 12.2 mmol, 2.0 equiv) drop wise via syringe. During the last few drops of the addition of *t*-BuLi, the yellow color of *t*-BuLi in THF persisted, indicating that all equivalents of the alkenyl bromide had been consumed. The resulting mixture was stirred for an additional 15 minutes at –78 °C. Meanwhile, in a separate 500 mL, round-bottom flask, epoxyketone **71** (2.13 g, 7.93 mmol, 1.3 equiv) was dissolved in THF (79 mL). **9** requires vigorous stirring or sonication at room temperature in order to dissolve in THF. After the epoxyketone had dissolved, it was cooled –94 °C (acetone/liquid N_2 bath) and stirred for 10 minutes at this temperature to ensure thorough cooling (some precipitate of **71** forms during this time, but this is not a problem). After the alkenyl lithium had been stirred for 15 minutes at –78 °C, the solution of alkenyl lithium was then cannulated over 10 minutes into the –94 °C solution of **71**. The reaction was stirred for an additional 30 minutes, allowing the reaction to warm to –78 °C (the acetone/liquid N_2 bath was replaced with a dry ice/acetone bath). TMSCl (1.55 mL, 12.2 mmol, 2.0 equiv) was added, and the mixture was warmed to 21 °C and stirred for 1 hour. The reaction was then quenched with saturated aqueous $NaHCO_3$ (150 mL), and

was allowed to warm to room temperature. The biphasic mixture was transferred to a separatory funnel, and the aqueous layer was extracted with EtOAc (3 x 200 mL), and the combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified by silica gel chromatography (5-10-20-30% EtOAc in hexanes) to afford silyl ether 9**8** (2.89 g, 4.67 mmol, 77% yield) as a white crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.03 (ddd, *J* = 9.6, 6.1, 1.1 Hz, 1H), 5.68 (ddd, *J* = 9.5, 4.3, 1.5, 1H), 5.57 (d, *J* = 3.7 Hz, 1H), 4.48 (t, *J* = 4.7 Hz, 1H), 4.26 (ddd, *J* = 4.1, 3.0, 0.7 Hz, 1H), 3.74 (s, 3H), 3.67 (s, 3H), 3.30 (d, *J* = 3.5 Hz, 1H), 3.08 – 3.03 (m, 1H), 2.90 (dd, *J* = 5.5, 4.8 Hz, 1H), 2.74 (t, *J* = 9.3 Hz, 1H), 2.61 (dddd, *J* = 12.8, 11.0, 8.9, 3.9 Hz, 1H), 2.43 – 2.25 (m, 2H), 2.12 (ddd, *J* = 12.7, 8.7, 3.9 Hz, 1H), 2.04 (ddd, *J* = 12.7, 11.0, 7.5 Hz, 1H), 1.96 (ddd, *J* = 15.1, 8.2, 3.7 Hz, 1H), 1.83 (ddt, *J* = 12.7, 9.4, 8.2, 1H), 1.45 (ddd, *J* = 13.3, 10.1, 8.4 Hz, 1H), 1.09 (s, 9H), 1.02 (s, 9H), 0.05 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.0, 170.4, 163.2, 135.1, 129.0, 122.5, 77.7, 77.6, 70.1, 66.1, 55.0, 54.0, 52.8, 52.1, 45.8, 44.9, 41.4, 34.5, 29.7, 28.9, 28.3, 22.2, 21.6, 21.2, 20.7, 2.2.

FTIR (NaCl, thin film): 3028, 2952, 2904, 2860, 1732, 1477, 1462, 1434, 1364, 1250, 1175, 1110, 1058, 992, 881, 842 cm^{-1}.

HRMS: (PPM) calc'd for $C_{32}H_{51}O_8Si_2$ $[M + H]^+$ 619.3117, found 619.3106.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +36° (*c* = 0.35, $CHCl_3$).

TLC (10%EtOAc/ 90% Hexanes), R_f: 0.4 (green/black in *p*-anisaldehyde)

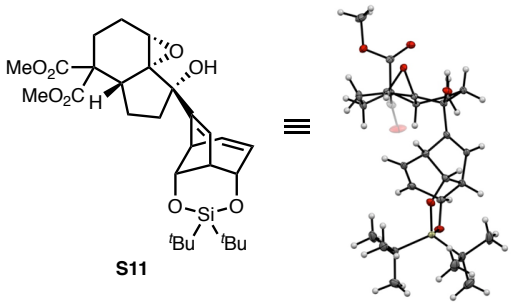
Notes:

(1) It is extremely important for this reaction to be rigorously dry. Trace water diminishes yield. To achieve this, both substrates were separately azeotroped with PhMe (from the solvent system, 3x) prior to use and dried under high vacuum. Additionally, the THF

from the solvent system was titrated. As long as the THF titrated at 7 ppm (or lower), good yields were achieved.

(2) Typically a smaller scale (300 mg) test reaction was done with the same reagent batches, solvent, and substrate prior to scaling up, to ensure that the scale-up run would proceed successfully.

The structure was confirmed via X-ray crystallography of the corresponding epoxy alcohol (**S11**).



Characterization of epoxy-alcohol S11:

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.10 (ddd, *J* = 9.6, 6.1, 1.1 Hz, 1H), 5.70 (ddd, *J* = 9.4, 4.3, 1.6 Hz, 1H), 5.65 (d, *J* = 3.8 Hz, 1H), 4.48 (t, *J* = 4.7 Hz, 1H), 4.25 (dd, *J* = 4.2, 2.8 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.32 (d, *J* = 3.6 Hz, 1H), 3.05 – 3.01 (m, 1H), 2.83 (ddd, *J* = 5.4, 4.9 Hz, 1H), 2.71 (dd, *J* = 10.7, 7.5 Hz, 1H), 2.53 – 2.42 (m, 2H), 2.42 – 2.29 (m, 2H), 2.10 – 1.98 (m, 2H), 1.97 – 1.86 (m, 2H), 1.61 – 1.47 (m, 1H), 1.08 (s, 9H), 1.02 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.7, 170.2, 161.6, 134.5, 129.2, 123.4, 77.7, 75.3, 71.2, 66.1, 56.5, 55.0, 52.9, 52.2, 45.6, 45.2, 44.4, 37.3, 29.3, 28.9, 28.3, 23.3, 21.6, 21.2, 20.7.

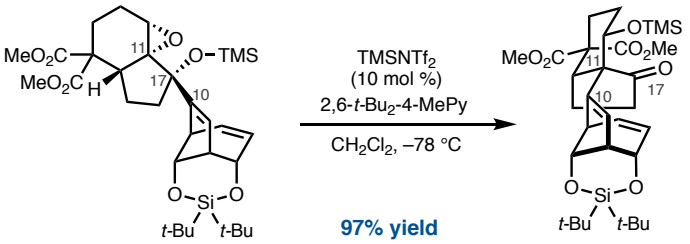
FTIR (NaCl, thin film): 3496, 3032, 2950, 2860, 1732, 1476, 1458, 1434, 1383, 1364, 1306, 1244, 1176, 1108, 991 cm^{-1}.

HRMS: (PPM) calc'd for $C_{29}H_{43}O_8Si$ $[M + H]^+$ 547.2722, found 547.2713.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = –5.1° (*c* = 0.30, $CHCl_3$).

TLC (33%EtOAc/ 67% Hexanes), R*f*: 0.5 (blue in *p*-anisaldehyde)

Preparation of ketone 99:



98 **99**

A 1 L, round-bottom flask was charged with epoxide 9**8** (4.27 g, 6.90 mmol, 1.0 equiv), 2,6-(*t*-Bu)$_2$-4-MePy (1.56 g, 7.59 mmol, 1.1 equiv) and CH_2Cl_2 (430 mL), and the solution was cooled to –78 °C in a dry ice/acetone bath. In an N_2-filled glovebox, a solution $TMSNTf_2$ (244 mg, 0.69 mmol, 0.10 equiv) in CH_2Cl_2 (2 mL) was taken up into a 3 mL syringe, which was plugged with a rubber stopper and removed from the glovebox. The $TMSNTf_2$ solution was immediately added dropwise over 2 minutes to the reaction mixture, causing the solution to turn yellow. After stirring for an additional 50 minutes at –78 °C, the reaction was quenched with sat. $NaHCO_3$ (250 mL), and the solution was allowed to warm to room temperature. The biphasic mixture was transferred to a separatory funnel and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 250 mL), and the combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (3% to 4% acetone in hexanes to elute the 2,6-*t*-Bu$_2$-4-MePy followed by 8% to 10% acetone in hexanes to elute the product) to afford ketone **99** (4.23 g, 6.70 mmol, 97% yield) as a white solid.

Notes:

(1) 2,6-(*t*-Bu)$_2$-4-MePy was purchased from Combi Blocks and repurified before use. The crude brown oil was dissolved in pentanes, and filtered over a plug of silica gel that

had been pre-equilibrated with pentanes, eluted with more pentanes and concentrated *in vacuo,* and dried under high-vacuum. Upon standing, the material turned into a white crystalline solid. This repurification step is crucial for high yields.

(2) If the starting material is not rigorously dry, the reaction may not reach full conversion. It is possible that trace amounts of water can quench $TMSNTf_2$ and result in early termination. In this case, the crude product can simply be resubjected to the reaction conditions. In order to ensure the starting material is sufficiently free of water, it should be azeotroped with toluene or benzene (1–3x) prior to the reaction.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.88 (ddd, *J* = 9.5, 6.1, 1.1 Hz, 1H), 5.65 (ddd, *J* = 9.5, 4.3, 1.9 Hz, 1H), 5.40 (d, *J* = 3.8 Hz, 1H), 4.66 (t, *J* = 4.7 Hz, 1H), 4.31 (br s, 1H), 4.23 (dd, *J* = 4.0, 3.1 Hz, 1H), 3.74 (s, 3H), 3.67 (s, 3H), 3.40 (dd, *J* = 11.7, 7.3 Hz, 1H), 3.03 – 2.94 (m, 2H), 2.48 (td, *J* = 14.1, 3.4 Hz, 1H), 2.38 – 2.26 (m, 1H), 2.17 – 2.05 (m, 3H), 1.80 – 1.71 (m, 1H), 1.65 – 1.60 (m, 1H), 1.52 (tdd, *J* = 14.3, 2.9, 1.9 Hz, 1H), 1.08 (s, 9H), 1.00 (s, 9H), 0.05 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 215.9, 170.7, 170.6, 158.9, 134.8, 128.2, 124.4, 76.7, 69.9, 66.2, 58.0, 56.2, 52.8, 52.6, 46.2, 46.1, 41.8, 38.8, 28.9, 28.3, 27.4, 23.7, 21.2, 20.7, 19.3, 0.0.

FTIR (NaCl, thin film): 3032, 2952, 2896, 2859, 1741, 1477, 1462, 1443, 1384, 1363, 1252, 1170, 1097, 991, 840 cm^{-1}.

HRMS: (PMM) calc'd for $C_{32}H_{51}O_8Si_2$ $[M + H]^+$ 619.3117, found 619.3105.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +92° (*c* = 0.73, $CHCl_3$).

TLC (10%EtOAc/ 90% Hexanes), R_f: 0.4 (blue in *p*-anisaldehyde)

2.7 NOTES AND REFERENCES

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(7) Arai, T.; Yamada, Y. M. A.; Yamamoto, N.; Sasai, H.; Shibasaki, M. *Chem. - Eur. J.* **1996**, *2* (11), 1368–1372.
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Chapter 3

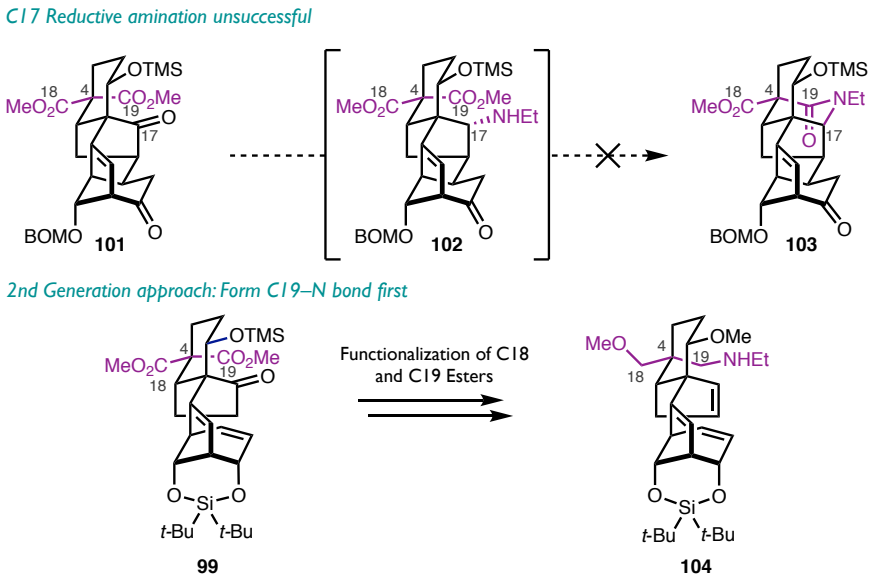
Towards C_{19}-Diterpenoid Alkaloids: Approaches to the C4 Chiral Quaternary Center

3.1 INTRODUCTION

Having accessed the product of the semipinacol rearrangement product **99**, which contains all of the carbon atoms of the aconitine core, our efforts turned to introducing the proper functionality for synthesis of the natural product. Functionalization of the C18 and C19 positions has presented a significant challenge in our efforts towards **1**. Our enantioselective synthesis of epoxy ketone fragment **71** relies on an enantioselective conjugate addition of dimethyl malonate (**74**) to 2-cyclopenten-1-one (**73**), followed by enolate alkylation to form the C4 quaternary center. This approach brings C18 and C19 in as diastereotopic esters which require diastereoselective functionalization to set the C4 chiral quaternary center. Our first-generation retrosynthesis included an intramolecular lactamization between a C17 amine and the C19 methyl ester (Figure 3.1). Efforts to introduce nitrogen through reductive amination at C17 were unsuccessful, which led us to modify our strategy such that the C19–N bond would

be formed before the C17–N bond.[1,2] This required selective incorporation of an amine by reaction with the C19 ester over its diastereotopic C18 ester. This chapter discusses efforts to differentiate the reactivity of these two sites in order to set the C4 chiral quaternary center, as well as an alternative approach to set that chiral center at an early stage in the synthesis, prior to the fragment coupling.

Figure 3.1 *Functionalization of C18 and C19 for the synthesis of talatisamine (**1**), liljestrandinine (**2**), and liljestrandisine (**3**).*[1,2]

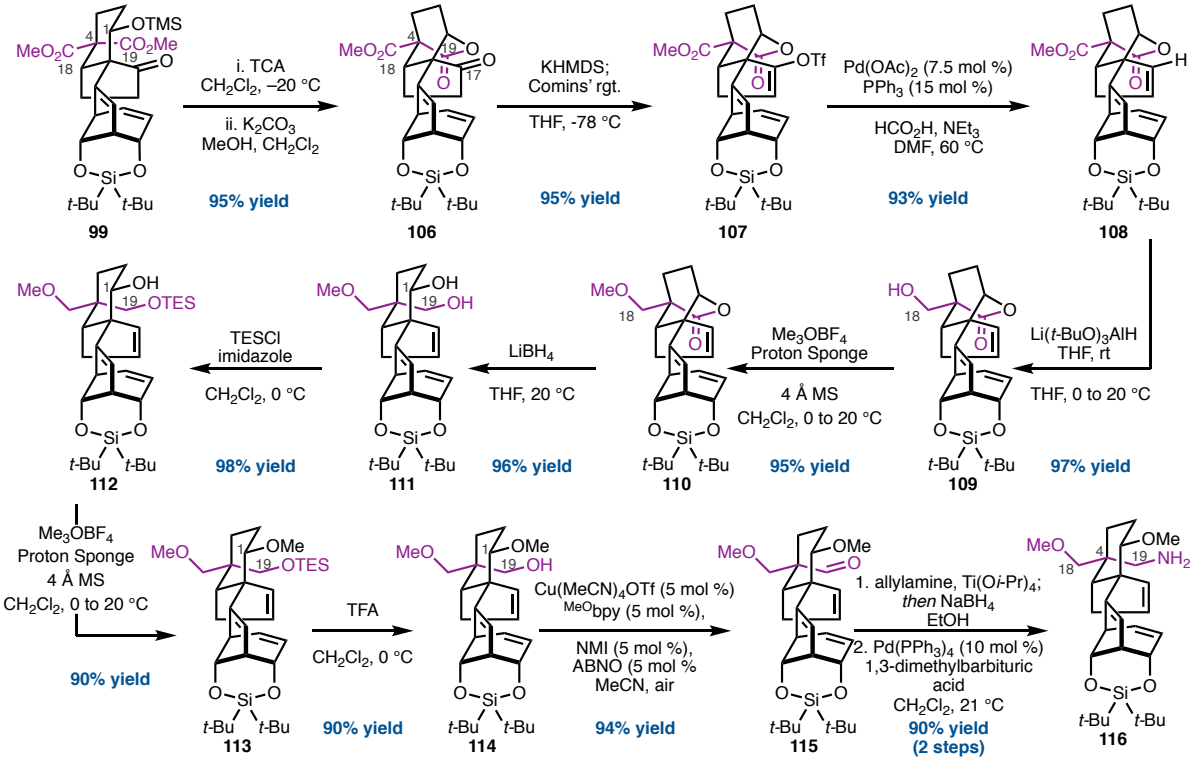


3.2 SEQUENTIAL REDUCTION OF C18 AND C19 ESTERS

Our first-generation approach to form the the C19-N bond was to reduce the C18 ester selectively (Scheme 3.1). In order to differentiate the reactivity of the two esters, the C1 TMS-ether of **99** was deprotected with trichloroacetic acid and subsequent treatment with potassium carbonate and methanol in dichloromethane effected lactonization with C19 to give **106**. The C17 ketone ins converted to the corresponding enol triflate **107**, which is then reduced under palladium-catalyzed conditions to cyclopentene **108**. The C18 ester of **108** can be selectively reduced to the alcohol using lithium tri-*tert*-butoxyaluminum hydride, a reducing agent with

unique reactivity with 1,3-diesters,[3] leaving the C19 lactone intact. Methylation of the C18 alcohol followed by reduction of the C19 lactone **110** with lithium borohydride furnishes the C1/C19 diol **111**. Selective TES protection of the primary C19 alcohol and methylation of the remaining C1 alcohol affords **113**. To introduce the amine at C19, the triethylsilyl ether of **113** is deprotected, and the resulting alcohol, **114**, is cleanly oxidized to the C19 aldehyde **115** using Stahl's conditions.[4] This aldehyde serves as a handle for reductive amination with *N*-allylamine followed by cleavage of the *N*-allyl group gives C19 primary amine **116**.

Scheme 3.1 *Sequential reduction of C18 and C19 esters to incorporate nitrogen at C19.*



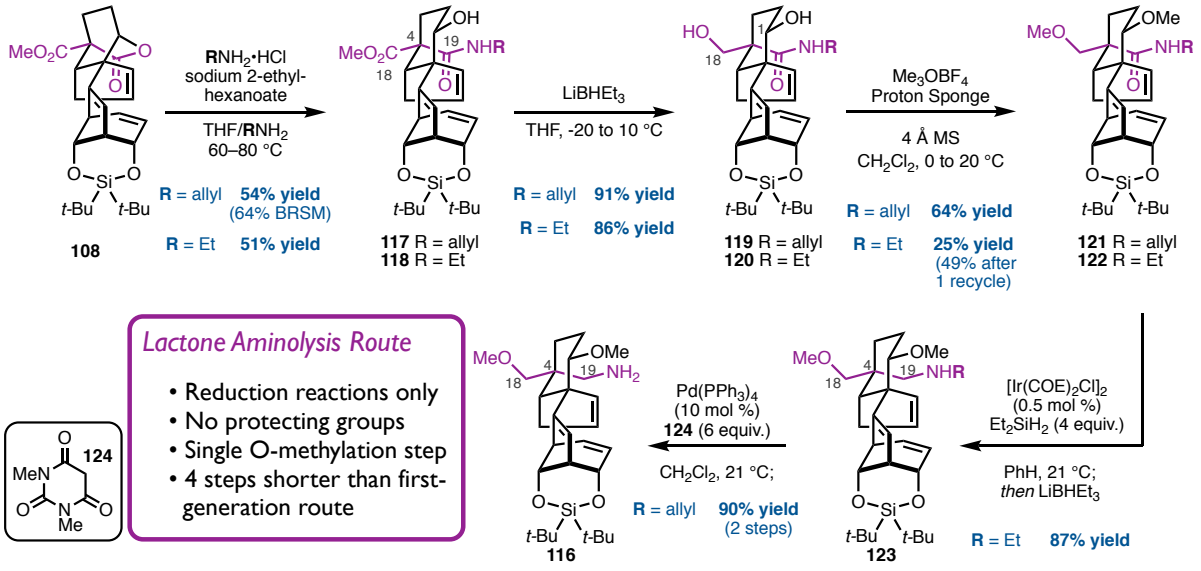
This route from semipinacol product **99** to primary amine **116** amounts to twelve steps, with nine of these twelve representing modification of functionality at C18 and C19. Four of the twelve steps represent redox manipulations at C18 or C19. We sought a more direct route to access amine **116** through a lactone-selective aminolysis.

3.3 SELECTIVE AMINOLYSIS OF C19 LACTONE

We wondered if we could leverage the ring strain of the [2.2.2]-bridged bicyclic lactone **108** for selective C19 ester aminolysis. Gratifyingly, we found that treatment of **108** with solvent quantities of amine and an ammonium carboxylate catalyst at elevated temperatures gave moderate yields of the desired *N*-allyl and *N*-ethyl amide products (**117** and **118**) (Scheme 3.2).[5,6] These reactions were stopped before complete conversion, as undesired aminolysis of the C18 methyl ester of the product occurred at longer reaction times. The C18 ester of **117** and **118** was reduced with lithium triethylborohydride to afford C1/C18 diols **119**/**120** in good yield. Accessing these diols enables methylation of the C1 and C18 alcohols in a single step with trimethyloxonium tetrafluoroborate. A small amount of mono-methylated products were isolated as well. Extending the reaction time led to lower yields and formation of the C19 methyl ester, presumably through amide *O*-methylation and imidate hydrolysis on workup. Reduction of the C19 amide was achieved using Brookhart's iridium-catalyzed hydrosilylation conditions.[7] These conditions proved uniquely effective for substrate **121** in reducing the amide without concomitant reduction of the *N*-allyl group to an *N*-propyl group. *N*-ethyl amine **123** was isolated in 87% yield, while the corresponding *N*-allyl amine was deprotected using the same palladium-catalyzed conditions as before to give primary amine **116**.

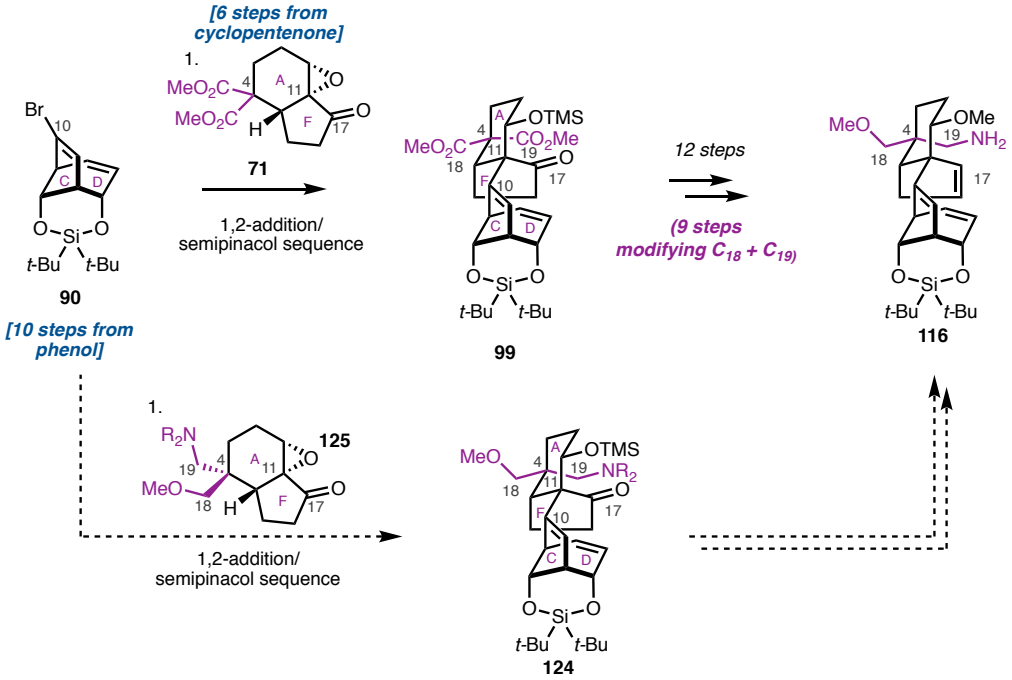
This lactone aminolysis route limits the redox manipulations necessary to access **116** and**123**. No protecting group manipulations are necessary on this route, and the diol intermediate **119/120** allows for methylation of the C1 and C19 alcohols in a single step. This route saves four steps over the first-generation route.

Scheme 3.2 *Lactone-selective aminolysis route to* ***116*** *and* ***123****.*



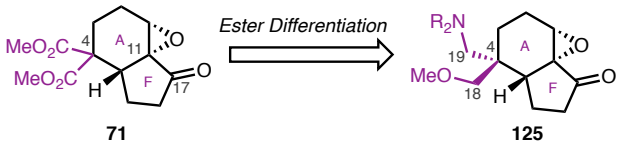
3.4 TOWARDS A C18/C19 FUNCTIONALIZED EPOXY KETONE FRAGMENT

Figure 3.2 *Opportunity to increase convergency of synthesis by properly functionalizing C18 and C19 prior to fragment coupling.*



For the key fragment coupling in our approach to the C_{19}-diterpenoid alkaloids, the epoxy ketone fragment **71** and alkenyl bromide fragment **90** are prepared in six and ten steps LLS, respectively. This disparity in step count required for the preparation of each of the fragments highlights an opportunity to make the synthesis more convergent by preparation of a more appropriately functionalized epoxy ketone fragment, such as **125** (Figure 3.2). In our elaboration of the fragment coupling product **99** to primary amine **116**, six of the eight steps required are spent modifying C18 and C19. Since these carbons are a part of the epoxy ketone fragment **71**, if these sites were properly functionalized prior to the fragment coupling to the synthesis would be more convergent, and therefore more efficient. We set out to evaluate approaches to differentiate the reactivity at C18 and C19 and introduce proper functionality at these positions for the epoxy ketone fragment.

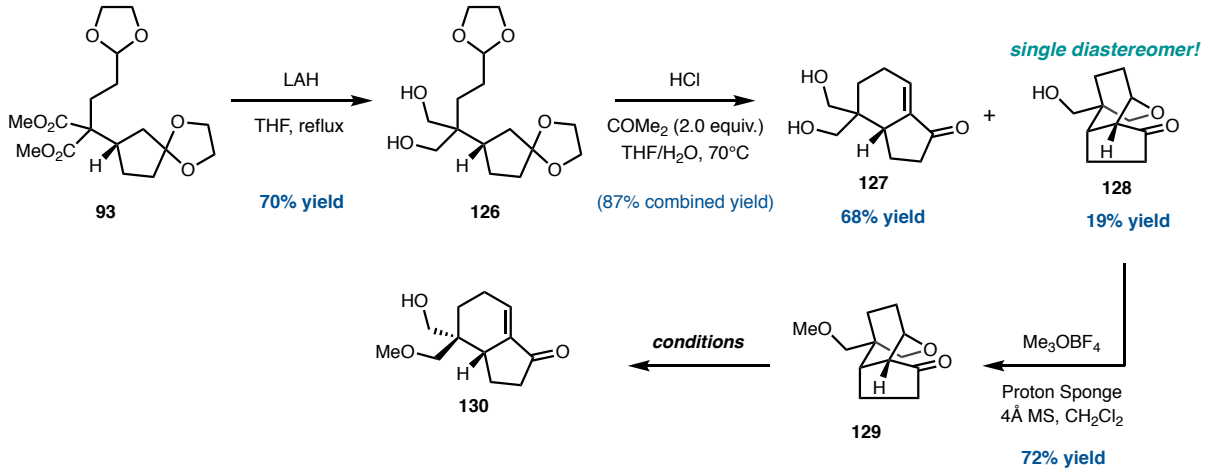
Figure 3.3 *Development of more complex A/F-ring fragment.*



3.4.1 Selective Functionalization of a C18/C19 Diol

Key to our enantioselective synthesis of epoxy ketone **71** is an asymmetric Michael addition of dimethyl malonate (**74**) to 2-cyclopenten-1-one (**73**) using a chiral bimetallic catalyst reported by Shibasaki and coworkers.[8,9] This brings C18 and C19 in at the ester oxidation state while the natural products are at the alcohol oxidation state at those positions. As a result, this strategy inherently requires reduction at those positions. For synthesis of of our desired epoxy ketone fragment, we sought to reduce at both positions and selectively functionalize one diastereotopic alcohol over the other.

Scheme 3.3 *Synthesis of C18/C19 diol* ***127*** *and unexpected oxy-Michael product* ***128****.*



To start, previously-synthesized diester **93** was reduced to 1,3-diol **126** with lithium aluminum hydride. Acid-catalyzed dioxolane deprotection and aldol condensation gave enone product, **127**, along with the unexpected oxy-Michael product **128** as a single diastereomer. We were excited by this result, as it amounts to a selective protection of the C18 alcohol. Methylation of the C19 alcohol of **128** affords **129**. Unfortunately, attempts to effect retro-oxy-Michael to regenerate the enone were plagued by low yields (Table 3.1). We believe this is due to the instability of the resulting enone **130** in the presence of base.

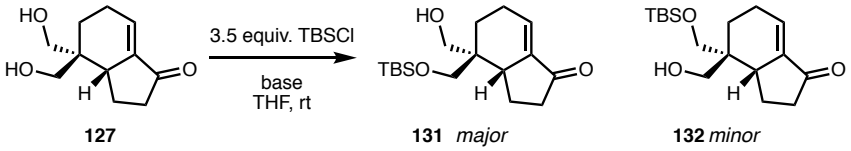
Table 3.1 *Retro-oxy-Michael conditions for synthesis of* ***130****.*

129 **130**

Entry	Scale	Solvent	Base	Temp.	Yield	comments
1	2 mg	THF	LiHMDS	50 °C	0%	no rxn
2	2 mg	THF	NaHMDS	50 °C	0%	—
3	2 mg	THF	KHMDS	0 °C	0%	no rxn
4	2 mg	THF	TMPMgCl•LiCl	-78 to 0 °C	0%	no rxn
5	2 mg	MeOH	0.2M LiOH	50 °C	0%	—
6	2 mg	MeOH	0.2M KOH	50 °C	0%	—
7	2 mg	MeOH	0.1 M NaOH	20 °C	10%	—
8	9 mg	MeOH	0.2 M NaOH	50 °C	24%	—

We turned back to a diastereoselective protection of C18/C19 diol **127**. Using an optimized ratio of triethylamine to imidazole with TBSCl, C18 TBS-ether **131** was isolated in 48% yield (Table 3.2). To install the epoxide, Luche reduction of **131** followed by alcohol directed epoxidation affords **134** (Scheme 3.4). At this point, we realized further elaboration with this route would result in a longer step count and less efficient synthesis of **116** than the routes described in sections 3.2 and 3.3 where C18 and C19 are functionalized after the fragment coupling. As such, we turned to an alternative approach to set the C4 quaternary center.

Table 3.2 *Diastereoselective TBS protection of* ***127****.*

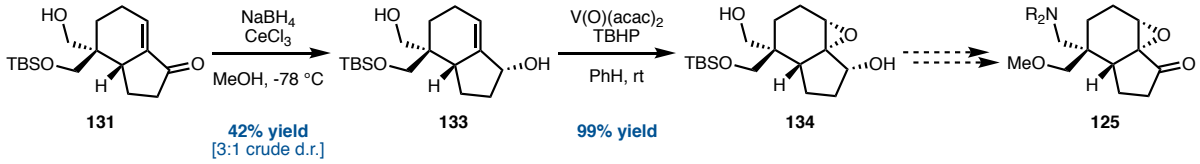


127 **131** *major* **132** *minor*

entry	scale	conditions	yield 131
1	50 mg	3.5 equiv. imid.	35%[b]
2	50 mg	5.3 equiv. imid.	28%[b]
3	50 mg	1.0 equiv imid, 3.5 equiv NEt_3	48%[b]
4	50 mg	0.5 equiv imid, 4.0 equiv NEt_3	66%, 2.6:1 d.r.[a]
5	50 mg	4.5 equiv. NEt_3	82%, 1.6:1 d.r.[a]
6	150 mg	1.0 equiv imid, 2.5 equiv. NEt_3	42%[b]

[a] **NMR yield**
[b] **Isolated major diast. yield**

Scheme 3.4 *Elaboration of* ***131*** *to epoxide* ***134****.*



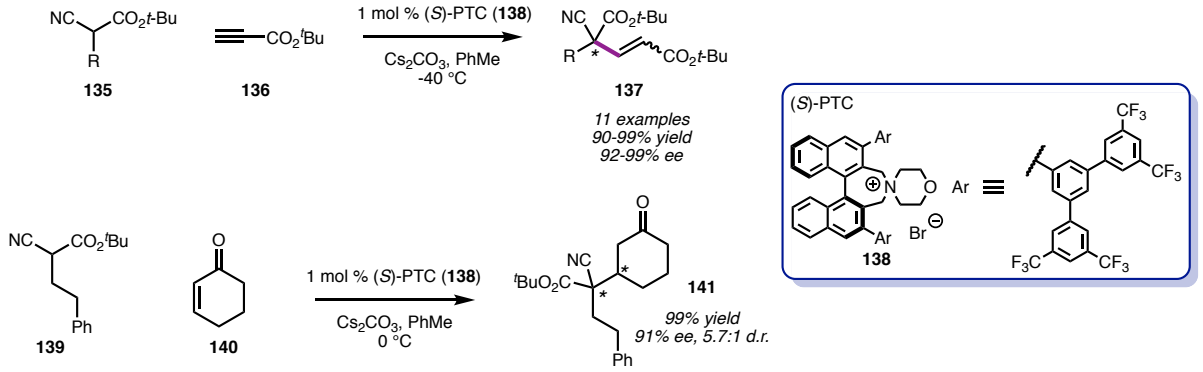
131 **42% yield** [3:1 crude d.r.] **133** **99% yield** **134** **125**

3.4.2 Setting C4 Quaternary Center by Michael Addition of a Prochiral Nucleophile

Previously discussed approaches relied on differentiation of diastereotopic C18 and C19 carbon centers about the C4 quaternary center. As an alternative, we considered the possibility of setting the C4 stereocenter directly through asymmetric catalysis. We were inspired by a report from Maruoka and coworkers detailing an enantioselective conjugate addition of prochiral α-cyanoacetate tertiary enolates to ynoate electrophiles to form quaternary centers (Figure 3.4).[10] They also reported a single example of a doubly stereoselective conjugate addition of these nucleophiles to 2-cyclohexen-1-one (**140**) to form

a β/γ-stereodiad in **141** with excellent yield, enantioselectivity and diastereoselectivity. Enticed by this result, we looked to apply it to our system.

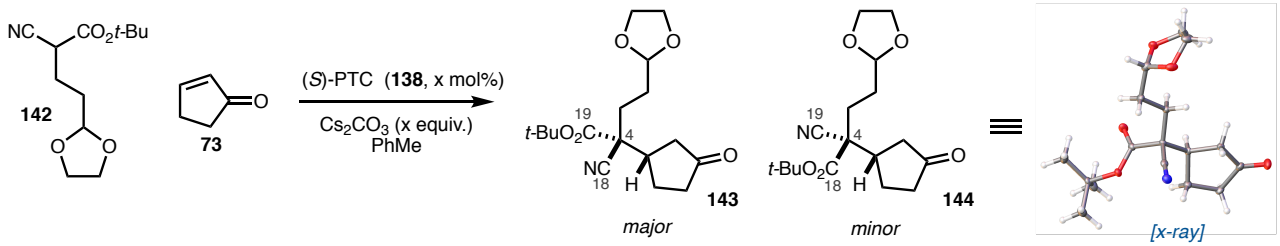
Figure 3.4 *Maruoka's enantioselective conjugate addition catalyzed by chiral ammonium salt.*



We started with Maruoka's optimal conditions using α-cyanoacetate **142** as the Michael donor and 2-cyclopenten-1-one (**73**) as the acceptor (Table 3.3, entry 1). To our delight, the major diastereomer was isolated in 50% ee and 1.5:1 d.r. Increasing the catalyst loading to 2 mol% gave significant improvements in enantioselectivity and diastereoselectivity, though any further increase in catalyst loading did not have any effect. Decreasing the loading of base improved the yield of the reaction with slight increase in ee. Decreasing the temperature had little effect on the reaction. Optimal conditions in entry 6 gave the product in quantitative yield, 3.3:1 d.r. and 74% ee. Control reactions show that base is necessary for the reaction (entry 9). Leaving out chiral catalyst, the reaction still proceeds in 80% yield (entry 10), suggesting that uncatalyzed reaction could be a problem.

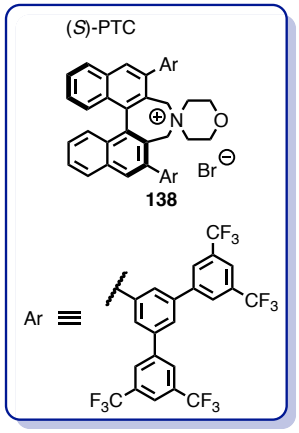
The relative stereochemistry of the product was determined by X-ray crystallography of the minor diastereomer. The major diastereomer has the ester at C19 and nitrile at C18. We could not envision a straightforward route from **143** which would incorporate the amine at C19, so we decided to move away from this strategy.

Table 3.3 *Doubly stereoselective Michael addition of α-cyanoacetate* ***142*** *to 2-cyclopenten-1-one (****73****)*



Entry	scale (mmol)	mol% (*S*)-PTC	equiv. Cs_2CO_3	T (°C)	Yield (%)	d.r.	ee of 143
1	0.20	1	0.5	0	98[a]	1.5:1	50%
2	0.05	2	0.5	0	63[a]	3.0:1	72%
3	0.05	5	0.5	0	80[a]	2.9:1	70%
4	0.05	2	0.5	-20	93[b]	3.0:1	71%
5	0.05	1	0.25	0	65[b]	2.9:1	77%
6	0.20	2	0.25	0	99[a]	3.3:1	74%
7	0.05	2	0.10	0	99	3.0:1	75%
8	0.20	1	0.05	0	56	3.6:1	67%
9	0.05	1	0	0	0	—	—
10	0.05	0	0.25	0	80	4.0:1	n/a

[a]NMR yield; [b]isolated yield incomplete conversion

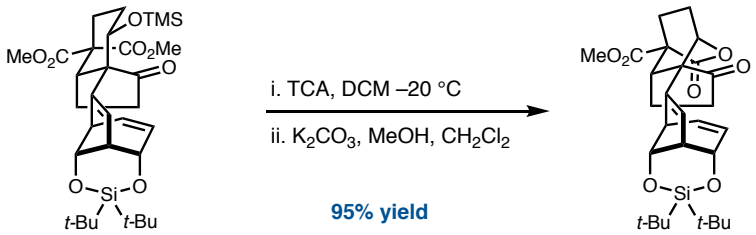


3.5 CONCLUDING REMARKS

Our synthesis of epoxy ketone fragment **71** requires the use of dimethyl malonate to introduce C18 and C19. Differentiating the reactivity at these two centers to introduce the proper functionality proved to be a significant challenge. Two routes to introduce the amine at C19 are described, one by sequential reduction of the two esters and one using a selective aminolysis of a strained C19 lactone. Strategies to incorporate the proper functionality at C18 and C19 prior to the fragment coupling are also described.

3.6 EXPERIMENTAL SECTION

Preparation of lactone 106:



99 **106**

A 250 mL, round-bottom flask was charged with silyl ether **99** (1.5 g, 2.43 mmol, 1.0 equiv), and CH_2Cl_2 (50 mL), and cooled to –20 °C in a cryocool. Trichloroacetic acid (15.86 g, 97.04 mmol, 40 equiv) was added, and the reaction vessel was sealed and allowed to continue stirring at –20 °C for 36 hours. The reaction was then carefully quenched with sat. $NaHCO_3$ (100 mL) at –20 °C, and let warm to room temperature. The biphasic mixture was then transferred to a 500 mL Erlenmeyer flask, and vigorously stirred for an additional 10 minutes. The aqueous phase was ensured to be basic with pH paper. The mixture was then transferred to a separatory funnel and the layers were separated. Aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL), and added to a round-bottom flask, and MeOH (20 mL) was added followed by K_2CO_3 (1.5 g). The mixture was allowed to stir at room temperature for 2 hours. The reaction was monitored by TLC and indicated full conversion. If the reaction is going slowly, more K_2CO_3 and MeOH can be added without deleterious effects. At this time, H_2O (20 mL) was added, and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 30 mL), and the organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (11% acetone in hexanes to 12.5% acetone in hexanes) to afford lactone **106** (1.185 g, 2.303 mmol, 95% yield) as a white foam.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.10 (ddd, *J* = 9.5, 6.2, 1.1 Hz, 1H), 5.79 (d, *J* = 3.8 Hz, 1H), 5.75 (ddd, *J* = 9.5, 4.3, 1.9 Hz, 1H), 4.93 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.35 (t, *J* = 4.7 Hz, 1H), 4.21 (ddd, *J* = 4.1, 3.1, 0.8 Hz, 1H), 3.83 (s, 3H), 3.13 – 3.07 (m, 2H), 3.03 (ttd, *J* = 4.2, 2.5, 1.1 Hz, 1H), 2.52 (dddd, *J* = 14.4, 10.6, 9.2, 4.1 Hz, 1H), 2.41 – 2.29 (m, 2H), 2.18 (ddd, *J* = 17.7, 8.8, 4.1 Hz, 1H), 2.04 (ddt, *J* = 13.2, 10.3, 1.9 Hz, 1H), 1.95 (ddd, *J* = 14.3, 6.7, 3.4 Hz, 1H), 1.91 – 1.82 (m, 1H), 1.75 (dddd, *J* = 14.3, 10.4, 8.9, 6.7 Hz, 1H), 1.05 (s, 9H), 0.99 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 212.0, 169.8, 169.6, 156.4, 134.1, 130.1, 127.0, 78.6, 77.5, 65.7, 58.0, 53.5, 52.9, 45.9, 44.8, 43.0, 35.3, 28.8, 28.2, 26.1, 23.5, 22.3, 21.2, 20.7.

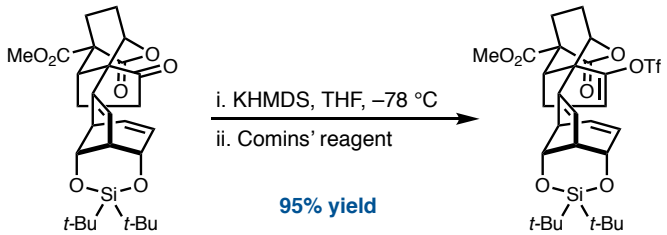
FTIR (NaCl, thin film): 3030, 2974, 2937, 2895, 2860, 1766, 1743, 1476, 1464, 1364, 1271, 1106, 1063, 995, 826 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{28}H_{42}O_7SiN$ $[M + NH_4]^+$ 532.2725, found 532.2720.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +9.9° (*c* = 0.66, $CHCl_3$).

TLC (30%EtOAc/70%Hexanes), R_f: 0.4 (UV, teal in *p*-anisaldehyde)

Preparation of enol triflate 107 from 106:



106 **107**

A 250 mL, round-bottom flask was charged with ketone **106** (2.99 g, 5.81 mmol, 1.0 equiv), and azeotroped PhMe from the solvent system (3 x 20 mL), and put under high vacuum overnight. The following day, the flask was equipped with a stir-bar and rubber septum, purged

with N_2, THF (58 mL) was added, and the solution was cooled to –78 °C in a dry ice/acetone bath. KHMDS solution (0.5 M in PhMe, 13.9 mL, 6.97 mmol, 1.2 equiv) was added dropwise via syringe causing the reaction mixture to turn yellow. Meanwhile, in a separate flame-dried 50 mL conical flask, Comins' reagent (2.74 g, 6.97 mmol, 1.2 equiv) was dissolved in THF (15 mL) under N_2. After the substrate and KHMDS solution had been stirring for 30 minutes at –78 °C, the Comins' reagent solution was added dropwise via cannula, and the solution was allowed to stir for an additional 20 minutes at –78 °C. The reaction was quenched with sat. $NaHCO_3$ (50 mL), the bath was removed and allowed to warm to room temperature. Diluted with Et_2O (75 mL), transferred to a separatory funnel, and the layers were separated. The aqueous phase was extracted with Et_2O (3 x 75 mL). The organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (11% acetone in hexanes to 12.5% acetone in hexanes) to afford enol triflate **107** (3.55 g, 5.52 mmol, 95% yield) as a white foam.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.06 (ddd, *J* = 9.5, 6.1, 1.2 Hz, 1H), 5.73 (ddd, *J* = 9.5, 4.4, 1.6 Hz, 1H), 5.70 (t, *J* = 2.6 Hz, 1H), 5.59 (dd, *J* = 3.8, 0.7 Hz, 1H), 4.78 (dd, *J* = 3.7, 1.7 Hz, 1H), 4.49 (t, *J* = 4.7 Hz, 1H), 4.23 (ddd, *J* = 4.2, 3.0, 0.8 Hz, 1H), 3.82 (s, 3H), 3.10 (m, 1H), 2.95 (ddd, *J* = 17.8, 9.3, 2.3 Hz, 1H), 2.89 – 2.83 (m, 2H), 2.50 (dt, *J* = 17.8, 2.7 Hz, 1H), 2.34 (ddd, *J* = 13.4, 11.4, 3.5 Hz, 1H), 2.20 – 2.04 (m, 2H), 1.79 (ddd, *J* = 13.4, 10.9, 6.6 Hz, 1H), 1.08 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.5, 169.0, 156.9, 145.2, 133.4, 129.9, 126.1, 118.3 (q, *J*=321 Hz, $SO_2\mathbf{C}F_3$), 114.3, 77.2, 75.3, 65.2, 56.8, 53.0, 52.7, 46.2, 46.2, 43.9, 32.5, 28.8, 28.2, 26.6, 21.9, 21.2, 20.7.

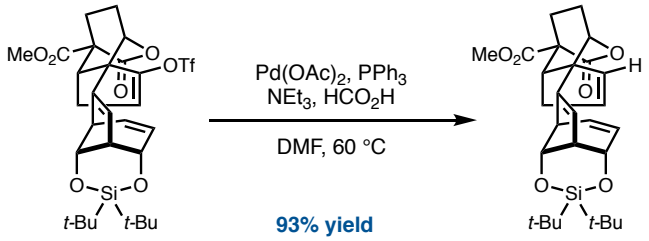
FTIR (NaCl, thin film): 3036, 2938, 2896, 2860, 1769, 1739, 1668, 1476, 1426, 1251, 1217, 1142, 1112, 998, 827 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{29}H_{41}O_9SF_3SiN$ $[M + NH_4]^+$ 664.2218, found 664.2216.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +123° (*c* = 0.67, $CHCl_3$).

TLC (20%EtOAc/80%Hexanes), R_f: 0.4 (UV, blue in *p*-anisaldehyde)

Preparation of cyclopentene 108:



107 **108**

A 200 mL, round-bottom flask was charged with enol triflate **107** (2.28 g, 3.53 mmol, 1.0 equiv), PPh_3 (139 mg, 0.53 mmol, 15 mol %), and $Pd(OAc)_2$ (60 mg, 0.265 mmol, 7.5 mol %). The flask was equipped with a rubber septum, purged with N_2, and dissolved in DMF (35 mL). Then, the reaction mixture was sparged with an Ar balloon for 5 minutes. NEt_3 (3.94 mL, 28.27 mmol, 8 equiv) was added followed by HCO_2H (0.66 mL, 17.67 mmol, 5 equiv) – a cloudy gas was observed upon addition. The reaction was lowered into a 60 °C oil bath, and allowed to continue to stir at that temperature for 20 minutes. The reaction turns black during this time, indicating its completion. The reaction was cooled to room temperature, diluted with sat. NH_4Cl (30 mL), transferred to a separatory funnel and diluted with Et_2O (30 mL). The layers were separated and the aqueous extracted with Et_2O (3 x 30 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (10% acetone in hexanes to 12.5% acetone in hexanes,

the product is very crystalline, it was loaded in PhMe where some of the product elutes but is collected) to afford olefin **108** (1.64 g, 3.28 mmol, 93% yield) as a crystalline solid.

Melting Point: 225–230 °C

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.06 (ddd, *J* = 9.5, 6.1, 1.2 Hz, 1H), 5.76 – 5.68 (m, 2H), 5.51 (d, *J* = 3.8 Hz, 1H), 5.48 – 5.44 (m, 1H), 4.61 (dd, *J* = 3.9, 1.6 Hz, 1H), 4.46 (td, *J* = 4.2, 0.9 Hz, 1H), 4.22 (ddd, *J* = 4.2, 3.1, 0.7 Hz, 1H), 3.80 (s, 3H), 3.04 (ttd, *J* = 4.2, 2.4, 1.0 Hz, 1H), 2.95 – 2.85 (m, 2H), 2.79 (dd, *J* = 4.9, 5.7, 1H), 2.54 – 2.42 (m, 1H), 2.27 (ddd, *J* = 13.1, 11.7, 3.2 Hz, 1H), 2.17 (dddd, *J* = 14.2, 11.1, 3.3, 1.6 Hz, 1H), 1.99 (dddd, *J* = 13.9, 11.6, 6.2, 3.8 Hz, 1H), 1.85 (ddd, *J* = 13.1, 11.0, 6.2 Hz, 1H), 1.07 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 170.3, 161.3, 134.7, 132.0, 131.3, 129.1, 121.8, 78.7, 77.3, 65.9, 59.8, 53.4, 52.7, 46.4, 45.7, 44.4, 38.2, 28.8, 28.2, 26.8, 22.4, 21.2, 20.7. A ^{13}C signal is observed to be overlapping with residual $CDCl_3$ at 77.3, resolved peaks are seen in the HSQC spectrum, provided below.

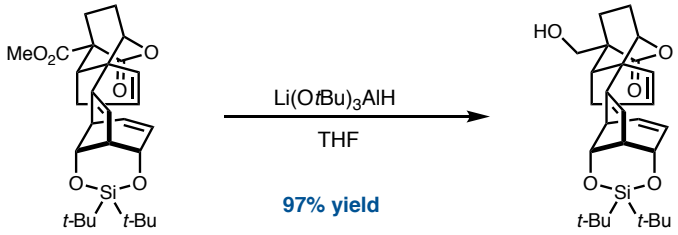
FTIR (NaCl, thin film): 3053, 2937, 2898, 2256, 1760, 1748, 1732, 1476, 1463, 1444, 1364, 1283, 1109, 1063, 993, 911 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{28}H_{39}O_6Si$ $[M + H]^+$ 499.2510, found 499.2512.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +166° (*c* = 0.40, $CHCl_3$).

TLC (20%EtOAc/80%Hexanes), R_f: 0.4 (UV, teal in *p*-anisaldehyde)

Preparation of alcohol 109:



108 **109**

A 250-mL, round-bottomed flask was charged with methyl ester **108** (1.56 g, 3.13 mmol, 1.0 equiv), equipped with a rubber septum, purged with N_2, and dissolved in THF (31 mL). Then, the reaction was cooled to 0 °C in an ice bath Li(O*t*-Bu)$_3$AlH (2.39 g, 9.39 mmol, 3 equiv) was added, and the ice bath was removed. The reaction was monitored by TLC, and after 100 minutes, trace starting material remained, so an additional portion of Li(O*t*-Bu)$_3$AlH (0.95 g, 3.66 mmol, 1.17 equiv) was added, and allowed to stir for an additional 70 minutes. The reaction was carefully quenched with water (10 mL) followed by sat. Rochelle's salt (30 mL). The biphasic mixture was allowed to stir for 30 minutes, then transferred to a separatory funnel with Et_2O (30 mL), and the layers were separated. The aqueous layer was extracted Et_2O (3 x 30 mL). The combined organics were washed with brine (1 x 30 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (20% acetone in hexanes to 25 % acetone in hexanes) to afford alcohol **109** (1.42 g, 3.02 mmol, 97% yield) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.06 (ddd, *J* = 9.5, 6.1, 1.2 Hz, 1H), 5.74 – 5.68 (m, 2H), 5.51 – 5.48 (m, 2H), 4.62 (dd, *J* = 3.8, 1.6 Hz, 1H), 4.45 (tt, *J* = 4.4, 1.0 Hz, 1H), 4.23 (ddd, *J* = 4.2, 2.9, 0.6 Hz, 1H), 4.03 (dd, *J* = 11.8, 3.7 Hz, 1H), 3.43 (dd, *J* = 11.8, 9.1 Hz, 1H), 3.04 (ddtt, *J* = 4.9, 2.8, 2.0, 1.0 Hz, 1H), 2.77 (dd, *J* = 5.5, 4.7 Hz, 1H), 2.58 (ddt, *J* =

17.9, 9.3, 2.3 Hz, 1H), 2.48 – 2.34 (m, 3H), 2.20 – 2.03 (m, 2H), 1.90 (dddd, *J* = 13.7, 11.4, 6.2, 3.7 Hz, 1H), 1.57 (ddd, *J* = 13.2, 11.1, 6.3 Hz, 1H), 1.07 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.6, 161.4, 134.7, 131.9, 131.2, 129.0, 121.6, 78.6, 65.9, 64.2, 60.4, 53.7, 46.4, 46.2, 45.7, 44.5, 35.0, 28.8, 28.2, 24.6, 22.3, 21.2, 20.7.

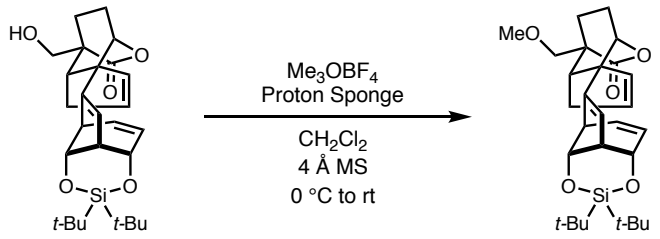
FTIR (NaCl, thin film): 3458, 2935, 2859, 2245, 1738, 1748, 1732, 1476, 1382, 1364, 1364, 1107, 1038, 995, 911 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{27}H_{39}O_5Si$ $[M + H]^+$ 471.2561, found 471.2555.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +168° (*c* = 0.51, $CHCl_3$).

TLC (50%EtOAc/50%Hexanes), R_f: 0.5 (UV, blue in *p*-anisaldehyde)

Preparation of methyl ether 110:



109 **95% yield** **110**

A 250-mL, round-bottomed flask was charged with alcohol **109** (1.41 g, 3.00 mmol, 1.0 equiv), equipped with a rubber septum, purged with N_2, and cooled to 0 °C in an ice bath. Meanwhile, Me_3OBF_4 (1.33 g, 9.00 mmol, 3 equiv), Proton Sponge (1.93 g, 9.00 mmol, 3 equiv), and activated 4 Å MS (2.8 g) were added to a 40 mL vial in the glovebox, brought out of the glovebox, and added to the flask containing the substrate. The mixture was then suspended in CH_2Cl_2 (30 mL), and allowed to stir for 24 hours, allowing the reaction to warm up to room temperature over this period. The reaction mixture was filtered through a plug of silica gel and celite that had been pre-packed with a 1:1 Hex/EtOAc mixture and rinsed further

with 1:1 Hex/EtOAc and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (15% ethyl acetate in hexanes to 18% ethyl acetate in hexanes) to afford methyl ether **110** (1.39 g, 2.85 mmol, 95% yield) as a white crystalline solid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.99 (ddd, *J* = 9.5, 6.1, 1.1 Hz, 1H), 5.67 – 5.59 (m, 2H), 5.43 (d, *J* = 3.7 Hz, 1H), 5.40 (dt, *J* = 5.7, 2.1 Hz, 1H), 4.54 – 4.52 (m, 1H), 4.39 (t, *J* = 4.7 Hz, 1H), 4.16 (ddd, *J* = 4.2, 2.9, 0.6 Hz, 1H), 3.58 (d, *J* = 10.0 Hz, 1H), 3.38 (d, *J* = 10.0 Hz, 1H), 3.30 (s, 3H), 2.96 (dtq, *J* = 5.0, 2.9, 0.8 Hz, 1H), 2.71 (dd, *J* = 5.6, 4.8 Hz, 1H), 2.62 – 2.49 (m, 2H), 2.28 (dq, *J* = 17.3, 2.2 Hz, 1H), 2.10 – 2.00 (m, 1H), 1.94 – 1.77 (m, 2H), 1.61 – 1.54 (m, 1H), 1.01 (s, 9H), 0.94 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.1, 161.6, 134.9, 132.2, 131.3, 128.8, 121.4, 77.9, 77.3, 72.8, 66.0, 59.8, 59.5, 46.4, 45.8, 44.8, 43.2, 35.0, 28.8, 28.2, 25.5, 21.9, 21.2, 20.7. A ^{13}C signal is observed to be overlapping with residual $CDCl_3$ at 77.3, resolved peaks are seen in the HSQC spectrum, provided below.

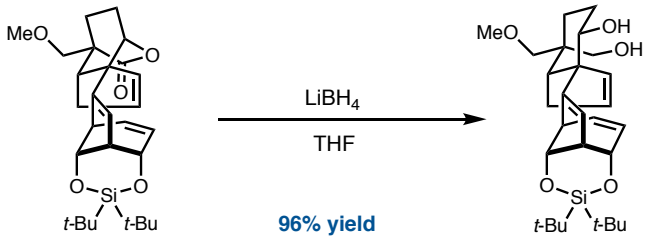
FTIR (NaCl, thin film): 2894, 2933, 2858, 1748, 1475, 1393, 1364, 1109, 994, 825 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{28}H_{41}O_5Si$ $[M + H]^+$ 485.2718, found 485.2716.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +156° (*c* = 0.75, $CHCl_3$).

TLC (20%EtOAc/80%Hexanes), R*f*: 0.5 (UV, blue in *p*-anisaldehyde)

Preparation of diol 111:



110 **111**

A 250-mL, round-bottomed flask was charged with lactone **110** (1.39 g, 2.88 mmol, 1.0 equiv), was equipped with a rubber septum, purged with N_2, and dissolved in THF (29 mL). $LiBH_4$ solution (2 M in THF, 7.2 mL, 14.4 mmol, 5 equiv) was added via syringe, and the reaction was allowed to continue stirring for 20 hours. The reaction was monitored by TLC, which indicated that it had not gone to completion. An additional portion of $LiBH_4$ solution (2 M in THF, 7.2 mL, 14.4 mmol, 5 equiv) was added via syringe. After an additional 3 hours another portion of $LiBH_4$ solution (2 M in THF, 7.2 mL, 14.4 mmol, 5 equiv) was added via syringe (15 equiv total). The reaction was allowed to continue to stir for another 24 hours at room temperature. The reaction was carefully quenched (bubbles evolve) with sat. $NaHCO_3$ (30 mL), and diluted with Et_2O (30 mL), and transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with 20%IPA/80%$CHCl_3$ (3 x 30 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (15% acetone in hexanes to 20% acetone in hexanes) to afford diol **111** (1.34 g, 2.76 mmol, 96% yield) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.19 (ddd, *J* = 5.8, 2.9, 1.7 Hz, 1H), 6.08 (ddd, *J* = 9.5, 6.1, 1.1 Hz, 1H), 5.67 (ddd, *J* = 9.3, 4.4, 1.9 Hz, 1H), 5.49 (d, *J* = 3.7 Hz, 1H), 5.44 (ddd, *J* = 5.8, 2.7, 1.1 Hz, 1H), 4.44 (td, *J* = 4.3, 0.9 Hz, 1H), 4.22 (ddd, *J* = 4.2, 3.0, 0.7 Hz, 1H), 4.03 (d, *J* = 4.1 Hz, 1H), 3.58 – 3.52 (m, 2H), 3.49 – 3.42 (m, 1H), 3.31 (s, 3H), 3.24 (d, *J* =

8.8 Hz, 1H), 3.08 – 3.01 (m, 2H), 2.91 (t, *J* = 5.3 Hz, 1H), 2.71 – 2.64 (m, 1H), 2.51 (dddd, *J* = 16.0, 8.4, 2.9, 1.1 Hz, 1H), 2.44 – 2.35 (m, 1H), 1.79 – 1.55 (m, 4H), 1.13 – 1.10 (m, 1H), 1.08 (s, 9H), 1.01 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.4, 135.9, 135.6, 133.6, 128.3, 120.9, 79.7, 77.1, 72.6, 68.2, 66.3, 59.1, 56.1, 46.5, 46.2, 41.5, 39.6, 35.0, 28.9, 28.3, 24.6, 21.2, 20.7, 20.7.

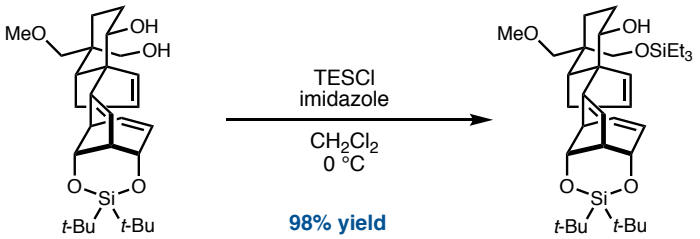
FTIR (NaCl, thin film): 2950, 2910, 2876, 1748, 1476, 1362, 1105, 996, 826 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{28}H_{45}O_5Si$ $[M + H]^+$ 489.3031, found 489.3020.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +152° (*c* = 0.42, $CHCl_3$).

TLC (50%EtOAc/50%Hexanes), R_f: 0.5 (UV, brown/pink in *p*-anisaldehyde)

Preparation of silyl ether 112:



111 **112**

A 200-mL, round-bottomed flask was charged with diol **111** (1.35 g, 2.76 mmol, 1.0 equiv), imidazole (0.42 g, 6.20 mmol, 2.25 equiv), dissolved in CH_2Cl_2 (55 mL), and cooled to 0 °C in an ice bath. TESCl (0.69 mL, 4.14 mmol, 1.5 equiv) added via syringe, and was allowed to continue to stir for 25 minutes at 0 °C. The reaction was monitored by TLC, which showed completion of the reaction. The reaction was quenched with sat. $NaHCO_3$ (30 mL), and transferred to a separatory funnel. The layers were separated, and the aqueous was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was purified by silica gel

chromatography (10% ethyl acetate in hexanes to 15% ethyl acetate in hexanes) to afford silyl ether **112** (1.63 g, 2.70 mmol, 98% yield) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.18 (dt, *J* = 5.9, 2.3 Hz, 1H), 6.07 (ddd, *J* = 9.5, 6.2, 1.1 Hz, 1H), 5.66 (ddd, *J* = 9.4, 4.3, 1.9 Hz, 1H), 5.44 (d, *J* = 3.8 Hz, 1H), 5.40 (dt, *J* = 5.9, 1.8 Hz, 1H), 4.49 (t, *J* = 4.7 Hz, 1H), 4.25 – 4.18 (m, 1H), 4.03 (t, *J* = 3.4 Hz, 1H), 3.49 (d, *J* = 9.3 Hz, 1H), 3.29–3.26 (m, 2H), 3.25 (s, 3H), 3.19 (d, *J* = 8.7 Hz, 1H), 3.08 – 3.04 (m, 1H), 2.87 (t, *J* = 5.3 Hz, 1H), 2.42 – 2.33 (m, 2H), 2.22 (t, *J* = 9.5 Hz, 1H), 1.80 (s, 1H), 1.71 (dt, *J* = 7.6, 3.9 Hz, 2H), 1.46 (dt, *J* = 13.6, 8.2 Hz, 1H), 1.31 (dt, *J* = 13.7, 4.0 Hz, 1H), 1.09 (s, 9H), 1.01 (s, 9H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.62 – 0.54 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.5, 136.1, 135.7, 133.9, 128.2, 120.9, 77.1, 72.3, 68.1, 66.3, 66.1, 58.8, 55.9, 46.3, 46.2, 43.1, 40.5, 34.4, 28.9, 28.3, 24.1, 21.3, 20.7, 18.6, 6.9, 4.3.

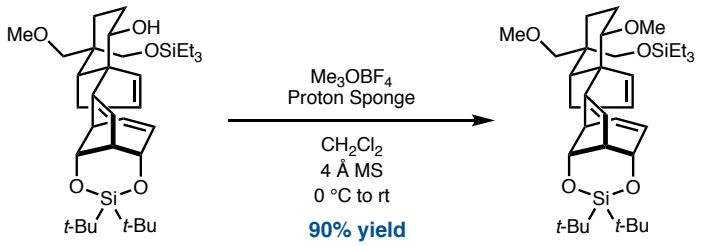
FTIR (NaCl, thin film): 2950, 2910, 2876, 1748, 1476, 1362, 1105, 996, 826 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{34}H_{59}O_5Si_2$ $[M + H]^+$ 603.3896, found 603.3881.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +103° (*c* = 0.38, $CHCl_3$).

TLC (15%EtOAc/85%Hexanes), R_f: 0.4 (UV, orange/pink in *p*-anisaldehyde)

Preparation of methyl ether 113:



112 **113**

A 250-mL, round-bottomed flask was charged with alcohol **112** (1.63 g, 2.71 mmol, 1.0 equiv), equipped with a rubber septum, purged with N_2, and cooled to 0 °C in an ice bath.

Meanwhile, Me_3OBF_4 (2.00 g, 13.55 mmol, 5 equiv), Proton Sponge (2.91 g, 13.55 mmol, 5 equiv), and activated 4 Å MS (3.3 g) were added to a 40 mL vial in the glovebox, brought out of the glovebox, and added to the flask containing the substrate. The mixture was then suspended in CH_2Cl_2 (27.1 mL), and allowed to stir for 24 hours, allowing the reaction to warm up to room temperature over this period. The reaction mixture was filtered through a plug of silica gel and celite that had been pre-packed with a 15% ethyl acetate/ 85% hexanes mixture and rinsed further with 15% ethyl acetate/ 85% hexanes and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (2% to 3% to 4% to 5% to 6% ethyl acetate in hexanes to) to afford methyl ether **113** (1.5 g, 2.43 mmol, 90% yield) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.08 (ddd, *J* = 9.5, 6.2, 1.1 Hz, 1H), 5.88 (dt, *J* = 5.8, 2.2 Hz, 1H), 5.65 (ddd, *J* = 9.3, 4.4, 1.9 Hz, 1H), 5.42 – 5.35 (m, 2H), 4.47 (td, *J* = 4.2, 0.9 Hz, 1H), 4.22 (ddd, *J* = 4.4, 3.0, 0.7 Hz, 1H), 3.55 (dd, *J* = 6.9, 2.7 Hz, 1H), 3.45 (d, *J* = 9.2 Hz, 1H), 3.30 (d, *J* = 9.3 Hz, 1H), 3.24 (s, 3H), 3.24 (s, 3H), 3.21 (d, *J* = 8.7 Hz, 1H), 3.16 (d, *J* = 8.7 Hz, 1H), 3.04 (ddddt, *J* = 5.8, 3.8, 2.9, 2.0, 1.0 Hz, 1H), 2.87 (dd, *J* = 6.4, 4.1 Hz, 1H), 2.35 – 2.27 (m, 2H), 2.23 (dd, *J* = 10.2, 7.8 Hz, 1H), 1.67 (dddd, *J* = 13.9, 8.4, 5.6, 2.7 Hz, 1H), 1.57 (dtd, *J* = 13.6, 6.8, 5.1 Hz, 1H), 1.40 – 1.24 (m, 2H), 1.09 (s, 9H), 1.01 (s, 9H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.63 – 0.52 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.6, 136.0, 134.0, 131.6, 128.0, 119.8, 79.7, 77.1, 73.4, 66.5, 66.0, 58.7, 57.2, 56.5, 46.2 (2 overlapping ^{13}C signals), 46.2, 43.7, 40.6, 34.8, 28.9, 28.3, 21.4, 21.3, 20.9, 20.7, 6.8, 4.3.

Two ^{13}C signals are observed to be overlapping at 46.2, resolved peaks are seen in the HSQC spectrum, provided below.

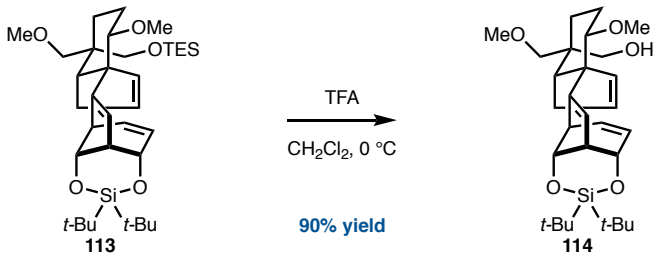
FTIR (NaCl, thin film): 3049, 2936, 2911, 2976, 2808 1476, 1103, 994 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{35}H_{61}O_5Si_2$ $[M + H]^+$ 617.4052, found 617.4045.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +87° (*c* = 0.57, $CHCl_3$).

TLC (5%EtOAc/95%Hexanes), R_f: 0.4 (UV, green in *p*-anisaldehyde)

Preparation of alcohol 114:



A 500-mL, round-bottomed flask was charged with silyl ether **113** (1.60 g, 2.59 mmol, 1.0 equiv), and CH_2Cl_2 (52 mL) and cooled to 0 °C in an ice bath. TFA (0.40 mL, 5.18 mmol, 2 equiv) was added via syringe. The reaction was monitored by TLC, and after 45 minutes at 0 °C, additional TFA (0.10 mL, 1.30 mmol, 0.5 equiv) was added. After a further 30 minutes, additional TFA (0.10 mL, 1.30 mmol, 0.5 equiv) was added (3 equiv total). After 15 more minutes, the reaction was done by TLC. The reaction was quenched with sat. $NaHCO_3$ (50 mL), and the pH of the aqueous layer was checked to make sure it was basic. The biphasic mixture was transferred to a separatory funnel, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (25% ethyl acetate in hexanes to 30% ethyl acetate in hexanes) to afford alcohol **114** (1.17 g, 2.33 mmol, 90% yield) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.08 (ddd, *J* = 9.5, 6.2, 1.1 Hz, 1H), 5.90 (ddd, *J* = 5.8, 2.7, 1.9 Hz, 1H), 5.66 (ddd, *J* = 9.3, 4.4, 1.9 Hz, 1H), 5.45 – 5.42 (m, 2H), 4.44 (td, *J* =

4.2, 0.9 Hz, 1H), 4.26 – 4.19 (m, 1H), 3.57 – 3.52 (m, 2H), 3.46 (dd, *J* = 8.9, 1.3 Hz, 2H), 3.27 (s, 3H), 3.26 (s, 3H), 3.21 (d, *J* = 8.7 Hz, 1H), 3.05 – 2.99 (m, 2H), 2.91 (dd, *J* = 5.9, 4.6 Hz, 1H), 2.64 (t, *J* = 9.2 Hz, 1H), 2.46 (dddd, *J* = 15.7, 8.7, 2.8, 1.4 Hz, 1H), 2.30 (ddt, *J* = 15.7, 9.9, 2.1 Hz, 1H), 1.67 – 1.61 (m, 1H), 1.61 – 1.42 (m, 2H), 1.17 – 1.10 (m, 1H), 1.08 (s, 9H), 1.01 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.5, 135.8, 133.7, 131.5, 128.1, 119.6, 80.5, 79.7, 77.0, 72.4, 66.5, 58.9, 57.2, 56.8, 46.4, 46.2, 42.3, 39.7, 35.5, 28.9, 28.3, 23.2, 21.6, 21.2, 20.7.

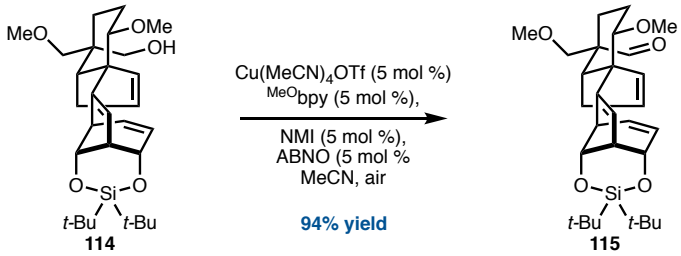
FTIR (NaCl, thin film): 3472, 3048, 2934, 2894, 2859, 1475, 1380, 1101, 991 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{29}H_{47}O_5Si$ $[M + H]^+$ 503.3187, found 503.3184.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +136° (*c* = 0.58, $CHCl_3$).

TLC (30%EtOAc/70%Hexanes), R_f: 0.4 (UV, pink/orange in *p*-anisaldehyde)

Preparation of aldehyde 115:



A 100-mL, round-bottomed flask was charged with alcohol **114** (218 mg, 0.434 mmol, 1.0 equiv) and MeCN (8.6 mL). 4,4'-dimethoxy-2,2'-bipyridine (^{MeO}bpy, 4.7 mg, 21.7 μmol, 5 mol %), *N*-methylimidazole (6.9 μL, 86.8 μmol, 20 mol %), and ABNO (3.0 mg, 21.7 μmol, 5 mol %). Lastly, $Cu(MeCN)_4OTf$ (8.2 mg, 21.7 μmol, 5 mol %) was added, and the clear red/brown reaction mixture was stirred until slightly yellow green, and the TLC indicated the reaction had gone to completion (ca. 90 min), at which point the solution was filtered through a short plug of silica, flushed with ethyl acetate, and concentrated *in vacuo*. Purification of the

crude residue by silica gel chromatography (10 to 12% EtOAc in hexanes) afforded aldehyde **115** (204 mg, 0.408 mmol, 94% yield) as a white foam.

Note: The product aldehyde **115** is prone to decomposition, prolonged storage should be avoided if possible. If necessary, it can be stored as a solid in the freezer and should be fine for at least a few weeks. Residual solvent accelerates the decomposition process. It is also possible to run the subsequent step without purification, and using the crude from the silica plug directly. Once the decomposition pathway was discovered, the aldehyde was reproducibly carried through as the crude in the subsequent reductive amination step, to keep the aldehyde for a minimum amount of time.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 9.53 (s, 1H), 6.09 (ddd, *J* = 9.5, 6.1, 1.1 Hz, 1H), 5.85 (dt, *J* = 5.8, 2.3 Hz, 1H), 5.68 (dddd, *J* = 9.5, 4.3, 1.9, 0.6 Hz, 1H), 5.62 (dt, *J* = 5.8, 1.9 Hz, 1H), 5.40 (dd, *J* = 3.9, 0.7 Hz, 1H), 4.45 (tt, *J* = 4.3, 0.9 Hz, 1H), 4.21 (ddd, *J* = 4.3, 3.0, 0.7 Hz, 1H), 3.49 (dd, *J* = 8.9, 3.3 Hz, 1H), 3.39 (d, *J* = 9.2 Hz, 1H), 3.31 (d, *J* = 9.2 Hz, 1H), 3.27 (s, 3H), 3.26 (s, 3H), 3.02 (ddddd, *J* = 4.9, 3.8, 2.9, 2.0, 0.8 Hz, 1H), 2.89 – 2.86 (m, 1H), 2.44 (t, *J* = 7.0 Hz, 1H), 2.29 (ddt, *J* = 16.0, 7.5, 2.2 Hz, 1H), 2.22 (ddt, *J* = 16.0, 6.6, 2.2 Hz, 1H), 2.12 (ddd, *J* = 14.2, 6.7, 4.5 Hz, 1H), 1.83 (dddd, *J* = 13.4, 6.7, 4.6, 3.3 Hz, 1H), 1.55 (dtd, *J* = 13.6, 9.3, 4.6 Hz, 1H), 1.40 (ddd, *J* = 14.3, 9.7, 4.6 Hz, 1H), 1.08 (s, 9H), 1.02 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 204.0, 164.5, 135.2, 134.0, 132.0, 128.5, 121.8, 79.5, 77.3, 76.1, 66.3, 59.3, 58.1, 56.9, 50.8, 46.2, 46.0, 44.1, 34.5, 28.9, 28.3, 21.5, 21.2, 21.1, 20.7.

A ^{13}C signal is observed to be overlapping with residual $CDCl_3$ at 77.3, resolved peaks are seen in the HSQC spectrum, provided below.

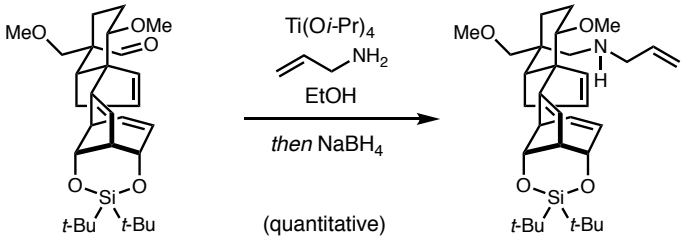
FTIR (NaCl, thin film): 2933, 2894, 2859, 2859, 1724, 1476, 1103, 993 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{29}H_{45}O_5Si$ $[M + H]^+$ 501.3031, found 501.3038.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +87° (*c* = 0.60, $CHCl_3$).

TLC (20%EtOAc/80%Hexanes), R*f*: 0.5 (UV, blue in *p*-anisaldehyde)

Preparation of *N*-allylamine 145:



114 **145**

A 100-mL, round-bottomed flask was charged with aldehyde **114** (311 mg, 0.621 mmol, 1 equiv), and azeotroped 3x with toluene (from the solvent system) to remove water, and put under high vacuum for 2 hours. The flask was equipped with a rubber septum, purged with N_2, and dissolved in EtOH (stored over 3 Å MS, 21 mL). Allylamine (freshly distilled over $CaCl_2$, 0.19 mL, 248 mmol, 4 equiv) was added followed by Ti(O*i*-Pr)$_4$ (0.39 mL, 1.24 mmol, 2 equv) and let stir for 90 minutes at room temperature. At this time, $NaBH_4$ (117 mg, 3.10 mmol, 5 equiv) was added in one portion, and let stir for 15 minutes further. The reaction was carefully quenched with aqueous 28–30% NH_3 solution (10 mL), and let stir for 10 minutes at room temperature. The reaction was then filtered through a basic alumina plug that had been pre-washed with EtOH, then flushed with ethyl acetate, and concentrated *in vacuo*. Then, the crude mixture was filtered through a silica plug, flushed with 100% CH_2Cl_2 to remove nonpolar impurities, and then with 5% 7 NH_3/95% CH_2Cl_2 to elute the product *N*-allyl amine **145**.

A sample of this material was purified by silica gel chromatography (to 2% to 3% to 4% 7 N NH_3/MeOH solution/ CH_2Cl_2) to afford analytically pure material for characterization:

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.06 (ddd, *J* = 9.5, 6.2, 1.1 Hz, 1H), 5.93 – 5.81 (m, 2H), 5.64 (ddd, *J* = 9.5, 4.4, 1.9 Hz, 1H), 5.43 – 5.38 (m, 2H), 5.16 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.08 (dq, *J* = 10.3, 1.3 Hz, 1H), 4.47 – 4.42 (m, 1H), 4.22 (ddd, *J* = 4.2, 3.0, 0.7 Hz, 1H), 3.55 (dd, *J* = 7.5, 2.8 Hz, 1H), 3.29 – 3.15 (m, 10H), 3.02 (tdd, *J* = 5.8, 2.8, 1.4 Hz, 1H), 2.90 – 2.86 (m, 1H), 2.49 (s, 2H), 2.41 (dd, *J* = 10.3, 8.0 Hz, 1H), 2.33 – 2.26 (m, 2H), 1.71 – 1.61 (m, 1H), 1.61 – 1.49 (m, 2H), 1.41 – 1.31 (m, 1H), 1.07 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.5, 136.8, 135.8, 134.0, 131.3, 128.0, 119.6, 116.1, 79.6, 77.0 (overlapping with $CDCl_3$), 76.5, 66.5, 58.8, 57.2, 56.8, 56.3, 53.0, 46.3, 46.2, 44.5, 39.3, 35.4, 28.9, 28.3, 24.3, 21.7, 21.2, 20.7.

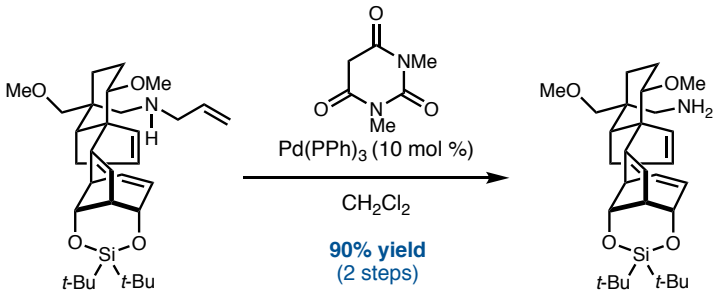
FTIR (NaCl, thin film): 3049, 2934, 2898, 2859, 2859, 1475, 1102, 1106, 992, 825, 732 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{32}H_{52}NO_4Si$ $[M + H]^+$ 542.3660, found 542.3653.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +104° (*c* = 2.20, $CHCl_3$).

TLC (5% 7N NH_3 in MeOH/95%CH_2Cl_2), R_f: 0.5 (UV, blue in *p*-anisaldehyde)

Preparation of primary amine 116 via deprotection of *N*-allyl 145:



145 **116**

A 100-mL, round-bottomed flask was charged with the crude allylamine **145** and 3,5-dimethylbarbituric acid (0.582 g, 3.72 mmol, 6 equiv), and dissolved in CH_2Cl_2 (12.4 mL) under N_2. Meanwhile, a solution of $Pd(PPh_3)_4$ (72 mg, 0.0621 mmol, 10 mol % in 3 mL

CH_2Cl_2) was made inside the glovebox, brought out, and added via syringe to the solution of substrate. The reaction was allowed to stir for 1 hour at room temperature, and was then quenched with sat. $NaHCO_3$ (20 mL). The mixture was then transferred to a separatory funnel, and extracted with 20%IPA/80% $CHCl_3$ (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (1% to 2% to 3% to 4% 7 N NH_3/MeOH solution/ CH_2Cl_2) to afford primary amine **116** (280 mg, 0.559 mmol, 90% yield) as a clear oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.06 (ddd, *J* = 9.5, 6.1, 1.1 Hz, 1H), 5.87 (dt, *J* = 5.9, 2.3 Hz, 1H), 5.65 (ddd, *J* = 9.4, 4.4, 1.9 Hz, 1H), 5.44 – 5.39 (m, 2H), 4.46 (t, *J* = 4.7 Hz, 1H), 4.23 (ddd, *J* = 4.3, 3.0, 0.7 Hz, 1H), 3.56 (dd, *J* = 7.7, 2.8 Hz, 1H), 3.26 – 3.24 (m, 6H), 3.22 – 3.19 (m, 1H), 3.18 (d, *J* = 9.2 Hz, 1H), 3.05 – 3.00 (m, 1H), 2.88 (dd, *J* = 5.9, 4.6 Hz, 1H), 2.63 (d, *J* = 13.1 Hz, 1H), 2.58 (d, *J* = 13.1 Hz, 1H), 2.39 (dd, *J* = 10.0, 8.4 Hz, 1H), 2.31 – 2.26 (m, 2H), 1.68 (dddd, *J* = 13.3, 8.0, 5.4, 2.7 Hz, 1H), 1.61 – 1.37 (m, 4H), 1.34 – 1.21 (m, 1H), 1.08 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.4, 135.8, 134.1, 131.1, 128.1, 119.7, 79.7, 77.0, 76.1, 66.5, 58.8, 57.2, 56.9, 49.5, 46.3, 46.2, 44.0, 39.7, 35.2, 28.9, 28.3, 23.9, 21.8, 21.2, 20.7.

A ^{13}C signal is observed to be overlapping with residual $CDCl_3$ at 77.00, the peak can be seen in the HSQC spectrum, provided below.

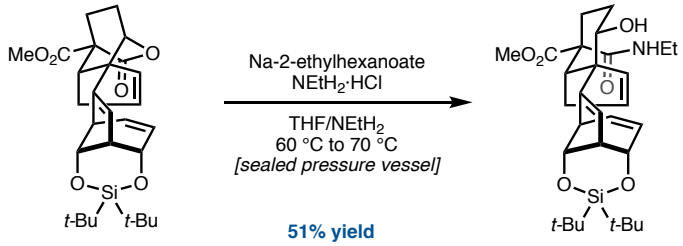
FTIR (NaCl, thin film): 3386, 3050, 2933, 2859, 2362, 1476, 1463, 1106, 992 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{29}H_{48}NO_4Si$ $[M + H]^+$ 502.3347, found 502.3344.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +105° (*c* = 0.67, $CHCl_3$).

TLC (10%MeOH/90%CH_2Cl_2), R*f*: 0.15 (UV, blue in *p*-anisaldehyde)

Preparation of *N*-ethyl amide 118:



108 **118**

To a 75 mL pressure vessel containing lactone **108** (437 mg, 0.877 mmol, 1 equiv), sodium 2-ethylhexanoate (657 mg, 3.95 mmol, 4.5 equiv), ethylamine hydrochloride (161 mg, 1.97 mmol, 2.25 equiv) were added, followed by THF (9 mL) and neat $NEtH_2$ (4 mL). The vessel was sealed (with a Teflon cap that had a perfluoro O-ring), and heated to 60 °C in an oil bath. The reaction was allowed to stir at 60 °C for 2 days, and the reaction progress was monitored. At this time, the reaction had not gone to completion, so the flask was re-sealed and the bath temperature was raised to 70 °C and stirred for another 2 days at this temperature. The reaction was then cooled to room temperature, and transferred to a separatory funnel with EtOAc (30 mL) and aqueous 0.5 M NaOH (20 mL). The layers were separated, and the aqueous phase was extracted with EtOAc (3 x 20 mL) and CH_2Cl_2 (2 x 20 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified by silica gel chromatography (20% to 30% to 40% ethyl acetate in hexanes) to afford secondary amide **118** as a white foam (243 mg, 0.447 mmol, 51% yield).

Note: Neat NH_2Et was obtained from distillation of 70%NH_2Et/ 30% H_2O solution, using a cold finger (with dry ice/acetone) to condense the very volatile NH_2Et, and stored over KOH pellets in the freezer.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.22 (t, *J* = 5.6 Hz, 1H), 6.16 – 6.05 (m, 2H), 5.65 (ddd, *J* = 9.4, 4.4, 1.9 Hz, 1H), 5.50 (dt, *J* = 5.9, 1.9 Hz, 1H), 5.33 (s, 1H), 4.54 (t, *J* = 4.8 Hz,

1H), 4.17 (ddd, *J* = 4.0, 2.9, 0.7 Hz, 1H), 3.91 (t, *J* = 4.4 Hz, 1H), 3.68 (s, 3H), 3.28 (dqd, *J* = 14.5, 7.2, 5.7 Hz, 1H), 3.22 – 3.10 (m, 2H), 3.01 – 2.96 (m, 1H), 2.90 (t, *J* = 5.3 Hz, 1H), 2.37 – 2.26 (m, 3H), 2.09 – 2.02 (m, 1H), 1.80 – 1.69 (m, 3H), 1.11 – 1.06 (m, 12H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.9, 168.6, 163.6, 135.6, 135.1, 132.8, 128.5, 122.0, 76.6, 66.9, 66.2, 56.9, 55.5, 52.9, 46.4, 46.3, 46.2, 35.2, 34.7, 28.9, 28.3, 25.6, 21.2, 20.7, 18.0, 14.6.

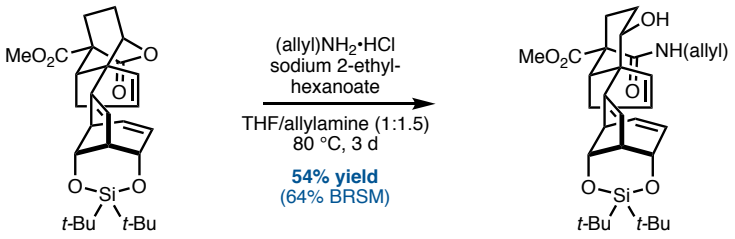
FTIR (NaCl, thin film): 3409, 3033, 3969, 6935, 2896, 2859, 2242, 1713, 1668, 1520, 1229, 1101, 826, 732 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{30}H_{46}O_6NSi$ $[M + H]^+$ 544.3089, found 544.3102.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +137° (*c* = 1.00, $CHCl_3$).

TLC (50%EtOAc/ 50% Hexanes), R*f*: 0.25 (UV, yellow in *p*-anisaldehyde)

Preparation of amide 117:



108 **117**

To a 150 mL pressure vessel containing lactone **108** (1.36 g, 2.73 mmol, 1.0 equiv), sodium 2-ethylhexanoate (2.04 g, 12.3 mmol, 4.5 equiv), allylamine hydrochloride (0.574 g, 6.14 mmol, 2.25 equiv) were added, followed by THF (10.7 mL) and neat *N*-allylamine (16 mL). The vessel was sealed (with a Teflon cap that had a perfluoro O-ring), and heated to 80 °C in an oil bath. The reaction was allowed to stir at 80 °C for 3 days. The reaction was then cooled to room temperature, and transferred to a separatory funnel with EtOAc (100 mL) and aqueous 0.5 M NaOH (30 mL). The layers were separated, and the aqueous phase was extracted with EtOAc (4 x 50 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and

concentrated *in vacuo*. The crude residue was purified by silica gel chromatography (20-30-40% EtOAc in hexanes) to afford *N*-allyl amide **117** (0.803 g, 1.47 mmol, 54% yield, 64% BRSM) and starting material **108** (0.203 g, 0.41 mmol, 15%).

Note: *N*-allylamine was purified by distillation over $CaCl_2$ prior to use.

^{1}H NMR (500 MHz, Chloroform-d): δ 6.33 (t, *J* = 5.7 Hz, 1H), 6.13 (dt, *J* = 5.9, 2.3 Hz, 1H), 6.10 (ddd, *J* = 9.5, 6.2, 1.1 Hz, 1H), 5.82 – 5.73 (m, 1H), 5.68 – 5.63 (m, 1H), 5.51 (dt, *J* = 5.9, 1.9 Hz, 1H), 5.34 (d, *J* = 3.9 Hz, 1H), 5.14 (t, *J* = 1.5 Hz, 1H), 5.11 (dq, *J* = 6.7, 1.4 Hz, 1H), 4.56 – 4.51 (m, 1H), 4.18 (ddd, *J* = 4.1, 3.0, 0.7 Hz, 1H), 3.92 (dd, *J* = 5.3, 3.4 Hz, 1H), 3.88 – 3.77 (m, 2H), 3.70 (s, 3H), 3.17 (td, *J* = 9.1, 1.5 Hz, 1H), 3.00 (dddp, *J* = 5.0, 3.1, 2.1, 1.0 Hz, 1H), 2.92 – 2.89 (m, 1H), 2.39 – 2.30 (m, 3H), 2.09 (dddd, *J* = 14.4, 5.6, 4.0, 1.5 Hz, 1H), 1.86 – 1.70 (m, 3H), 1.08 (s, 9H), 1.01 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.9, 168.6, 163.5, 135.6, 135.2, 133.7, 132.8, 128.5, 122.0, 116.7, 76.6, 66.9, 66.2, 57.0, 55.6, 52.9, 46.4, 46.3, 46.2, 42.1, 35.3, 28.9, 28.3, 25.5, 21.2, 20.7, 18.1.

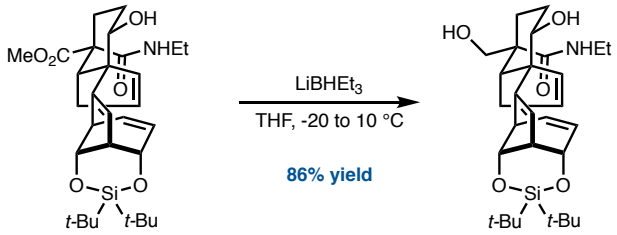
FTIR (NaCl, thin film): 3413, 2934, 3858, 1714, 1674, 1519, 1476, 1252, 1230, 1101, 992, 827, 731 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{31}H_{46}NO_6Si$ $[M + H]^+$ 556.3089, found 556.3085

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +129° (*c* = 1.34, $CHCl_3$).

TLC (70% EtOAc/30% Hexanes), R_f: 0.5 (brown in *p*-anisaldehyde)

Preparation of diol 120:



118 **120**

A flame-dried 100 mL round-bottom flask was charge with ester **118** (360 mg, 0.67 mmol, 1.0 equiv). The starting material was dried by azeotroping with toluene (3 x 25 mL). The flask was put under N_2 before THF (13 mL) was added and the solution cooled to -20 °C. In a separate flame-dried 50 mL pear-shaped flask, a solution of $LiBHEt_3$ (1M in THF, 3.3 mL, 3.3 mmol, 5.0 equiv) was diluted with THF (5 mL). The solution of $LiBHEt_3$ was cooled to -20 °C and transferred to the flask of **118** by cannula over 10 minutes. After stirring at -20 °C for an additional 5 minutes, the reaction was warmed to 0 °C and stirred for 45 min. The reaction quenched with 0.5 M NaOH (aq., 15 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 10 minutes. The mixture was transferred to a separatory funnel and extracted with EtOAc (6 x 50 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated *in vacuo* to give the crude product as a colorless oil. The product was purified by column chromatography (SiO_2, 75-100% EtOAc in hexanes) to give diol **120** (293 mg, 0.58 mmol, 86% yield) as a white foam.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.18 (dt, *J* = 5.8, 2.3 Hz, 1H), 6.11 – 5.98 (m, 2H), 5.65 (ddd, *J* = 9.4, 4.4, 2.0 Hz, 1H), 5.54 (d, *J* = 3.7 Hz, 1H), 5.44 (dt, *J* = 5.8, 1.8 Hz, 1H), 4.58 – 4.49 (m, 1H), 4.21 (ddt, *J* = 3.8, 3.0, 1.4 Hz, 1H), 4.04 – 3.98 (m, 1H), 3.75 (dd, *J* = 10.9, 7.8 Hz, 1H), 3.52 (dd, *J* = 10.9, 3.8 Hz, 1H), 3.41 – 3.16 (m, 3H), 3.07 – 2.99 (m, 1H), 2.95 (t, *J* = 5.3 Hz, 1H), 2.86 (t, *J* = 9.6 Hz, 1H), 2.33 – 2.12 (m, 3H), 1.98 – 1.90 (m, 1H), 1.90 – 1.78 (m, 2H), 1.46 – 1.34 (m, 1H), 1.13 (t, *J* = 7.3 Hz, 3H), 1.07 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.44, 164.58, 136.42, 135.74, 133.95, 128.66, 121.89, 77.04, 67.34, 66.40, 65.63, 56.13, 47.38, 46.64, 46.40, 41.63, 36.17, 34.45, 29.06, 28.45, 24.23, 21.35, 20.85, 18.20, 14.89.

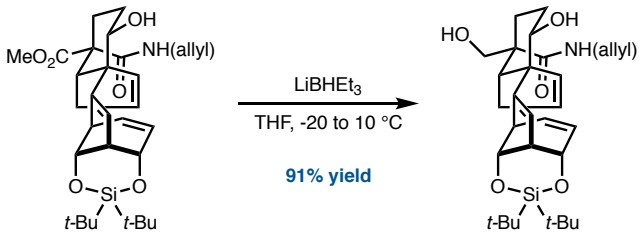
FTIR (NaCl, thin film): 3386, 2934, 2861, 2356, 1635, 1529, 1476, 1332, 1226, 1102, 1060, 1012, 993, 824, 810, 757, 732, 643 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{29}H_{46}NO_5Si$ $[M + H]^+$ 516.3140, found 516.3148

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{22}}$ = +111° (*c* = 1.0, $CHCl_3$).

TLC (100%EtOAc): Rf: 0.4 (brown/purple in *p*-anisaldehyde).

Preparation of diol 119:



117 **119**

A flame-dried 250 mL round-bottom flask was charge with ester **117** (1.830 g, 3.29 mmol, 1.0 equiv). The starting material was dried by azeotroping with toluene (3 x 25 mL). The flask was put under N_2 before THF (45 mL) was added and the solution cooled to -20 °C. In a separate flame-dried 100 mL pear-shaped flask, a solution of $LiBHEt_3$ (1M in THF, 16.5 mL, 16.5 mmol, 5.0 equiv) was diluted with THF (20 mL). The solution of $LiBHEt_3$ was cooled to -20 °C and transferred to the flask of **30** by cannula over 30 minutes. After stirring at -20 °C for an additional 15 minutes, the reaction was warmed to 10 °C and stirred for 1h. The reaction was cooled to 0 °C before quenching with 0.5 M NaOH (aq., 20 mL). The mixture was warmed to room temperature and stirred for 1 hour. The mixture was extracted with EtOAc (2 x 100 mL; 6 x 40 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and

concentrated *in vacuo* to give the crude product as a colorless oil. The product was purified by column chromatography (SiO_2, 25-50-75-100% EtOAc in hexanes) to give diol **119** (1.574 g, 2.99 mmol, 91% yield) as a white foam.

^{1}H NMR (400 MHz, Chloroform-d): δ 6.19 (dt, *J* = 5.9, 2.3 Hz, 1H), 6.13 (t, *J* = 5.7 Hz, 1H), 6.06 (ddd, *J* = 9.5, 6.1, 1.1 Hz, 1H), 5.82 (ddt, *J* = 17.2, 10.2, 5.7 Hz, 1H), 5.66 (ddd, *J* = 9.3, 4.4, 1.9 Hz, 1H), 5.54 (d, *J* = 3.7 Hz, 1H), 5.44 (dt, *J* = 5.8, 1.9 Hz, 1H), 5.22 –5.13 (m, 2H), 4.53 (td, *J* = 4.3, 0.9 Hz, 1H), 4.21 (ddd, *J* = 4.2, 3.0, 0.7 Hz, 1H), 4.02 (t, *J* = 3.1 Hz, 1H), 3.94 (dtt, *J* = 15.6, 5.7, 1.6 Hz, 1H), 3.84 (dtt, *J* = 15.7, 5.7, 1.5 Hz, 1H), 3.76 (d, *J* = 10.8 Hz, 1H), 3.55 (d, *J* = 10.9 Hz, 1H), 3.14 – 3.01 (m, 2H), 2.95 (dd, *J* = 5.9, 4.6 Hz, 1H), 2.86 (t, *J* = 9.7 Hz, 1H), 2.32 – 2.18 (m, 3H), 1.88 – 1.81 (m, 2H), 1.48 – 1.38 (m, 2H), 1.08 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, CDCl3): δ 176.2, 164.4, 136.3, 135.6, 133.9, 133.8, 128.5, 121.8, 116.8, 76.9, 67.2, 66.2, 65.5, 56.0, 47.6, 46.5, 46.2, 41.8, 41.6, 36.1, 28.9, 28.3, 24.1, 21.2, 20.7, 18.0.

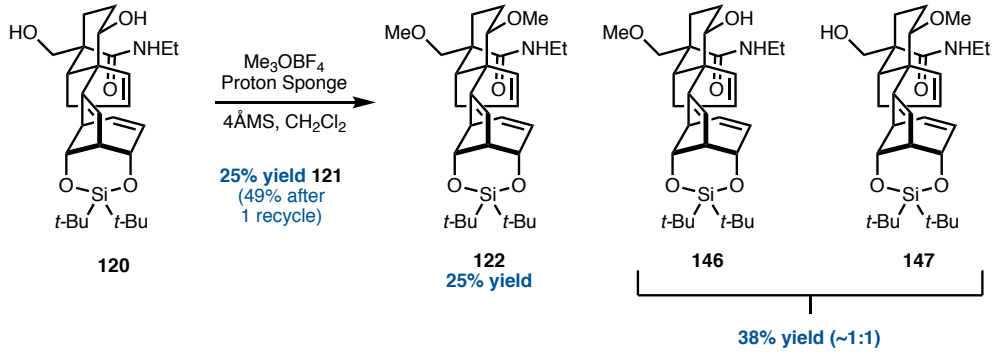
FTIR (NaCl, thin film): 3352, 2931, 2858, 1634, 1539, 1475, 1103, 994, 827, 733 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{30}H_{46}NO_5Si$ $[M + H]^+$ 528.3140, found 528.3130

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +104° (*c* = 1.08, $CHCl_3$).

TLC (100%EtOAc): R_f: 0.5 (pink/brown in p-anisaldehyde).

Preparation of Amide 122:



An oven-dried 20 mL scintillation vial with a cross stir bar was charged with diol **120** (122 mg, 0.24 mmol, 1.0 equiv). CH_2Cl_2 (4.8 mL) was added, followed by Proton Sponge® (406 mg, 1.9 mmol, 8.0 equiv), trimethyloxonium tetrafluoroborate (210 mg, 14.2 mmol, 6.0 equiv), and 4Å molecular sieve powder (120 mg). The vial was stirred (1000 rpm) at 20 °C for 14 hours. HOAc (0.1 mL) was added, and the mixture was passed over a plug of silica gel, eluting with 50-100% EtOAc in hexanes. The filtrate was concentrated to give the crude product as a yellow oil. The product was purified by column chromatography (SiO_2, 20-30-40-50-60-70-80% EtOAc in hexane) to give di-methylated product **122** (32.2 mg, 0.059 mmol, 25% yield) and a ~1:1 mixture of isomeric mono-methylated products **146** and **147** (47.6 mg, 0.090 mmol, 38% yield).

The mixture of **146** and **147** (47.6 mg) was resubjected to the same set of conditions to yield an additional 31.0 mg (0.057 mmol, 65% yield) of **122**. This represents a combined 49% yield of **122** after 1 recycle of **146** and **147**.

Characterization data for 122:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.66 (t, *J* = 5.5 Hz, 1H), 6.06 (ddd, *J* = 9.4, 6.1, 0.6 Hz, 1H), 5.84 (dt, *J* = 4.7, 2.3 Hz, 1H), 5.66 (ddd, *J* = 9.2, 4.4, 1.8 Hz, 1H), 5.42 (d, *J* = 3.8

Hz, 1H), 5.40 – 5.32 (m, 1H), 4.49 (t, *J* = 4.7 Hz, 1H), 4.29 – 4.19 (m, 1H), 3.59 (dd, *J* = 8.2, 2.8 Hz, 1H), 3.40 (d, *J* = 9.4 Hz, 1H), 3.27 (s, 3H), 3.26 – 3.21 (m, 5H), 3.18 (d, *J* = 9.3 Hz, 1H), 3.06 – 3.00 (m, 1H), 2.87 (t, *J* = 5.3 Hz, 1H), 2.65 (t, *J* = 9.4 Hz, 1H), 2.57 (dt, *J* = 13.7, 6.5 Hz, 1H), 2.33 – 2.24 (m, 1H), 2.24 – 2.14 (m, 1H), 1.81 – 1.66 (m, 2H), 1.66 – 1.55 (m, 1H), 1.09 (d, *J* = 7.7 Hz, 12H), 1.01 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.99, 166.16, 135.80, 133.51, 131.78, 128.36, 119.52, 79.04, 76.98, 76.14, 66.61, 58.53, 57.32, 57.03, 46.93, 46.52, 46.35, 43.58, 36.59, 34.40, 29.03, 28.44, 21.66, 21.39, 21.14, 20.81, 15.01.

FTIR (NaCl, thin film): 3355, 2932, 2902, 2859, 1648, 1556, 1534, 1476, 1380, 1265, 1228, 1102, 991, 935, 912, 843, 829, 755, 642 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{31}H_{50}NO_5Si$ $[M + H]^+$ 544.3453, found 544.3451

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{22}}$ = +94° (*c* = 1.07, $CHCl_3$).

TLC (2:1 EtOAc:Hexanes), R_f: 0.6 (blue in *p*-anisaldehyde)

Characterization data for C_1-O methyl ether 147:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.16 (t, *J* = 5.6 Hz, 1H), 6.07 (ddd, *J* = 9.5, 6.2, 1.1 Hz, 1H), 5.87 (dt, *J* = 6.0, 2.3 Hz, 1H), 5.65 (ddd, *J* = 9.5, 4.5, 1.9 Hz, 1H), 5.46 (d, *J* = 3.7 Hz, 1H), 5.39 (ddd, *J* = 5.8, 2.3, 1.4 Hz, 1H), 4.51 (t, *J* = 4.7 Hz, 1H), 4.26 – 4.18 (m, 1H), 3.71 (d, *J* = 10.9 Hz, 1H), 3.59 – 3.42 (m, 2H), 3.40 – 3.26 (m, 1H), 3.25 (s, 4H), 3.10 – 2.98 (m, 2H), 2.97 – 2.89 (m, 1H), 2.71 (t, *J* = 9.3 Hz, 1H), 2.30 – 2.05 (m, 3H), 1.75 (q, *J* = 4.7 Hz, 2H), 1.41 – 1.32 (m, 1H), 1.13 (t, *J* = 7.3 Hz, 3H), 1.07 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.34, 165.99, 135.90, 133.95, 131.96, 128.40, 120.89, 78.80, 66.47, 66.23, 57.96, 56.46, 47.74, 46.56, 46.35, 42.82, 36.22, 34.46, 29.06, 28.45, 21.91, 21.35, 20.84, 19.66, 14.89.

FTIR (NaCl, thin film): 3354, 2933, 1633, 1462, 1358, 1101, 991, 825, 755, 637 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{30}H_{48}NO_5Si$ $[M + H]^+$ 530.3296, found 530.3311.

$[\alpha]_D^{22}$ = +103° (*c* = 0.755, $CHCl_3$).

TLC (2:1 EtOAc:Hexanes), R_f: 0.3 (blue in *p*-anisaldehyde)

Characterization data for C_{18}-O methyl ether 146:

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.48 (t, *J* = 5.5 Hz, 1H), 6.11 (dt, *J* = 5.3, 2.2 Hz, 1H), 6.05 (dd, *J* = 9.4, 6.1 Hz, 1H), 5.66 (ddd, *J* = 9.5, 4.4, 1.9 Hz, 1H), 5.49 (d, *J* = 3.8 Hz, 1H), 5.40 (dd, *J* = 6.0, 2.5 Hz, 1H), 4.46 (t, *J* = 4.6 Hz, 1H), 4.21 (t, *J* = 3.6 Hz, 1H), 4.03 (dd, *J* = 5.2, 2.4 Hz, 1H), 3.48 (d, *J* = 9.2 Hz, 1H), 3.32 – 3.21 (m, 6H), 3.06 – 3.01 (m, 1H), 2.89 (t, *J* = 5.3 Hz, 1H), 2.62 (t, *J* = 9.6 Hz, 1H), 2.40 (ddd, *J* = 13.6, 11.4, 4.7 Hz, 1H), 2.36 – 2.29 (m, 1H), 2.24 (ddd, *J* = 16.6, 8.9, 3.0 Hz, 1H), 1.80 – 1.69 (m, 2H), 1.33 (dt, *J* = 13.8, 4.5 Hz, 1H), 1.10 (t, *J* = 7.3 Hz, 3H), 1.08 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.01, 165.12, 135.84, 135.66, 133.52, 128.56, 121.07, 77.03, 75.39, 67.69, 66.41, 58.88, 56.48, 47.00, 46.58, 46.38, 42.75, 36.18, 34.34, 29.01, 28.43, 24.78, 21.38, 20.81, 18.64, 15.00.

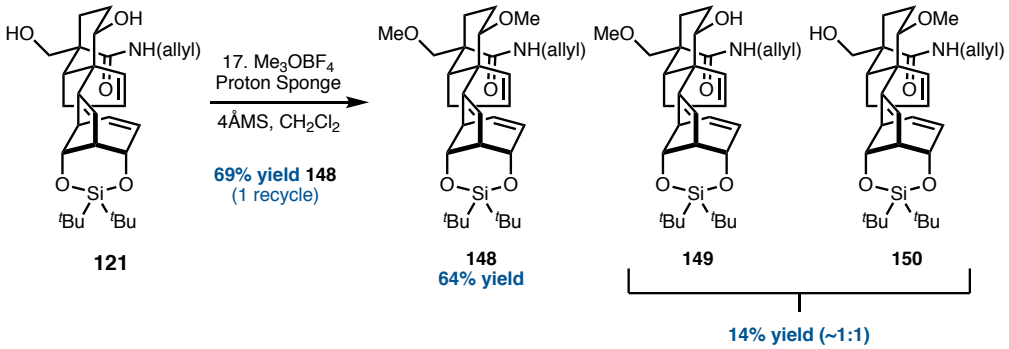
FTIR (NaCl, thin film): 3363, 2934, 2861, 1653, 1530, 1475, 1378, 1265, 1103, 1058, 993, 827, 812, 779, 760, 640 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{30}H_{48}NO_5Si$ $[M + H]^+$ 530.3296, found 530.3306

$[\alpha]_D^{22}$ = +134° (*c* =1.15, $CHCl_3$).

TLC (2:1 EtOAc:Hexanes), R_f: 0.2 (purple in *p*-anisaldehyde)

Preparation of Amide 148:



5 oven-dried 20 mL scintillation vials with cross stir bars were charged with 0.250 g (1.25 g total, 2.37 mmol, 1.0 equiv) of diol **121**, each. CH_2Cl_2 (9.5 mL) was added to each vial, followed by Proton Sponge® (0.610 g each, 0.35 g total, 14.2 mmol, 6.0 equiv), trimethyloxonium tetrafluoroborate (0.420 g each, 2.10 g total, 14.2 mmol, 6.0 equiv), and 4Å molecular sieve powder (250 mg to each vial). The vials were stirred (1000 rpm) at 20 °C for 18 hours. The contents of the vials were combined, HOAc (0.5 mL) was added, and the mixture was passed over a plug of silica gel, eluting with 50-100% EtOAc in hexanes. The eluent was concentrated to give the crude product as a yellow oil. The product was purified by column chromatography (SiO_2, 20-30-40-50-60-70-80% EtOAc in hexane) to give di-methylated product **148** (0.839 g, 1.52 mmol, 64% yield) and a ~1:1 mixture of isomeric mono-methylated products **149** and **150** (0.175 g, 0.33 mmol, 14% yield).

The mixture of **149** and **150** (0.175 g) was resubjected to the same set of conditions to yield an additional 77.0 mg (0.15 mmol, 43%) of **148**, along with 70.0 mg (40%) of a mixture of **149** and **150**. This represents a 69% yield of **148** after 1 recycle of **149** and **150**.

Characterization data for 148:

^{1}H NMR (400 MHz, Chloroform-d): δ 6.80 (t, *J* = 5.7 Hz, 1H), 6.06 (ddd, *J* = 9.5, 6.2, 1.1 Hz, 1H), 5.88 – 5.77 (m, 2H), 5.67 (ddd, *J* = 9.4, 4.4, 1.9 Hz, 1H), 5.44 (d, *J* = 3.8 Hz, 1H), 5.39 (ddd, *J* = 5.9, 2.6, 1.4 Hz, 1H), 5.19 – 5.08 (m, 2H), 4.49 (t, *J* = 4.7, 1H), 4.24 (ddd, *J* = 4.1, 3.0, 0.7 Hz, 1H), 3.94 – 3.78 (m, 2H), 3.60 (dd, *J* = 8.2, 2.8 Hz, 1H), 3.42 (d, *J* = 9.4 Hz, 1H), 3.28 (s, 3H), 3.26 (s, 3H), 3.21 (d, *J* = 9.4 Hz, 1H), 3.06 – 3.01 (m, 1H), 2.87 (dd, *J* = 5.9, 4.6 Hz, 1H), 2.69 (t, *J* = 9.4 Hz, 1H), 2.59 (ddd, *J* = 13.9, 7.5, 5.9 Hz, 1H), 2.30 (ddt, *J* = 16.1, 9.8, 2.2 Hz, 1H), 2.20 (dddd, *J* = 16.1, 9.0, 2.7, 1.4 Hz, 1H), 1.79 – 1.69 (m, 1H), 1.66 – 1.62 (m, 1H), 1.22 – 1.13 (m, 1H), 1.08 (s, 9H), 1.01 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.9, 166.0, 135.6, 134.6, 133.4, 131.6, 128.2, 119.4, 115.8, 78.9, 76.8, 76.0, 66.5, 58.4, 57.2, 56.9, 47.0, 46.4, 46.2, 43.3, 41.8, 36.5, 28.9, 28.3, 21.5, 21.3, 21.1, 20.7.

FTIR (NaCl, thin film): 3362, 2932, 2859, 1652, 1531, 1476, 1380, 1258, 1102, 991, 911, 825, 732 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{32}H_{50}NO_5Si$ $[M + H]^+$ 556.3453, found 556.3454

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +103° (*c* = 0.50, $CHCl_3$).

TLC (30% EtOAc/70% Hexanes), R*f*: 0.4 (blue in *p*-anisaldehyde)

Characterization data for C_1-O methyl ether 150:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.30 (t, *J* = 5.8 Hz, 1H), 6.07 (ddd, *J* = 9.5, 6.1, 1.1 Hz, 1H), 5.92 – 5.73 (m, 2H), 5.65 (ddd, *J* = 9.5, 4.5, 2.1 Hz, 1H), 5.46 (d, *J* = 3.7 Hz, 1H), 5.39 (ddd, *J* = 5.9, 2.4, 1.4 Hz, 1H), 5.19 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.14 (dq, *J* = 10.2, 1.3 Hz,

1H), 4.50 (t, *J* = 4.7 Hz, 1H), 4.27 – 4.19 (m, 1H), 3.95 – 3.78 (m, 2H), 3.73 (d, *J* = 11.0 Hz, 1H), 3.65 – 3.47 (m, 2H), 3.24 (s, 3H), 3.07 – 2.98 (m, 1H), 2.92 (t, *J* = 5.3 Hz, 1H), 2.70 (t, *J* = 9.3 Hz, 1H), 2.33 – 2.13 (m, 3H), 1.79 – 1.69 (m, 2H), 1.40 (dt, *J* = 13.0, 4.8 Hz, 1H), 1.08 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 165.8, 135.7, 134.1, 133.8, 131.8, 128.3, 120.8, 116.6, 78.6, 66.3, 66.1, 57.8, 56.3, 47.9, 46.4, 46.2, 42.8, 41.8, 36.2, 28.9, 28.3, 21.7, 21.2, 20.7, 19.5.

FTIR (NaCl, thin film): 3359, 2934, 2860, 1641, 1526, 1475, 1461, 1382, 1228, 1168, 1102, 1060, 1012, 994, 931, 852, 826, 810, 756, 724, 682, 665, 642 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{31}H_{48}NO_5Si$ $[M + H]^+$ 542.3302, found 542.3326

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{22}}$ = +96.9° (*c* = 1.19, $CHCl_3$).

Characterization data for C_{18}-O methyl ether 149:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.62 (t, *J* = 5.6 Hz, 1H), 6.11 (ddd, *J* = 5.9, 2.8, 1.7 Hz, 1H), 6.06 (ddd, *J* = 9.5, 6.2, 1.1 Hz, 1H), 5.82 (ddt, *J* = 17.2, 10.2, 5.6 Hz, 1H), 5.66 (ddd, *J* = 9.7, 4.5, 1.9 Hz, 1H), 5.50 (d, *J* = 3.8 Hz, 1H), 5.41 (ddd, *J* = 5.9, 2.7, 1.2 Hz, 1H), 5.16 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.11 (dq, *J* = 10.3, 1.4 Hz, 1H), 4.46 (td, *J* = 4.2, 0.9 Hz, 1H), 4.28 – 4.15 (m, 1H), 4.04 (dd, *J* = 5.0, 2.5 Hz, 1H), 3.98 – 3.76 (m, 2H), 3.50 (d, *J* = 9.2 Hz, 1H), 3.29 (s, 4H), 3.15 – 2.98 (m, 1H), 2.98 – 2.81 (m, 1H), 2.65 (t, *J* = 9.6 Hz, 1H), 2.53 – 2.14 (m, 3H), 1.95 – 1.62 (m, 2H), 1.47 – 1.27 (m, 1H), 1.16 – 1.04 (m, 9H), 1.00 (s, 9H).

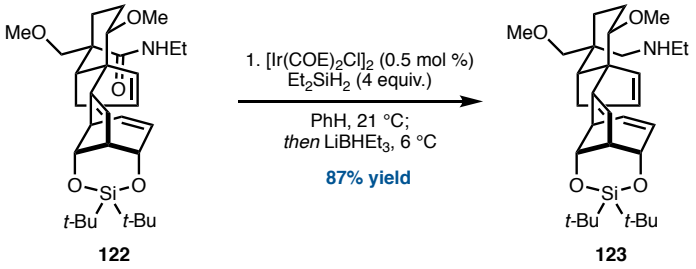
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 165.0, 135.7, 135.5, 134.5, 133.4, 128.5, 121.0, 116.0, 76.9, 75.3, 67.6, 66.3, 58.8, 56.4, 47.1, 46.5, 46.3, 42.5, 41.8, 36.2, 28.9, 28.9, 28.3, 24.6, 21.3, 20.7, 18.6.

FTIR (NaCl, thin film): 3362, 2934, 2897, 2859, 1651, 1520, 1476, 1461, 1382, 1258, 1227, 1168, 1102, 1058, 1012, 993, 934, 888, 853, 826, 811, 755, 736, 682, 642 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{31}H_{48}NO_5Si$ $[M + H]^+$ 542.3302, found 542.3305

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{22}}$ = +123° (*c* = 1.19, $CHCl_3$).

Preparation of amine 123:[7]



Following a modified procedure from Brookhart and coworkers, a 2-dram vial was charged with amide **122** (40.2 mg, 74 μmol, 1.0 equiv.) and brought into an N_2-filled glovebox. Benzene (1.0 mL) was added. Also in the glovebox, a stock solution of catalyst was prepared:$[Ir(COE)_2Cl]_2$ (1.0 mg, 1.1 μmol, 0.015 equiv.) was suspended in benzene (0.9 mL) and Et_2SiH_2 (6.0 mg) was added. After stirring for 5 minutes, the portion of the catalyst solution (0.3 mL, 0.5 mol % $[Ir(COE)_2)Cl]_2$) was added to the reaction vial. An additional 24 mg of and Et_2SiH_2 (300 μmol, 4.0 equiv.) in benzene (0.1 mL) was added, and the reaction was stirred brought out of the glovebox and stirred for 12 hours at 21 °C. The reaction was cooled to 6 °C before a solution of $LiBHEt_3$ (1 M in THF, 0.08 mL, 80 μmol, 1.10 equiv.) was added dropwise. The solution was stirred at 6 °C for 15 minutes before the reaction was quenched at 6 °C with 0.5 M NaOH (aq., 1 mL). The mixture was warmed to room temperature and stirred for 30 minutes. The mixture was extracted with EtOAc (6 x 5 mL) and the combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo* to give the crude product as a

yellow foam. The product was purified by silica gel chromatography (SiO_2, 1-2-3% (7N NH_3 in MeOH) in CH_2Cl_2) to give amine **123** (34.2 mg, 64 μmol, 87% yield) as a white foam.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.06 (ddd, *J* = 9.5, 6.2, 1.1 Hz, 1H), 5.88 (dt, *J* = 5.9, 2.2 Hz, 1H), 5.65 (ddd, *J* = 9.3, 4.4, 1.9 Hz, 1H), 5.41 (dd, *J* = 5.5, 2.7 Hz, 2H), 4.46 (t, *J* = 4.7 Hz, 1H), 4.32 – 4.06 (m, 1H), 3.56 (dd, *J* = 7.7, 2.8 Hz, 1H), 3.25 (s, 3H), 3.24 (s, 3H), 3.19 (d, *J* = 1.5 Hz, 2H), 3.05 – 2.99 (m, 1H), 2.93 – 2.85 (m, 1H), 2.65 – 2.53 (m, 2H), 2.46 (s, 2H), 2.40 (dd, *J* = 10.5, 7.7 Hz, 1H), 2.36 – 2.26 (m, 2H), 1.74 – 1.61 (m, 1H), 1.61 – 1.44 (m, 2H), 1.44 – 1.31 (m, 1H), 1.07 (d, *J* = 7.7 Hz, 12H), 1.01 (s, 9H).

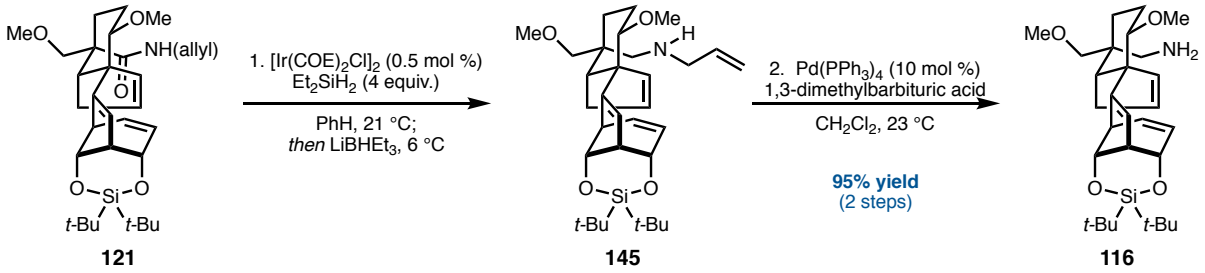
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.80, 136.06, 134.18, 131.52, 128.20, 119.72, 79.92, 76.52, 66.69, 58.93, 57.31, 56.98, 56.89, 46.43, 46.35, 45.06, 44.81, 39.48, 35.51, 29.06, 28.46, 24.58, 21.94, 21.40, 20.83, 15.57.

FTIR (NaCl, thin film): 2936, 2860, 2338, 1606, 1476, 1359, 1107, 993, 860, 825, 816, 782, 744, 730, 668, 644 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{31}H_{52}NO_4Si$ $[M + H]^+$ 530.3660, found 530.3652

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{22}}$ = +112° (*c* = 0.95, $CHCl_3$).

Preparation of primary amine 116:[7,11]



Following a modified procedure from Brookhart and coworkers, a 50 mL round-bottom flask was charged with *N*-allylamide **121** (0.839 g, 1.51 mmol, under N_2 and before benzene

(22 mL) was added. In a nitrogen-filled glovebox, $[Ir(COE)_2Cl]_2$ (6.8 mg, 7.6 μmol, 0.005 equiv) was suspended in benzene (5 ml) and Et_2SiH_2 (0.533 g, 6.04 mmol, 4.0 equiv) was added dropwise. After stirring for 5 minutes, the catalyst solution was drawn up into a syringe, taken out of the glovebox and added to the reaction dropwise at 21 °C. The reaction was stirred for 16 hours at 21 °C. The reaction was cooled to 6 °C before a solution of $LiBHEt_3$ (1M in THF, 1.66 mL, 1.66 mmol, 1.10 equiv) was added dropwise over 10 minutes. The solution was stirred at 6 °C for 30 minutes before the reaction was quenched at 6 °C with 0.5 M NaOH (aq., 15 mL). The mixture was warmed to room temperature and stirred for 30 minutes. The mixture was extracted with EtOAc (6 x 30 mL) and the combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo* to give the crude *N*-allylamine **145** as a yellow foam. **145** was carried on to the following step without purification.

A 50 mL round-bottom flask charged with crude **S17** and 1,3-dimethylbarbituric acid (1.41 g, 9.06 mmol, 6.0 equiv), put under N_2, and CH_2Cl_2 (30 mL) was added. In a nitrogen-filled glovebox, $Pd(PPh_3)_4$ (0.174 g, 0.15 mmol, 0.10 equiv) was taken up in CH_2Cl_2 (3 mL), and this solution was added to the reaction mixture. The reaction was stirred at 23 °C for 1h before quenching with saturated aq. $NaHCO_3$ (25 mL). The mixture was extracted with 3:1 $CHCl_3$:^{i}PrOH (5 x 30 mL). The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo* to give the crude product as a red foam. The product was purified by column chromatography (SiO_2, 1-2-3-4-5-6-7% 7N NH_3 in MeOH/CH_2Cl_2) to give primary amine **116** (0.720 g, 1.43 mmol, 95% yield, 2 steps) as a white foam.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.06 (ddd, *J* = 9.5, 6.1, 1.1 Hz, 1H), 5.87 (dt, *J* = 5.9, 2.3 Hz, 1H), 5.65 (ddd, *J* = 9.4, 4.4, 1.9 Hz, 1H), 5.44 – 5.39 (m, 2H), 4.46 (t, *J* = 4.7 Hz, 1H), 4.23 (ddd, *J* = 4.3, 3.0, 0.7 Hz, 1H), 3.56 (dd, *J* = 7.7, 2.8 Hz, 1H), 3.26 – 3.24 (m, 6H), 3.22

– 3.19 (m, 1H), 3.18 (d, *J* = 9.2 Hz, 1H), 3.05 – 3.00 (m, 1H), 2.88 (dd, *J* = 5.9, 4.6 Hz, 1H), 2.63 (d, *J* = 13.1 Hz, 1H), 2.58 (d, *J* = 13.1 Hz, 1H), 2.39 (dd, *J* = 10.0, 8.4 Hz, 1H), 2.31 – 2.26 (m, 2H), 1.68 (dddd, *J* = 13.3, 8.0, 5.4, 2.7 Hz, 1H), 1.61 – 1.37 (m, 4H), 1.34 – 1.21 (m, 1H), 1.08 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.4, 135.8, 134.1, 131.1, 128.1, 119.7, 79.7, 77.0, 76.1, 66.5, 58.8, 57.2, 56.9, 49.5, 46.3, 46.2, 44.0, 39.7, 35.2, 28.9, 28.3, 23.9, 21.8, 21.2, 20.7.

A ^{13}C signal is observed to be overlapping with residual $CDCl_3$ at 77.00, the peak can be seen in the HSQC spectrum, provided below.

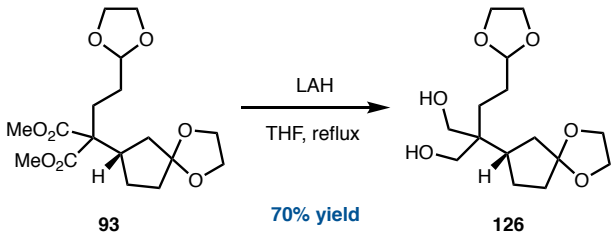
FTIR (NaCl, thin film): 3386, 3050, 2933, 2859, 2362, 1476, 1463, 1106, 992 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{29}H_{48}NO_4Si$ $[M + H]^+$ 502.3347, found 502.3344.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +105° (*c* = 0.67, $CHCl_3$).

TLC (10%MeOH/90%CH_2Cl_2), R_f: 0.15 (UV, blue in *p*-anisaldehyde)

Preparation of diol 126:



A flame-dried 2 L round-bottom flask was charged with diester **93** (24.0 g, 66.9 mmol, 1.0 equiv.). THF (670 mL) added, and the solution was cooled to 0 °C. LAH (12.7 g, 335 mmol, 5.0 equiv.) was added slowly in portions over 30 minutes. The suspension was warmed to room temperature and then heated to reflux for 6 hours. The reaction was cooled to 0 °C and quenched using the Fieser procedure: the mixture was diluted with ether (500 mL) before water (13 mL) was added slowly. 15 % aqueous NaOH (13 mL) was added, followed by water (50

mL). The mixture was warmed to room temperatrure and stirred vigorously for 15 minutes. MgSO4 was added and the mixture was filtered to remove the solids. The filtrate was concentrated *in vacuo*. The product was purified by silica gel chromatography (50-70% acetone in hexanes) to give **126** (14.5 g, 47.6 mmol, 70% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.86 (t, *J* = 4.5 Hz, 1H), 4.03 – 3.95 (m, 2H), 3.95 – 3.81 (m, 6H), 3.74 – 3.64 (m, 2H), 3.65 – 3.50 (m, 2H), 2.60 (q, *J* = 7.7, 5.5 Hz, 2H), 2.14 (dddd, *J* = 19.3, 10.6, 6.3, 4.0 Hz, 1H), 1.96 – 1.79 (m, 2H), 1.76 – 1.66 (m, 5H), 1.60 – 1.45 (m, 3H).

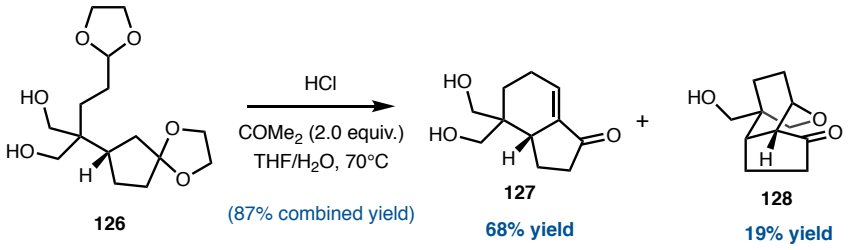
^{13}C NMR (101 MHz, $CDCl_3$) δ 117.35, 104.95, 67.20, 65.11, 64.49, 64.34, 42.10, 39.59, 36.75, 35.82, 27.33, 24.46, 23.90.

FTIR (NaCl, thin film): 3450, 2949, 2882, 2340, 1407, 1332, 1115, 1030, 947 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{15}H_{26}O_6$ $[M + H]^+$ 325.1622, found 325.1510.

$[\alpha]_D^{22} = -1.3°$ (*c* = 1.0, $CHCl_3$).

Preparation of 127 and 128:



A 250 mL round-bottom flask was charged with diol **126** (3.00 g, 9.9 mmol, 1.0 equiv.). THF (40 mL), 2 M HCl (*aq.*, 10 mL) and acetone (1.5 mL) were added. The flask was fitted with a reflux condenser and heated to reflux for 2 days. The reaction was cooled to room temperature before quenching with saturated aqueous $NaHCO_3$ (50 mL). The mixture was extracted with EtOAc (4 x 60 mL). The combined organic extracts were dried (Na_2SO_4),

filtered and concentrated *in vacuo*. The product was purified by silica gel chromatography (20-30-40-50-60-70% acetone in hexanes) to give enone **127** (1.30 g, 7.8 mmol, 79% yield) and oxy-Michael product **128** (0.381 g, 1.9 mmol, 19% yield).

Characterization data for enone **127**:

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.82 (q, *J* = 3.5 Hz, 1H), 3.96 (d, *J* = 10.4 Hz, 1H), 3.82 (d, *J* = 10.8 Hz, 1H), 3.72 – 3.67 (m, 1H), 3.54 (d, *J* = 10.8 Hz, 1H), 2.63 – 2.56 (m, 1H), 2.41 – 2.32 (m, 2H), 2.29 – 2.17 (m, 6H), 1.58 – 1.49 (m, 1H), 1.31 (dd, *J* = 12.4, 6.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.86, 138.24, 132.79, 71.63, 63.51, 43.61, 39.43, 38.33, 27.04, 23.11, 22.61.

FTIR (NaCl, thin film): 3415, 2940, **2883, 1707,** 1648, 1423, 1216, 1178, 1098, 1032, 924, 865, 789, 754, 666 cm^{-1}.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{21}}$ = –93° (*c* = 1.0, $CHCl_3$).

TLC (8%MeOH/92%CH_2Cl_2), R_f: 0.3 (UV, blue in *p*-anisaldehyde)

Characterization data for oxy-Michael product **128**:

^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.16 (td, *J* = 2.7, 1.4 Hz, 1H), 3.77 (dd, *J* = 9.4, 3.4 Hz, 1H), 3.63 (dd, *J* = 9.3, 1.6 Hz, 1H), 3.48 (d, *J* = 10.9 Hz, 1H), 3.43 (d, *J* = 10.9 Hz, 1H), 2.61 (dddd, *J* = 11.1, 9.1, 7.3, 1.6 Hz, 1H), 2.38 – 2.27 (m, 2H), 2.24 (d, *J* = 11.6 Hz, 1H), 2.15 – 2.02 (m, 2H), 1.97 (dtd, *J* = 13.6, 9.6, 7.6 Hz, 1H), 1.78 (ddd, *J* = 12.9, 10.9, 2.1 Hz, 1H), 1.72 – 1.67 (m, 1H), 1.55 – 1.48 (m, 1H).

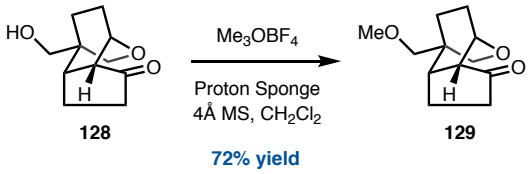
^{13}C NMR (101 MHz, $CDCl_3$) δ 211.14, 67.96, 66.34, 65.66, 50.37, 38.85, 37.69, 36.18, 27.66, 25.66, 21.32.

FTIR (NaCl, thin film): 3445, 2940, 2868, 2352, 1735, 1456, 1407, 1268, 1168, 1140, 1095, 1021, 922, 847, 822 cm^{-1}.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{21}}$ = +59° (*c* = 1.0, $CHCl_3$).

TLC (30% acetone/70% hexanes), R_f: 0.15 (blue/green in *p*-anisaldehyde)

Preparation of C18 Methyl Ether 129:



An oven-dried 20 mL scintillation vial was charged with **128** (30.5 mg, 0.16 mmol, 1.0 equiv.) and brought into a N_2 filled glovebox. CH_2Cl_2 (6.2 mL) was added, followed by Me_3OBF_4 (69.0 mg, 0.47 mmol, 3.0 equiv.), Proton Sponge (100 mg, 0.47 mmol, 3.0 equiv.), and 4 Å molecular sieve powder (61 mg). The vial was capped, removed from the glovebox and stirred for 3 hours at 20 °C. The reaction was quenched with saturated aqueous $NaHCO_3$ (5 mL) and extracted with EtOAc (4 x 5 mL). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (10-30-40-60% EtOAc in hexanes) to afford the product **129** as a colorless oil (23.6 mg, 0.11 mmol, 72% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.17 (td, *J* = 2.7, 1.4 Hz, 1H), 3.80 (dd, *J* = 9.4, 3.3 Hz, 1H), 3.65 (dd, *J* = 9.5, 1.5 Hz, 1H), 3.34 (s, 3H), 3.21 – 3.13 (m, 2H), 2.65 – 2.53 (m, 1H), 2.42 – 2.29 (m, 2H), 2.24 (d, *J* = 11.6 Hz, 1H), 2.16 – 2.05 (m, 2H), 2.05 – 1.96 (m, 1H), 1.82 (ddd, *J* = 12.9, 10.9, 2.1 Hz, 1H), 1.74 – 1.65 (m, 1H), 1.56 – 1.42 (m, 1H).

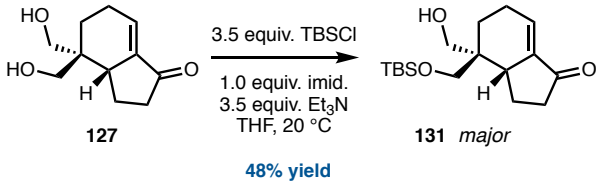
^{13}C NMR (101 MHz, $CDCl_3$) δ 220.43, 76.24, 67.99, 66.57, 59.67, 50.48, 38.89, 38.36, 35.57, 28.32, 25.76, 21.53.

FTIR (NaCl, thin film): 2940, 2869, 1737, 16541, 1457, 1389, 1268, 1195, 1167, 1106, 1044, 902, 848 cm^{-1}.

$[\alpha]_D^{21}$ = +83° (*c* = 1.0, $CHCl_3$).

TLC (30% acetone/70% hexanes), R_f: 0.5 (green in *p*-anisaldehyde)

Preparation of C18 silyl ether 131:



An oven-dried 20 mL scintillation vial was charged with **127** (50 mg, 0.25 mmol, 1.0 equiv.) and THF (3.5 mL). Imidazole (17.0 mg, 0.25 mmol, 1.0 equiv.), triethylamine (0.12 mL, 0.89 mmol, 3.5 equiv.), and TBSCl (134 mg, 0.89 mmol, 3.5 equiv.) were added. The reaction was stirred at 20 °C for 4 hours. The reaction was quenched with saturated aqueous $NaHCO_3$ (5 mL) and extracted with EtOAc (4 x 5 mL). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (10-15-20% EtOAc in hexanes) to afford the product **131** as a colorless oil (37.3 mg, 0.12 mmol, 48% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.80 (q, *J* = 3.5 Hz, 1H), 3.89 (d, *J* = 9.5 Hz, 1H), 3.74 (dd, *J* = 11.1, 3.2 Hz, 1H), 3.56 (dd, *J* = 9.6, 1.4 Hz, 1H), 3.42 (ddd, *J* = 10.8, 8.7, 1.4 Hz, 1H), 2.65 (dd, *J* = 8.5, 3.2 Hz, 1H), 2.48 (tt, *J* = 7.1, 3.7 Hz, 1H), 2.31 (qd, *J* = 14.1, 13.4, 6.9 Hz,

3H), 2.23 – 2.12 (m, 2H), 2.06 (dt, *J* = 12.1, 7.6 Hz, 1H), 1.47 (qd, *J* = 12.4, 7.8 Hz, 1H), 1.20 (ddd, *J* = 13.5, 11.1, 6.3 Hz, 1H), 0.93 (d, *J* = 1.0 Hz, 9H), 0.11 (d, *J* = 2.3 Hz, 5H).

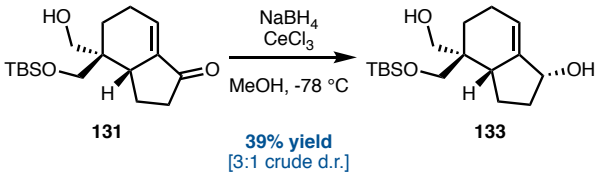
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.77, 138.04, 133.18, 72.30, 63.43, 43.33, 39.30, 38.30, 27.09, 26.00, 23.27, 22.10, 18.32, -5.45, -5.53.

FTIR (NaCl, thin film): 3449, 2951, 2892, 2855, 2340, 1716, 1651, 1470, 1424, 1255, 1216, 1176, 1084, 1049, 836, 777, 680, 667 cm^{-1}.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{21}}$ = +59° (*c* = 1.0, $CHCl_3$).

TLC (40%$COMe_2$/60%hexanes), R_f: 0.6 (UV, blue in *p*-anisaldehyde)

Preparation of allylic alcohol 133:



A 50 mL round-bottom flask was charged with **131** (0.217 mg, 0.70 mmol, 1.0 equiv.), MeOH (14 mL) and $CeCl_3 \bullet 7H_2O$ (0.391 g, 1.05 mmol, 1.5 equiv.). The mixture was cooled to –78 °C, and $NaBH_4$ (32 mg, 0.84 mmol, 1.2 equiv.) was added in one portion. The reaction was stirred for 45 minutes. The reaction was quenched with saturated aqueous 0.1 M NaOH (10 mL), warmed to room temperature and stirred for 20 minutes. The mixture was extracted with EtOAc (4 x 5 mL). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (30-40-50% EtOAc in hexanes) to afford the product **133** as a colorless oil (84.5 mg, 0.27 mmol, 39% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.84 (t, *J* = 3.4 Hz, 1H), 4.48 – 4.40 (m, 1H), 3.85 (d, *J* = 9.5 Hz, 1H), 3.68 (d, *J* = 10.9 Hz, 1H), 3.45 (ddd, *J* = 18.9, 10.2, 1.7 Hz, 2H), 2.88 (s, 1H),

2.45 – 2.26 (m, 1H), 2.23 – 2.10 (m, 3H), 2.09 – 1.98 (m, 1H), 1.87 – 1.75 (m, 1H), 1.52 – 1.37 (m, 1H), 1.32 – 1.10 (m, 3H), 0.91 (s, 9H), 0.09 (s, 3H), 0.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.24, 122.53, 74.08, 73.39, 64.08, 43.11, 39.14, 34.23, 27.22, 26.01, 24.01, 22.74, 18.31, -5.48, -5.55.

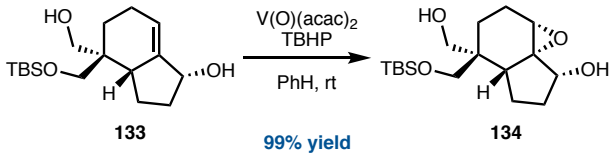
FTIR (NaCl, thin film): 3347, 2952, 2928, 2856, 1461, 1252, 1085, 1006, 813, 776 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{17}H_{33}O_3Si$ $[M + H]^+$ 313.2193, found 313.2192.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{21}}$ = +37° (*c* = 0.75, $CHCl_3$).

TLC (50% EtOAc/50%hexanes), R_f: 0.5 (purple in *p*-anisaldehyde)

Preparation of epoxide **134**:



Alcohol **133** (4.2 mg, 13 mmol, 1.0 equiv.) was added to an oven-dried 1-dram vial. Benzene (1 mL) was added, followed by $V(O)(acac)_2$ (0.7 mg, 2.6 mmol, 20 mol %) and TBHP (5 M in decane, 5 mL, 26 mmol, 2.0 equiv.). The reaction was stirred at 20 °C for 1.5 hours. The reaction was quenched with saturated aqueous Na_2SO_3 (1 mL) and the mixture was extracted with EtOAc (4 x 2 mL). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (50% EtOAc in hexanes) to afford the product **134** as a colorless oil (4.5 mg, 13 μmol, 99% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.26 (dd, *J* = 6.0, 3.1 Hz, 1H), 4.17 (d, *J* = 4.2 Hz, 1H), 3.71 – 3.60 (m, 2H), 3.61 – 3.50 (m, 2H), 3.31 (br, 1H), 2.58 (t, *J* = 8.7 Hz, 1H), 2.33 – 2.18 (m, 1H), 1.99 – 1.75 (m, 2H), 1.70 – 1.60 (m, 3H), 1.56 – 1.41 (m, 2H), 0.87 (s, 9H), 0.06 – -0.02 (m, 6H).

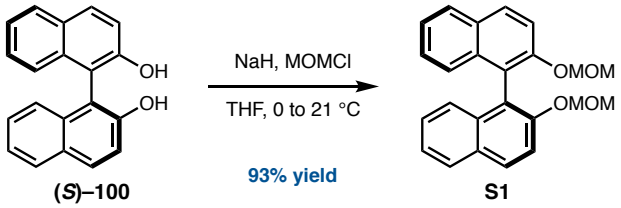
^{13}C NMR (101 MHz, $CDCl_3$) δ 94.54, 79.43, 72.14, 70.62, 65.94, 50.62, 46.46, 35.88, 29.89, 27.79, 25.99, 22.57, 18.38, -5.41, -5.44.

FTIR (NaCl, thin film): 3354, 2950, 2929, 2858, 1462, 1360, 1255, 1223, 1098, 1070, 1002, 958, 838, 776, 668 cm^{-1}.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{21}}$ = +37° (*c* = 0.75, $CHCl_3$).

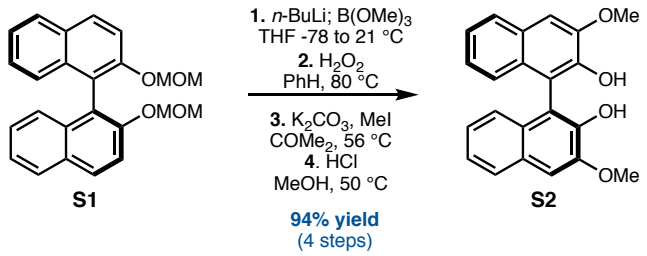
TLC (30% acetone in hexanes), R_f: 0.61 (green in *p*-anisaldehyde)

Preparation of S1:



A flame-dried 1L round-bottom flask was charged with (*S*)–BINOL (**(*S*)–100**) (14.3 g, 50 mmol, 1.0 equiv.) and THF (500 mL). The solution was cooled to 0 °C and NaH (60 wt.% dispersion in mineral oil, 5.0 g, 125 mmol, 2.5 equiv.) was added slowly in portions. After complete addition of NaH, the mixture was stirred at 0 °C for 15 minutes. MOMCl (9.5 mL, 125 mmol, 2.5 equiv.) was added dropwise and the mixture was warmed to 21 °C. The mixture was stirred for 4.5 hours before quenching with water (200 mL) and saturated aqueous $NaHCO_3$ (100 mL). The mixture was extracted with EtOAc (3 x 400 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude product was recrystallized from hot MeOH (~400 mL) to give **S1** (17.4 g, 46.5 mmol, 93% yield) as white, needle-shaped crystals. ^{1}H NMR of **S1** matches previously reported spectroscopic data.[12]

Preparation of S2:



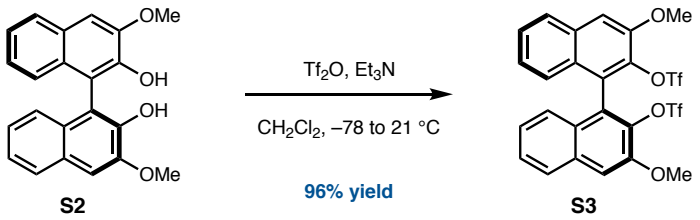
Directed lithiation of **S1** was employed to introduce oxidation at C3/3'.[13] A flame-dried 250 mL round-bottom flask was charged with **S1** (3.74 g, 10 mmol, 1.0 equiv.) and put under N_2. THF (30 mL) was added and the solution was cooled to –78 °C. A solution of *n*-BuLi (2.5M in hexanes, 9.6 mL, 24 mmol, 2.4 equiv.) was added dropwise. The mixture was warmed to 0 °C and stirred for 1 hour. The solution was then cooled to –78 °C before $B(OMe)_3$ (3.3 mL, 30 mmol, 3.0 equiv.) was added dropwise. The reaction was warmed to 21 °C and stirred for 24 hours. The reaction was concentrated *in vacuo* to give a white solid. Benzene (35 mL) was added, and the solution was cooled to 0 °C. H_2O_2 (50 wt.% in water, 2.9 mL) was added dropwise and the reaction was then heated to reflux. After stirring for 2 hours, the reaction was cooled to 0 °C and quenched with saturated aqueous $Na_2S_2O_3$ (100 mL). The reaction was extracted with Et_2O (4 x 100 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude product was carried on to the next step.

The crude product of the boronic ester oxidation was dissolved in acetone (135 mL) in a 250 mL round-bottom flask. K_2CO_3 (4.15 g, 30 mmol, 3.0 equiv.) was added, followed by MeI (3.1 mL, 50 mmol, 5.0 equiv.). The reaction flask was fitted with a reflux condenser and the reaction was heated to reflux for 14 hours. The reaction was cooled to room temperature and quenched with water (100 mL). The reaction was extracted with Et_2O (4 x 100 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude product was carried on to the next step.

The crude methyl ether product was dissolved in MeOH (20 mL) in a 100 mL round-bottom flask. HCl (4M, *aq.*) (10 mL, 40 mmol, 4 equiv.) was added and the reaction flask was fitted with a reflux condenser. The mixture was heated to 50 °C for 48 hours. The reaction was then cooled to room temperature and quenched with saturated aqueous $NaHCO_3$ (100 mL). The mixture was extracted with EtOAc (4 x 100 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (50% EtOAc in hexanes) to afford the product **S2** (2.821 g, 8.1 mmol, 81% yield) as a white solid. The ^{1}H NMR of **S2** matches previously reported spectroscopic data.[14]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.32 (ddd, *J* = 8.1, 6.3, 1.8 Hz, 2H), 7.30 (s, 2H), 7.18 – 7.12 (m, 4H), 4.10 (s, 6H).

Preparation of aryl triflate S3:



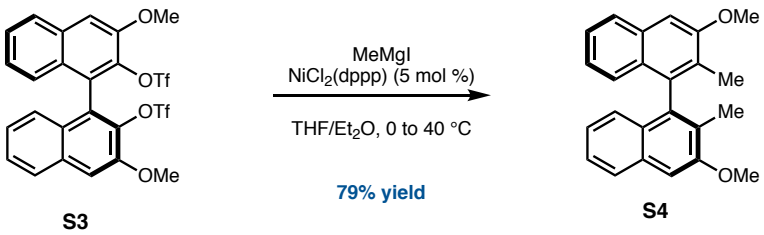
A flame-dried 250 mL round-bottom flask was charged with **S2** (1.88 g, 5.42 mmol, 1.0 equiv.) and put under N_2 atmosphere. CH_2Cl_2 (108 mL) and Et_3N (2.3 mL, 16.3 mmol, 3.0 equiv.) were added, and the mixture was cooled to –78 °C. Tf_2O (2.0 mL, 11.9 mmol, 2.2 equiv.) was added dropwise, and the reaction was warmed to 21 °C. After stirring for 4 hours, the reaction mixture was poured into a stirring solution of HCl (1M, *aq.*) (100 mL). Et_2O (100 mL) was added, and the mixture was transferred to a separatory funnel. The phases were separated, and the organic phase was extracted with Et_2O (2 x 100 mL). The combined organic

phases were washed with saturated aqueous $NaHCO_3$ (2 x 100 mL), then with brine (100 mL). The organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to yield the crude product as an orange foam. Purification by silica gel chromatography (10-20% EtOAc in hexanes) afforded **S3** (3.17 g, 5.20 mmol, 96% yield) as a white solid. The ^{1}H NMR of **S3** matches previously reported spectroscopic data.[14]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.52 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 2H), 7.49 (s, 2H), 7.24 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 4.11 (s, 6H).

TLC (25%EtOAc/ 75% Hexanes), R_f: 0.3 (UV)

Preparation of S4:[14,15]



A solution of MeMgI was prepared as follows: A flame-dried 250 mL 3-neck round-bottom flask was charged with oven-dried Mg (4.56 g, 188 mmol, 2.5 equiv.), fitted with a reflux condenser, and put under argon atmosphere. Et_2O (5 mL) was added, followed by neat DIBAL (0.02 mL), and the mixture was stirred vigorously for 15 minutes. The flask was heated to 30 °C in an oil bath before a solution of MeI (4.7 mL, 75 mmol, 1.0 equiv.) in Et_2O (75 mL) was added slowly until the reaction began to reflux. At this point, the oil bath was removed, and the solution of MeI was added at a rate just fast enough to maintain reflux. After addition of MeI was complete, the mixture was heated to reflux in an oil bath for 1 hour. The mixture was cooled to room temperature. Titration with salicylaldehyde phenylhydrazone indicated the

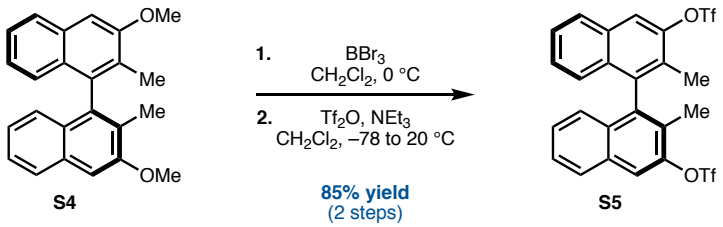
concentration of the MeMgI solution was 0.8 M. The solution was transferred to a flame-dried Schlenk flask under argon for storage.

For the Kumada coupling, a flame-dried 50 mL round-bottom flask was charged with aryl triflate **S3** (1.10 g, 1.8 mmol, 1.0 equiv.) and $NiCl_2$•dppp (49.0 mg, 0.09 mmol, 5 mol %). The flask was fitted with a reflux condenser and put under argon atmosphere. Et_2O (1.8 mL) was added, followed by a solution of MeMgI (0.8 M in Et_2O, 11.3 mL, 9.0 mmol, 5.0 equiv.). The reaction was heated to reflux for 11 hours. The reaction was quenched with 1M HCl (*aq.*) (15 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (2 x 50 mL) then with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by silica gel chromatography (5-10-20% EtOAc in hexanes) afforded **S4** (0.492 g, 1.44 mmol, 80% yield) as a white powder. The ^{1}H NMR of **S4** matches previously reported spectroscopic data.[14]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.35 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 2H), 7.23 (s, 2H), 7.06 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 4.04 (s, 6H), 1.93 (s, 5H).

TLC (25%EtOAc/ 75% Hexanes), R_f: 0.5 (UV)

Preparation of bis-aryltriflate S5:



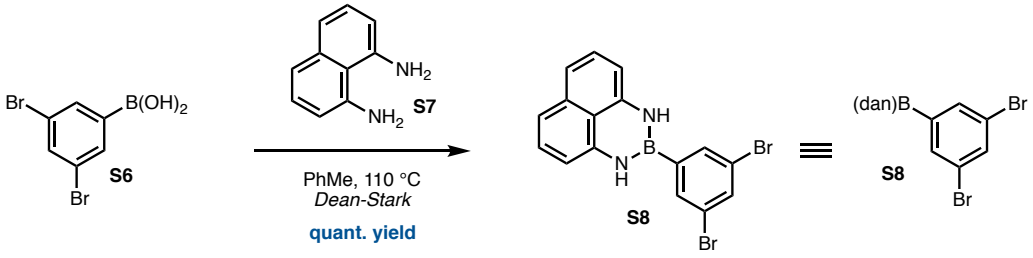
A flame-dried 10 mL round-bottom flask was charged with bis-methylether **S4** (0.200 g, 0.58 mmol, 1.0 equiv.) and put under a N_2-atmosphere. CH_2Cl_2 (2.4 mL) was added, and the solution was cooled to 0 °C. BBr_3 (0.13 mL, 1.4 mmol, 2.4 equiv.) was added dropwise, and the reaction was stirred at 0 °C for 4.5 hours. Water (5 mL) was added, and the mixture was filtered through a pad of celite. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude product was carried on to the next reaction

The crude product from the demethylation reaction was dissolved in CH_2Cl_2 (in a flame-dried 50 mL round-bottom flask. Triethylamine (0.24 mL, 1.7 mmol, 3.0 equiv.) was added, and the solution was cooled to –78 °C. Triflic anhydride (0.21 mL, 1.3 mmol, 2.2 equiv.) was added dropwise and the mixture was stirred at –78 °C for 10 minutes before warming to room temperature. After stirred for 3 hours, the reaction was quenched with 1M HCl (*aq*.) (10 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (4 x 20 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (2 x 50 mL) then with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by silica gel chromatography (5:1 hexanes:EtOAc) afforded **S5** (0.287 g, 0.50 mmol, 85% yield over 2 steps) as a white foam. The ^{1}H NMR of **S5** matches previously reported spectroscopic data.[14]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 – 7.90 (m, 4H), 7.53 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 2H), 7.33 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 2H), 6.98 (dd, *J* = 8.5, 1.0 Hz, 2H), 2.05 (s, 6H).

TLC (25%EtOAc/ 75% Hexanes), R_f: 0.6 (UV)

Preparation of 1,8-diaminonaphthalene-protected boronic acid S8:

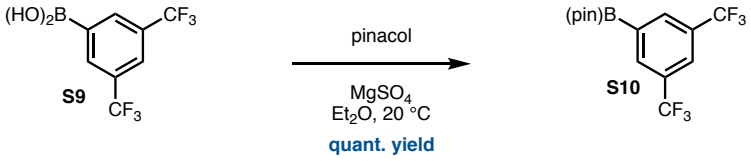


An oven-dried 250 mL round-bottom flask was charged with 3,5-dibromophenylboronic acid (3.55 g, 12.7 mmol, 1.0 equiv.), 1,8-diaminonaphthalene (2.21 g, 14.0 mmol, 1.1 equiv.) and toluene (160 mL). The flask was fitted with a Dean-Stark apparatus, and the mixture was heated to a vigorous reflux for 5 hours. The reaction was concentrated *in vacuo* and the product was purified by silica gel chromatography (50% CH_2Cl_2 in hexanes) to afford **S8** (5.10 g, 12.7 mmol., 100% yield) as a light orange solid. The ^{1}H NMR of **S8** matches previously reported spectroscopic data.[16]

Note: S8 was stored in a N_2-filled glovebox, as it begins to change color to purple under air.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76 (t, *J* = 1.8 Hz, 1H), 7.68 (d, *J* = 1.8 Hz, 2H), 7.15 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.08 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.43 (dd, *J* = 7.2, 1.1 Hz, 2H), 5.94 (s, 2H).

Preparation of boronic ester S10:

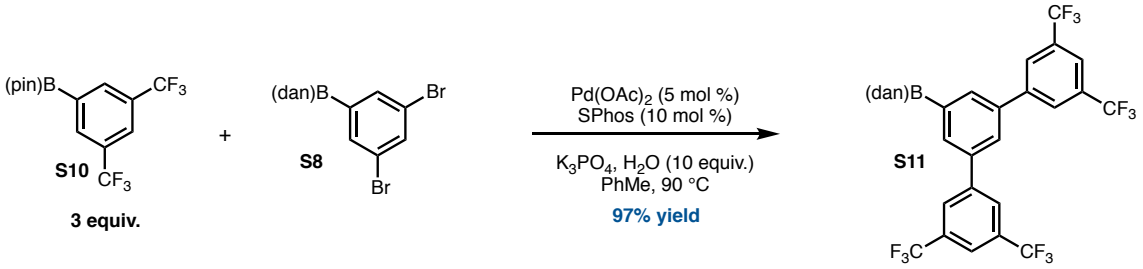


A 250 mL round-bottom flask was charged with 3,5-bis(trifluoromethyl)phenylboronic acid (3.82 g, 14.8 mmol, 1.0 equiv.), pinacol (1.92 g, 16.3 mmol, 1.1 equiv.), $MgSO_4$ (10 g),

and Et_2O (130 mL). The mixture was stirred vigorously at 20 °C for 20 hours. The mixture was filtered and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (20% EtOAc in hexanes) to give boronic ester **S10** (4.98 g, 14.8 mmol, 100% yield) as a white solid. The ^{1}H NMR of **S8** matches previously reported spectroscopic data.[17]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.24 (s, 2H), 7.94 (s, 1H), 1.38 (s, 12H).

Preparation of protected boronic acid S11:

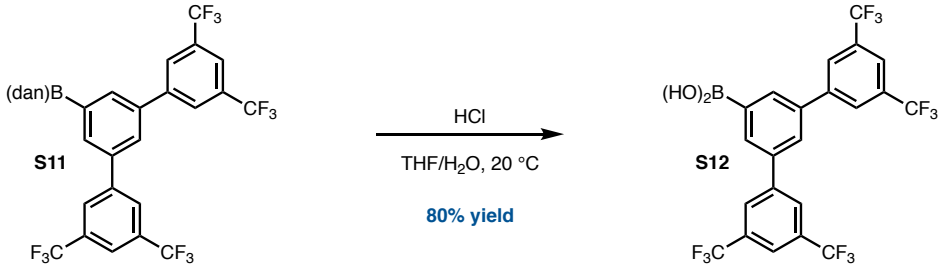


A flame-dried 50 mL round-bottom flask was charged with aryl bis-bromide **S8** (0.804 g, 2.0 mmol, 1.0 equiv.) and boronic ester **S10** (2.040 g, 6.0 mmol, 3.0 equiv.). The flask was brought into a N_2-filled glovebox. $Pd(OAc)_2$ (22.5 mg, 0.10 mmol, 5 mol %), SPhos (82.1 mg, 0.20 mmol, 10 mol %), and K_3PO_4 (1.274 g, 6.0 mmol, 3.0 equiv.). The flask was sealed with a rubber septum and removed from the glovebox. Toluene (20 mL) was added along with water (0.36 mL, 20 mmol, 10 equiv.) and the mixture was heated to 90 °C. After stirring for 30 hours, the reaction was cooled to room temperature before water (80 mL) was added. The phases were separated, and the aqueous phase was extracted with Et_2O (3 x 100 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by silica gel chromatography (10:1 hexanes:EtOAc) afforded **S11** (1.298 g, 1.94 mmol, 97% yield) as an orange powder. Boronic ester **S10** (152 mg, 0.45 mmol, 0.22 equiv.) was also recovered.

Note: This procedure is modified from a literature procedure which used THF as solvent.[17] In our hands, only mono-cross-coupled product with protodebromination was obtained under the previously reported conditions.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.09 (s, 4H), 7.95 (s, 2H), 7.90 (d, *J* = 1.8 Hz, 2H), 7.83 (t, *J* = 1.8 Hz, 1H), 7.18 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.11 (dd, *J* = 8.4, 1.0 Hz, 2H), 6.51 (dd, *J* = 7.3, 1.0 Hz, 2H), 6.13 (s, 2H).

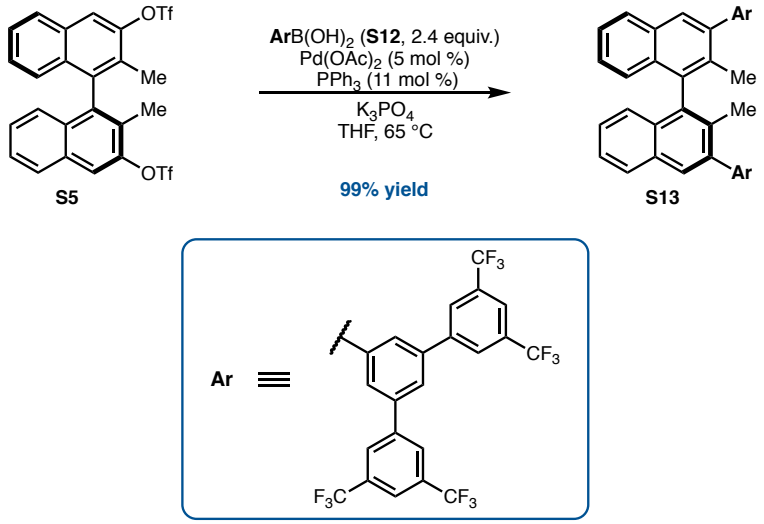
Preparation of boronic acid S12:



A 50 mL round-bottom flask was charged with **S11** (0.780 g, 1.17 mmol, 1.0 equiv.). THF (25 mL) and 5M HCl (*aq*.) were added, and the mixture was stirred at 20 °C for 22 hours. 3M HCl (*aq*.) (35 mL) was added, and the mixture was extracted with Et_2O (4 x 40 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to yield **S12** (0.518 g, 0.95 mmol, 80% yield) as a white solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 (s, 4H), 8.04 (d, *J* = 1.8 Hz, 2H), 7.93 (s, 2H), 7.86 (t, *J* = 1.9 Hz, 1H).

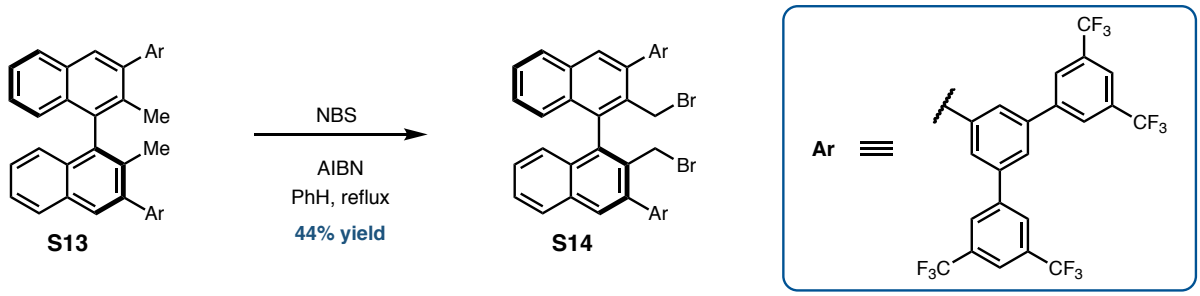
Suzuki Coupling to synthesize S13:



An oven–dried 1-dram vial with a stir bar was charged with **S5** (75 mg, 0.13 mmol, 1.0 equiv.), **S12** (170 mg, 0.31 mmol, 2.4 equiv.), K_3PO_4 (90 mg, 0.39 mmol, 3.0 equiv.), and PPh_3 (3.8 mg, 14 µmol, 11 mol %). The vial was brought into a N_2–filled glovebox. $Pd(OAc)_2$ (1.5 mg, 6.6 µmol, 5 mol %) and THF (1.3 mL) were added. The vial was capped and removed from the glovebox, and the reaction was heated to 65 °C for 20 hours. Saturated aqueous NH_4Cl (2 mL) was added, and the mixture was filtered over a short pad of celite. The aqueous phase was extracted with Et_2O (5 x 2 mL), and the combined extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The product was purified via silica gel chromatography (16:4:1 hexanes:PhMe:EtOAc) to afford **S13** (164 mg, 0.13 mmol, 99% yield) as an colorless, amorphous solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (s, 8H), 7.97 (s, 4H), 7.93 (s, 4H), 7.80 – 7.76 (m, 6H), 7.53 – 7.45 (m, 2H), 7.33 (ddd, J = 8.2, 6.8, 1.3 Hz, 2H), 7.18 (d, J = 8.6 Hz, 2H), 2.07 (s, 6H).

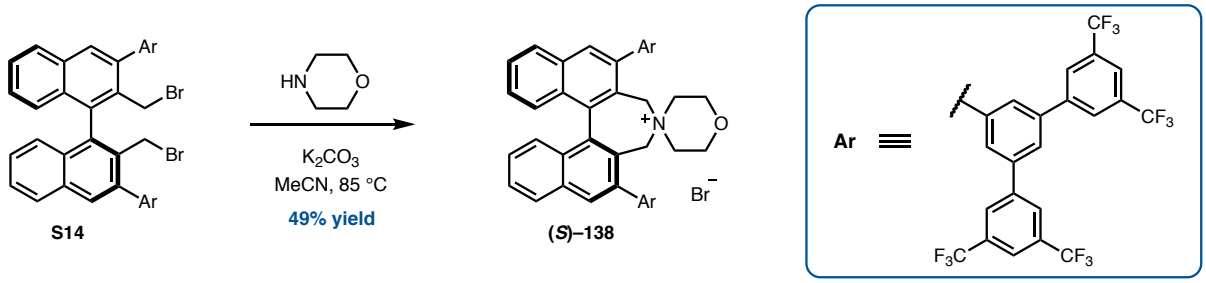
Synthesis of bis-benzylic bromide S14:



An oven–dried 1-dram vial with a stir bar was charged with **S13** (163 mg, 0.13 mmol, 1.0 equiv.), *N*-bromosuccinimide (50 mg, 0.28 mmol, 2.2 equiv.), AIBN (2.1 mg, 13 µmol, 0.10 equiv.). The vial was brought into a N_2–filled glovebox, and benene was added. The vial was capped and removed from the glovebox. The reaction was heated to 80 °C for 3 hours. After cooling to room temperature, water (1.5 mL) was added, and the aqueous phase was extracted with EtOAc (5 x 2 mL), and the combined extracts were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The product was purified via silica gel chromatography (16:4:1 hexanes:PhMe:EtOAc) to afford **S14** (80 mg, 56 µmol, 44% yield) as a white solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.16 (s, 8H), 8.06 (s, 2H), 8.01 – 7.97 (m, 6H), 7.94 (s, 4H), 7.87 (t, *J* = 1.7 Hz, 2H), 7.60 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 2H), 7.38 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 2H), 4.37 (d, *J* = 10.3 Hz, 2H), 4.32 (d, *J* = 10.1 Hz, 2H).

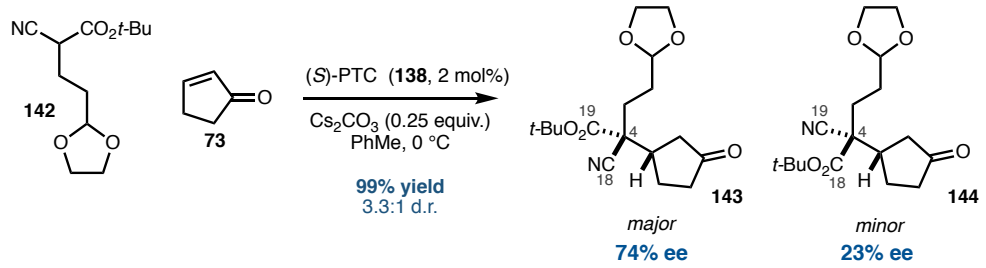
Preparation of quaternary ammonium bromide catalyst (*S*)–138:



An oven-dried 1-dram vial with a stir bar was charged with **S14** (80 mg, 56 μmol, 1.0 equiv.), K_2CO_3 (39 mg, 0.28 mmol, 5.0 equiv.), MeCN (1.1 mL), and freshly-distilled morpholine (15 mg, 0.17 mmol, 3.0 equiv.). The mixture was heated to 85 °C for 14 hours. After the reaction was allowed to cool to room temperature, the mixture was filtered over celite, and the filtrate was concentrated *in vacuo*. The product was purified by silica gel chromatography, taking precautions to avoid contaminating the product with impurities from the silica gel: 3 column volumes of MeOH was passed through a column pre-equilibrated with MeOH. The column was then flushed with the mobile phase before loading the crude product. Purification (2-4-5-10-20% MeOH in CH_2Cl_2) afforded **(*S*)–138** (39.4 mg, 28 μmol, 49% yield) as a white solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.21 (s, 2H), 8.16 – 8.08 (m, 10H), 7.98 (s, 2H), 7.94 (s, 2H), 7.90 (t, *J* = 1.7 Hz, 2H), 7.89 (s, 2H), 7.75 – 7.67 (m, 4H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.48 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 2H), 5.28 (d, *J* = 12.5 Hz, 1H), 5.24 (s, 1H), 4.04 (d, *J* = 13.4 Hz, 2H), 3.95 – 3.84 (m, 2H), 3.56 – 3.44 (m, 2H), 3.18 – 3.06 (m, 2H), 3.07 – 2.93 (m, 2H).

Stereoselective conjugate addition:



An oven-dried 1-dram vial was charged with α-cyanoacetate **141** (12.1 mg, 0.05 mmol, 1.0 equiv.), 2-cyclopenten-1-one (8.2 mg, 0.10 mmol, 2.0 equiv.), and quaternary ammonium catalyst (*S*)–**138** (1.4 mg, 0.001 mmol, 2 mol %). Toluene (1 mL) was added, and the vial was put under Argon with a balloon and cooled to 0 °C in a cryocool. After 15 minutes of cooling, Cs_2CO_3 (1.6 mg, 0.005 mmol, 0.10 equiv.) was added, and the mixture was stirred at 0 °C for 11 hours. The reaction was quenching with saturated aqueous NH_4Cl (1 mL) and extracted with EtOAc (5 x 2 mL). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. Quantitative NMR with dimethyl fumarate as an internal standard showed a 3.3:1 ratio of **143**:**144** in 99% yield. Clean samples of each diastereomer were obtained by silica gel chromatography (5-10-15-20% EtOAc in hexanes). Enantiopurity of **143** and **144** were determined to be 74% ee and 23% ee, respectively, using chiral SFC.

Characterization data for major diastereomer **143**:

^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.92 (t, *J* = 4.2 Hz, 1H), 4.01 – 3.96 (m, 2H), 3.91 – 3.84 (m, 2H), 2.65 (tdd, *J* = 11.7, 7.8, 6.2 Hz, 1H), 2.50 – 2.43 (m, 1H), 2.37 – 2.27 (m, 3H), 2.27 – 2.15 (m, 1H), 2.06 – 1.93 (m, 3H), 1.92 – 1.83 (m, 1H), 1.74 – 1.64 (m, 1H), 1.52 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.03, 117.69, 103.11, 85.04, 65.21, 65.19, 54.21, 43.03, 41.27, 38.22, 29.89, 29.55, 27.95, 25.19.

HRMS: (ESI-TOF) calc'd for $C_{13}H_{17}NO_5$ $[M + H - CH_2C(CH_3)_2]^+$ 268.1179, found 268.1179.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{22}}$ = +39° (*c* = 0.33, $CHCl_3$).

TLC (50%EtOAc/50%Heaxanes), R_f: 0.35 (blue in *p*-anisaldehyde)

Characterization data for minor diastereomer **144**:

^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.90 (t, *J* = 4.2 Hz, 1H), 4.02 – 3.93 (m, 2H), 3.92 – 3.80 (m, 2H), 2.73 – 2.62 (m, 1H), 2.55 – 2.40 (m, 2H), 2.33 – 2.16 (m, 2H), 2.16 – 2.05 (m, 1H), 2.05 – 1.83 (m, 4H), 1.74 – 1.64 (m, 1H), 1.54 (s, 9H).

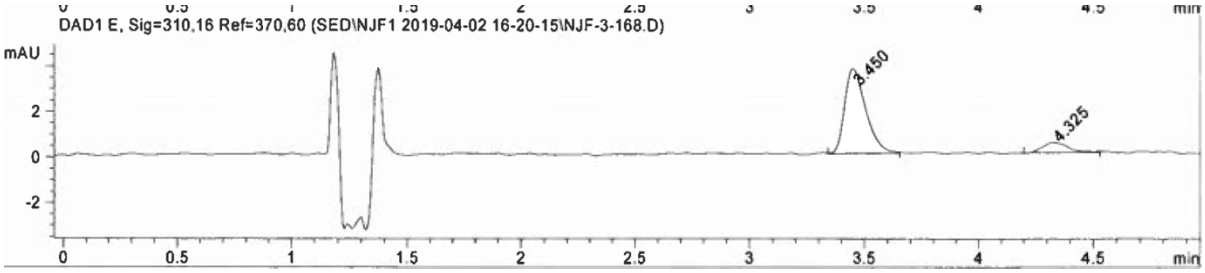
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.95, 117.63, 103.02, 85.01, 65.19, 65.17, 54.57, 43.32, 40.64, 38.27, 30.83, 29.89, 28.01, 27.94, 25.84.

TLC (50%EtOAc/50%Heaxanes), R_f: 0.35 (blue in *p*-anisaldehyde)

Chiral SFC Traces:

Major diastereomer **143**, 74% ee.

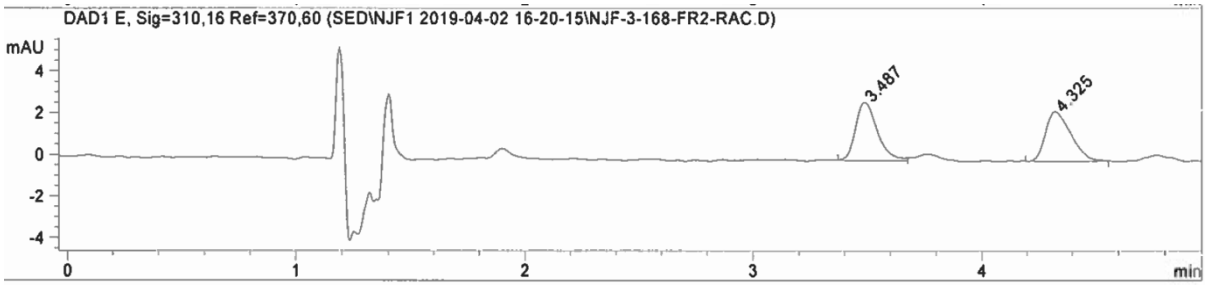
Conditions: 10% *i*PrOH, OD-H column, 2.5 mL/min, 5 minute run.



Signal 4: DAD1 E, Sig=310,16 Ref=370,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.450	BB	0.0981	23.60655	3.71444	87.4752
2	4.325	BB	0.1022	3.38001	4.46909e-1	12.5248
Totals :				26.98656	4.16134	

Major diastereomer **143**, racemic trace.

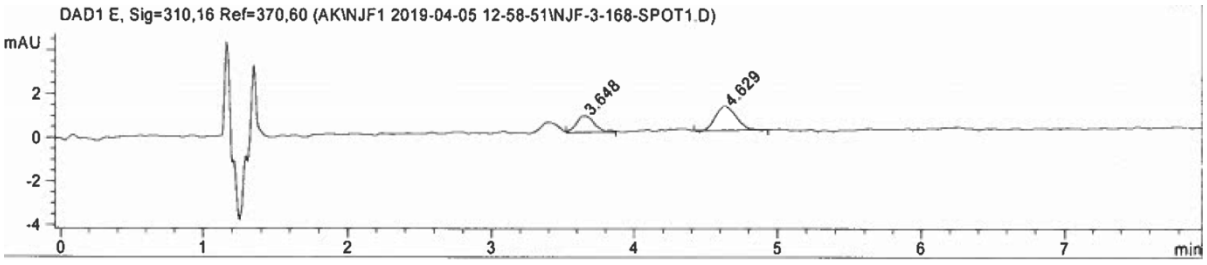


Signal 4: DAD1 E, Sig=310,16 Ref=370,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.487	BB	0.1038	18.74980	2.81238	50.7048
2	4.325	BB	0.1234	18.22854	2.37961	49.2952
Totals :				36.97834	5.19199	

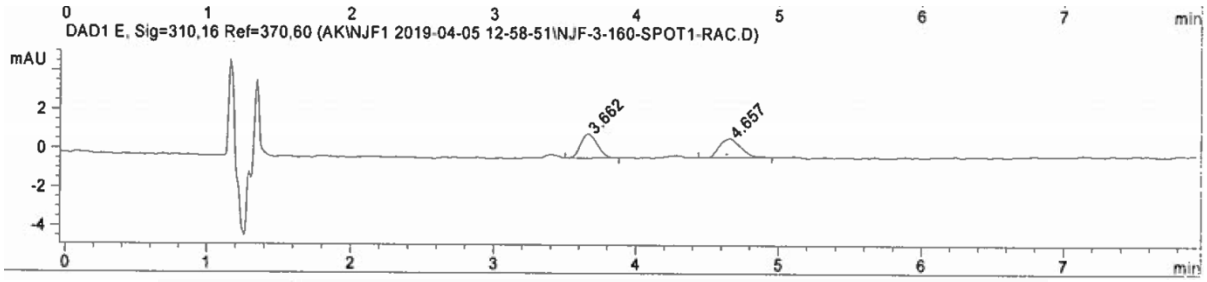
Minor diastereomer **144**, 23% ee:

Conditions: 10% *i*PrOH, OD-H column, 2.5 mL/min, 8 minute run.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.648	VB	0.1308	6.69269	7.74426e-1	38.6076
2	4.629	BB	0.1461	10.64245	1.08860	61.3924
Totals :				17.33513	1.86303	

Minor diastereomer **144**, racemic trace:



Signal 4: DAD1 E, Sig=310,16 Ref=370,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.662	BB	0.1294	10.40502	1.24587	50.6880
2	4.657	BB	0.1552	10.12257	9.74508e-1	49.3120
Totals :				20.52759	2.22038	

3.7 NOTES AND REFERENCES

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Chapter 4

Completion of Aconitine Core and Synthesis of (–)-Talatisamine, (–)-Liljestrandisine, and (–)-Liljestrandinine

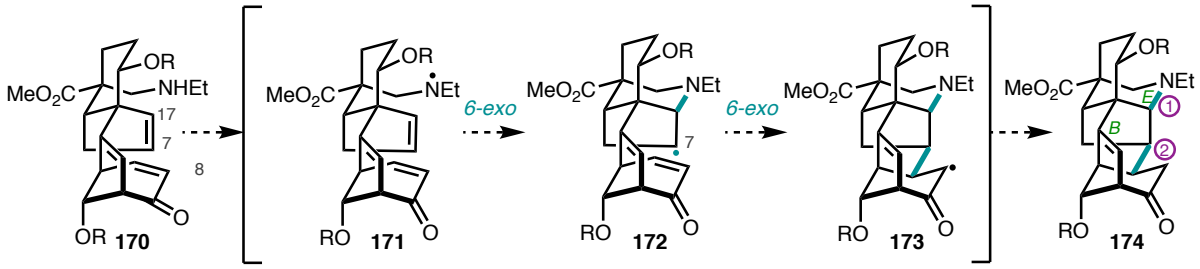
4.1 INTRODUCTION

This chapter describes studies on the completion of the B and E rings of the aconitine core, as well as the completion of the total synthesis of (–)-talatisamine, (–)-liljestrandisine, and (–)-liljestrandinine.

4.2 RADICAL CYCLIZATION CASCADE

With all carbon atoms of the natural product framework in place, all that remains to access the core is C17–N and C7–C8 bond formation. To do so, we envisioned an olefin carboamination with *anti*-stereoselectivity to form two rings in a single step (Figure 4.1). In order to effect this transformation, we investigated a radical cascade approach, wherein an N-centered radical would undergo 6-exo-trig cyclization to form the E-ring and generate a C7-radical which would engage in Giese addition to a D-ring enone. To test this approach, we targeted *N*-chloro amines as *N*-centered radical precursors.

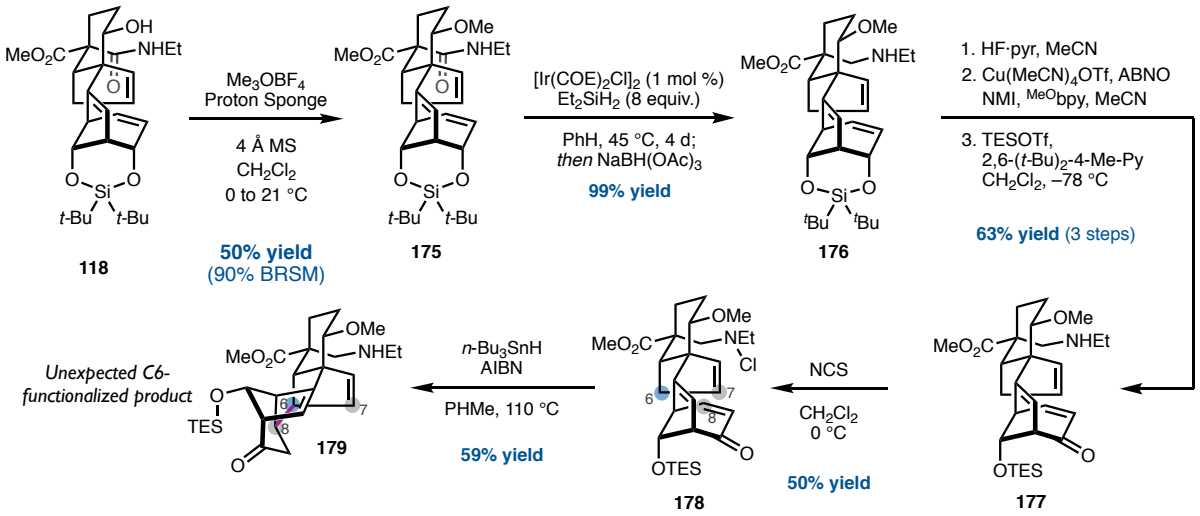
Figure 4.1 *Proposed radical cyclization cascade to form aconitine core.*



4.2.1 *Reaction of Neutral Aminyl Radical*

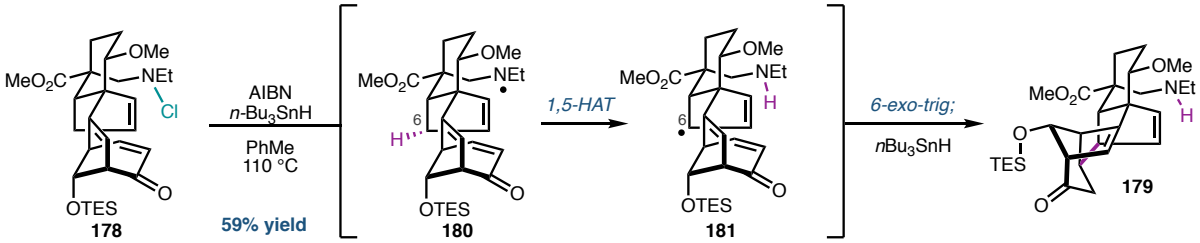
Starting from *N*-ethyl amide **118**, *O*-methylation with trimethyloxonium tetrafluoroborate proceeds in moderate yield to afford **175** along with recovered starting material. The amide was reduced selectively using iridium-catalyzed hydrosilylation to afford amine **176**. Next, the D-ring was functionalized to introduce the radical acceptor enone. The siliconide is deprotected with HF•pyridine to afford a diol, which can undergo selective oxidation at the allylic site under Stahl's conditions. The remaining C16 alcohol is protected as the triethylsilyl ether to give **177**. Treatment of **177** with NCS affords the *N*-chloroamine **178**. In the key attempted radical cascade reaction, when **178** was treated with AIBN and tributyltin hydride, an unexpected C6-functionalized product **179** was obtained.

Scheme 4.1 *Synthesis of N-centered radical precursor* ***178*** *and unexpected reactivity.*



Our proposed mechanism for the formation of **179** is a Hoffmann-Löffler-Freytag type reaction, the mechanism of which is shown in Scheme 4.2. *N*-centered radical intermediate **180** undergoes a 1,5-hydrogen atom transfer at C6 to afford allyl-radical intermediate **181**. The radical then undergoes Giese addition to the D-ring enone at C6 to afford the observed product **179** after quenching of the resulting α-radical. It is worth noting that there are very few examples of 6-*exo* cyclizations of neutral aminyl radicals with olefins, especially those with allylic H-atoms. This observed reactivity led us to consider less nucleophilic *N*-centered radical intermediates with the hope that this would minimize HAT pathways.

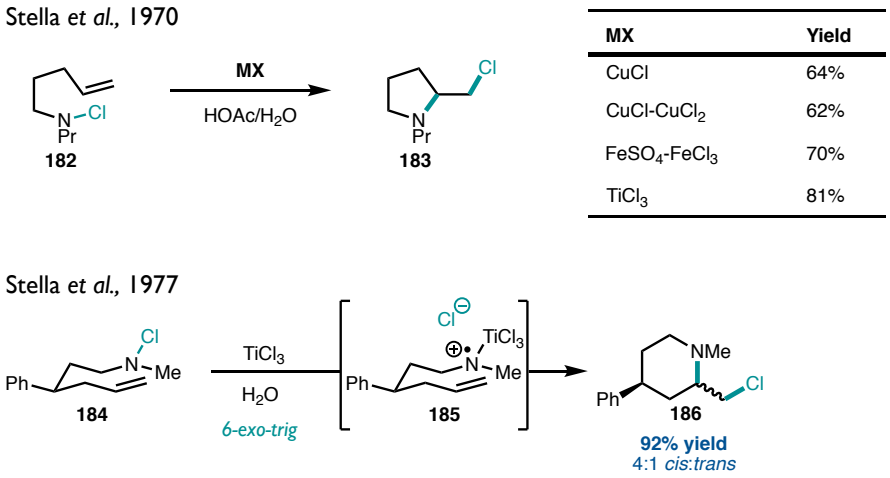
Scheme 4.2 *Hoffmann-Löffler-Freytag type reaction of aminyl radical* ***180*** *to afford* ***179***.



4.2.2 *Reactivity of Aminyl Radical Cations*

We turned to methods of generating aminyl radical cations. Lewis-acidic single-electron reducing catalysts have been used to effect 1,2-aminochlorination of alkenes.[1–5] Especially relevant are examples of 6-*exo*-trig cyclizations on substrates with allylic hydrogen atoms with the potential for 1,5-HAT to occur (Figure 4.2). To quickly evaluate conditions for radical cyclization to form the E-ring piperidine, we turned to a simplified model system.

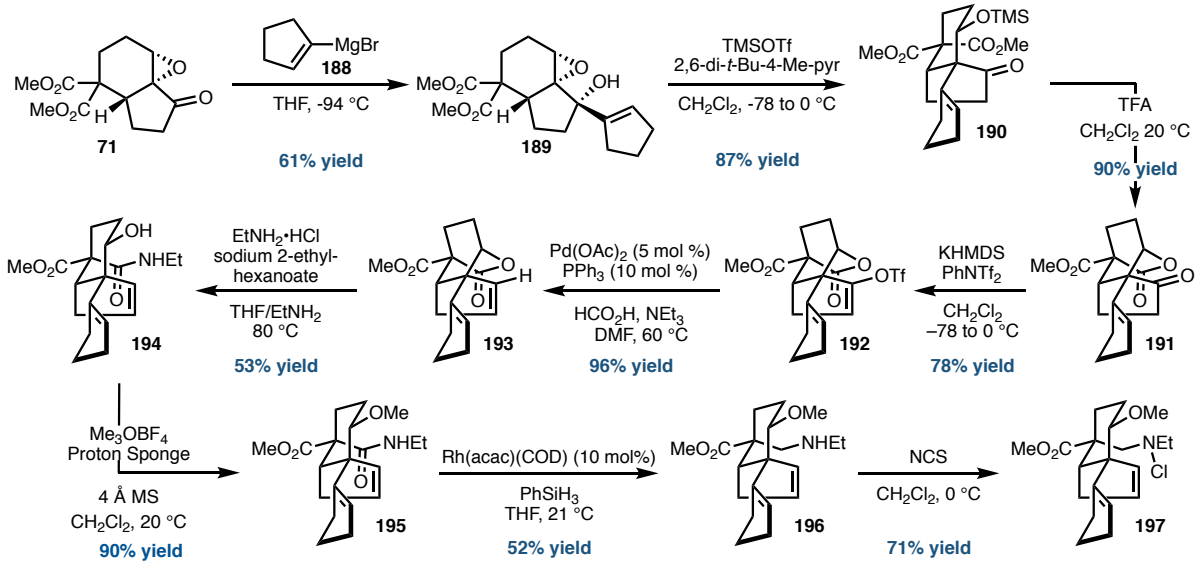
Figure 4.2 *Aminyl radical cations generated from Lewis-acidic single-electron reductants engaging in intramolecular aminochlorination of alkenes.*



We chose to test conditions for *N*-centered radical conditions using a simplified model system synthesized via a route analogous to the lactone-aminolysis route presented in Chapter 3 (Scheme 4.3). The [3.2.1]-bicyclooctene C/D-ring bicycle substituent off of the C11 quaternary center was replaced with a simple cyclopentene. 1,2-addition of an cyclopentenylmagnesium bromide (**182**) to epoxy ketone **71** affords 1,2-addition product **189**. Subjection to TMSOTf effects semipinacol rearrangement to afford **190**. C1 silyl-ether deprotection and *in situ* lactonization was achieved by treatment with trifluoroacetic acid to give **191**. The ketone of **191** was converted to the enol triflate **192** and then reduced under

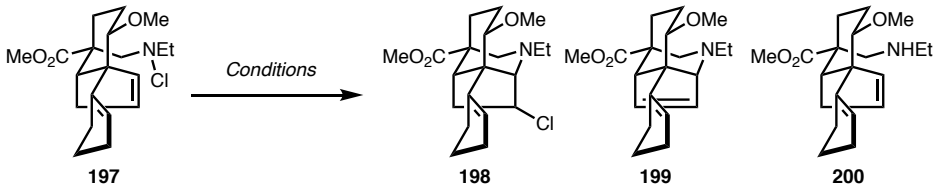
palladium-catalyzed conditions to afford **193**. Lactone-opening aminolysis with ethylamine affords C19 amide **194**. The C1 alcohol was converted to the methyl ether **195** upon treatment with trimethyloxonium tetrafluoroborate. The amide of **195** was reduced to the amine via rhodium-catalyzed hydrosilylation.[6] Lastly, the amine **196** was *N*-chlorinated to give the radical cyclization substrate **197**.

Scheme 4.3 *Synthesis of model system for N-centered radical cyclization cascade.*



A small series of single-electron reducing metal reagents were tested on our model substrate **197** to see if 6-*exo*-trig cyclization to afford the E-ring piperidine could occur (Table 4.1). While Stella's stoichiometric $TiCl_3$ conditions gave only protodechlorination, treatment with catalytic copper (I) chloride yielded **199** which represents cyclization and formal loss of HCl. With this result in hand, we sought to apply these conditions to a substrate which would lead to the aconitine core.

Table 4.1 *Conditions for N-centered radical cyclization cascade evaluated on model substrate* ***197****.*



197 **198** **199** **200**

Entry	Reductant	Temperature	Solvent	Result
1	$TiCl_3$ (1.1 equiv)	0 °C	1:1 HOAc:H_2O	**200**
2	CuCl (0.2 equiv.)	70 °C	THF	60% yield 198

N-chlorination of **123** gave a radical cyclization substrate with an unactivated D-ring olefin (**201**, Scheme 4.4). Subjection of **201** to catalytic copper (I) chloride again resulted in E-ring piperidine formation, although the final C7–C8 bond of the aconitine core was not formed. The product isolated is tentatively assigned as olefin 1,2-aminochlorination product **203**, though we have been unable to confirm the relative stereochemistry at C7. We sought to oxidize the C16 alcohol to the ketone in order to increase the reactivity of the C8-C15 alkene. To do so, the siliconide of **123** was deprotected, the allylic C16 alcohol was oxidized selectively, and the C14 alcohol was protected as the triethylsilyl ether (Scheme 4.4). Unfortunately, this 3 step sequence resulted in epimerization at C14 to give an inseparable 1.7:1 mixture of diastereomers (**204**). N-chlorination of **204** gave **205**. Subjecting this mixture to a variety of single-electron reductant catalysts again did not result in formation of the aconitine core, as evidenced by the diagnostic ^{1}H NMR signal from the β-position of the D-ring enone (C8) (Table 4.2). The lack of reactivity of these substrates led us to question the mechanism of this reaction.

Scheme 4.4 *Synthesis of radical cascade substrates* ***201*** *and* ***205****.*

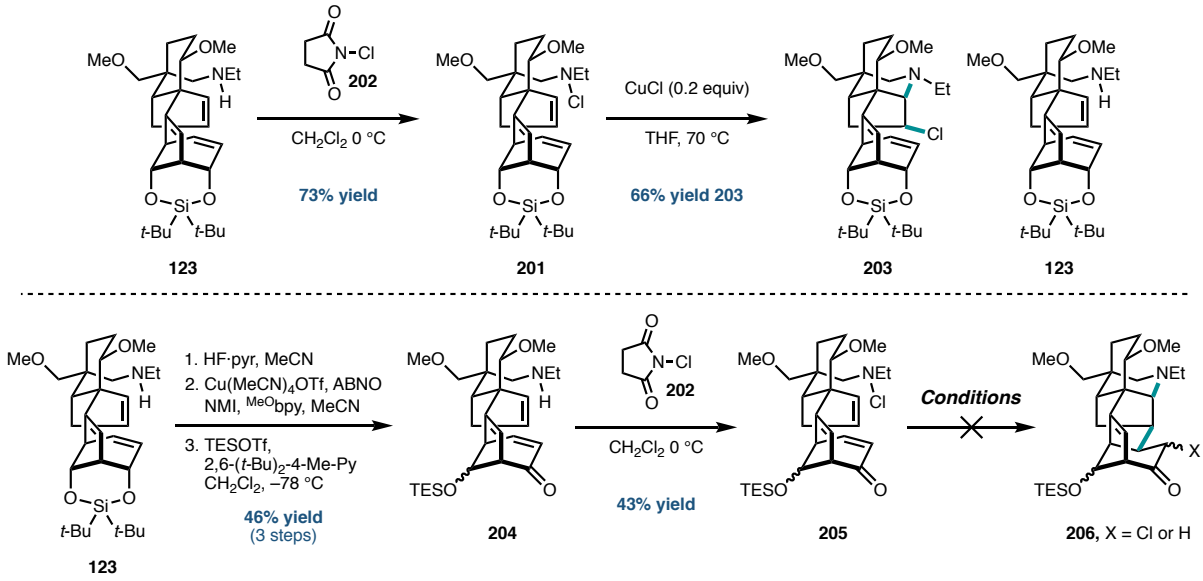
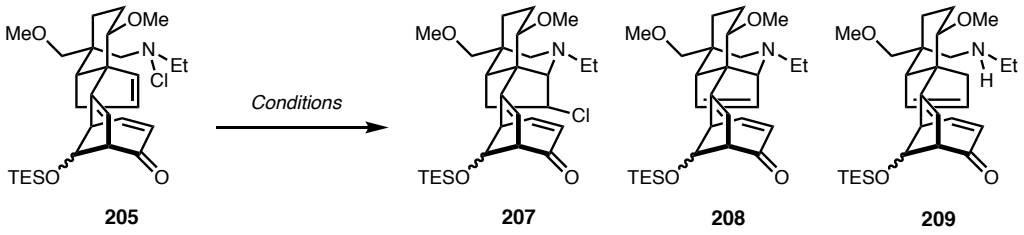
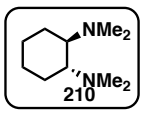


Table 4.2 *Evaluating radical cyclization cascade conditions on a substrate with a D-ring enone.*



Entry	Catalyst	Temperature	Solvent	product
1	CuCl (0.5 equiv.)	70 °C	THF	**208 + 209**
2	CuCl (0.2 equiv.)	50 °C	THF	**208 + 209**
3	CuCl (0.2 equiv.), hv (halogen lamp)	~35 °C	THF	decomp
4	CuI (0.5 equiv.)	70 °C	PhMe	**208 + 209**
5	$[Cu(MeCN)_4]PF_6$, (±)–**210** (0.1 equiv. each)	70 °C	THF	**208 + 209**
6	$FeCl_2$ (0.2 equiv.)	50 °C	THF	**208 + 209**
7	$FeCl_2$ (0.2 equiv.)	50 °C	THF/H_2SO_4	decomp
8	$FeCl_2$ (0.2 equiv.), hv (halogen lamp)	~35 °C	THF	**208 + 209**
9	$FeCl_2$ (0.2 equiv.), hv (halogen lamp)	~35 °C	THF/H_2SO_4	decomp
10	$TiCl_3$ (0.2 equiv.)	35 °C	THF	209



Previous synthetic work from Gin and coworkers as well as work from our lab (*vide infra*) suggests that a C7 radical should readily cyclize with a D-ring enone to close the central B-ring (Figure 4.3).[7] The lack of C7–C8 bond formation under copper (I) catalyzed conditions

suggests that this system does not go through a C7 radical intermediate. One potential mechanism which accounts for these observations is shown in Figure 4.4. After the copper (I) catalyst reduces the *N*-chloroamine substrate, aminyl radical cation **213** may undergo a 6-*exo*-trig cyclization with the undesired regioselectivity, forming a C7–N bond to give C17 radical **214**. The regioselectivity of this cyclization may be the result of steric hindrance at the neopentyl C17 position. If the C17 radical **214** is unable to cyclize with the D-ring enone, it may abstract a chlorine atom from another equivalent of substrate or from copper (II) chloride to turn over the catalyst. This would give the 1,2-aminochlorination product **215**, which may undergo intramolecular S_N2 displacement of the C17 chloride by the amine to give aziridinium **216**. S_N2 aziridinium opening by chloride at C7 would give the observed 1,2-aminochlorination product **207**. Alternatively, deprotonation of aziridinium **216** at C6 would effect E2-elimination to give the observed C6–C7 olefin product **208**. This proposal is purely hypothetical at this point, and computational and synthetic investigations are ongoing to shed light on this mechanism.

Figure 4.3 *Previous example of radical C7–C8 bond formation to close central B-ring.*

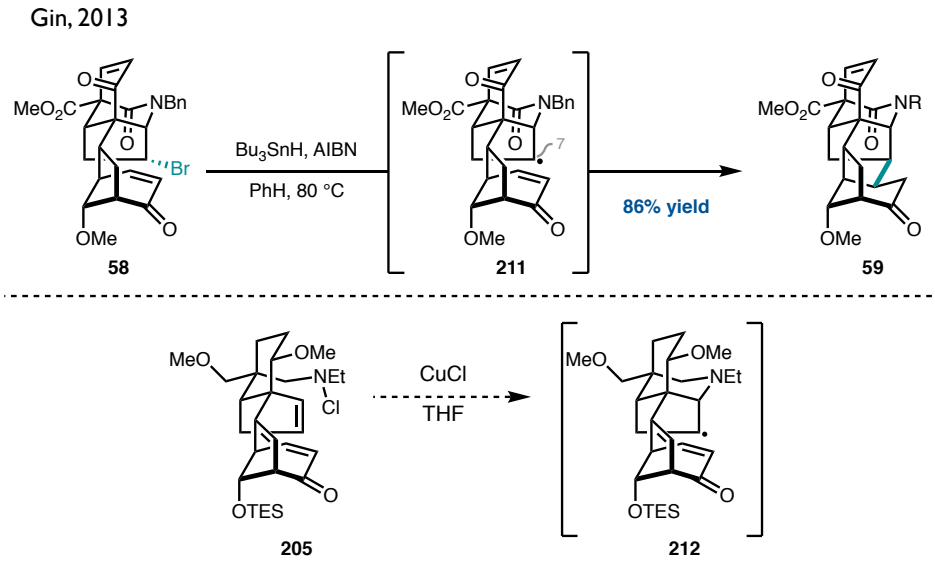
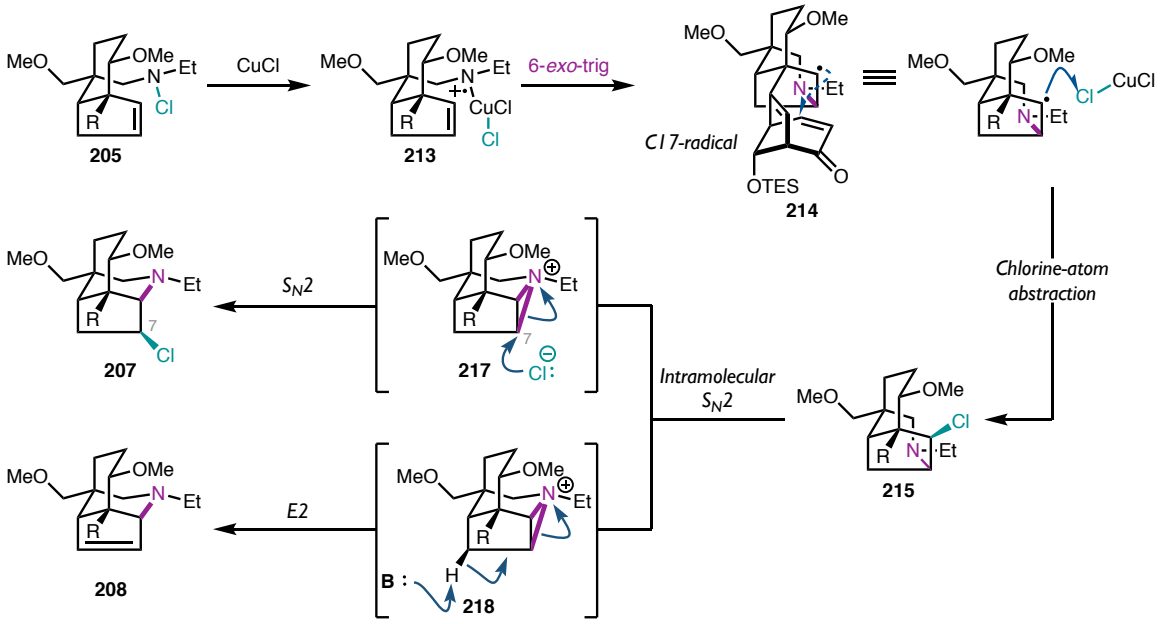


Figure 4.4 *Possible mechanism to explain observed reactivity of N-chloroamines* ***197***, ***191*** *and* ***205***.



4.3 SYNTHESIS OF C_{19} DITERPENOID ALKALOIDS (–)-TALATISAMINE (1), (–)-LILJESTRANDISINE (238), AND (–)-LILJESTRANDININE (3)

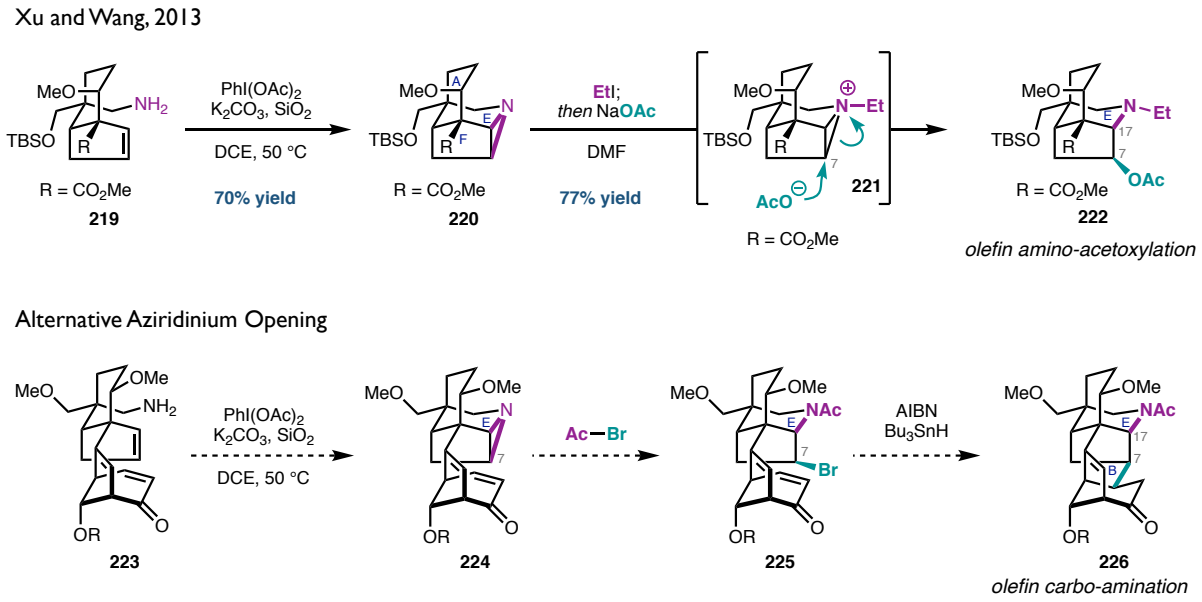
The following sections describe the successful completion of the total syntheses of C_{19} diterpenoid alkaloids (–)-talatisamine (**1**), (–)-liljestrandisine (**238**), and (–)-liljestrandinine (**3**). A stepwise approach was taken for the formation of the final two rings of the aconitine core. Reduction/oxidation manipulations of the D-ring at a late stage allow for divergent synthesis of the three natural products named above. The synthesis of talatisamine (**1**) and liljestrandisine from the same C16 alcohol diastereomer led to a revision of the structure of liljestrandisine from **2** to **238**.

4.3.1 *Completion of the Aconitine Core*

Unable to effect the desired radical cyclization cascade discussed above, we turned to a stepwise approach to closing the E-ring piperidine and central B-ring cyclohexane. A report

from Xu, Wang and coworkers describing a synthesis of the A/E/F-tricycle of the aconitine-type diterpenoid alkaloids detailed a strategy for E-ring piperidine formation which mapped on well to intermediates we had been able to access (Figure 4.5).[8] Intramolecular aziridination between the C19 primary amine and C7–C17 alkene of **219** efficiently closes the E-ring. In addition to forming the C17–N bond of the aconitine core, this strategy allows for functionalization of C7. Activation of aziridine **220** with ethyl iodide forms intermediate aziridinium **221**, which is subsequently opened via S_N2 displacement by acetate at the less-hindered C7. We imagined changing the nucleophile in this aziridinium opening from acetate to a halide would provide a functional group handle for C7–C8 bond formation.

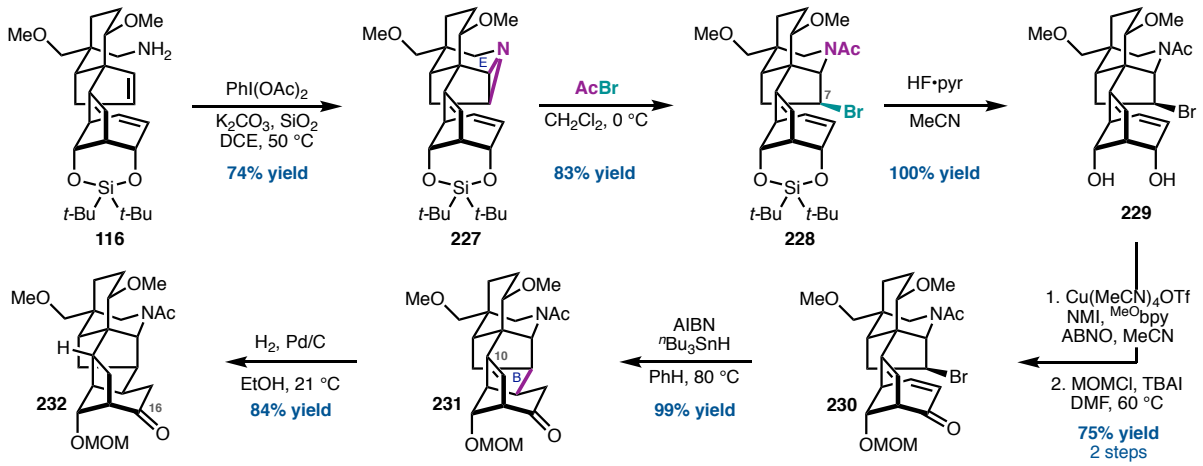
Figure 4.5 *Functionalization at C7 and C17 enabled by intramolecular aziridination.*



We were pleased to find that subjecting intermediate **116** to Xu and Wang's aziridination conditions, (diacetoxyiodo)benzene (PIDA) with potassium carbonate and silica gel, resulted in clean conversion to our desired aziridine **227** (Scheme 4.5). Gratifyingly, treating **27** with acetyl bromide gave aziridine-opened product **228** in good yield. In addition to forging the E-ring piperidine, this two-step sequence efficiently introduces a radical-precursor at C7 and an

N-acetyl group, which will later be reduced to the *N*-ethyl group found in many C_{19}-diterpenoid alkaloids. Having achieved E-ring formation, we turned to closing the B-ring and completing the aconitine core.

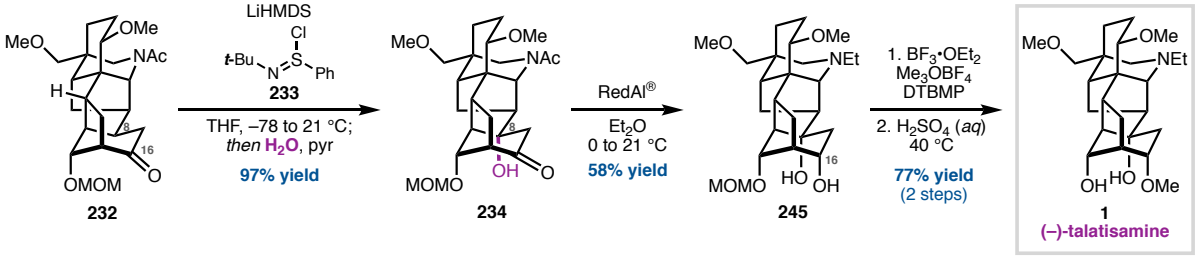
Scheme 4.5 *Completion of the aconitine core.*



To form the final C7–C8 bond of the aconitine core, we envisioned a Giese addition of a C7 radical generated from **230** to a D-ring enone. To introduce the D-ring enone, the siliconide was deprotected with HF•pyridine to yield C14/C16 diol **229**. The allylic C16 alcohol was oxidized, selectively, and the remaining C14 alcohol was protected at its MOM ether to give Giese reaction substrate **230**. We were elated to find that subjecting **230** to AIBN and tributyltin hydride resulted in formation of **231** in quantitative yield, validating our fragment coupling approach to this family of natural products. The C10–C12 olefin was hydrogenated with Pd on carbon. Having demonstrated retrosynthetic disconnection through the central B-ring as a viable strategy to access the aconitine core, reduction/oxidation manipulations of the D-ring were the only remaining challenges to accessing natural products **1**, **238,** and **3**.

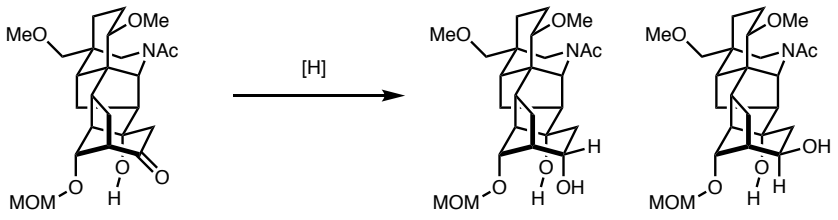
4.3.2 *Reduction/Oxidation of D-ring for Divergent Syntheses of (–)-Talatisamine (1), (–)-Liljestrandisine (238) and (–)-Liljestrandinine (3)*

Scheme 4.6 *Total synthesis of (–)-talatisamine (**1**).*



For the synthesis of **1**, **2,** and **238**, Giese reaction product **232** is dehydrogenated using Mukaiyama's reagent to form a strained enone which then undergoes spontaneous oxy-Michael reaction when treated with water and pyridine to give **234** with the proper oxidation at C8 (Scheme 4.6).[9]. From there, conditions for diastereoselective reduction of the C16 ketone were evaluated (Table 4.3). Lithium aluminum hydride and sodium borohydride each favored formation of the axial alcohol **235**, while samarium (II) iodide favored the equatorial alcohol **236** 2:1 in excellent yield. Talatisamine (**1**) and the reported structure of liljestrandisine (**2**) are epimeric at C16, so preferential access to either diastereomer is valuable. The optimal reagent for accessing talatisamine was found to be sodium bis(2-methoxyethoxy)aluminum hydride (RedAl ®), as it also reduced the acetamide to the *N*-ethylamine to give a 58% yield of **245**. Using an equivalent of BF_3•OEt_2 to protect the basic amine, the C8/C16 diol was per-methylated, then treated with aqueous sulfuric acid at 40 °C to effect selective hydrolysis at C8 and afford (–)-talatisamine (**1**) in 77% yield over two steps. This represents a 31 step synthesis in the longest linear sequence (LLS) starting from phenol, the shortest synthesis reported to date.

Table 4.3 *Evaluating conditions for diastereoselective C16 ketone reduction.*

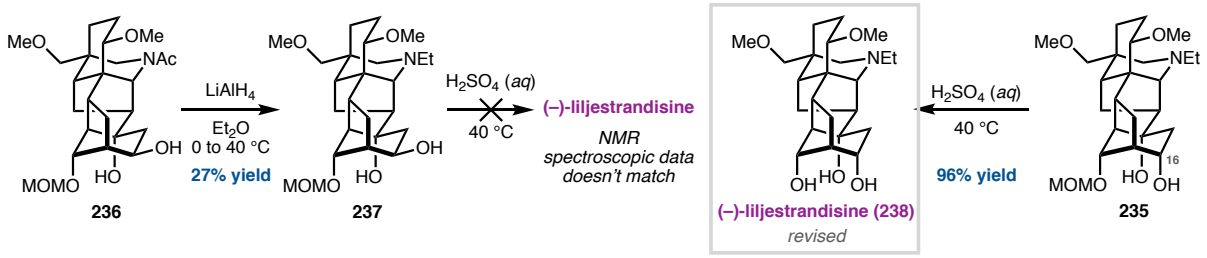


234 **235** **236**

Entry	Reductant	Solvent	Temp	**S20**:**S21**	yield
1	SmI_2, Et_3N, H_2O	THF	-78 to 21 °C	1:2	87%
2	$NaBH_4$	MeOH	0 °C	2:1	62%
3	LAH	THF	0 °C	1.2:1	n.d.
4	LAH	THF	-78 to 0 °C	1.8:1	n.d.
5	LAH	Et_2O	-78 to 0 °C	2.4:1	n.d.
6	LAH	DME	0 °C	1.3:1	n.d.

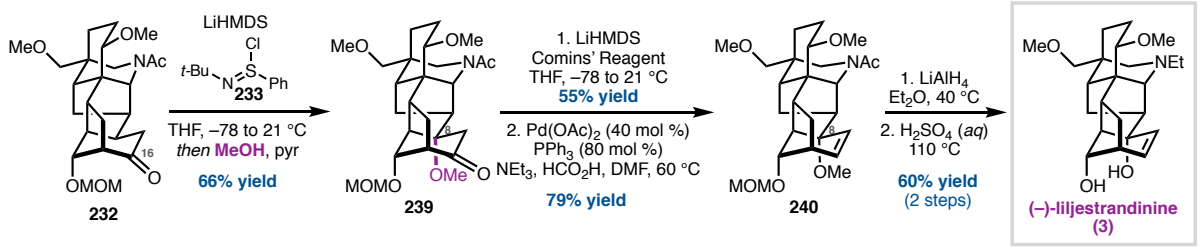
To access the reported structure of liljestrandisine (**2**), the equatorial C16 alcohol **236** was treated with lithium aluminum hydride to reduce the acetamide to the *N*-ethylamine **237** (Scheme 4.7). Deprotection of the C14 MOM ether of **237** gave a product with ^{1}H NMR spectrum which varied significantly from that of the material isolated from nature.[10] The reported structure **2** represents the only reported C_{19}-diterpenoid alkaloid natural product with the equatorial alcohol stereochemistry at C16. As such, we hypothesized that the reported structure of liljestrandisine is epimeric at C16 of the actual natural product structure. Indeed, when C16 axial alcohol was treated with sulfuric acid to deprotect the C14 MOM ether, the material isolated had characterization data which matched that reported by the isolation chemists. As such, we propose the structure of (–)-liljestrandisine be revised from **2** to **238**.

Scheme 4.7 *Total synthesis and structural revision of (–)-liljestrandisine (**238**).*



The sequence to access (–)-liljestrandinine (**3**) varies slightly from the one above (Scheme 4.8). **232** is treated with Mukaiyama's reagent again, now quenching with methanol and pyridine to afford the C8 methyl ether. The C16 ketone is converted to the corresponding enol-triflate, then reduced under palladium-catalyzed conditions to afford **240**. Amide reduction with lithium aluminum hydride followed by heating to 110 °C in aqueous sulfuric acid effects C14 MOM ether deprotection and S_N1 substitution with water at C8 to afford (–)-liljestrandinine (**3**) in 60% yield over 2 steps.

Scheme 4.8 *Total synthesis of (–)-liljestrandinine (**3**).*



4.4 CONCLUDING REMARKS

In summary, we report syntheses of the C_{19} diterpenoid alkaloids (–)-talatisamine (**1**), (–)-liljestrandisine (**238**), and (–)-liljestrandinine (**3**) using a fragment coupling strategy. A two-step sequence of 1,2-addition of an alkenyl lithium to an epoxy ketone electrophile followed by a Lewis Acid-catalyzed semipinacol rearrangement enables this fragment coupling and forms the key C11 all-carbon quaternary center. Creative syntheses of C_{19} diterpenoid alkaloids

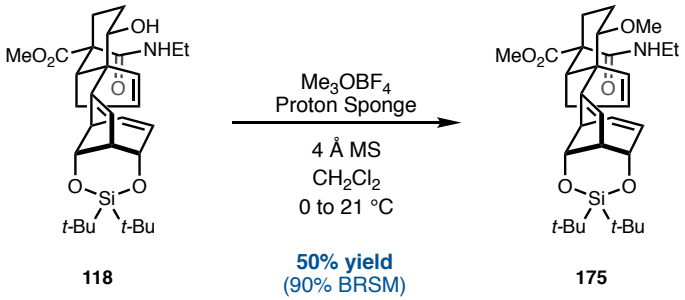
have been reported for nearly 50 years at the time of this publication. We believe the success of this novel approach demonstrates that there are still opportunities for strategic innovation to access these highly-bridged natural product scaffolds.

This project has exposed opportunities for innovations in methodology as well. Significant synthetic effort was spent on functional group interconversion at the diastereotopic C18/C19 methyl esters after the key fragment coupling. The synthesis could be more convergent if the epoxy ketone coupling partner which bears these centers had the proper functionality installed prior to the coupling event. Work is ongoing to develop a doubly-stereoselective Michael-reaction of prochiral tertiary enolates to α,β-unsaturated ketones to form β/γ-stereodiads.

We will seek to apply our fragment coupling strategy to the synthesis of other subfamilies of diterpenoid alkaloids, the C_{20} denudatine and C_{20} napelline-type natural products in particular, by varying the bridged bicyclic coupling partner. We also hope to learn from our experience studying radical cyclization cascades to potentially try revised radical cascade approaches in pursuit of these C_{20} cores.

4.5 EXPERIMENTAL SECTION

Preparation of methyl ether 178:



118 **175**

A 250 mL, round-bottom flask was charged with alcohol **26** (787 mg, 1.447 mmol, 1.0 equiv.), equipped with a rubber septum, purged with N_2, and cooled to 0 °C in an ice bath. Meanwhile, Me_3OBF_4 (0.856 g, 5.79 mmol, 4 equiv.), Proton Sponge (1.24 g, 5.79 mmol, 4 equiv.), and activated 4 Å MS (2.36 mg) were added to a 40 mL vial in the glovebox, brought out of the glovebox, and added to the flask containing the substrate. The mixture was then suspended in CH_2Cl_2 (14.5 mL), and allowed to stir for 48 hours, allowing the reaction to warm up to room temperature over this period. The reaction mixture was filtered through a plug of silica gel and celite that had been pre-packed with EtOAc and rinsed further with EtOAc and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (15% in hexanes to elute the product to 20% acetone in hexanes to elute the starting material) to afford methyl ether **175** (399 mg, 71.6 mmol, 50% yield) as a white solid and recovered alcohol **26** (350 mg, 0.637 mmol, 44% yield).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.9, 168.7, 164.6, 135.9, 132.8, 131.7, 128.2, 121.1, 77.2, 76.8, 66.4, 57.5, 57.0, 55.7, 52.8, 46.6, 46.1, 46.0, 35.4, 34.8, 28.9, 28.3, 22.0, 21.2, 20.7, 19.2, 14.6.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.18 (ddd, J = 9.5, 6.1, 1.1 Hz, 1H), 6.11 (t, J = 5.6 Hz, 1H), 5.87 (dt, J = 5.9, 2.3 Hz, 1H), 5.66 (ddd, J = 9.3, 4.4, 1.9 Hz, 1H), 5.45 (dt, J = 5.9,

2.0 Hz, 1H), 5.25 (d, *J* = 3.5 Hz, 1H), 4.51 (td, *J* = 4.2, 0.9 Hz, 1H), 4.19 (ddd, *J* = 4.2, 3.1, 0.8 Hz, 1H), 3.70 (s, 3H), 3.38 (dd, *J* = 7.8, 4.0 Hz, 1H), 3.34 – 3.24 (m, 1H), 3.21 (s, 3H), 3.19 – 3.14 (m, 1H), 3.14 – 3.05 (m, 1H), 3.00 – 2.96 (m, 1H), 2.89 – 2.81 (m, 1H), 2.37 (ddt, *J* = 16.4, 8.7, 2.2 Hz, 1H), 2.28 – 2.10 (m, 3H), 1.79 (dddd, *J* = 13.2, 9.0, 7.0, 4.0 Hz, 1H), 1.62 – 1.54 (m, 1H), 1.11 – 1.06 (m, 12H), 1.01 (s, 9H).

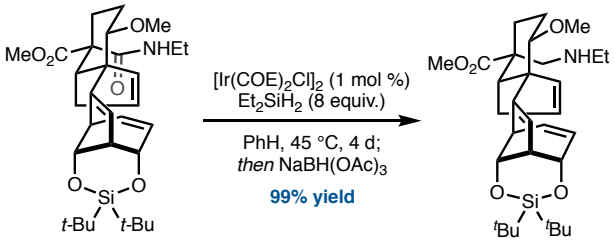
FTIR (NaCl, thin film): 3375, 2970, 2936, 2896, 2860, 1731 1715, 1668, 1652, 1519, 1476, 1463, 1255, 1780, 1104, 991, 826, 732 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{31}H_{48}O_6NSi$ $[M + H]^+$ 558.3245, found 558.3240.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +122° (*c* = 0.4, $CHCl_3$).

TLC (50%EtOAc/ 50% Hexanes), R*f*: 0.6 (UV, blue in *p*-anisaldehyde)

Preparation of *N*-ethylamine 176:[11]



175 **176**

A 2-dram vial charged with amide **175** (30 mg. 54 µmol, 1.0 equiv.) was brought into a N_2 filled glovebox. In a separate vial, a stock solution of $[Ir(COE)_2Cl]_2$ (1.5 mg, 1.7 µmol, 0.03 equiv.) and Et_2SiH_2 (7 mg, 79 µmol, 1.5 equiv.) in PhH (1.5 mL) was prepared. Amide **175** was dissolved in PhH (2.0 mL) before [Ir] and Et_2SiH_2 solution (0.5 mL, 0.01 equiv. $[Ir(COE)_2Cl]_2$, 0.5 equiv. Et_2SiH_2) was added, followed by a solution of E_2SiH_2 (16.6 mg, 0.19 mmol, 3.5 equiv.) in PhH (0.5 mL). The reaction was stirred at 45 °C for 1 day before more Et_2SiH_2 (9.2 mg, 0.10 mmol, 2.0 equiv.) was added. The reaction was stirred for an additional 1 day before more Et_2SiH_2 (9.2 mg, 0.10 mmol, 2.0 equiv.) was added. The reaction was stirred

an additional 2 days (4 days total) before TLC indicated conversion to the imine was complete. The reaction was cooled to 19 °C and $NaBH(OAc)_3$ was prepared from $NaBH_4$ (20.3 mg, 0.54 mmol, 10 equiv.) and HOAc (0.09 mL, 1.50 mmol, 30 equiv.). The $NaBH(OAc)_3$ was added dropwise by pipette to the reaction, and the mixture stirred for 10 minutes. The reaction was quenched with 0.5 M NaOH (3 mL) and stirred for 30 minutes. The reaction was extracted with 3:1 $CHCl_3$:^{i}PrOH (4 x 5 mL). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude mixture was purified by column chromatography to give amine **176** (29.0 mg, 54 μmol, 99% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.05 (ddd, *J* = 9.5, 6.1, 1.1 Hz, 1H), 5.89 (dt, *J* = 5.9, 2.3 Hz, 1H), 5.64 (ddd, *J* = 9.3, 4.4, 1.9 Hz, 1H), 5.46 (ddd, *J* = 5.8, 2.4, 1.4 Hz, 1H), 5.27 (d, *J* = 3.7 Hz, 1H), 4.45 – 4.37 (m, 1H), 4.23 – 4.19 (m, 1H), 3.58 (s, 3H), 3.54 (dd, *J* = 9.2, 3.3 Hz, 1H), 3.23 (s, 3H), 2.99 – 2.95 (m, 1H), 2.82 – 2.73 (m, 3H), 2.63 – 2.49 (m, 3H), 2.43 (dddd, *J* = 16.0, 9.1, 2.7, 1.5 Hz, 1H), 2.36 – 2.25 (m, 2H), 1.88 – 1.79 (m, 1H), 1.59 – 1.40 (m, 3H), 1.07 (s, 9H), 1.04 – 0.98 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.9, 164.6, 135.6, 133.4, 131.1, 128.2, 119.8, 77.7, 76.7, 66.6, 58.7, 57.7, 57.1, 51.5, 47.9, 46.2, 46.1, 46.0, 44.5, 35.4, 28.9, 28.3, 23.7, 21.8, 21.2, 20.6, 15.1.

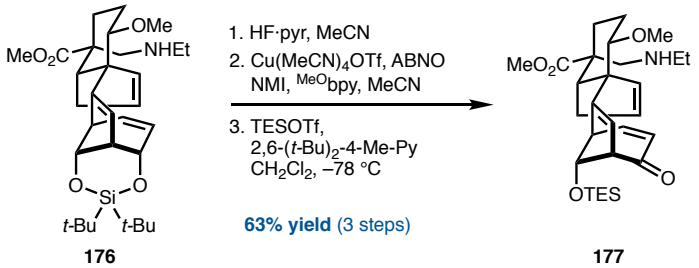
FTIR (NaCl, thin film): 3449, 2965, 2935, 2898, 2859, 1732, 1476, 1103, 992, 827, 731 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{31}H_{50}O_5NSi$ $[M + H]^+$ 544.3453, found 544.3463.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +84.5° (*c* = 1.26, $CHCl_3$).

TLC (5% 7 N NH_3 in MeOH/ 95% CH_2Cl_2), R_f: 0.5 (UV, blue in *p*-anisaldehyde)

Preparation of enone 177:



176 177

A 2-dram vial was charged with silylene **176** (20.2 mg, 0.037 mmol, 1 equiv.) and MeCN (1 mL). A solution of HF•Py (pyridine ~30%, HF ~70%, 20.2 mg) in MeCN (0.2 mL) was added, and the reaction was allowed to stir for 40 minutes at 20 °C. The reaction was quenched by filtering through a silica gel plug and flushing with lots of 10% 7N NH_3 in MeOH/ 90% CH_2Cl_2 solution, and concentrated *in vacuo*. The crude material was used without further purification.

A 2-dram vial was charged with the crude diol, and dissolved in MeCN (1 mL). A homemade stock-solution [see note below] 0.05M 4,4'-dimethoxy-2,2'-bipyridine (^{MeO}bpy), 0.05 M in ABNO, and 0.2 M *N*-methylimidazole was added to the solution of diol (74 µL, 0.0037 mmol, 0.1 equiv.) followed by $Cu(MeCN)_4OTf$ (1.4 mg, 0.0037 mmol, 0.1 equiv.) was added, and the clear red/brown reaction mixture was stirred at 20 °C until slightly yellow green, and the TLC indicated the reaction had gone to completion (ca. 90 min), at which point the solution was filtered through a short plug of silica that had been pre-packed with 10% 7N NH_3 in MeOH/ 90% CH_2Cl_2 and flushed with more 10% 7N NH_3 in MeOH/ 90% CH_2Cl_2 to elute the product, and concentrated *in vacuo*. The crude enone was subjected to the next step without further purification.

A 2-dram vial was charged with crude enone, and azeotroped with PhMe (from the solvent system, 2 x 1 mL), and dried under high vacuum. 2,6-(*t*-Bu)$_2$-4-MePy (76 mg, 0.371 mmol, 10 equiv.) was added, followed by CH_2Cl_2 (2 mL). The solution was cooled to –78 °C,

and TESOTf (40 μL, 0.186 mmol, 5 equiv.) was added dropwise via microsyringe. After 10 minutes of stirring at –78 °C, the reaction was quenched via the addition of aqueous sat. $NaHCO_3$ solution 2 mL), and was allowed to warm to room temperature. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (5 x 3 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was filtered through a plug of silica gel and filtered with hexanes (to remove the 2,6-(*t*-Bu)$_2$-4-MePy) and then 3% 7N NH_3 solution in MeOH/ 97% CH_2Cl_2 to elute the product, and then concentrated *in vacuo*. The crude residue was purified by preparative thin layer chromatography (3% 7N NH_3 solution in MeOH/ 97% CH_2Cl_2) to afford enone **177** (12 mg, 0.023 mmol, 63% yield) as a clear oil.

Notes for the Stahl oxidation step:

(1) A 0.05 M solution of 4,4'-dimethoxy-2,2'-bipyridine, 0.05M ABNO and 0.2M NMI solution in MeCN could be pre-made and kept in an 8 °C freezer and was stable and good to use for an extended time (>4 months). This homemade stock solution was used in this reaction, and makes it easy to add more catalyst.

(2) This selective oxidation to the enone is very clean and performs well, but oxidation to the diketone has been observed if too much catalyst is added. It is important to monitor this reaction by TLC. It is best to run this reaction carefully, and start with less catalyst, because more can be added if needed to reach full conversion to the desired product.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.94 (ddd, *J* = 9.8, 6.4, 1.6 Hz, 1H), 5.98 – 5.94 (m, 1H), 5.76 (ddd, *J* = 9.8, 2.0, 0.7 Hz, 1H), 5.50 (d, *J* = 3.7 Hz, 1H), 5.38 – 5.35 (m, 1H), 4.65

(td, J = 4.5, 1.6 Hz, 1H), 3.61 (s, 3H), 3.46 (dd, J = 7.0, 3.0 Hz, 1H), 3.19 (s, 3H), 3.13 – 3.05 (m, 2H), 2.92 (t, J = 9.2 Hz, 1H), 2.77 (d, J = 11.3 Hz, 1H), 2.64 – 2.52 (m, 3H), 2.43 (dddd, J = 15.7, 8.7, 2.6, 1.5 Hz, 1H), 2.33 (ddt, J = 15.6, 9.7, 2.2 Hz, 1H), 2.24 – 2.16 (m, 1H), 1.83 – 1.73 (m, 1H), 1.65 – 1.54 (m, 3H), 1.03 (t, J = 7.1 Hz, 3H), 0.93 (t, J = 7.9 Hz, 9H), 0.64 – 0.53 (m, 6H).

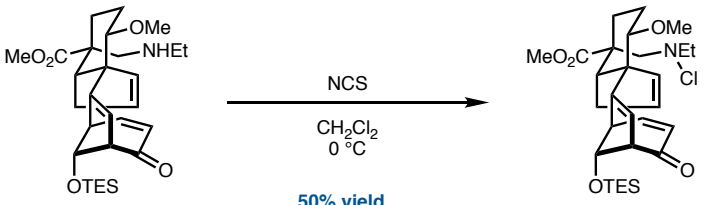
^{13}C NMR (101 MHz, $CDCl_3$): δ 197.0, 176.8, 161.4, 149.2, 132.8, 132.2, 126.6, 120.6, 84.6, 78.2, 62.1, 58.5, 57.4, 57.2, 51.7, 48.2, 47.9, 45.6, 44.5, 34.9, 22.9, 22.5, 15.1, 6.7, 4.7.

HRMS: (ESI-TOF) calc'd for $C_{29}H_{46}O_5NSi$ $[M + H]^+$ 516.3140, found 516.3122.

$[\alpha]_D^{25}$ = +163° (c = 0.085, $CHCl_3$).

TLC (5% 7 N NH_3 in MeOH/ 95% CH_2Cl_2), R_f: 0.5 (UV, blue in *p*-anisaldehyde)

Preparation of *N*-chloroamine 178:



A 10 mL round-bottom flask was charged with amine **177** (12 mg, 0.0233 mmol, 1 equiv.), and CH_2Cl_2 (2.3 mL). The solution was cooled to 0 °C, and *N*-chlorosuccinimide (3.7 mg, 0.028 mmol, 1 equiv.) was added. The reaction was allowed to stir for 1 hour at 0 °C, and then the reaction was filtered through a plug of silica gel and flushed with EtOAc. The crude residue was purified by preparative thin layer chromatography (20% EtOAc/ 80% Hexanes) to afford *N*-chloroamine **178** (6 mg, 0.011 mmol, 47% yield) as a clear oil.

Note: This reaction is fairly clean and the poor yield in this case resulted from incomplete conversion (procedure is not optimized). Some starting material was recovered.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.93 (ddd, *J* = 9.8, 6.4, 1.6 Hz, 1H), 5.98 – 5.90 (m, 1H), 5.76 (dd, *J* = 9.5, 1.8 Hz, 1H), 5.51 (d, *J* = 3.8 Hz, 1H), 5.37 (ddd, *J* = 5.9, 2.6, 1.5 Hz, 1H), 4.68 (td, *J* = 4.6, 1.6 Hz, 1H), 3.60 (s, 3H), 3.49 (dd, *J* = 7.9, 3.0 Hz, 1H), 3.28 (d, *J* = 14.0 Hz, 1H), 3.19 (s, 3H), 3.13 – 3.01 (m, 3H), 2.97 – 2.88 (m, 3H), 2.46 – 2.26 (m, 3H), 1.84 – 1.75 (m, 1H), 1.70 (dt, *J* = 13.9, 6.6 Hz, 1H), 1.62 – 1.56 (m, 1H), 1.16 (t, *J* = 6.9 Hz, 3H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.58 (q, *J* = 7.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.9, 175.9, 161.2, 149.1, 133.0, 131.8, 126.6, 120.6, 84.6, 77.9, 72.3, 62.0, 60.4, 57.3, 57.3, 51.7, 48.4, 47.9, 45.9, 35.3, 23.1, 22.3, 12.8, 6.7, 4.7.

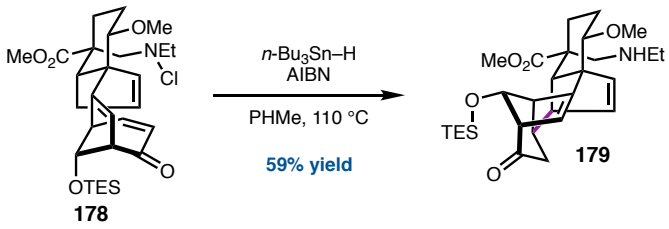
FTIR (NaCl, thin film): 2953, 2933, 2877, 1738, 1731, 1722, 1682, 1455, 1176, 1121, 1100, 1013, 739 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{29}H_{45}O_5NSiCl$ $[M + H]^+$ 550.2750, found 550.2774.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +122° (*c* = 0.2, $CHCl_3$).

TLC (20%EtOAc/ 80%Hexanes), R_f: 0.5 (UV, blue in *p*-anisaldehyde)

Preparation of cyclization product 179:



A 1-dram vial was charged with *N*-chloroamine **178** (5 mg, 9.1 μmol, 1 equiv.) and PhMe (1 mL). The reaction was heated to 110 °C in an oil bath, and *n*-Bu_3SnH (1 M in cyclohexane, 0.05 mL, 0.05 mmol, 5 equiv.) and AIBN (0.7 mg, 4.3 μmol, 0.5 equiv.) was added dropwise as a PhMe solution (0.5 mL). The reaction was heated to 110 °C for 30 min. The reaction was then cooled to room temperature, loaded onto a plug of silica gel which was

flushed with CH_2Cl_2 to remove excess Bu_3SnH, followed by 10% 7N NH_3 in MeOH/90% CH_2Cl_2 to elute the product. The crude residue was purified by column chromatography (0.5-1-2-3-4% 7N NH_3 in MeOH/CH_2Cl_2) to afford cyclized **179** (2.8 mg, 5.4 μmol, 63% yield) as a clear oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.78 – 5.73 (m, 1H), 5.70 (dt, *J* = 5.9, 1.8 Hz, 1H), 4.92 – 4.87 (m, 1H), 4.78 (dd, *J* = 6.3, 5.0 Hz, 1H), 3.76 (d, *J* = 6.6 Hz, 1H), 3.71 (s, 3H), 3.54 (s, 1H), 3.39 (dd, *J* = 11.7, 5.0 Hz, 1H), 3.28 (s, 1H), 3.20 (s, 3H), 3.16 – 3.13 (m, 1H), 2.90 (t, *J* = 6.0 Hz, 1H), 2.72 – 2.69 (m, 1H), 2.63 – 2.59 (m, 2H), 2.50 (dd, *J* = 18.6, 9.2 Hz, 1H), 2.41 (dd, *J* = 18.6, 1.9 Hz, 1H), 2.27 – 2.21 (m, 1H), 2.15 – 2.10 (m, 1H), 2.06 – 2.00 (m, 1H), 1.43 – 1.39 (m, 1H), 1.25 (s, 1H), 1.06 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 8.0 Hz, 9H), 0.59 (q, *J* = 8.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.8, 177.4, 156.7, 135.2, 131.1, 114.7, 74.7, 71.7, 63.0, 61.1, 56.1, 54.9, 53.7, 52.1, 48.7, 48.0, 44.5, 41.9, 33.9, 25.2, 21.3, 15.0, 6.8, 4.7.

FTIR (NaCl, thin film): 3340, 2932, 1722, 1714, 1514, 1462, 1234, 1102, 1013, 743 cm^{-1}.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{21}}$ = +78° (*c* = 0.22, $CHCl_3$).

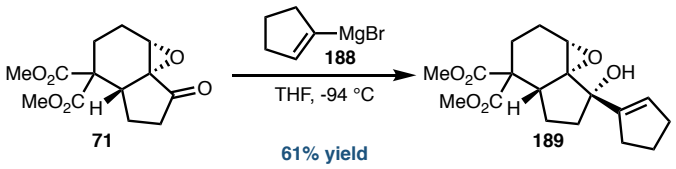
HRMS: (ESI-TOF) calc'd for $C_{29}H_{46}O_5NSi$ $[M + H]^+$ 516.3140, found 516.3144.

TLC (5% 7 N NH_3 in MeOH/ 95% CH_2Cl_2), R_f: 0.5 (UV, yellow in *p*-anisaldehyde)

Notes:

1) PhMe was degassed via Freeze-Pump-Thaw (3 cycles) prior to use.

Preparation of epoxy alcohol 189:



In a 200-mL, round-bottomed flask, epoxyketone **71** (1.59 g, 5.93 mmol, 1.0 equiv.) was dissolved in THF (59 mL) and cooled to –78 °C. To this solution was added cyclopentyl magnesium bromide (prepared from cyclopentenyl bromide, Mg(0) and I_2 activation, 0.3M in THF, 25 mL, 7.50 mmol, 1.27 equiv.) via cannula. The reaction was allowed to stir for an additional 10 minutes at –78 °C, then quenched with sat. NH_4Cl solution (30 mL) and H_2O (30 mL), and was allowed to warm to room temperature. The biphasic mixture was then transferred to a separatory funnel with Et_2O (50 mL), and the layers were separated. The aqueous layer was extracted with more Et_2O (3 x 75 mL). The combined organics were washed with brine (1 x 100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified by silica gel chromatography (12% to 13% to 14% acetone in hexanes to elute the product and then 20% acetone in hexanes to recover the unreacted epoxy ketone starting material) to afford epoxy alcohol **189** (1.20 g, 3.61 mmol, 61% yield) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.67 (t, *J* = 1.8 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.34 (d, *J* = 3.8 Hz, 1H), 2.74 (dd, *J* = 10.5, 7.8 Hz, 1H), 2.52 – 2.40 (m, 2H), 2.39 – 2.28 (m, 6H), 2.19 – 2.08 (m, 1H), 2.05 – 1.96 (m, 1H), 1.95 – 1.85 (m, 4H), 1.62 – 1.52 (m, 1H).

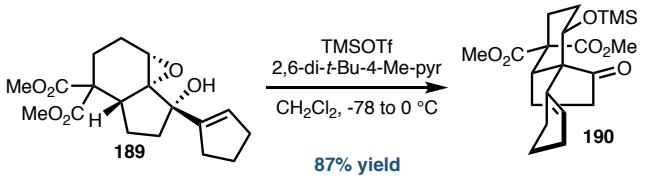
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9, 170.3, 145.4, 126.0, 75.4, 71.4, 56.5, 55.1, 52.9, 52.1, 44.0, 37.8, 32.3, 31.7, 29.3, 23.4, 23.2, 21.4.

FTIR (NaCl, thin film): 3503, 2952, 1732, 1433, 1244, 1218, 1174 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{18}H_{25}O_6$ $[M + H]^+$ 337.1646, found 337.1635.

TLC (33%EtOAc/ 67% Hexanes), R_f: 0.40 (blue/purple in *p*-anisaldehyde)

Semipinacol rearrangement of 189 to prepare 190:



A 100-mL, round-bottomed flask was charged with epoxy alcohol **189** (1.37 g, 4.07 mmol, 1.0 equiv.), 2,6-*t*-Bu_2-4-MePy (2.51 g, 12.2 mmol, 3 equiv.) and CH_2Cl_2 (41 mL), and the solution was cooled to –78 °C in a dry/ice acetone bath. TMSOTf added dropwise via syringe (1.47 mL, 8.15 mmol, 2 equiv.), causing the solution to turn a faint pink color. The reaction was allowed to stir at – 78 °C for 5 minutes, and then the dry//ice acetone bath was replaced with an ice bath, allowing the reaction to warm to 0 °C. The reaction was allowed to stir for an additional 10 minutes at 0 °C, then the reaction was quenched with sat. $NaHCO_3$ (50 mL), and the mixture was allowed to warm to room temperature. The biphasic mixture was transferred to a separatory funnel and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 75 mL), and the combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (10% to 12% to 15% ethyl acetate in hexanes) to afford ketone **190** (1.45 g, 4.07 mmol, 87% yield) as a white solid.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.38 (t, *J* = 2.2 Hz, 1H), 4.33 (t, *J* = 2.5 Hz, 1H), 3.74 (s, 3H), 3.64 (s, 3H), 3.37 (dd, *J* = 12.5, 6.9 Hz, 1H), 2.57 – 2.49 (m, 1H), 2.45 (td, *J* = 13.9, 3.9 Hz, 1H), 2.41 – 2.23 (m, 3H), 2.22 – 2.08 (m, 3H), 1.97 – 1.89 (m, 1H), 1.87 – 1.81 (m, 2H), 1.81 – 1.71 (m, 2H), 1.68 (dq, *J* = 14.3, 3.6 Hz, 1H), 0.06 (s, 9H).

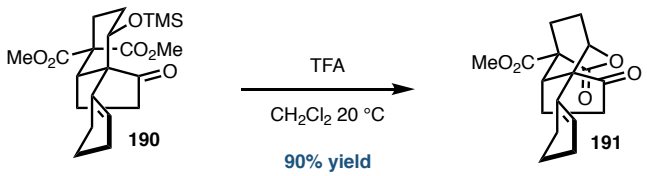
^{13}C NMR (126 MHz, $CDCl_3$): δ 219.2, 170.8, 170.5, 142.9, 127.3, 70.3, 57.8, 56.1, 52.7, 52.5, 41.9, 39.1, 32.9, 32.7, 27.8, 23.5, 22.8, 19.6, -0.0.

FTIR (NaCl, thin film): 2952, 2846, 1740, 1434, 1252, 1171, 1058, 841 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{21}H_{33}O_6Si$ $[M + H]^+$ 409.2041, found 409.2056.

TLC (15%EtOAc/ 85% Hexanes), R_f: 0.4 (grey/blue/black in *p*-anisaldehyde)

Preparation of lactone 191:

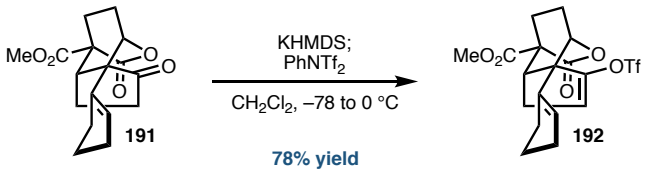


In a 250 mL round-bottom flask, silyl ether **190** (1.445 g, 3.54 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (70 mL) and TFA (0.82 mL, 10.6 mmol, 3 equiv.) was added dropwise. The reaction was stirred for 7 hours when TLC indicated complete conversion of starting material. The reaction was quenched with saturated aqueous $NaHCO_3$ (50 mL) and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL) and the combined extracts were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The reaction was purified by silica gel chromatography (30% EtOAc/70% hexanes) to afford lactone **191** (0.956 g, 3.14 mmol, 90% yield) as a white powder.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.78 (t, *J* = 2.2 Hz, 1H), 5.10 – 4.99 (m, 1H), 3.84 (s, 3H), 3.23 (t, *J* = 9.2, 7.5 Hz, 1H), 2.63 – 2.52 (m, 1H), 2.49 – 2.40 (m, 2H), 2.21 – 2.12 (m, 2H), 2.01 – 1.76 (m, 5H), 1.75 – 1.64 (m, 1H).

TLC (30%EtOAc/ 70% Hexanes), R_f: 0.4 (blue in *p*-anisaldehyde)

Preparation of enol triflate 192:



An oven-dried 100 mL round-bottom flask was charged with **191** (0.946 g, 3.11 mmol, 1.0 equiv.) and put under N_2. THF (31 mL) was added, and the solution was cooled to –78 °C. A solution of KHMDS (0.5 M in PhMe, 7.5 mL, 3.8 mmol, 1.2 equiv.) was added dropwise by syringe and the mixture was stirred at –78 °C for 40 minutes. In an oven-dried 50 mL pear-shaped flask, $PhNTf_2$ (1.33 g, 3.73 mmol, 1.2 equiv.) was put under N_2 and dissolved in THF (10 mL). The solution of $PhNTf_2$ was transferred to the reaction flask by cannula, and the reaction was stirred at –78 °C for 10 minutes. The reaction was quenched with saturated aqueous $NaHCO_3$ (50 mL), and the mixture was allowed to warm to room temperature. The mixture was transferred to a separatory funnel and was extracted with Et_2O (3 x 50 mL). The combined organic extracts were washed with 0.5 M NaOH (aq.) (3 x 50 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The reaction was purified by silica gel chromatography (20% EtOAc/80% hexanes) to afford enol triflate **192** (1.059 g, 2.43 mmol, 78% yield) as a white solid.

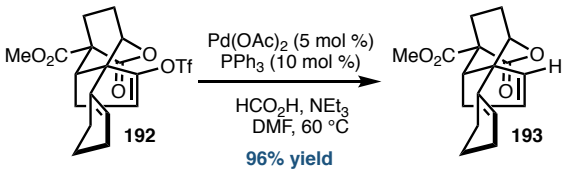
^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.68 (t, *J* = 2.6 Hz, 1H), 5.64 (t, *J* = 2.0 Hz, 1H), 4.91 (dd, *J* = 3.8, 1.7 Hz, 1H), 3.83 (s, 3H), 3.05 (dd, *J* = 9.4, 2.9 Hz, 1H), 2.92 (ddd, *J* = 18.2, 9.4, 2.4 Hz, 1H), 2.51 – 2.40 (m, 3H), 2.39 – 2.31 (m, 2H), 2.18 – 2.07 (m, 2H), 1.96 – 1.79 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.98, 169.79, 146.02, 139.86, 129.91, 116.90, 116.34, 76.26, 56.45, 53.11, 53.03, 43.60, 33.14, 33.05, 32.35, 26.65, 22.83, 21.89.

HRMS: (ESI-TOF) calc'd for $C_{18}H_{19}O_7F_3SNa$ $[M + Na]^+$ 459.0696, found 459.0708.

TLC (20%EtOAc/ 80% Hexanes), R*f*: 0.2 (brown in *p*-anisaldehyde)

Preparation of cyclopentene 193:



A 100 mL, round-bottom flask was charged with enol triflate **192** (1.046 g, 2.40mmol, 1.0 equiv.), PPh_3 (63 mg, 0.24 mmol, 10 mol %), and $Pd(OAc)_2$ (27 mg, 0.12 mmol, 5 mol %). The flask was equipped with a rubber septum, purged with N_2, and DMF (24 mL) was added. Then, the reaction mixture was sparged with N_2 for 5 minutes. NEt_3 (2.68 mL, 19.2 mmol, 8 equiv.) was added, followed by HCO_2H (0.45 mL, 12.0 mmol, 5 equiv.) – a cloudy gas was observed upon addition. The reaction was heated to 60 °C allowed stirred at that temperature for 15 minutes. The reaction turns black during this time, indicating its completion. The reaction was cooled to room temperature, diluted with sat. NH_4Cl (20 mL), transferred to a separatory funnel and diluted with Et_2O (30 mL). The layers were separated and the aqueous extracted with Et_2O (5 x 30 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (15-16% EtOAc in hexanes) to afford olefin **193** (0.657 g, 2.3 mmol, 96% yield) as a white crystalline solid.

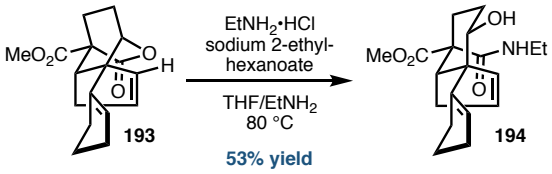
^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.69 (dt, *J* = 5.7, 2.3 Hz, 1H), 5.59 (t, *J* = 2.1 Hz, 1H), 5.51 (dt, *J* = 5.8, 2.3 Hz, 1H), 4.70 (dd, *J* = 3.2, 2.2 Hz, 1H), 3.81 (s, 3H), 3.08 (dd, *J* = 9.5, 3.5 Hz, 1H), 2.91 (ddt, *J* = 18.7, 9.4, 2.3 Hz, 1H), 2.45 (ddt, *J* = 18.7, 3.5, 2.3 Hz, 1H), 2.40 – 2.32 (m, 3H), 2.30 – 2.22 (m, 2H), 2.01 – 1.97 (m, 2H), 1.95 – 1.83 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.86, 170.78, 145.07, 132.39, 130.90, 125.13, 79.50, 59.31, 54.02, 52.79, 44.87, 38.25, 32.92, 32.45, 26.62, 23.65, 22.50.

HRMS: (ESI-TOF) calc'd for $C_{17}H_{21}O_4$ $[M + H]^+$ 289.1434, found 289.1441.

TLC (20%EtOAc/ 80% Hexanes), R*f*: 0.2 (brown in *p*-anisaldehyde)

Preparation of *N*-ethyl amide 194:



To a 75 mL pressure vessel containing lactone **193** (0.647 g, 2.24 mmol, 1.0 equiv.), sodium 2-ethylhexanoate (1.680 g, 10.1 mmol, 4.5 equiv.), ethylamine hydrochloride (0.412 g, 5.1 mmol, 2.25 equiv.) were added, followed by THF (5 mL) and neat $EtNH_2$ (10 mL). The vessel was sealed (with a Teflon cap that had a perfluoro O-ring), and heated to 80 °C in an oil bath. The reaction was allowed to stir at 80 °C for 2 days, and the reaction progress was monitored. The reaction was then cooled to room temperature and transferred to a separatory funnel with EtOAc (30 mL) and aqueous 0.5 M NaOH (20 mL). The layers were separated, and the aqueous phase was extracted with Et_2O (3 x 20 mL) and EtOAc (2 x 20 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified by silica gel chromatography (30% to 50% to 100% EtOAc in hexanes) to afford secondary amide **194** as a white foam (400 mg, 1.20 mmol, 53% yield).

Note: Neat NH_2Et was obtained from distillation of 70%NH_2Et/ 30% H_2O solution, using a cold finger (with dry ice/acetone) to condense the very volatile NH_2Et, and stored over KOH pellets in the freezer.

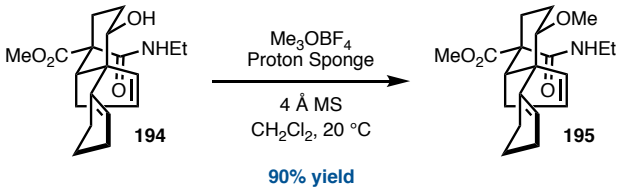
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.23 (s, 1H), 6.10 (dt, *J* = 5.9, 2.3 Hz, 1H), 5.50 (dt, *J* = 5.9, 2.0 Hz, 1H), 5.41 (t, *J* = 2.1 Hz, 1H), 3.96 (t, *J* = 4.5 Hz, 1H), 3.35 – 3.15 (m, 3H), 2.47 (m, 1H), 2.39 – 2.16 (m, 6H), 2.13 – 2.02 (m, 1H), 1.95 – 1.77 (m, 5JH), 1.11 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.64, 169.11, 146.86, 134.74, 134.38, 125.44, 67.89, 57.00, 55.75, 52.87, 46.45, 35.46, 34.85, 33.24, 33.14, 25.75, 23.38, 18.60, 14.81.

HRMS: (ESI-TOF) calc'd for $C_{19}H_{27}NO_4Na$ $[M + Na]^+$ 356.1832, found 356.1850.

TLC (50%EtOAc/ 50% Hexanes), R*f*: 0.2 (teal in *p*-anisaldehyde)

Preparation of methyl ether 195:



In a N_2-filled glovebox, an oven-dried 15 mL round-bottom flask with a stir bar was charged with **194** (150 mg, 0.45 mmol, 1.0 equiv.). CH_2Cl_2 (4.5 mL) was added, followed by Proton Sponge® (289 mg, 1.35 mmol, 3.0 equiv.), trimethyloxonium tetrafluoroborate (200 mg, 1.35 mmol, 3.0 equiv.), and 4Å molecular sieve powder (750 mg). The reaction was stirred at 20 °C for 18 hours. The mixture was passed over a plug of silica gel, eluting with 50-100% EtOAc in hexanes. The filtrate was concentrated to give the crude product as a yellow oil. The product was purified by column chromatography (SiO_2, 20-30-40-50% EtOAc in hexanes) to give methyl ether **195** (140 mg, 0.41 mmol, 90% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.10 (s, 1H), 5.85 (dt, *J* = 5.8, 2.4 Hz, 1H), 5.49 (dt, *J* = 5.9, 2.1 Hz, 1H), 5.34 (t, *J* = 2.0 Hz, 1H), 3.70 (s, 3H), 3.44 (dd, *J* = 8.4, 4.2 Hz, 1H), 3.34

– 3.27 (m, 1H), 3.25 (s, 3H), 3.23 – 3.05 (m, 2H), 2.52 – 2.08 (m, 8H), 1.97 – 1.89 (m, 1H), 1.85 (p, J = 7.5 Hz, 2H), 1.63 – 1.57 (m, 1H), 1.10 (t, J = 7.2 Hz, 3H).

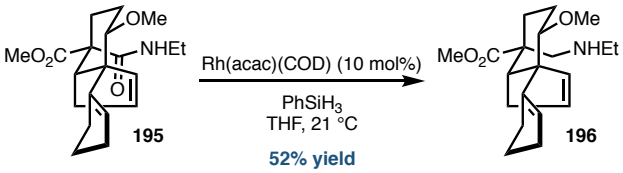
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.77, 169.33, 148.58, 134.36, 130.81, 124.10, 78.47, 57.46, 57.06, 55.98, 52.82, 47.32, 35.72, 34.87, 32.84, 32.53, 23.52, 22.12, 19.95, 14.75.

FTIR (NaCl, thin film): 3353, 2933, 1727, 1654, 1522, 1439, 1377, 1203, 1101, 754 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{20}H_{29}NO_4$ $[M + H]^+$ 370.1989, found 370.1994.

TLC (2:1 Hexanes:EtOAc), R_f: 0.4 (blue in *p*-anisaldehyde)

Preparation of amine 196:



A flame-dried 100 mL round-bottom flask was charged with amide **195** (100 mg, 0.29 mmol, 1.0 equiv.) and brought into a N_2-filled glovebox. THF was added, followed by Rh(acac)cod (8.9 mg, 0.029 mmol, 10 mol%) and phenylsilane (0.71 mL, 5.8 mmol, 20 equiv.). The flask was sealed with a rubber septum, brought out of the glovebox and put under Ar atmosphere with a balloon. The reaction was stirred at room temperature for 16 hours. The reaction was diluted with THF (5 mL) and quenched with careful addition of saturated aqueous NH_4F (5 mL), at which point reaction bubbles vigorously. The mixture was stirred for 90 minutes before diluting with water (5 mL) and EtOAc (15 mL). The phases were separated and the aqueous phase was extracted with 4:1 $CHCl_3$: *i*PrOH mixture (5 x 15 mL). The organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude residue was purified by silica gel chromatography (1-2% (7N NH_3 in MeOH) in CH_2Cl_2) to afford the amine **196** as a colorless oil (49.1 mg, 0.15 mmol, 52 % yield).

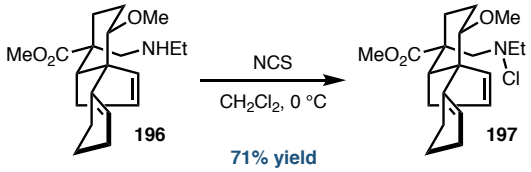
^{1}H NMR (400 MHz, Benzene-d_6) δ 5.83 (dt, *J* = 5.9, 2.3 Hz, 1H), 5.65 (dt, *J* = 5.8, 2.0 Hz, 1H), 5.45 (p, *J* = 1.9 Hz, 1H), 3.69 (dd, *J* = 7.7, 3.1 Hz, 1H), 3.36 (s, 3H), 3.11 (s, 3H), 3.10 – 3.04 (m, 1H), 2.77 (d, *J* = 11.1 Hz, 1H), 2.60 – 2.50 (m, 1H), 2.48 (d, *J* = 11.2 Hz, 1H), 2.45 – 2.37 (m, 3H), 2.36 – 2.24 (m, 5H), 2.05 (dddd, *J* = 13.8, 7.8, 6.2, 3.1 Hz, 1H), 1.81 (p, *J* = 7.4 Hz, 2H), 1.66 (ddd, *J* = 13.7, 7.7, 6.5 Hz, 1H), 1.61 – 1.48 (m, 1H), 0.91 (t, *J* = 7.1 Hz, 4H).

^{13}C NMR (101 MHz, C_6D_6) δ 176.56, 148.73, 136.23, 130.36, 123.68, 79.90, 59.16, 57.52, 57.16, 51.16, 48.39, 46.74, 44.91, 35.40, 33.43, 33.35, 23.93, 23.72, 23.06, 15.52.

HRMS: (ESI-TOF) calc'd for $C_{20}H_{32}NO_3$ $[M + H]^+$ 334.2377, found 334.2377.

TLC (8% MeOH/ 92% CH_2Cl_2), R_f: 0.4 (blue in *p*-anisaldehyde)

Preparation of *N*-chloroamine 197:

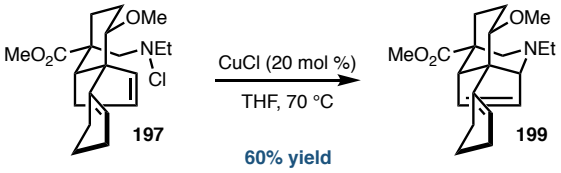


A solution of secondary amine **196** (20 mg, 60 μmol, 1.0 equiv.) in CH_2Cl_2 (2.0 mL) was cooled to 0 °C before NCS (8.0 mg, 60 μmol, 1.0 equiv.) was added in one portion. The reaction was stirred for 60 minutes before filtering over a short pad of silica gel, eluting with 1:1 hexanes:EtOAc. The filtrate was concentrated *in vacuo*. The crude product was purified by column chromatography (10-20-30-40% EtOAc in hexanes) to afford *N*-chloroamine **197** (15.6 mg, 42 μmol, 71% yield) as a white powder.

^{1}H NMR (500 MHz, Chloroform-d) δ 5.85 (dt, *J* = 5.8, 2.3 Hz, 1H), 5.44 (ddd, *J* = 5.8, 2.5, 1.4 Hz, 1H), 5.41 – 5.38 (m, 1H), 3.70 (dd, *J* = 9.4, 3.3 Hz, 1H), 3.57 (s, 3H), 3.33 (d, *J* = 14.0 Hz, 1H), 3.28 (s, 3H), 3.00 (d, *J* = 14.0 Hz, 1H), 2.94 (qd, *J* = 6.8, 2.9 Hz, 2H), 2.86 (td, *J* =

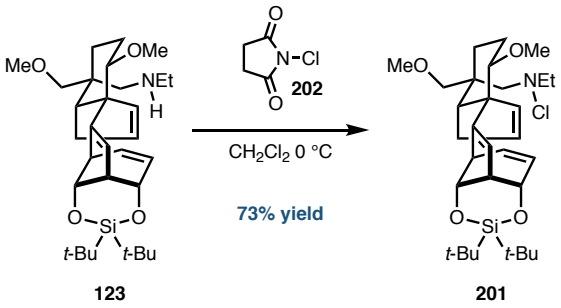
9.2, 1.3 Hz, 1H), 2.62 – 2.49 (m, 1H), 2.46 – 2.22 (m, 5H), 2.23 – 2.07 (m, 1H), 1.94 (dddd, *J* = 13.1, 7.0, 5.6, 3.3 Hz, 1H), 1.90 – 1.68 (m, 3H), 1.56 – 1.42 (m, 1H), 1.15 (t, *J* = 6.9 Hz, 3H).

Reaction of *N*-chloroamine 197 with Copper (I) Chloride:



CuCl (0.5 mg, 5.4 μmol, 0.2 equiv.) was added to a 1-dram vial followed by a solution of *N*-chloroamine **197** (10.0 mg, 27 μmol, 1.0 equiv.) in THF (2.0 mL), and the mixture was heated to 70 °C for 12 hours. Saturated aqueous $NaHCO_3$ (2 mL) was added, and the mixture was extracted with 4:1 $CHCl_3$: *i*PrOH mixture (3 x 5 mL). The organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification by preparative TLC (1% (7 N NH_3 in MeOH) in CH_2Cl_2) gave a product tentatively assigned as **199** (5.2 mg, 16 μmol, 60% yield). **^{1}H NMR (400 MHz, Benzene-d_6)** δ 6.29 (dd, *J* = 5.9, 1.5 Hz, 1H), 5.77 (dd, *J* = 5.8, 1.5 Hz, 1H), 5.51 (p, *J* = 2.1 Hz, 1H), 4.31 (dt, *J* = 7.2, 1.6 Hz, 1H), 3.67 (d, *J* = 7.1 Hz, 1H), 3.43 – 3.38 (m, 1H), 3.37 (d, *J* = 3.2 Hz, 4H), 3.29 (d, *J* = 8.8 Hz, 1H), 3.12 (d, *J* = 1.0 Hz, 4H), 2.69 – 2.57 (m, 1H), 2.54 – 2.39 (m, 5H), 2.31 (dtq, *J* = 11.0, 6.5, 2.1 Hz, 4H), 2.09 – 1.76 (m, 4H), 1.70 (dq, *J* = 12.5, 4.2 Hz, 2H), 1.64 – 1.43 (m, 2H), 1.43 – 1.30 (m, 2H), 1.03 (t, *J* = 7.2 Hz, 3H).

Preparation of *N*-chloroamine 201:



123 **201**

A solution of secondary amine **123** (24 mg, 65 μmol, 1.0 equiv.) in CH_2Cl_2 (2.2 mL) was cooled to 0 °C before NCS (17 mg, 130 μmol, 2.0 equiv.) was added in one portion. The reaction was stirred for 90 minutes before filtering over a short pad of silica gel, eluting with 1:1 hexanes:EtOAc. The filtrate was concentrated *in vacuo*. The crude product was purified by column chromatography (10-20-30-40% EtOAc in hexanes) to afford *N*-chloroamine **201** (27 mg, 47 μmol, 73% yield) as a white powder.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.07 (ddd, *J* = 9.5, 6.1, 1.1 Hz, 1H), 5.87 (dt, *J* = 5.8, 2.2 Hz, 1H), 5.65 (ddd, *J* = 9.3, 4.4, 1.9 Hz, 1H), 5.46 – 5.38 (m, 2H), 4.47 (t, *J* = 4.8 Hz, 1H), 4.26 – 4.17 (m, 1H), 3.57 (dd, *J* = 7.5, 2.6 Hz, 1H), 3.29 – 3.24 (m, 5H), 3.22 (s, 3H), 3.08 – 2.93 (m, 5H), 2.93 – 2.84 (m, 1H), 2.47 (t, *J* = 9.2 Hz, 1H), 2.42 – 2.20 (m, 2H), 1.71 – 1.52 (m, 3H), 1.49 – 1.40 (m, 1H), 1.19 (t, *J* = 6.9 Hz, 3H), 1.09 (s, 9H), 1.01 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.56, 136.04, 134.27, 131.37, 128.25, 119.94, 79.64, 77.36, 74.37, 69.55, 66.68, 60.90, 58.33, 57.36, 57.26, 46.45, 46.36, 44.59, 40.82, 35.61, 29.07, 28.48, 24.01, 21.86, 21.41, 20.84, 13.25.

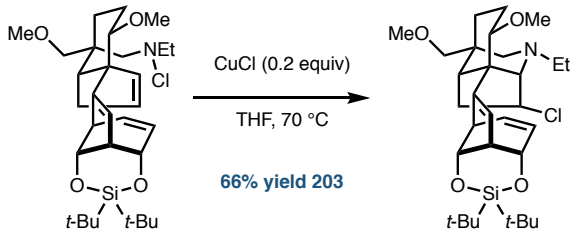
FTIR (NaCl, thin film): 2933, 1476, 1102, 992, 812, 780, 762, 641cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{31}H_{51}NO_4ClSi$ $[M + H]^+$ 564.3270, found 564.3279

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{22}}$ = +126° (*c* = 0.40, $CHCl_3$).

TLC (3:1 Hexanes:EtOAc), R_f: 0.8 (UV, white/green in *p*-anisaldehyde)

Reaction of *N*-chloroamine 201 with Copper (I) Chloride:

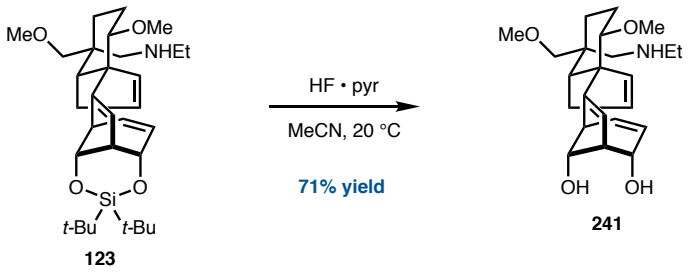


201 **203**

CuCl (0.18 mg, 1.8 μmol, 0.2 equiv.) was dispensed as a stock solution in MeCN to a ½ dram vial. The MeCN was removed *in vacuo*. The vial of CuCl was brought into a N_2 filled glovebox and a solution of *N*-chloroamine **201** (5.0 mg, 8.9 μmol, 1.0 equiv.) in THF (0.5 mL) was added, and the mixture was heated to 70 °C for 4 hours. Saturated aqueous $NaHCO_3$ (2 mL) was added, and the mixture was extracted with 4:1 $CHCl_3$: *i*PrOH mixture (3 x 5 mL). The organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification by preparative TLC (5% (7 N NH_3 in MeOH) in CH_2Cl_2) gave a product tentatively assigned as **203** (3.3 mg, 5.9 μmol, 66% yield). Assignments were made using ^{1}H, COSY, HSQC, HMBC and TOCSY NMR experiments.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.07 (ddd, *J* = 9.5, 6.0, 1.1 Hz, 1H), 5.74 (ddd, *J* = 9.5, 4.4, 1.9 Hz, 1H), 5.64 (d, *J* = 3.9 Hz, 1H), 4.57 (d, *J* = 4.9 Hz, 1H), 4.47 (t, *J* = 4.7 Hz, 1H), 4.25 (t, *J* = 3.7 Hz, 1H), 3.94 – 3.83 (m, 1H), 3.81 – 3.72 (m, 3H), 3.41 – 3.36 (m, 1H), 3.35 (s, 3H), 3.32 (s, 3H), 3.27 – 3.19 (m, 3H), 3.16 (d, *J* = 13.1 Hz, 1H), 3.08 (s, 1H), 2.83 (t, *J* = 5.2 Hz, 1H), 2.58 (d, *J* = 14.9 Hz, 1H), 2.37 – 2.26 (m, 2H), 2.11 – 2.05 (m, 1H), 1.41 – 1.38 (m, 3H), 1.08 (s, 9H), 1.00 (s, 9H).

Preparation of diol 241:



123 **241**

A 20 mL Teflon vial was charged with siliconide **123** (0.116 g, 0.22 mmol, 1.0 equiv.) and MeCN (8 mL). HF•pyridine (0.116 g, ~70% HF) was diluted with MeCN (1.6 mL) and this solution was added dropwise to the vial of **123** and the reaction was stirred at 20 °C for 1 hour. The reactions was quenched with saturated aqueous $NaHCO_3$ (10 mL) and the mixture was extracted with 4:1 $CHCl_3$: *i*PrOH mixture (5 x 10 mL). The organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude residue was purified by silica gel chromatography (2-3-4-5-6% (7N NH_3 in MeOH) in CH_2Cl_2) to afford the diol **241** as a colorless oil (60.0 mg, 0.16 mmol, 71 % yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.96 (dd, *J* = 9.5, 6.4 Hz, 1H), 5.88 (dt, *J* = 5.7, 2.2 Hz, 1H), 5.76 (ddd, *J* = 9.6, 3.6, 2.0 Hz, 1H), 5.47 (d, *J* = 3.6 Hz, 1H), 5.37 (dt, *J* = 5.8, 1.8 Hz, 1H), 4.38 (t, *J* = 4.7 Hz, 1H), 4.06 – 3.88 (m, 1H), 3.54 (dd, *J* = 7.3, 2.8 Hz, 1H), 3.25 (s, 3H), 3.24 (s, 3H), 3.19 (s, 2H), 2.81 (dd, *J* = 6.3, 4.3 Hz, 1H), 2.76 – 2.67 (m, 1H), 2.67 – 2.53 (m, 2H), 2.47 (d, *J* = 1.6 Hz, 2H), 2.39 (dd, *J* = 10.7, 7.7 Hz, 1H), 2.31 (dt, *J* = 8.3, 2.3 Hz, 2H), 1.70 – 1.45 (m, 3H), 1.38 – 1.28 (m, 1H), 1.07 (t, *J* = 7.0 Hz, 3H).

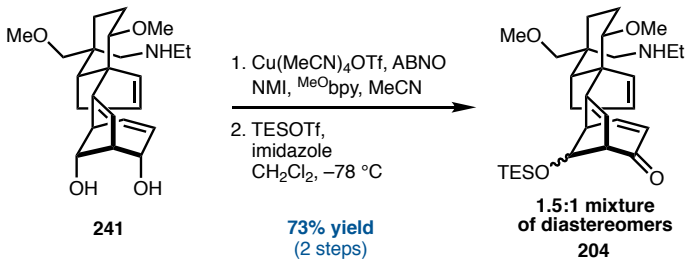
^{13}C NMR (101 MHz, $CDCl_3$): δ 165.03, 134.31, 132.42, 131.58, 129.34, 120.14, 79.80, 77.36, 76.51, 74.85, 66.16, 59.05, 57.37, 56.97, 56.72, 47.78, 44.99, 44.74, 39.38, 35.45, 24.47, 21.91, 15.35.

FTIR (NaCl, thin film): 3374, 2923, 2352, 1453, 1362, 1218, 1100, 1010, 960, 935, 817, 758, 733 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{23}H_{35}NO_4$ $[M + H]^+$ 390.2639, found 390.2621

$[\alpha]_D^{25}$ = +98.2° (*c* = 0.82, $CHCl_3$).

Preparation of enone 242:



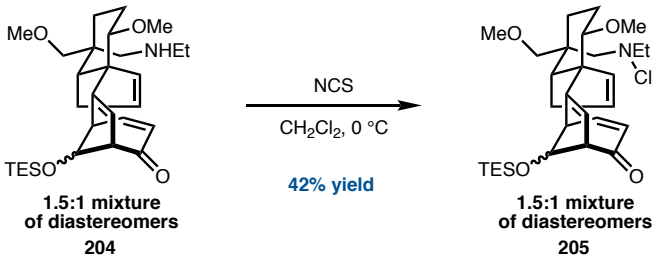
0.64 mL of a stock solution of ABNO (1 mM), ^{MeO}bpy (1 mM) and NMI (6 mM) (0.05 equiv. ABNO; 0.05 equiv. ^{MeO}bpy; 0.40 equiv. NMI) was added to a ½ dram vial. $Cu(MeCN)_4OTf$ (0.2 mg, 0.64 μmol, 0.05 equiv.) was added, and the catalyst solution was stirred for 5 minutes. Diol **241** (5.0 mg, 13 μmol, 1.0 equiv.) in MeCN (0.5 mL) was added, and the mixture was stirred for 90 minutes at room temperature. The reaction mixture was filtered over a short pad of silica gel, eluting with 10% (7N NH_3 in MeOH) in CH_2Cl_2. The filtrate was concentrated and taken on crude to the next step.

The crude isolate from the Stahl oxidation was added to an oven-dried 10 mL round-bottom flask along with imidazole (3.3 mg, 48 μmol, 3.8 equiv.). The flask was put under N_2 atmosphere before THF (1.0 mL) was added and the mixture was cooled to –78 °C. TESCl (4.9 mg, 32 μmol, 2.5 equiv.) in THF (0.1 mL) was added dropwise, and the mixture was stirred at –78 °C for 10 minutes. The reaction was quenched with saturated aqueous $NaHCO_3$ (2 mL) and the mixture was extracted with 4:1 $CHCl_3$: *i*PrOH mixture (3 x 5 mL). The organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude residue was purified by silica gel chromatography (2-3% (7N NH_3 in MeOH) in CH_2Cl_2) to afford **204** (4.7

mg, 9.5 μmol, 73% yield) as a ~1.5:1 mixture of diastereomers. The ^{1}H NMR spectrum of the major diastereomer is reported below:

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.94 (ddd, *J* = 9.8, 6.4, 1.7 Hz, 1H), 5.94 (dt, *J* = 5.9, 2.3 Hz, 1H), 5.78 (dd, *J* = 9.7, 1.9 Hz, 1H), 5.66 (d, *J* = 3.8 Hz, 1H), 5.34 (dt, *J* = 5.9, 1.9 Hz, 1H), 4.66 (td, *J* = 4.5, 1.7 Hz, 1H), 3.52 (dd, *J* = 7.3, 2.7 Hz, 1H), 3.24 (d, *J* = 2.3 Hz, 3H), 3.22 (s, 3H), 3.21 – 3.16 (m, 2H), 3.13 (t, *J* = 5.5 Hz, 1H), 2.67 – 2.57 (m, 2H), 2.57 – 2.43 (m, 3H), 2.36 (dt, *J* = 10.1, 2.2 Hz, 2H), 1.71 – 1.62 (m, 1H), 1.57 (dtt, *J* = 12.7, 8.4, 3.8 Hz, 4H), 1.34 (q, *J* = 7.1, 6.1 Hz, 1H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.57 (q, *J* = 7.9 Hz, 6H).

Preparation of *N*-chloroamine 205:

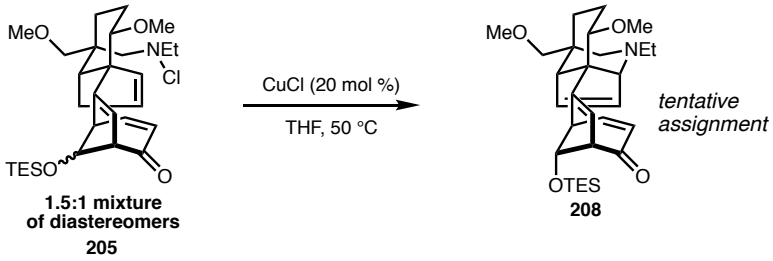


A solution of secondary amine **204** (4.7 mg, 9.5 μmol, 1.0 equiv.) in CH_2Cl_2 was cooled to 0 °C before NCS (3.1 mg, 24 μmol, 2.5 equiv.) was added in one portion. The reaction was stirred for 30 minutes before filtering over a short pad of silica gel, eluting with EtOAc. The filtrate was concentrated *in vacuo*. The crude product was purified by column chromatography (10-20-30-40% EtOAc in hexanes) to afford *N*-chloroamine **205** (2.1 mg, 3.9 μmol, 42% yield) as a mixture of diastereomers.

The ^{1}H NMR spectrum of the major diastereomer is reported below:

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.94 (ddd, *J* = 9.8, 6.5, 1.7 Hz, 1H), 5.93 (dt, *J* = 5.8, 2.3 Hz, 1H), 5.78 (dd, *J* = 9.6, 1.4 Hz, 1H), 5.66 (d, *J* = 3.7 Hz, 1H), 5.39 – 5.33 (m, 1H), 4.66 (td, *J* = 4.6, 1.7 Hz, 1H), 3.53 (dd, *J* = 7.6, 2.4 Hz, 1H), 3.29 (s, 2H), 3.25 – 3.21 (m, 6H), 3.18 (s, 1H), 3.14 – 3.09 (m, 1H), 3.10 – 3.05 (m, 1H), 3.02 – 2.93 (m, 3H), 2.54 (t, *J* = 9.3 Hz, 1H), 2.39 – 2.23 (m, 2H), 1.80 – 1.64 (m, 2H), 1.64 – 1.56 (m, 1H), 1.50 – 1.42 (m, 1H), 1.20 (t, *J* = 6.9 Hz, 3H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.57 (q, *J* = 8.0 Hz, 6H).

Tentative identification of cyclized product 208:



1.5:1 mixture of diastereomers 205 **208**

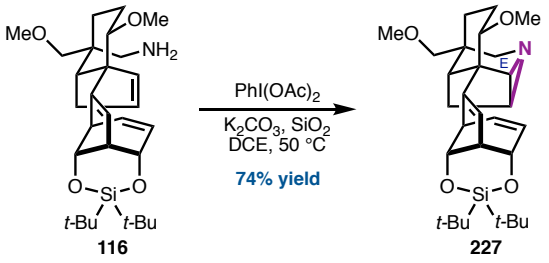
CuCl (0.04 mg, 0.4 μmol, 0.2 equiv.) was dispensed as a stock solution in MeCN to a ½ dram vial. The MeCN was removed *in vacuo*. A solution of *N*-chloroamine **205** (1.0 mg, 1.9 μmol, 1.0 equiv.) in THF (0.2 mL) was added, and the mixture was heated to 50 °C for 12 hours. Saturated aqueous $NaHCO_3$ (1 mL) was added, and the mixture was extracted with 4:1 $CHCl_3$: *i*PrOH mixture (3 x 5 mL). The organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification by preparative TLC (5% (7 N NH_3 in MeOH) in CH_2Cl_2) gave a trace amount of a product tentatively assigned as **208** based on HRMS and ^{1}H NMR.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.06 (s, 1H), 5.96 (s, 1H), 5.92 (s, 1H), 5.77 (d, *J* = 9.8 Hz, 1H), 5.47 (s, 1H), 4.64 (s, 1H), 4.14 (s, 1H), 3.65 (s, 2H), 3.37 (s, 4H), 3.33 (s, 4H), 3.17 (s, 2H), 3.11 (s, 1H), 3.04 (s, 1H), 2.65 (s, 1H), 2.47 (d, *J* = 9.9 Hz, 2H), 2.38 (d, *J* = 6.6 Hz,

1H), 2.19 – 2.08 (m, 2H), 1.12 – 1.05 (m, 4H), 0.92 (t, *J* = 7.8 Hz, 9H), 0.57 (q, *J* = 7.9 Hz, 6H).

HRMS: (ESI-TOF) calc'd for $C_{29}H_{46}NO_4Si$ $[M + H]^+$ 500.3196, found 500.3172

Preparation of aziridine 227:[8]



A 100 mL, round-bottom flask was charged with primary amine **116** (0.348 g, 0.694 mmol, 1 equiv.), $PhI(OAc)_2$ (0.357 g, 1.11 mmol, 1.6 equiv.), K_2CO_3 (0.256 g, 1.85 mmol, 2.7 equiv.), SiO_2 gel (17.3 g), and suspended in DCE (70 mL) under N_2. The mixture was stirred for 30 minutes at room temperature, and then heated to 50 °C in an oil bath and was allowed to stir at 50 °C for 1 hour. At this time, the reaction was allowed to cool to room temperature, and was filtered through a plug of SiO_2 and flushed with 8% 7 N NH_3/ 92% CH_2Cl_2 solution to elute the product aziridine, and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (4% to 6% MeOH in CH_2Cl_2) to afford aziridine **227** (0.257 g, 0.514 mmol, 74% yield) as a clear oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.11 (ddd, *J* = 9.5, 6.1, 1.1 Hz, 1H), 5.67 (ddd, *J* = 9.3, 4.4, 1.9 Hz, 1H), 5.45 (dd, *J* = 3.9, 0.7 Hz, 1H), 4.51 (t, *J* = 4.7 Hz, 1H), 4.24 – 4.17 (m, 1H), 3.38 – 3.32 (m, 4H), 3.27 (s, 3H), 3.09 (d, *J* = 8.9 Hz, 1H), 3.05 – 3.01 (m, 1H), 2.99 – 2.91 (m, 2H), 2.88 (dd, *J* = 6.0, 4.6 Hz, 1H), 2.78 (d, *J* = 14.3 Hz, 1H), 2.60 – 2.58 (m, 1H), 2.48 – 2.46 (m, 1H), 2.17 – 2.08 (m, 1H), 1.82 (d, *J* = 13.4 Hz, 1H), 1.69 – 1.56 (m, 2H), 1.50 – 1.43 (m, 2H), 1.30 (td, *J* = 14.2, 3.7 Hz, 1H), 1.07 (s, 9H), 1.01 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 135.0, 128.8, 123.9, 78.9 (2 overlapping ^{13}C signals), 77.3, 66.3, 59.3, 56.8, 50.2, 50.0, 46.0, 45.1, 38.1, 35.9, 35.6, 33.7, 32.9, 28.9, 28.3, 24.0, 22.6, 21.2, 20.7. Two ^{13}C signals are observed to be overlapping at 78.9. Additionally, a ^{13}C signal is observed to be overlapping with residual $CDCl_3$ at 77.3. Resolved peaks are seen in the HSQC spectrum, provided below.

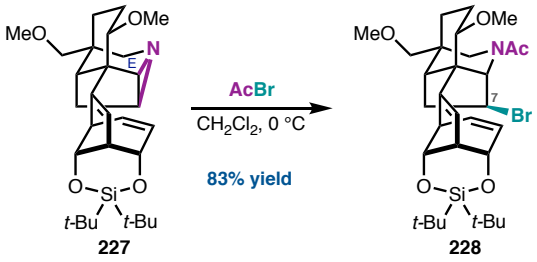
FTIR (NaCl, thin film): 2938, 2859, 2824, 2362, 1476, 1463, 1110, 993 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{29}H_{46}NO_4Si$ $[M + H]^+$ 500.3191, found 500.3178

$[\alpha]_D^{25}$ = +24.6° (*c* = 1.30, $CHCl_3$).

TLC (10%MeOH/90%CH_2Cl_2), R_f: 0.5 (UV, teal in *p*-anisaldehyde)

Preparation of bromide 228:



A 100 mL, round-bottom flask was charged with aziridine **227** (198 mg, 0.397 mmol, and CH_2Cl_2 (7.8 mL) under N_2, and cooled to 0 °C in an ice bath. Acetyl bromide (86.1 µL, 1.1645 mmol, 3 equiv.) added dropwise via microsyringe, and was allowed to stir for an additional 15 minutes while maintained at 0 °C. Reaction quenched with sat. $NaHCO_3$ (10 mL), transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (30% to 40% to 50% ethyl acetate in hexanes) to afford bromide **228** (206 mg, 0.330 mmol, 83% yield) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.17 (ddd, *J* = 9.6, 6.1, 1.1 Hz, 1H), 5.73 – 5.68 (m, 2H), 4.76 – 4.71 (m, 1H), 4.65 (s, 1H), 4.24 – 4.19 (m, 1H), 4.09 – 4.03 (m, 2H), 3.29 (s, 3H), 3.23 (s, 3H), 3.14 (d, *J* = 9.2 Hz, 1H), 3.09 – 3.05 (m, 1H), 3.04 – 2.98 (m, 2H), 2.51 (dd, *J* = 14.6, 8.8 Hz, 1H), 2.38 (d, *J* = 14.4 Hz, 1H), 2.34 – 2.23 (m, 2H), 2.18 (s, 3H), 2.07 – 1.98 (m, 1H), 1.74 – 1.67 (m, 1H), 1.50 – 1.32 (m, 2H), 1.16 – 1.08 (m, 1H), 1.08 (s, 9H), 1.03 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.0, 135.9, 128.2, 124.9, 80.6, 78.1, 77.6, 66.6, 66.2, 59.4, 55.7, 53.1, 47.3, 46.3, 46.0, 45.7, 42.8, 35.5, 35.4, 32.2, 29.7, 29.0, 28.3, 24.6, 21.8, 21.3, 20.8.

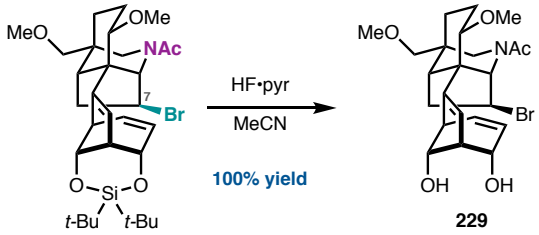
FTIR (NaCl, thin film): 2935, 2867, 2826, 1658, 1631, 1471, 1462, 1427, 1232, 1109 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{31}H_{49}BrNO_5Si$ $[M + H]^+$ 622.2558, found 622.2540

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +50.9° (*c* = 1.32, $CHCl_3$).

TLC (50%EtOAc/50%hexanes), R_f: 0.4 (UV, green in *p*-anisaldehyde)

Preparation of diol 229:



A 100 mL, round-bottom flask was charged with silylene **228** (206 mg, 0.331 mmol, 1 equiv.) and MeCN (6 mL). A solution of HF•Py (pyridine ~30%, HF ~70%, 206 mg) in MeCN (1 mL) was added, and the reaction was allowed to stir for 30 minutes at room temperature. The reaction was quenched with sat. $NaHCO_3$ (20 mL), transferred to a separatory funnel and extracted with 20%IPA/80%$CHCl_3$ (5 x 20 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was dissolved in CH_2Cl_2, filtered through a plug of SiO_2, flushed with CH_2Cl_2 to remove the nonpolar impurities

and then 5% MeOH/95% CH_2Cl_2 to elute the product to afford diol **229** (160 mg, 0.331 mmol, 100% yield) as a clear oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.10 (ddt, *J* = 9.6, 6.3, 1.1 Hz, 1H), 5.84 – 5.78 (m, 2H), 4.70 – 4.61 (m, 2H), 4.09 – 4.02 (m, 2H), 3.96 (s, 1H), 3.29 (s, 3H), 3.21 (s, 3H), 3.18 (dd, *J* = 7.8, 2.4 Hz, 1H), 3.13 (d, *J* = 9.2 Hz, 1H), 3.03 (d, *J* = 9.1 Hz, 1H), 2.96 – 2.88 (m, 1H), 2.84 – 2.78 (m, 1H), 2.77 – 2.73 (m, 1H), 2.55 – 2.47 (m, 1H), 2.38 (dd, *J* = 14.4, 2.1 Hz, 1H), 2.31 – 2.24 (m, 2H), 2.19 (s, 3H), 2.06 – 1.98 (m, 1H), 1.74 – 1.66 (m, 2H), 1.46 (dddd, *J* = 17.2, 12.6, 4.4, 2.2 Hz, 1H), 1.41 – 1.27 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.1, 132.4, 129.0, 125.1, 80.8, 78.0, 75.1, 66.6, 65.6, 59.4, 55.8, 52.9, 47.4, 47.4, 45.5, 44.5, 42.8, 35.5, 35.4, 32.2, 24.5, 21.8.

A 13C signal is observed to be missing in the ^{13}C NMR, but can be seen in the HMBC spectrum at 159.5, which is provided below.

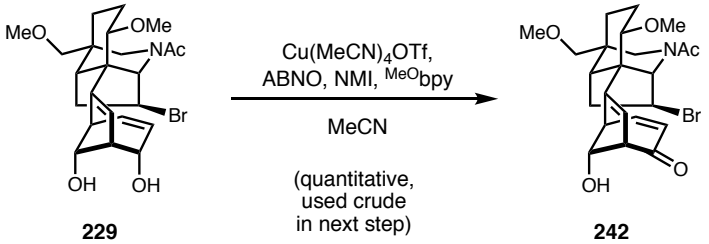
FTIR (NaCl, thin film): 3367, 2930, 2877, 2826, 2239, 1624, 1426, 1234, 1094, 917 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{23}H_{33}BrNO_5$ $[M + H]^+$ 482.1537, found 482.1539

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +39.1° (*c* = 0.55, $CHCl_3$).

TLC (100%EtOAc), R_f: 0.25 (UV, green/blue in *p*-anisaldehyde)

Preparation of enone 242:[12]



229 **242**

A 100 mL, round-bottom flask was charged with diol **229** (159 mg, 0.3308 mmol, 1.0 equiv.) and MeCN (3.3 mL). A homemade stock-solution [see note below] 0.05M 4,4'-

dimethoxy-2,2'-bipyridine (^{MeO}bpy), 0.05 M in ABNO, and 0.2 M *N*-methylimidazole was added to the solution of diol (0.61 mL, 0.031 mmol, 0.1 equiv.) followed by $Cu(MeCN)_4OTf$ (11.6 mg, 0.031 mmol, 0.1 equiv.) was added, and the clear red/brown reaction mixture was stirred until slightly yellow green, and the TLC indicated the reaction had gone to completion (ca. 90 min), at which point the solution was filtered through a short plug of silica that had been pre-packed with 5%MeOH/95% CH_2Cl_2, and flushed with more 5%MeOH/95% CH_2Cl_2 to elute the product, and concentrated *in vacuo*. The crude enone was subjected to the next step without further purification. For characterization purposes, **242** could be purified via silica gel chromatography (1% to 2% to 3% to 4% to 5% MeOH in CH_2Cl_2).

Notes:

(1) A 0.05 M solution of 4,4'-dimethoxy-2,2'-bipyridine, 0.05M ABNO and 0.2M NMI solution in MeCN could be pre-made and kept in an 8 °C freezer and was stable and good to use for an extended time (>4 months). This homemade stock solution was used in this reaction, and makes it easy to add more catalyst.

(2) This selective oxidation to the enone is very clean and performs well, but oxidation to the diketone has been observed if too much catalyst is added. It is important to monitor this reaction by TLC. It is best to run this reaction carefully, and start with less catalyst, because more can be added if needed to reach full conversion to the desired product.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.19 (ddd, *J* = 9.8, 6.4, 1.6 Hz, 1H), 5.95 – 5.90 (m, 2H), 5.18 – 5.11 (m, 1H), 4.71 (s, 1H), 4.13 – 4.04 (m, 2H), 3.46 (dd, *J* = 6.4, 4.4 Hz, 1H), 3.33 (dddd, *J* = 4.8, 3.9, 2.0, 1.0 Hz, 1H), 3.29 (s, 3H), 3.29 – 3.20 (m, 1H), 3.21 (s, 3H), 3.14 (d, *J* = 9.2 Hz, 1H), 3.04 (d, *J* = 9.2 Hz, 1H), 2.64 – 2.56 (m, 2H), 2.41 (dd, *J* = 14.6, 2.3 Hz,

1H), 2.36 (d, J = 6.3 Hz, 1H), 2.28 (dt, J = 15.3, 6.0 Hz, 1H), 2.21 (s, 3H), 2.05 – 1.98 (m, 1H), 1.75 – 1.69 (m, 1H), 1.51 – 1.32 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 195.1, 169.0, 160.1 (br), 150.9, 126.3, 124.1, 85.0, 82.0, 77.9, 66.8, 60.9, 59.4, 55.1, 52.9, 47.8, 47.5, 45.4, 42.7, 35.5, 35.3, 32.0, 24.5, 21.9.

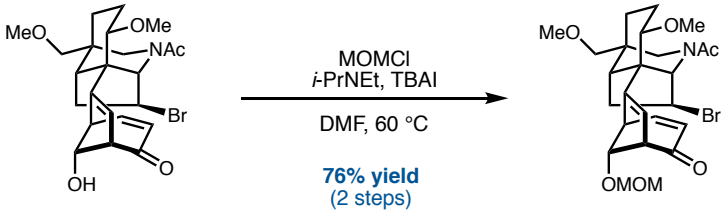
FTIR (NaCl, thin film): 3367, 2930, 2877, 2826, 2239, 1624, 1426, 1234, 1094, 917 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{23}H_{31}BrNO_5$ $[M + H]^+$ 480.1380, found 480.1367

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +169° (c = 0.50, $CHCl_3$).

TLC (100%EtOAc), R_f: 0.25 (UV, pink in *p*-anisaldehyde)

Preparation of methoxymethyl ether 230:



242 **230**

A 100 mL, round-bottom flask was charged with crude enone **242** (159 mg, 0.3308 mmol, 1.0 equiv.), TBAI (61 mg, 0.165 mmol, 0.50 mol %), and DMF (6.6 mL). *i*-Pr_2NEt (0.87 mL, 4.96 mmol, 15.0 equiv.) added followed by dropwise addition of MOMCl (0.25 mL, 3.31 mmol, 10 equiv.), causing a smokiness to evolve from the reaction. The flask was then lowered into a 60 °C oil bath, and let stir for 16 hours at this temperature. The reaction was then cooled to room temperature, diluted with sat. NH_4Cl (20 mL), transferred to a separatory funnel and extracted with EtOAc (4 x 20 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (10% to 20% to 30% to 40% acetone in hexanes) to afford methoxy methyl ether **230** (131 mg, 0.251 mmol, 76% yield over two steps) as a white foam.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.11 (ddd, *J* = 9.8, 6.4, 1.6 Hz, 1H), 5.95 (d, *J* = 4.0 Hz, 1H), 5.81 (ddd, *J* = 9.8, 1.9, 0.6 Hz, 1H), 4.92 (q, *J* = 4.5 Hz, 1H), 4.70 (s, 1H), 4.65 (s, 2H), 4.12 – 4.04 (m, 2H), 3.50 – 3.46 (m, 1H), 3.41 – 3.37 (m, 1H), 3.32 (s, 3H), 3.27 (s, 3H), 3.27 – 3.19 (m, 1H), 3.19 (s, 3H), 3.13 (d, *J* = 9.2 Hz, 1H), 3.03 (d, *J* = 9.2 Hz, 1H), 2.62 – 2.54 (m, 1H), 2.42 – 2.33 (m, 2H), 2.31 – 2.23 (m, 1H), 2.21 (s, 3H), 2.04 – 1.96 (m, 1H), 1.74 – 1.66 (m, 1H), 1.47 – 1.33 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 195.6, 168.9, 160.0 (br), 150.6, 125.4, 123.9, 96.1, 90.6, 82.0, 77.9, 66.7, 59.4, 59.3, 55.9, 55.1, 52.9, 47.6, 46.2, 45.5, 42.7, 35.4, 35.3, 31.9, 24.5, 21.9.

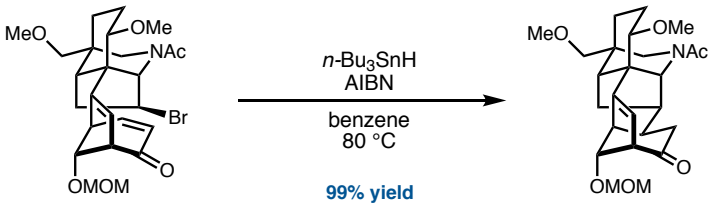
FTIR (NaCl, thin film): 3454, 3056, 2920, 2825, 2244, 1703, 1682, 1654, 1621, 1454, 1109, 1035, 918 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{25}H_{35}BrNO_6$ $[M + H]^+$ 524.1642, found 524.1689

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +179° (*c* = 0.50, $CHCl_3$).

TLC (100%EtOAc), R_f: 0.5 (UV, pink in *p*-anisaldehyde)

Preparation of hexacycle 231:



230 **231**

A 100 mL, round-bottom flask was charged with enone **230** (234 mg, 0.45 mmol, 1.0 equiv.) and dissolved in benzene (89 mL). The solution was degassed (freeze-pump-thaw with N_2, 3 cycles) and the headspace was purged with argon. Meanwhile, a solution of AIBN (36.6 mg, 0.22 mmol, 0.5 equiv.) and *n*-Bu_3SnH (0.72 mL, 2.68 mmol, 6.0 equiv.) in benzene (7 mL) was degassed in the same manor. The round-bottom flask containing the substrate was

then heated to 80 °C in an oil bath, and the AIBN/*n*-Bu_3SnH solution was added over 7 hours to the substrate solution via syringe pump. After the addition of the AIBN/*n*-Bu_3SnH solution was complete, the reaction was cooled to room temperature and concentrated *in vacuo*. The resulting crude residue was purified by chromatography with a 90% SiO_2/ 10% ground K_2CO_3 solid support[13] eluting (20% to 30% to 40% to 50% acetone in hexanes) to afford hexacycle **231** (205 mg, 0.45 mmol, 99% yield) as a clear oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.83 (d, *J* = 2.6 Hz, 1H), 4.68 – 4.64 (m, 2H), 4.48 (t, *J* = 5.6 Hz, 1H), 4.07 (s, 1H), 3.74 (d, *J* = 14.6 Hz, 1H), 3.58 (dd, *J* = 10.4, 7.2 Hz, 1H), 3.34 (s, 3H), 3.30 (s, 3H), 3.29 (s, 3H), 3.24 – 3.19 (m, 2H), 3.03 (d, *J* = 9.0 Hz, 1H), 2.91 (t, *J* = 5.7 Hz, 1H), 2.73 – 2.62 (m, 2H), 2.33 – 2.22 (m, 3H), 2.16 – 2.06 (m, 5H), 2.01 – 1.94 (m, 1H), 1.78 – 1.67 (m, 2H), 1.44 (dddd, *J* = 14.9, 13.2, 4.0, 1.7 Hz, 1H), 1.35 – 1.30 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 204.6, 169.8, 153.4, 121.4, 96.3, 80.0, 79.0, 78.2, 65.0, 59.7, 59.4, 55.9, 55.1, 51.5, 46.2, 45.4, 42.5, 42.2, 39.2, 37.7, 33.8, 31.9, 30.5, 24.7, 22.5.

2-dimensional NMR data is included below (HSQC, HMBC, COSY, NOESY).

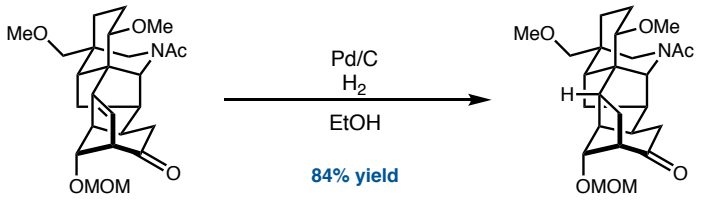
FTIR (NaCl, thin film): 2924, 2825, 1708, 1644, 1418, 1405, 1150, 1112, 1091, 1045, 1001, 919 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{25}H_{39}N_2O_6$ $[M + NH_4]^+$ 463.2803, found 463.2797

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +84.5° (*c* = 1.0, $CHCl_3$).

TLC (100%EtOAc), R_f: 0.3 (UV, brown in *p*-anisaldehyde)

Preparation of carbocycle 232:



231 **232**

A 50 mL, round-bottom flask was charged with alkene **231** (100 mg, 0.224 mmol), Pd/C (10% wt % palladium, contains 67% H_2O, 300 mg, 0.282 mmol, 1.25 equiv.), and EtOH (5 mL). The flask was then equipped with a rubber septum, and the suspension was sparged with an H_2 balloon for 10 minutes, then let stir under H_2 for an additional 20 minutes. The reaction was monitored by TLC and LCMS, indicating that the reaction had gone to completion. The reaction mixture was then sparged with an argon balloon for 20 minutes, then filtered through a plug of SiO_2 and celite that had been pre-packed with 5%MeOH/95% CH_2Cl_2, flushed with more 5%MeOH/95% CH_2Cl_2, and then concentrated *in vacuo*. The resulting crude residue was purified by silica gel chromatography (20% to 30% to 40% to 50% acetone in hexanes) to afford **232** (84 mg, 0.187 mmol, 84% yield) as a white foam.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 4.60 (s, 2H), 4.11 (t, *J* = 5.0 Hz, 1H), 3.99 (s, 1H), 3.86 (d, *J* = 14.4 Hz, 1H), 3.31 (s, 3H), 3.28 (s, 3H), 3.20 (m, 5H), 3.09 (dd, *J* = 10.4, 7.1 Hz, 1H), 2.98 (d, *J* = 9.1 Hz, 1H), 2.76 (dd, *J* = 7.8, 5.6 Hz, 1H), 2.70 (dd, *J* = 19.6, 11.4 Hz, 1H), 2.58 (d, *J* = 15.0 Hz, 1H), 2.56 – 2.47 (m, 1H), 2.44 – 2.37 (m, 1H), 2.37 – 2.29 (m, 1H), 2.06 (d, *J* = 8.2 Hz, 7H), 1.92 – 1.85 (m, 2H), 1.71 – 1.64 (m, 2H), 1.43 (tdd, *J* = 13.4, 4.4, 1.9 Hz, 1H), 1.33 – 1.25 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 212.9, 169.7, 96.0, 84.0, 79.7, 78.2, 59.4, 56.8, 55.8, 55.6, 52.3, 48.3, 46.8, 46.1, 44.5, 43.9, 39.1, 37.4, 36.6, 33.8, 32.0, 28.6, 27.3, 25.2, 22.5.

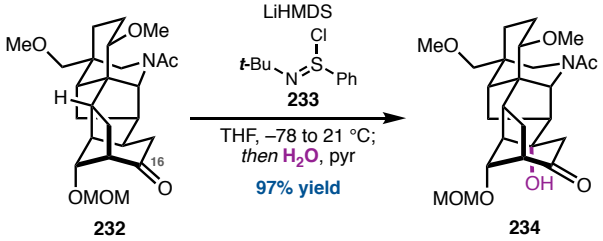
TLC (100%EtOAc), R_f: 0.3 (UV, yellow in *p*-anisaldehyde)

FTIR (NaCl, thin film): 2913, 2241, 1714, 1698, 1650, 1644, 1634, 1614, 1470, 1454, 1108, 1041, 919 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{25}H_{38}NO_6$ $[M + H]^+$ 448.2694, found 448.2687

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = –57.4° (*c* = 2.47, $CHCl_3$).

Preparation of β-hydroxy ketone 234:



A 50 mL round-bottom flask was charged with ketone **232** (50.0 mg, 0.11 mmol, 1.0 equiv.) and put under N_2. THF (4.5 mL) was added and the solution cooled to -78 °C. A solution of LiHMDS (1M in THF, 0.25 mL, 0.25 mmol, 2.2 equiv.) was added dropwise over 10 minutes. The mixture was stirred at -78 °C for 15 minutes before a solution of *N-tert*-butyl-phenylsulfinyl chloride (193 mg, 0.89 mmol, 8 equiv.) in THF (2.1 mL) was added dropwise over 5 minutes. The reaction was stirred at -78 °C for 15 minutes, then warmed to 21 °C and stirred 1 hour. Pyridine (0.05 mL) and water (1.7 mL) were added, and the mixture stirred at 21 °C for 16 hours. The reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL), and extracted with 3:1 $CHCl_3$:^{i}PrOH (5 x 10 mL). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated to give the crude product as a yellow oil. The reaction was purified by column chromatography (1-2-3-4-5-6-7% MeOH in CH_2Cl_2) to give *β*-hydroxy ketone **234** (50.0 mg, 0.11 mmol, 97% yield) as a white solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 4.69 – 4.64 (m, 2H), 4.27 (t, *J* = 5.1 Hz, 1H), 3.98 (s, 1H), 3.90 (d, *J* = 14.3 Hz, 1H), 3.35 (s, 3H), 3.31 (s, 3H), 3.25 – 3.10 (m, 6H), 3.03 (s, 1H),

2.88 (dd, *J* = 7.8, 5.2 Hz, 1H), 2.79 (d, *J* = 2.3 Hz, 1H), 2.63 (d, *J* = 13.9 Hz, 1H), 2.51 – 2.44 (m, 2H), 2.21 – 2.04 (m, 8H), 2.02 (d, *J* = 8.0 Hz, 1H), 1.92 (d, *J* = 7.5 Hz, 1H), 1.80 (dd, *J* = 15.1, 7.8 Hz, 1H), 1.71 (ddd, *J* = 13.6, 5.1, 2.8 Hz, 1H), 1.46 (tdd, *J* = 13.7, 4.7, 1.9 Hz, 1H), 1.34 – 1.26 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 210.4, 169.7, 96.3, 82.7, 80.5, 78.0, 73.4, 59.5, 58.5, 56.1, 55.5, 52.2, 51.7, 50.6, 48.3, 45.6, 45.3, 44.4, 44.3, 37.4, 31.9, 27.0, 25.3, 25.2, 22.5.

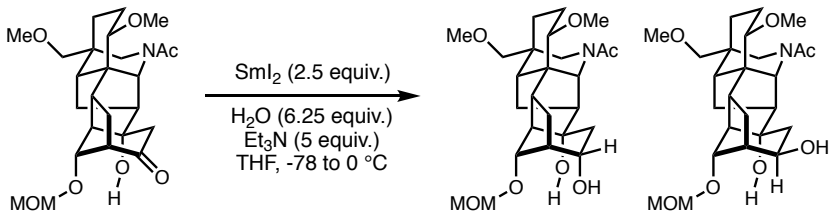
FTIR (NaCl, thin film): 3422, 2926, 2891, 2826, 2242, 1713, 1633, 1462, 1434, 1153, 1106, 1043, 920 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{25}H_{38}NO_7$ $[M + H]^+$ 464.2643, found 464.2646

$[\alpha]_D^{25}$ = –52.6° (*c* = 0.70, $CHCl_3$).

TLC (10%MeOH/90%CH_2Cl_2), R_f: 0.5 (UV, yellow in *p*-anisaldehyde)

SmI_2/NEt_3/H_2O Reduction of Ketone 234 to diols 235 and 236:[14]



234 **235** 29% yield **236** 58% yield

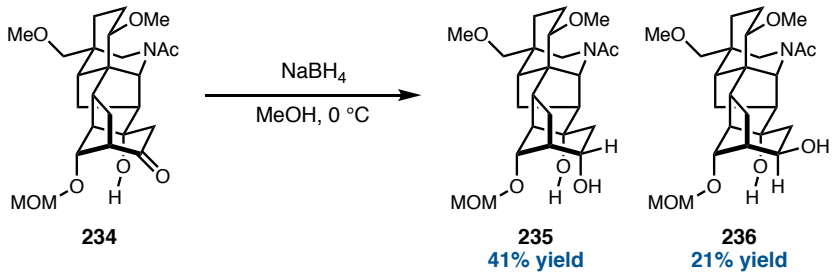
Preparation of SmI_2: 1,2-diiodoethane was purified prior to use as follows: 1,2-diiodoethane (1.6 g) was dissolved in Et_2O (50 mL) and washed with sat. aq. $Na_2S_2O_3$ (3 x 10 mL) and deionized water (2 x 10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 1.41 g of a white solid. A 100 mL Schlenk flask containing a stir bar was charged with freshly filed Sm metal (650 mg). The system was flame-dried under high vacuum then cooled to ambient temperature before adding freshly purified 1,2-diiodoethane (700 mg). The

atmosphere was exchanged three times for argon. Subsequently, the flask was charged with anhydrous THF (25 mL) that had been submitted to five freeze-pump-thaw cycles. Note: The THF used for the synthesis of SmI_2 must contain <50 ppm H_2O; THF containing greater quantities of water resulted in excessive induction times for the synthesis of SmI_2. The suspension was stirred for 2 min and the flask was cautiously and briefly (5 s) placed under partial high vacuum, then purged with argon. This process was repeated two additional times to remove ethylene gas formed from insertion of Sm metal into 1,2-diiodoethane. The resulting heterogeneous suspension was rapidly (930 rpm) stirred; after 5 min, the reaction turned dark green, and within 10 min, a dark blue color was observed. After stirring under argon for 3 h at 19 °C, the system was cautiously and briefly placed under high vacuum, then purged with argon. This process was repeated two additional times, then stirring was halted. The mixture was allowed to settle for 15 min prior to use.

A 5 mL round-bottom flask charged with ketone **234** (12.0 mg, 26 μmol, 1.0 equiv.) and put under argon. THF (1.2 mL) degassed by 3 freeze-pump-thaw cycles was added, and the mixture was cooled to -78 °C. In a separate flask, a stock solution of NEt_3 (0.20 mL, 1.4 mmol, 50 equiv.) and water (30 μL, 1.7 mmol, 65 equiv.) in THF (4.8 mL). 0.50 mL of the Et_3N/H_2O stock solution (5.0 equiv Et_3N, 6.5 equiv H_2O) was added to a third flask containing freshly prepared SmI_2 solution (~0.1 M in THF, 0.65 mL, 65 μmol, 2.5 equiv.). The $SmI_2/Et_3N/H_2O$ solution was added dropwise to the substrate, and the mixture stirred at -78 °C for 5 minutes before warming to 0 °C and stirring an additional 90 minutes. The reaction was quenched with saturated aqueous $NaHCO_3$ (3 mL). The mixture was extracted with 3:1 $CHCl_3$:^{i}PrOH (5 x 4 mL). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude residue was purified via column chromatography (SiO_2 2-3-

4-5-6% MeOH in CH_2Cl_2) to afford C16-equitorial diol **236** (7.0 mg, 15 µmol, 58% yield) and C16-axial diol **235** (3.5 mg, 7.5 µmol, 29% yield) as colorless oils.

$NaBH_4$ Reduction of Ketone 234 to diols 235 and 236:



234 **235** 41% yield **236** 21% yield

MeOH (5 mL) was added to a 25 mL round-bottom flask charged with ketone **234** (22 mg, 47 µmol, 1.0 equiv.) and the solution cooled to 0 °C. $NaBH_4$ (36 mg, 0.47 mmol, 10 equiv.) was added slowly in portions (granual by granual). After complete addition of the reductant, the reaction was stirred for an additional 30 minutes before quenching with 0.5 M NaOH (5 mL). The mixture was stirred for 30 minutes, then extracted with 3:1 $CHCl_3$:^{i}PrOH (5 x 10 mL). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude residue was purified via column chromatography (SiO_2 2-3-4-5-6% MeOH in CH_2Cl_2) to afford C16-axial diol **235** (9.0 mg, 19 µmol, 41% yield) and C16-equitorial diol **236** (4.6 mg, 9.9 µmol, 21% yield) as colorless oils.

Characterization of axial C16-alcohol 235:

^{1}H NMR (600 MHz, Chloroform-*d*) δ 4.75 (s, 2H), 4.12 (t, *J* = 5.0 Hz, 1H), 4.01 (s, 1H), 3.87 (d, *J* = 14.3 Hz, 1H), 3.72 (t, *J* = 9.7 Hz, 1H), 3.43 (s, 3H), 3.31 (s, 3H), 3.22 (s, 3H), 3.20 (d, *J* = 1.8 Hz, 1H), 3.20 – 3.05 (m, 2H), 3.00 (t, *J* = 4.6 Hz, 1H), 2.67 – 2.54 (m, 2H), 2.38 – 2.29 (m, 2H), 2.15 (s, 3H), 2.10 – 2.02 (m, 4H), 1.91 (d, *J* = 7.7 Hz, 1H), 1.88 – 1.79 (m, 3H), 1.74 – 1.64 (m, 2H), 1.43 (td, *J* = 14.2, 4.4 Hz, 1H), 1.38 – 1.24 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 970, 83.1, 81.8, 78.3, 72.9, 72.4, 59.6, 59.1, 56.20, 55.8, 53.2, 48.4, 45.6, 44.7, 44.0, 41.2, 37.6, 32.2, 27.6, 25.4, 22.7.

FTIR (NaCl, thin film): 3480, 3451, 2926, 2824, 2530, 2508, 2490, 2044, 1686, 1618, 1435, 1212, 1152, 1166, 1106, 1058, 1038, 913, 868, 825, 777, 755, 732, 685, 668 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{25}H_{39}NO_7Na$ $[M + Na]^+$ 488.2619, found 488.2603 diff.: 3.41 ppm.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{21}}$ = –57.5° (*c* = 0.21, $CHCl_3$).

TLC (6% MeOH/94% CH_2Cl_2), R_f: 0.5 (Blue in *p*-anisaldehyde)

Characterization of C16-equitorial alcohol 236:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.67 (d, *J* = 3.1 Hz, 2H), 4.45 (d, *J* = 4.7 Hz, 2H), 4.05 (dd, *J* = 6.0, 4.3 Hz, 1H), 3.79 (d, *J* = 14.4 Hz, 1H), 3.40 (s, 3H), 3.30 (s, 3H), 3.26 (s, 3H), 3.21 (d, *J* = 8.9 Hz, 1H), 3.15 (dd, *J* = 10.6, 7.0 Hz, 1H), 3.00 (d, *J* = 9.0 Hz, 1H), 2.68 (d, *J* = 14.3 Hz, 1H), 2.36 – 2.24 (m, 3H), 2.24 – 2.15 (m, 4H), 2.11 – 2.05 (m, 2H), 1.92 (d, *J* = 7.6 Hz, 1H), 1.89 – 1.76 (m, 3H), 1.72 – 1.63 (m, 3H), 1.44 – 1.38 (m, 1H), 1.32 – 1.29 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 96.1, 83.7, 80.5, 78.3, 75.3, 66.1, 59.7, 59.6, 56.1, 56.0, 52.4, 49.0, 45.4, 45.4, 44.9, 44.5, 41.9, 40.7, 37.8, 32.41, 29.9, 25.7, 25.0, 23.0, 22.6.

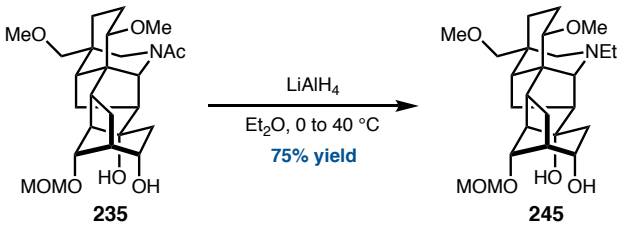
FTIR (NaCl, thin film): 3897, 3413, 2928, 1721, 1622, 1429, 1379, 1258, 1212, 1166, 1152, 1106, 1061, 1039, 996, 942, 918, 884, 798, 766, 748, 664 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{25}H_{39}NO_7Na$ $[M + Na]^+$ 488.2619, found 488.2612 diff.: 1.85 ppm

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{21}}$ = –19.4° (*c* = 0.17, $CHCl_3$).

TLC (6% MeOH/94% CH_2Cl_2), R_f: 0.5 (Blue in *p*-anisaldehyde)

Preparation of amine 245 from amide 235:

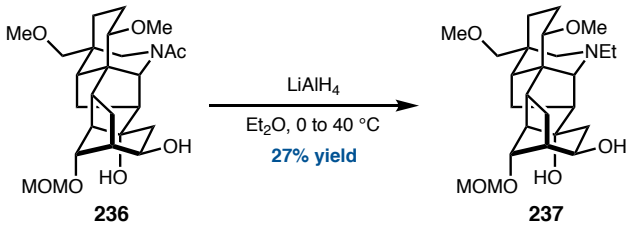


235 **245**

A 1-dram vial charged with amide **235** (4.0 mg, 8.6 µmol, 1.0 equiv.) and Et_2O (1 mL) was cooled to 0 °C. A solution of $LiAlH_4$ (1 M in THF, 0.04 mL, 40 µmol, 5 equiv.) was added dropwise. The reaction was heated to 40 °C and stirred for 4 hours. The reaction was cooled to 0 °C before quenching with 0.5 M NaOH (1 mL). The mixture was extracted with 3:1 $CHCl_3$:^{i}PrOH (4 x 2 mL). The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude mixture was purified by column chromatography (SiO_2, 1-2-3-4-5% 7N NH_3 in MeOH/CH_2Cl_2) to afford **245** as a colorless oil (3.0 mg, 6.6 µmol, 77% yield).

Characterization below.

Preparation of amine 237 from amide 236:



236 **237**

A 1-dram vial charged with amide **236** (5.0 mg, 11 µmol, 1.0 equiv.) and Et_2O (1 mL) was cooled to 0 °C. A solution of $LiAlH_4$ (1 M in THF, 0.06 mL, 60 µmol, 5.5 equiv.) was added dropwise. The reaction was heated to 40 °C and stirred for 4 hours. The reaction was cooled to 0 °C before quenching with 0.5 M NaOH (1 mL). The mixture was extracted with

3:1 $CHCl_3$:^{i}PrOH (4 x 2 mL). The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude mixture was purified by column chromatography (SiO_2, 1-2-3-4-5% 7N NH_3 in MeOH/CH_2Cl_2) to afford amine **237** as a colorless oil (1.3 mg, 2.8 μmol, 27% yield).

^{1}H NMR (600 MHz, Benzene-d_6) δ 4.41 – 4.29 (m, 3H), 3.87 (t, *J* = 5.3 Hz, 1H), 3.74 (s, 1H), 3.22 (s, 1H), 3.13 (s, 3H), 3.12 – 3.10 (m, 6H), 3.09 – 3.03 (m, 1H), 2.99 – 2.92 (m, 2H), 2.81 (d, *J* = 8.6 Hz, 1H), 2.56 – 2.43 (m, 4H), 2.35 – 2.26 (m, 3H), 2.20 – 2.12 (m, 2H), 2.10 – 2.01 (m, 3H), 1.99 – 1.95 (m, 1H), 1.92 – 1.87 (m, 1H), 1.62 (d, *J* = 7.4 Hz, 1H), 1.53 – 1.49 (m, 2H), 1.41 – 1.32 (m, 2H), 1.05 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, C_6D_6) δ 95.8, 86.2, 81.0, 79.6, 75.7, 66.3, 63.4, 59.1, 55.8, 55.4, 53.8, 49.7, 46.4, 46.1, 45.8, 45.6, 42.7, 41.2, 39.1, 33.4, 30.2, 26.2, 25.8, 23.8, 13.9.

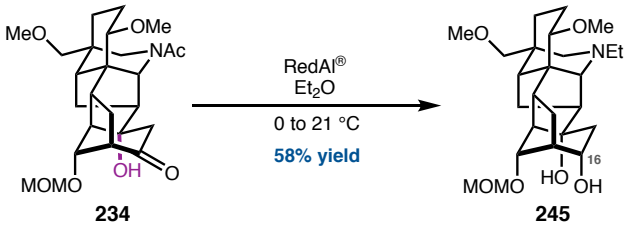
FTIR (NaCl, thin film): 3420, 2924, 2820, 1719, 1453, 1388, 1290, 1260, 1203, 1170, 1150, 1110, 1040, 966, 919, 804, 753, 724, 657 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{25}H_{42}NO_6$ $[M+H]^+$ 452.3003, found: 452.3007 diff: 0.92 ppm

$[\alpha]_D^{21}$ = –9.3° (*c* = 0.18, $CHCl_3$).

TLC (6% MeOH/94% CH_2Cl_2), R_f: 0.2 ($KMnO_4$)

Preparation of diol 245:



β-hydroxy ketone **234** (13 mg, 28 μmol, 1 equiv.) was dissolved in Et_2O (1.5 mL) under N_2 and cooled to 0 °C. A solution of RedAl in toluene (>46%, ~3M, 0.16 mL, 0.48 mmol, 17 equiv.) was added dropwise over 10 minutes. The reaction was stirred at 0 °C for 30 min. before warming to room temp and stirring an additional 2h. The solution was cooled to 0 °C and quenched with 0.5 M NaOH (aq., 2 mL) and stirred for 15 minutes. The mixture was extracted with 3:1 $CHCl_3$:^{i}PrOH (5 x 3 mL). The combined organic phase was dried (Na_2SO_4), filtered and concentrated. The crude was purified by column chromatography (1-6% 7N NH_3 in MeOH/CH_2Cl_2) to give **245** (7.3 mg, 16 μmol, 58%) as a thin film.

^{1}H NMR (600 MHz, C_6D_6): δ 4.33 (s, 2H), 3.91 (t, *J* = 5.0 Hz, 1H), 3.79 (t, *J* = 9.2 Hz, 1H), 3.21 (s, 1H), 3.18 (d, *J* = 10.2 Hz, 1H), 3.11 (s, 3H), 3.07 (s, 3H), 3.07 (s, 3H), 2.97 (d, *J* = 8.8 Hz, 1H), 2.87 (dd, *J* = 10.6, 6.6 Hz, 1H), 2.80 (m, 2H), 2.68 (dd, *J* = 16.9, 9.2 Hz, 1H), 2.51 (d, *J* = 11.4 Hz, 1H), 2.36-2.48 (m, 2H), 2.18-2.30 (m, 5H), 2.06-2.10 (m, 2H), 1.94-1.98 (m, 2H), 1.88 (ddd, *J* = 13.4, 5.0, 2.6 Hz, 1H), 1.48-1.63 (m, 4H), 1.34 (dt, *J* = 11.4, 6.7 Hz, 1H), 1.03 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, C_6D_6): δ 96.2, 85.8, 81.4, 79.7, 73.2, 72.7, 62.5, 59.2, 55.7, 55.5, 53.8, 49.5, 49.0, 46.7, 46.2, 46.0, 45.6, 44.9, 41.5, 38.9, 33.3, 28.6, 26.6, 25.5, 13.8.

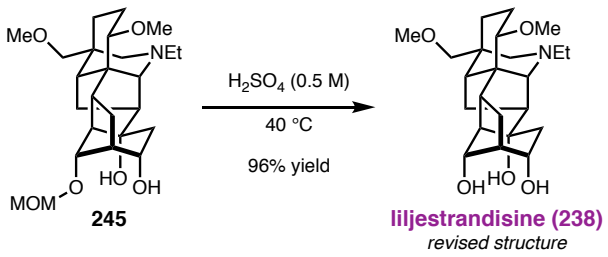
FTIR (NaCl, thin film): cm^{-1}. 3434, 2928, 2822, 1461, 1448, 1375, 1201, 1148, 1110, 1052, 922, 754, 640.

HRMS: calc'd for $C_{25}H_{42}NO_6$ $[M + H]^+$: 452.3003 found: 452.3023 diff: 0.94 ppm

$[\alpha]_D^{21}$ = -20.1 (*c* = 0.52, $CHCl_3$)

TLC (6% 7N NH_3 in MeOH/90%CH_2Cl_2), R_f: 0.5 ($KMnO_4$)

Preparation of (–)-liljestrandisine (238):



A 1-dram vial was charged with diol **245** (2.5 mg, 5.6 μmol, 1.0 equiv.) and 0.5 M H_2SO_4 (aq., 1 mL). The solution was heated to 40 °C for 4 hours before quenching with 0.5 M NaOH (1.5 mL) and saturated aqueous $NaHCO_3$ (2 mL). The mixture was extracted with 3:1$CHCl_3$:^{i}PrOH (5 x 3 mL). The combined organic phases were dried (Na_2SO_4), filtered and concentrated. The product was purified on column chromatography (SiO_2, 1-2-3-4-5-6% 7N NH_3 in MeOH/CH_2Cl_2) to give (–)-liljestrandisine (**238**) (2.2 mg, 5.4 μmol. 96%) as a thin film.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 4.25 (t, *J* = 5.3 Hz, 1H), 4.16 (br, 1H), 3.87 (d, *J* = 8.7 Hz, 1H), 3.30 (s, 3H), 3.26 (s, 3H), 3.20 (br, 1H), 3.18 (s, 1H), 3.11 (ABq, *J* = 9.0 Hz, 1H), 3.07 (dd, *J* = 10.8, 6.5 Hz, 1H), 2.99 (ABq, *J* = 9.0 Hz, 1H), 2.89 (br, 1H), 2.64 (dd, *J* = 17.4, 8.9 Hz, 1H), 2.56 – 2.47 (m, 2H), 2.45 – 2.33 (m, 1H), 2.32 – 2.19 (m, 3H), 2.08 (d, *J* = 7.8 Hz, 1H), 2.05 – 1.86 (m, 4H), 1.83 (dd, *J* = 10.3, 5.5 Hz, 2H), 1.80 – 1.74 (m, 1H), 1.74 – 1.69 (m, 1H), 1.66 (d, *J* = 7.4 Hz, 1H), 1.49 (dd, *J* = 14.9, 7.9 Hz, 1H), 1.45 – 1.35 (m, 1H), 1.06 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 86.2, 79.4, 76.1, 73.6, 72.6, 63.1, 59.5, 56.3, 53.1, 49.55, 48.6, 46.57, 46.47, 46.08, 45.7, 42.5, 40.9, 38.7, 32.8, 27.9, 25.8, 24.6, 13.7.

FTIR (NaCl, thin film): 3330, 2923, 2883, 2814, 1455, 1094 cm^{-1}.

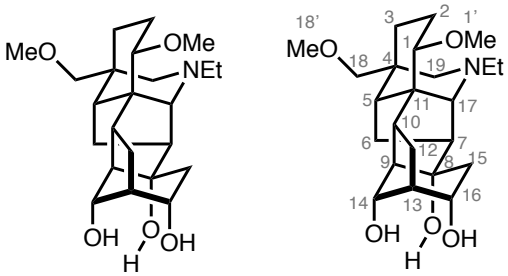
HRMS: (ESI-TOF) calc'd for $C_{23}H_{38}NO_5$ $[M + H]^+$ 408.2744, found 408.2736

$[\alpha]_D^{25}$ = –9.5° (*c* = 0.15, $CHCl_3$).

TLC (10%7N NH_3 in MeOH/90%CH_2Cl_2), R_f: 0.5 (ninhydrin)

^{1}H and ^{13}C line list comparison tables are shown below with natural liljestrandisine.[10]

The following carbon numbering system is used in the line list comparisons:



(–)-liljestrandisine (238)
revised

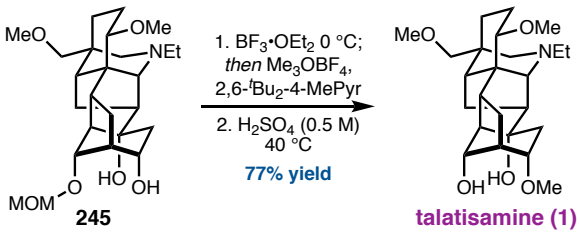
	authentic liljestrandisine Wang, 2004 (*ref.* 10) (400 MHz, $CHCl_3$) $[\alpha]_D$=–12 ° (c =0.5, $CHCl_3$)	synthetic liljestrandisine this report (600 MHz, $CHCl_3$) $[\alpha]_D$=–9.5 ° (c =0.15, $CHCl_3$)
Carbon #, multiplicity	^{1}H (δ) ppm	^{1}H (δ) ppm
1 d	3.07, dd(10.4, 6.4)	3.07 (dd (10.8, 6.5), 1H)
2 t	1.98, m; 2.19, m	1.96 (m, 4H); 2.25 (m, 3H)
3 t	1.38, dd(11.6); 1.74, m	1.39 (m, 1H); 1.77 (m, 1H)
4 s	–	–
5 d	1.64, d(7.2)	1.66 (d (7.4), 1H)
6 t	1.47, dd(14.4, 7.6; 1.89, d(7.6)	1.49 (dd (14.9, 7.9), 1H); 1.96 (m, 4H)
7 d	2.07, d(8.0)	2.08 (d (7.8), 1H)
8 s	–	–
9 d	2.25, m	2.25 (m, 3H)
10 d	1.70, m	1.71 (m, 1H)
11 s	–	–
12 t	1.78, m; 1.78, m	1.83 (m, 2H); 1.83 (m, 2H)
13 d	2.23, m	2.25 (m, 3H)
14 d	4.22, t(5.0)	4.25 (t (5.3), 1H)
15 t	1.95, m; 2.58, m	1.96 (m, 4H); 2.64 (dd (17.4, 8.9), 1H)
16 d	3.82, d(8.0)	3.87 (t (8.7), 1H)
17 d	3.18, s	3.18 (s, 1H)
18 t	2.99, ABq(9.2); 3.11, ABq(8.4)	2.99, ABq (9.0), 1H; 3.11, ABq(9.0), 1H
19 t	2.02, d(11.6); 2.51, m	1.96 (m, 4H); 2.52 (m, 2H)
N CH2	2.39, m; 2.56, m	2.38 (m, 1H); 2.52 (m, 2H)
NCH2CH3	1.05, t(7.2)	1.06 (t (7.1), 3H)
1’	3.26 s	3.26 (s, 3H)
18’	3.29 s	3.30 (s, 3H)
8-OH	—	2.89 (br, 1H)
14-OH	—	4.25 (br, 1H)
16-OH	—	3.20 (br, 1H)

Table 4.4 *Comparison of ^{1}H NMR data for Authentic (ref. 10) vs. Synthetic (–)-liljestrandisine.*

	authentic liljestrandisine Wang, 2004 (*ref.* 10) (100 MHz, $CHCl_3$) $[\alpha]_D$=–12 ° (c =0.5, $CHCl_3$)	synthetic liljestrandisine this report (151 MHz, $CHCl_3$) $[\alpha]_D$=–9.5 ° (c =0.15, $CHCl_3$)	chemical shift difference
Carbon #, multiplicity	^{13}C (δ) ppm	^{13}C (δ) ppm	^{13}C (Δδ) ppm
1 d	86.2	86.2	0
2 t	25.7	25.8	+0.1
3 t	32.7	32.8	+0.1
4 s	38.7	38.7	0
5 d	46.0	46.1	0
6 t	24.6	24.6	0
7 d	46.4	46.47	+0.1
8 s	73.6	73.6	0
9 d	46.5	46.57	+0.1
10 d	45.8	45.7	-0.1
11 s	48.7	48.6	-0.1
12 t	27.9	27.9	0
13 d	40.8	40.9	+0.1
14 d	75.8	76.0	+0.2
15 t	42.3	42.5	+0.2
16 d	72.5	72.6	+0.1
17 d	63.0	63.2	+0.2
18 t	79.4	79.4	0
19 t	53.2	53.1	-0.1
N CH2	49.5	49.5	0
NCH2CH3	13.6	13.7	+0.1
1’	56.2	56.3	+0.1
18’	59.5	59.5	0

Table 4.5 *Comparison of ^{13}C NMR data for Authentic (ref. 10) vs. Synthetic (–)-liljestrandisine.*

Preparation of (–)-talatisamine (1):



A stock solution of BF_3•OEt_2 (12 μL/mL) in CH_2Cl_2 was prepared by 10x dilution of a solution of BF_3•OEt_2 (0.12 mL) in CH_2Cl_2 (0.88 mL).

A 1-dram vial was charged with diol **245** (4.2 mg, 9.3 μmol, 1.0 equiv.) and CH_2Cl_2 (2.1 mL). The mixture was cooled to 0 °C before 0.10 mL of a stock solution of BF_3•OEt_2 (12 μL/mL, 0.10 mL ,1.2 μL, 9.3 μmol, 1.0 equiv.) was added dropwise. The mixture was warmed to 20 °C before 2,6-di-*tert*-butyl-4-methylpyridine (7.6 mg, 37 μmol, 4.0 equiv.) was added, followed by Me_3OBF_4 (5.5 mg, 37 μmol, 4.0 equiv.). The mixture was stirred (750 rpm) for 2 hours before quenching with saturated aqueous $NaHCO_3$ (1 mL). The mixture was extracted with 3:1 $CHCl_3$:^{i}PrOH (8 x 2 mL) and the combined extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was carried onto the next step without purification.

A 1-dram vial was charged with the crude methylation product and 0.5 M H_2SO_4 (1 mL). The reaction was heated to 40 °C for 5 hours. The reaction was transferred to a 20 mL vial and quenched with saturated aqueous $NaHCO_3$ (10 mL). The mixture was extracted with 3:1 $CHCl_3$:^{i}PrOH (8 x 2 mL) and the combined extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The product was purified by column chromatography (SiO_2, 0.25-0.5-1-2% 7N NH_3 in MeOH/CH_2Cl_2) to give (–)-talatisamine (**1**) (3.0 mg, 7.2 mmol, 77% yield, 2 steps) as a colorless oil.

^{1}H NMR (600 MHz, Benzene-d_6) δ 4.82 (d, *J* = 4.1 Hz, 1H), 4.15 (dd, *J* = 9.7, 5.1 Hz, 1H), 3.99 (s, 1H), 3.26 (s, 1H), 3.12 (s, 3H), 3.08 (s, 3H), 3.06 – 3.02 (m, 1H), 2.94 (d, *J* = 8.8 Hz, 1H), 2.89 – 2.86 (m, 1H), 2.87 – 2.84 (m, 4H), 2.84 (d, *J* = 8.8 Hz, 1H), 2.56 (d, *J* = 11.3 Hz, 1H), 2.50 – 2.41 (m, 2H), 2.38 (dd, *J* = 17.2, 8.7 Hz, 1H), 2.35 – 2.29 (m, 2H), 2.27 (d, *J* = 7.8 Hz, 1H), 2.23 (d, *J* = 17.4 Hz, 1H), 2.21 – 2.12 (m, 2H), 2.04 (dd, *J* = 11.3, 2.4 Hz, 1H), 1.99 – 1.90 (m, 2H), 1.85 (dd, *J* = 15.5, 7.6 Hz, 1H), 1.65 – 1.57 (m, 1H), 1.55 (d, *J* = 7.5 Hz, 1H), 1.53 – 1.43 (m, 2H), 1.37 (ddd, *J* = 11.2, 7.6, 6.0 Hz, 1H), 1.06 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, C_6D_6) δ 86.1, 82.7, 79.8, 76.0, 72.8, 62.8, 59.2, 56.1, 55.7, 53.9, 49.7, 49.0, 47.6, 46.3, 46.2, 39.1, 38.5, 33.2, 28.1, 26.3, 25.6, 13.9.

FTIR (NaCl, thin film): 3436, 2926, 2814, 1670, 1495, 1456, 1412, 1392, 1204, 1160, 1091, 770, 751, 682, 666, 650, 624, 614 cm^{-1}

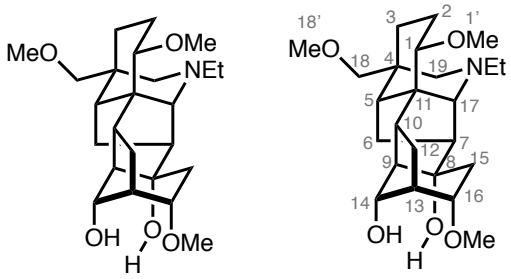
HRMS: (ESI-TOF) calc'd for $C_{24}H_{40}NO_5$ $[M + H]^+$: 422.2905 found: 422.2894 diff: 2.49 ppm

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{21}}$ = -3.2 (*c* = 0.23, $CHCl_3$)

TLC (8% 7N NH_3 MeOH/92%CH_2Cl_2), R_f: 0.3 ($KMnO_4$)

^{1}H and ^{13}C line list comparison tables are shown below with natural talatisamine.[15,16]

The following carbon numbering system is used in the line list comparisons:



(–)-talatisamine (1)

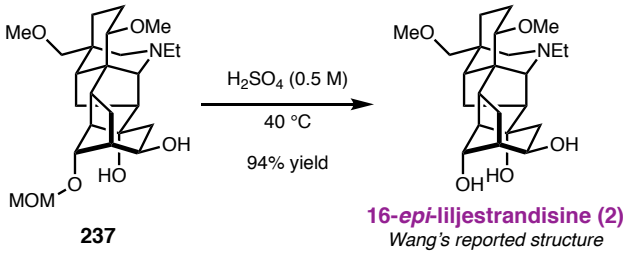
	authentic talatisamine Inoue, 2020 (*ref.* 15) (500 MHz, $CHCl_3$) $[\alpha]_D$=0 ° (c =0.6, $CHCl_3$) (*ref.* 16)	synthetic talatisamine this report (600 MHz, C_6D_6) $[\alpha]_D$=–3.2 ° (c =0.23, $CHCl_3$)
Carbon #, multiplicity	^{1}H (δ) ppm	^{1}H (δ) ppm
1 d	2.83-2.88 (m, 2H)	2.83-2.88 (m, 2H)
2 t	1.92-1.98 (m, 2H)	1.90-1.99 (m, 2H); 2.41-2.50 (m, 2H)
3 t	1.43-1.62 (m, 4H); 1.92-1.98 (m, 2H)	1.43-1.53 (m, 2H); 1.90-1.99 (m, 2H)
4 s	–	-
5 d	1.43-1.62 (m, 4H)	1.55 (d(7.5), 1H)
6 t	1.43-1.62 (m, 4H); 2.15-2.22 (m, 3H)	1.43-1.53 (m, 2H); 2.12-2.21 (m, 2H)
7 d	2.25-2.38 (m, 3H)	2.27 (d(7.8), 1H)
8 s	–	-
9 d	2.25-2.38 (m, 3H)	2.27-2.35 (m, 2H)
10 d	1.37 (ddd (9.8, 7.5, 7.3), 1H)	1.37 (ddd(11.2, 7.6, 6.0), 1H)
11 s	–	-
12 t	1.43-1.62 (m, 4H), 1.85 (dd (15.5, 7.5), 1H)	1.57-1.65 (m, 1H); 1.85 (dd(15.5, 7.6), 1H)
13 d	2.15-2.22 (m, 3H)	2.12-2.21 (m, 2H)
14 d	4.15 (dd (5.5, 7.5), 1H)	4.15 (dd(9.7, 5.1), 1H)
15 t	2.15-2.22 (m, 3H), 2.40-2.49 (m, 3H)	2.23 (d(17.4), 1H); 2.38 (dd (8.7, 17.2), 1H)
16 d	3.04 (d (9.2), 1H)	3.02-3.06 (m, 1H)
17 d	3.26 (s, 1H)	3.26 (s, 1H)
18 t	2.83-2.88 (m, 2H); 2.94 (d(8.6), 1H)	2.83-2.88 (m, 2H); 2.94 (d(8.8), 1H)
19 t	2.03 (dd (11.5, 2.3), 1H); 2.56 (d (11.5), 1H)	2.04 (dd(11.3, 2.4), 1H); 2.56 (d(11.3), 1H)
N CH2	2.25-2.38 (m, 3H); 2.40-2.49 (m, 3H)	2.27-2.35 (m, 2H); 2.41-2.50 (m, 2H)
NCH2CH3	1.06 (dd(7.5, 7.5), 3H)	1.06 (t(7.2), 3H)
1’	3.08 (s, 3H)	3.08 (s, 3H)
16’	2.85 (s, 3H)	2.85 (s, 3H)
18’	3.11 (s, 3H)	3.12 (s, 3H)
8-O*H*	4.01 (s, 1H)	3.99 (s, 1H)
14-O*H*	4.84 (d(4.0), 1H)	4.82 (d(4.1), 1H)

Table 4.6 *Comparison of ^{1}H NMR data for Authentic (ref. 15) vs. Synthetic (–)-talatisamine.*[15]

	authentic talatisamine Inoue, 2020 (*ref.* 15) (125 MHz, C_6D_6) $[\alpha]_D$=0 ° (c =0.6, $CHCl_3$) (*ref.* 16)	synthetic talatisamine this report (151 MHz, C_6D_6) $[\alpha]_D$=–3.2 ° (c =0.23, $CHCl_3$)	chemical shift difference
Carbon #, multiplicity	^{13}C (δ) ppm	^{13}C (δ) ppm	^{13}C (Δδ) ppm
1 d	86.1	86.2	+0.1
2 t	26.3	26.4	+0.1
3 t	33.2	33.3	+0.1
4 s	38.99/39.03	39.05/39.10	0
5 d	46.16/46.18/46.27	46.23/46.26/46.33	+0.1
6 t	25.5	25.6	+0.1
7 d	46.16/46.18/46.27	46.23/46.26/46.33	+0.1
8 s	72.8	72.8	0
9 d	47.6	47.6	0
10 d	46.16/46.18/46.27	46.23/46.26/46.33	+0.1
11 s	48.9	49.0	+0.1
12 t	28.0	28.1	+0.1
13 d	38.4	38.5	+0.1
14 d	75.9	76.0	+0.1
15 t	38.99/39.03	39.05/39.10	0
16 d	82.7	82.8	+0.1
17 d	62.8	62.8	0
18 t	79.7	79.8	+0.1
19 t	53.8	53.9	+0.1
N CH2	49.6	49.7	+0.1
NCH2CH3	13.9	13.9	0
1’	55.7	55.7	0
16’	56.0	56.1	+0.1
18’	59.1	59.2	+0.1

Table 4.7 *Comparison of ^{13}C NMR data for Authentic (ref. 15) vs. Synthetic (–)-talatisamine.*

Preparation of Wang's reported structure of (–)-liljestrandisine (16-*epi*-liljestrandisine, 2):



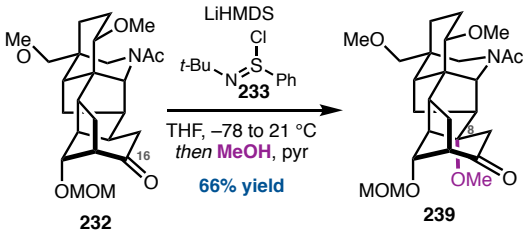
0.5 M H_2SO_4 (1 mL) was added to a 1-dram vial charged with diol **237** (2.0 mg, 4.4 µmol, 1.0 equiv.) and the mixture was heated to 40 °C for 16 hours. The reaction was cooled to 0 °C and quenched with 1 M NaOH (1.5 mL) and sat. $NaHCO_3$ (2 mL). The mixture was extracted with 3:1 $CHCl_3$:^{i}PrOH (8 x 5 mL). The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The product was purified by silica gel chromatography (1-2-3-4-5-6-7 % 7N NH_3 in MeOH/CH_2Cl_2) to give **2** (1.7 mg, 4.1 µmol, 91% yield) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 4.62 – 4.49 (m, 1H), 4.16 (s, 1H), 3.54 (s, 1H), 3.30 (s, 6H), 3.11 (d, *J* = 8.9 Hz, 1H), 2.98 (d, *J* = 9.1 Hz, 1H), 2.53 (d, *J* = 11.3 Hz, 2H), 2.45 – 2.34 (m, 2H), 2.23 (dd, *J* = 14.9, 7.2 Hz, 2H), 2.20 – 2.12 (m, 2H), 2.12 – 2.01 (m, 3H), 1.97 (br, 1H), 1.90 (dd, *J* = 15.8, 8.5 Hz, 2H), 1.77 (d, *J* = 13.3 Hz, 1H), 1.71 – 1.59 (m, 3H), 1.49 (dd, *J* = 14.7, 7.6 Hz, 1H), 1.38 (t, *J* = 14.8 Hz, 2H), 1.06 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 86.29, 79.31, 76.01, 66.20, 63.69, 59.50, 56.41, 53.14, 49.62, 49.39, 46.42, 46.30, 45.82, 45.56, 42.83, 41.50, 38.72, 32.79, 29.69, 25.61, 24.95, 23.60, 13.69.

TLC (10% 7N NH_3 MeOH/92%CH_2Cl_2), R_f: 0.3 ($KMnO_4$)

Preparation of β-methoxy ketone 239:



Ketone **232** (11.2 mg, 25 μmol, 1 equiv.) was dried by azeotroping with PhMe (3 x 5 mL) in a 2 dram vial. The vial was put under N_2, THF (1.0 mL) was added, and the mixture was cooled to – 78 °C. A solution of LiHMDS (1M in THF, 0.06 mL, 60 μmol, 2.2 equiv.) was added dropwise over 1 minute. The mixture was stirred at -78 °C for 15 minutes before a solution of *N*-tert-butyl-phenylsulfinyl chloride (43.2 mg. 0.20 mmol, 8.0 equiv.) in THF (0.50 mL) was added dropwise over 5 minutes. The reaction was stirred at -78 °C for 15 minutes, then warmed to 21 °C and stirred an additional 1 hour. Pyridine (0.05 mL) was added, followed by freshly-distilled MeOH (0.25 mL) and the mixture was stirred for 60 hours. The reaction was quenched with sat. aq. $NaHCO_3$ (2 mL). The mixture was extracted with 3:1 $CHCl_3$:^{i}PrOH (5 x 2 mL). The combined extracts were dried (Na_2SO_4), filtered and concentrated. The reaction was purified by column chromatography (SiO_2, 1-2-3-4-5-6-7% MeOH/CH_2Cl_2) to give β-methoxy ketone **239** (7.9 mg, 17 μmol, 66% yield) and β-hydroxy ketone **234** (3.5 mg, 7.5 μmol, 30% yield)

^{1}H NMR (400 MHz, Chloroform-*d*): δ 4.77 (d, *J* = 6.8 Hz, 1H), 4.57 (d, *J* = 6.8 Hz, 1H), 4.13 (t, *J* = 4.8 Hz, 1H), 3.91 (d, *J* = 14.4 Hz, 1H), 3.74 (s, 1H), 3.33 (s, 3H), 3.30 (s, 3H), 3.22 – 3.18 (m, 4H), 3.14 (dd, *J* = 9.8, 7.2 Hz, 1H), 3.10 (s, 3H), 3.05 – 2.96 (m, 2H), 2.78 (dd, *J* = 7.6, 4.3 Hz, 1H), 2.61 – 2.50 (m, 2H), 2.44 (t, *J* = 5.7 Hz, 1H), 2.39 (d, *J* = 18.3 Hz, 1H), 2.25

(d, J = 7.8 Hz, 1H), 2.10 – 2.02 (m, 7H), 1.88 (d, J = 7.4 Hz, 1H), 1.72 – 1.64 (m, 2H), 1.45 (tdd, J = 13.2, 4.5, 1.7 Hz, 1H), 1.37 – 1.26 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 211.3, 169.7, 95.8, 82.5, 78.2, 77.7, 76.8, 59.5, 58.3, 55.7, 55.5, 52.3, 48.7 (2 overlapping peaks), 47.6, 45.4, 45.3, 44.2, 44.1, 42.7, 37.4, 31.6, 26.8, 25.4, 24.0, 22.4.

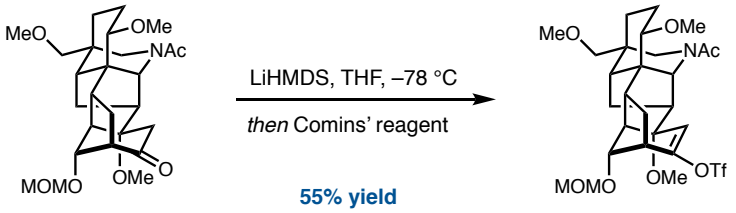
FTIR (NaCl, thin film): 2930, 2890, 2825, 1710, 1639, 1430, 1151, 1114, 1092, 1048 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{26}H_{40}NO_7$ $[M + H]^+$ 478.2799, found 478.2790

$[\alpha]_D^{25}$ = –120° (c = 1.5, $CHCl_3$).

TLC (5%MeOH/95%CH_2Cl_2), R_f: 0.5 (UV, yellow in *p*-anisaldehyde)

Preparation of enol triflate 247:



239 **247**

A 50 mL, round-bottom flask was charged with ketone **239** (20 mg, 42 μmol, 1 equiv.), and azeotroped with PhMe (from the solvent system, 2 x 3 mL) to remove H_2O and put under high vacuum for two hours. The flask was then equipped with a rubber septum, purged with N_2, dissolved in THF (2 mL), and cooled to –78 °C in a dry ice/acetone bath. LiHMDS (1M in THF, 84 μL, 84 μmol, 2 equiv.) was added dropwise via syringe, causing the solution to turn yellow. The LiHMDS/**239** solution was allowed to stir for 30 minutes at –78 °C, and then Comins' reagent (36.9 mg, 94 μmol, 2.25 equiv.) solution in THF (1 mL) was added dropwise via syringe. This was allowed to stir for an additional 5 minutes at –78 °C, the bath was then removed, and this was allowed to stir for 20 minutes at room temperature. The reaction was

quenched with 0.5 M NaOH (5 mL), and the biphasic mixture was transferred to a separatory funnel with EtOAc (10 mL). The layers were separated, and the aqueous layer was extracted EtOAc (4 x 10 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was purified by preparative thin layer silica gel chromatography (mobile phase: 100% ethyl acetate) to afford enol triflate **247** (14 mg, 23 μmol, 55% yield) as a clear oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.85 (t, *J* = 1.6 Hz, 1H), 4.71 (d, *J* = 6.9 Hz, 1H), 4.60 (d, *J* = 6.9 Hz, 1H), 3.93 – 3.85 (m, 3H), 3.36 (s, 3H), 3.30 (s, 3H), 3.21 (s, 3H), 3.19 – 3.17 (m, 4H), 3.14 – 3.10 (m, 1H), 3.02 (d, *J* = 9.1 Hz, 1H), 2.86 (dd, *J* = 14.2, 5.3 Hz, 1H), 2.72 – 2.64 (m, 1H), 2.61 (d, *J* = 14.4 Hz, 1H), 2.34 (t, *J* = 5.5 Hz, 1H), 2.27 (d, *J* = 7.8 Hz, 1H), 2.09 – 2.03 (m, 6H), 1.96 – 1.90 (m, 1H), 1.83 (d, *J* = 7.4 Hz, 1H), 1.76 – 1.68 (m, 2H), 1.43 (tdd, *J* = 13.2, 4.5, 1.8 Hz, 1H), 1.33 – 1.27 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.5, 153.9,114.2, 96.0, 82.6, 78.4, 78.2, 77.2, 59.5, 59.1, 55.6, 55.5, 49.4, 48.0, 45.2, 45.1, 44.3, 43.9, 42.8, 42.6, 37.4, 32.0, 30.7, 25.4, 23.7, 22.5. (Note: triflate carbon was not observed).

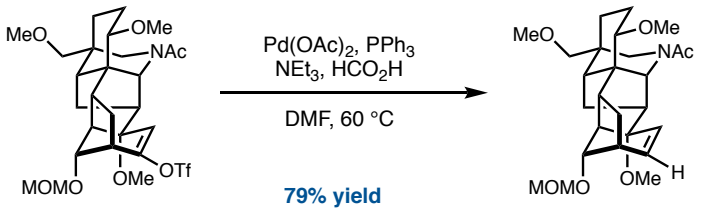
FTIR (NaCl, thin film): 2938, 2829, 1636, 1418, 1210, 1142, 1094 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{27}H_{39}NF_3O_9S$ $[M + H]^+$ 610.2292, found 610.2281

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = –37.7° (*c* = 0.50, $CHCl_3$).

TLC (100%EtOAc), R_f: 0.4 (yellow in *p*-anisaldehyde)

Preparation of alkene 240:



247 **240**

A 50 mL, round-bottom flask was charged with enol triflate **247** (10 mg, 16.4 μmol, 1.0 equiv.), PPh_3 (3.4 mg, 12.96 μmol, 0.80 equiv.), and $Pd(OAc)_2$ (1.5 mg, 6.68 μmol, 0.40 equiv.). The flask was equipped with a rubber septum, purged with N_2, and dissolved in DMF (0.8 mL). Then, the reaction mixture was sparged with an Ar balloon for 5 minutes. NEt_3 (46 μL, 328 μmol, 20 equiv.) was added followed by HCO_2H (3 μL, 82.1 μmol, 5 equiv.)—a cloudy gas was observed upon addition. The reaction was lowered into a 60 °C oil bath, and allowed to continue to stir at that temperature for 20 minutes. The reaction turns black during this time indicating its completion. The reaction was cooled to room temperature, diluted with sat. NH_4Cl (5 mL), transferred to a separatory funnel and diluted with EtOAc (10 mL). The layers were separated and the aqueous extracted with EtOAc (4 x 10 mL). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was purified by preparative thin layer silica gel chromatography (mobile phase: 100% ethyl acetate) to afford olefin **240** (6.0 mg, 13.0 μmol, 79% yield) as a clear oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.17 (ddd, *J* = 9.8, 6.7, 1.1 Hz, 1H), 5.85 (dd, *J* = 9.8, 1.9 Hz, 1H), 4.75 (d, *J* = 6.8 Hz, 1H), 4.59 (d, *J* = 6.8 Hz, 1H), 3.88 (d, *J* = 14.2 Hz, 1H), 3.84 (t, *J* = 4.5 Hz, 1H), 3.79 (s, 1H), 3.36 (s, 3H), 3.30 (s, 3H), 3.23 – 3.18 (m, 4H), 3.17 (s, 3H), 3.11 (dd, *J* = 10.3, 7.6 Hz, 1H), 3.04 (d, *J* = 9.1 Hz, 1H), 2.64 – 2.54 (m, 2H), 2.41 (dd, *J* = 13.9, 5.3 Hz, 1H), 2.33 (t, *J* = 5.5 Hz, 1H), 2.14 (d, *J* = 7.8 Hz, 1H), 2.08 – 1.98 (m, 6H), 1.88 – 1.79 (m, 2H), 1.74 – 1.65 (m, 2H), 1.50 – 1.36 (m, 1H), 1.34 – 1.26 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.9, 134.3, 125.3, 95.5, 82.9, 78.6, 77.2, 76.6, 59.5, 59.5, 55.6, 55.5, 49.2, 48.0, 45.6, 45.2, 44.3, 44.2, 42.7, 37.5, 37.4, 32.0, 31.5, 25.5, 23.5, 22.5.

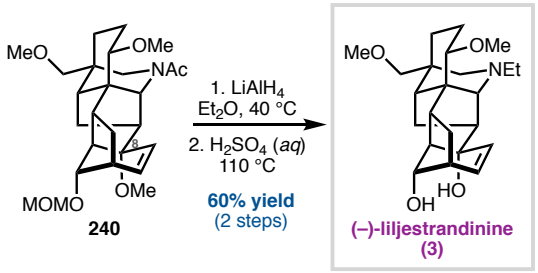
FTIR (NaCl, thin film): 2928, 2886, 2822, 1634, 1428, 1149, 1114, 1091, 1044 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{26}H_{40}NO_6$ $[M + H]^+$ 462.2850, found 462.2835

$[\alpha]_D^{25}$ = –78.2° (*c* = 0.21, $CHCl_3$).

TLC (100%EtOAc), R_f: 0.3 (grey/purple in *p*-anisaldehyde)

Preparation of (–)-liljestrandinine (3):



A 2-dram vial was charged with acetamide **240** (6 mg, 13 μmol, 1 equiv.), azeotroped with toluene (from the solvent system, 2 x 1 mL) and put under high vacuum for 1 hour. The vial was then equipped with a rubber septum, purged with N_2, and charged with Et_2O (1 mL) to dissolve the substrate, and $LiAlH_4$ solution (1 M in THF, 52 μL, 52 μmol, 4 equiv.) was added dropwise via microsyringe. The rubber septum was replaced with a vial cap, and heated to 40 °C in a pre-heated heating block. The reaction was allowed to stir at 40 °C for 40 minutes, and then was removed from the heating block and allowed to cool to room temperature. The reaction was carefully quenched with aqueous 10% NaOH solution (4 mL), and diluted with Et_2O (4 mL). The layers were separated, and the aqueous layer was extracted with 20%IPA/80%$CHCl_3$ (5 x 5 mL). The combined organic extracts were dried over Na_2SO_4,

filtered, and concentrated *in vacuo*. The crude residue was then transferred to a new 2-dram vial, and used in the next step without further purification.

The 2-dram vial containing the crude residue from the $LiAlH_4$ reduction was dissolved in aqueous 0.5 M H_2SO_4 (1.5 mL), sealed with a cap, and heated to 110 °C in a pre-heated heating block. The reaction was allowed to stir at 110 °C for 3 hours, and then was cooled to room temperature. Monitoring by LCMS indicated full conversion to the product. The reaction as then carefully quenched with aqueous 10% NaOH solution (2 mL), and diluted with 20%IPA/80%$CHCl_3$ (4 mL). The layers were separated, and the aqueous layer was extracted with 20%IPA/80%$CHCl_3$ (8 x 4 mL). As an additional precaution, the aqueous layer was made sure to be basic with pH paper, and an LCMS sample of the aqueous layer was taken to ensure that no product was left behind. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified by preparative thin layer chromatography (mobile phase: 10% 7 N NH_3 in MeOH/ 90% CH_2Cl_2) to furnish (–)-liljestrandinine (**3**) (3 mg, 7.8 μmol, 60% yield over 2 steps).

Notes:

(1) Due to rapid protonation and other dynamic effects, the ^{1}H NMR and ^{13}C NMR spectra in $CDCl_3$ are inconsistent and often display broadened and poorly resolved resonances and extra peaks arising from the protonated material. Characterization data was therefore obtained in benzene-d6, and was compared with synthetic liljestrandinine that had been characterized in benzene-d6.[4] Data collected in chloroform was only of satisfactory resolution and used only to compare to the reported tabulated data for isolated liljestrandinine.[18]

^{1}H NMR (400 MHz, Benzene-d_6): δ 5.70 (ddd, J = 9.5, 6.7, 1.1 Hz, 1H), 5.61 (dd, J = 9.4, 1.8 Hz, 1H), 3.78 (q, J = 4.8 Hz, 1H), 3.12 (s, 3H), 3.10 – 3.08 (m, 1H), 3.05 (s, 3H), 2.96 (d, J =

8.8 Hz, 1H), 2.90 – 2.82 (m, 2H), 2.60 – 2.50 (m, 3H), 2.49 – 2.43 (m, 1H), 2.43 – 2.35 (m, 1H), 2.29 (dq, J = 12.0, 7.1 Hz, 1H), 2.19 – 2.11 (m, 2H), 2.10 – 2.07 (m, 1H), 2.05 – 1.97 (m, 2H), 1.97 – 1.88 (m, 2H), 1.76 – 1.72 (m, 1H), 1.64 – 1.47 (m, 5H), 1.04 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 131.9, 129.8, 85.8, 79.6, 74.6, 74.3, 63.2, 59.5, 56.3, 53.2, 49.5, 48.4, 46.4, 45.8, 45.6, 42.4, 39.0, 38.5, 33.1, 32.7, 23.5, 22.7, 13.5.

^{13}C NMR (101 MHz, C_6D_6): δ 132.5, 129.7, 85.6, 80.0, 75.0, 74.5, 63.0, 59.2, 55.7, 53.9, 49.6, 48.6, 46.8, 46.3, 46.0, 42.7, 39.6, 38.9, 33.4, 33.3, 26.7, 24.2, 13.7.

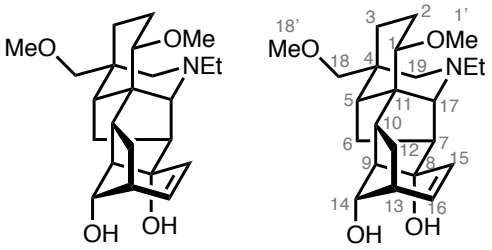
TLC (10%7N NH_3 in MeOH/90%CH_2Cl_2), R_f: 0.5 (ninhydrin)

FTIR (NaCl, thin film): 3332, 2921, 2823, 1642, 1462, 1095 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{23}H_{36}NO_4$ $[M + H]^+$ 390.2639, found 390.2622

$[\alpha]_D^{25}$ = –17.6° (c = 0.21, $CHCl_3$).

The following carbon numbering system is used in the line list comparisons:



(–)-liljestrandinine (3)

	authentic liljestrandinine Wang, 2003 (*ref.* 18) (100 MHz, $CHCl_3$) $[\alpha]_D$=–10 ° (c =0.5, $CHCl_3$)	synthetic liljestrandinine this report (101 MHz, $CHCl_3$) $[\alpha]_D$=–17.6 ° (c =0.21, $CHCl_3$)	chemical shift difference
Carbon #, multiplicity	^{13}C (δ) ppm	^{13}C (δ) ppm	^{13}C (Δδ) ppm
1 d	85.7	85.8	+0.1
2 t	22.6	22.7	+0.1
3 t	32.6	32.7	+0.1
4 s	38.5	38.5	0
5 d	45.6	45.6	0
6 t	23.4	23.5	+0.1
7 d	42.3	42.4	+0.1
8 s	74.3	74.3	0
9 d	46.3	46.4	+0.1
10 d	45.8	45.8	0
11 s	48.2	48.4	+0.2
12 t	33.0	33.1	+0.1
13 d	38.9	39.0	+0.1
14 d	74.5	74.6	+0.2
15 t	131.7	131.9	+0.2
16 d	129.8	129.8	0
17 d	63.2	63.2	+0.1
18 t	79.6	79.6	0
19 t	53.1	53.2	+0.1
N CH2	49.4	49.5	+0.1
NCH2CH3	13.4	13.5	+0.1
1’	56.2	56.3	+0.1
18’	59.4	59.5	+0.1

Table S2.5.6. Comparison of ^{13}C NMR data for Authentic (*ref.* 18) vs. synthetic (–)-liljestrandinine.

synthetic liljestrandinine Sarpong, 2015 (*ref.* 17) (151 MHz, C_6D_6)	synthetic liljestrandinine this report (101 MHz, C_6D_6) $[\alpha]_D$=–17.6 ° (c =0.21, $CHCl_3$)	chemical shift difference
^{13}C (δ) ppm	^{13}C (δ) ppm	^{13}C (Δδ) ppm
132.4	132.5	+0.1
129.7	129.7	0
85.6	85.6	0
80.0	80.0	0
74.9	75.0	+0.1
74.5	74.5	0
63.0	63.0	0
59.1	59.2	+0.1
55.6	55.7	+0.1
53.9	53.9	0
49.5	49.6	+0.1
48.6	48.6	0
46.8	46.8	0
46.3	46.3	0
46.0	46.0	0
42.7	42.7	0
39.6	39.6	0
38.9	38.9	0
33.4	33.4	0
33.2	33.3	+0.1
26.7	26.7	0
24.2	24.2	0
13.7	13.7	0

Table S2.5.7. Comparison of ^{13}C NMR data in C_6D_6 of Synthetic (*ref.* 17) vs. Synthetic (–)-liljestrandinine (this report).

4.6 NOTES AND REFERENCES

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ABOUT THE AUTHOR

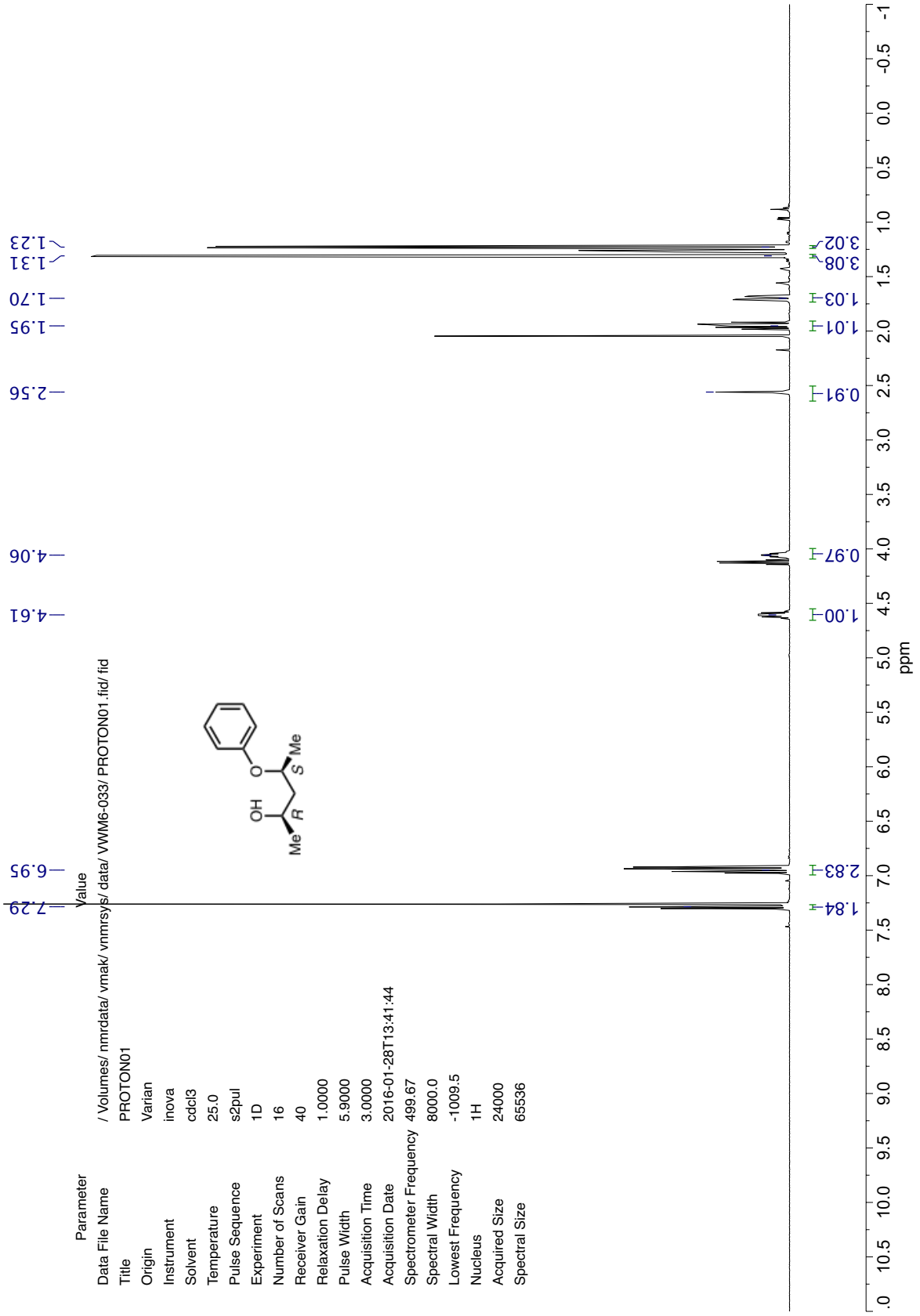
Nicholas James Fastuca was born on June 4th, 1993 in Raleigh, NC, to parents Debra Fastuca and Stephen Fastuca. He grew up in West Chester, PA, where he spent his childhood surrounded by his extended family and friends. His interest in chemistry was sparked by his high school teacher, Josh Gellner. This led him to pursue a B.S. in chemistry at The Pennsylvania State University from 2012-2016 where he received encouragement and support from his academic adviser Dr. Joseph Keiser. During his time at Penn State, he had the opportunity to join Professor Alexander Radosevich's laboratory where he was first exposed to the world of synthetic chemistry.

After graduating from Penn State, he moved to Pasadena, CA, to pursue a Ph.D. in organic chemistry at Caltech in the lab of Professor Sarah Reisman. During his time at Caltech, he had the opportunity to learn from many excellent synthetic chemists. Upon completion of his Ph.D., he will move to Princeton, NJ to work as a postdoctoral scholar at Princeton University in the lab of Professor Robert Knowles.

Appendix 1

Spectra Relevant to Chapter 2:

Convergent Approach to C_{19}-Diterpenoid Alkaloids via 1,2-Addition/Semipinacol Sequence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0.91
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1.03
3.08
3.02
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R
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Acquisition Time 3.0000
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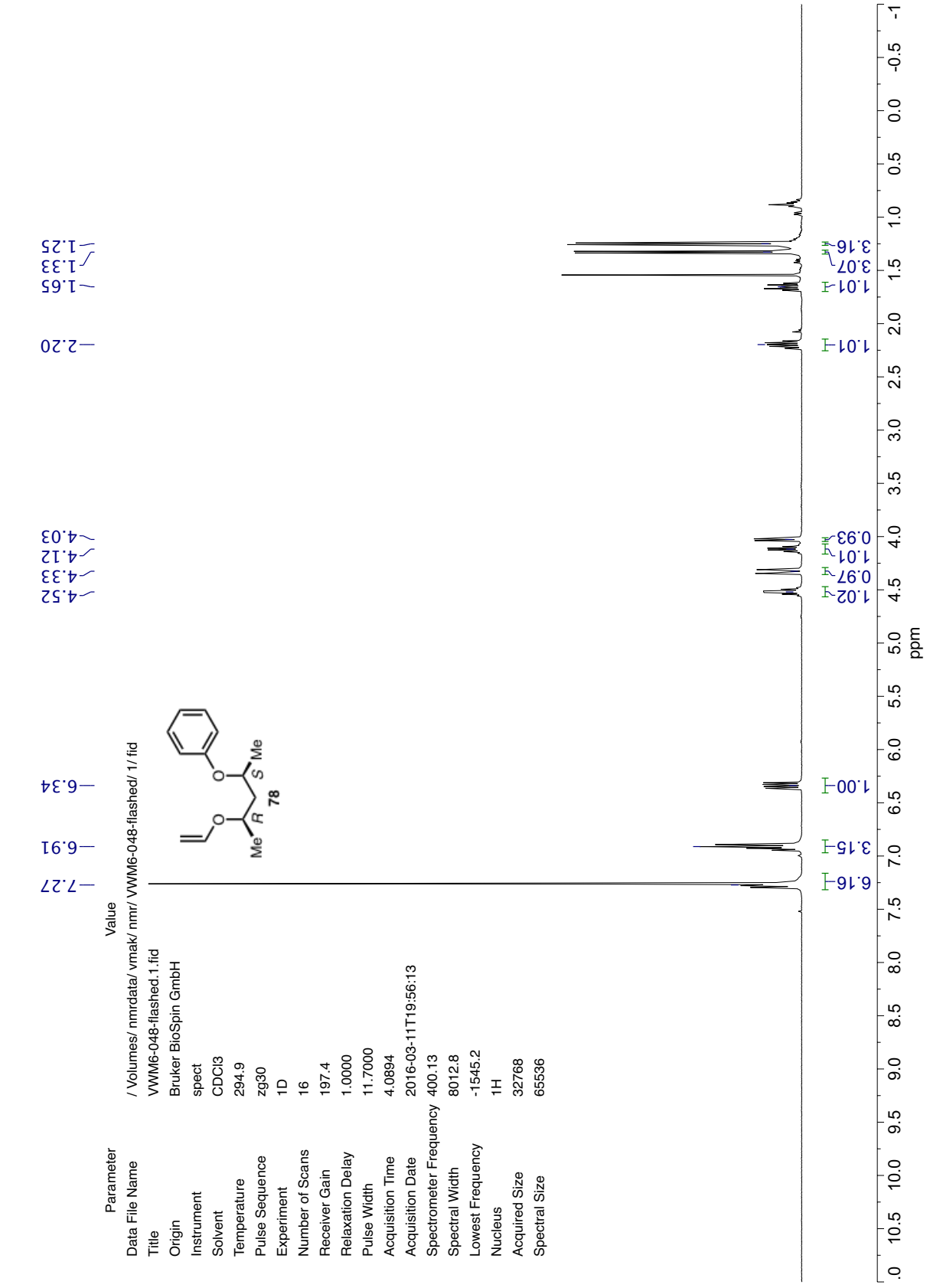
Spectral Size 65536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Instrument spect
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Nucleus 1H
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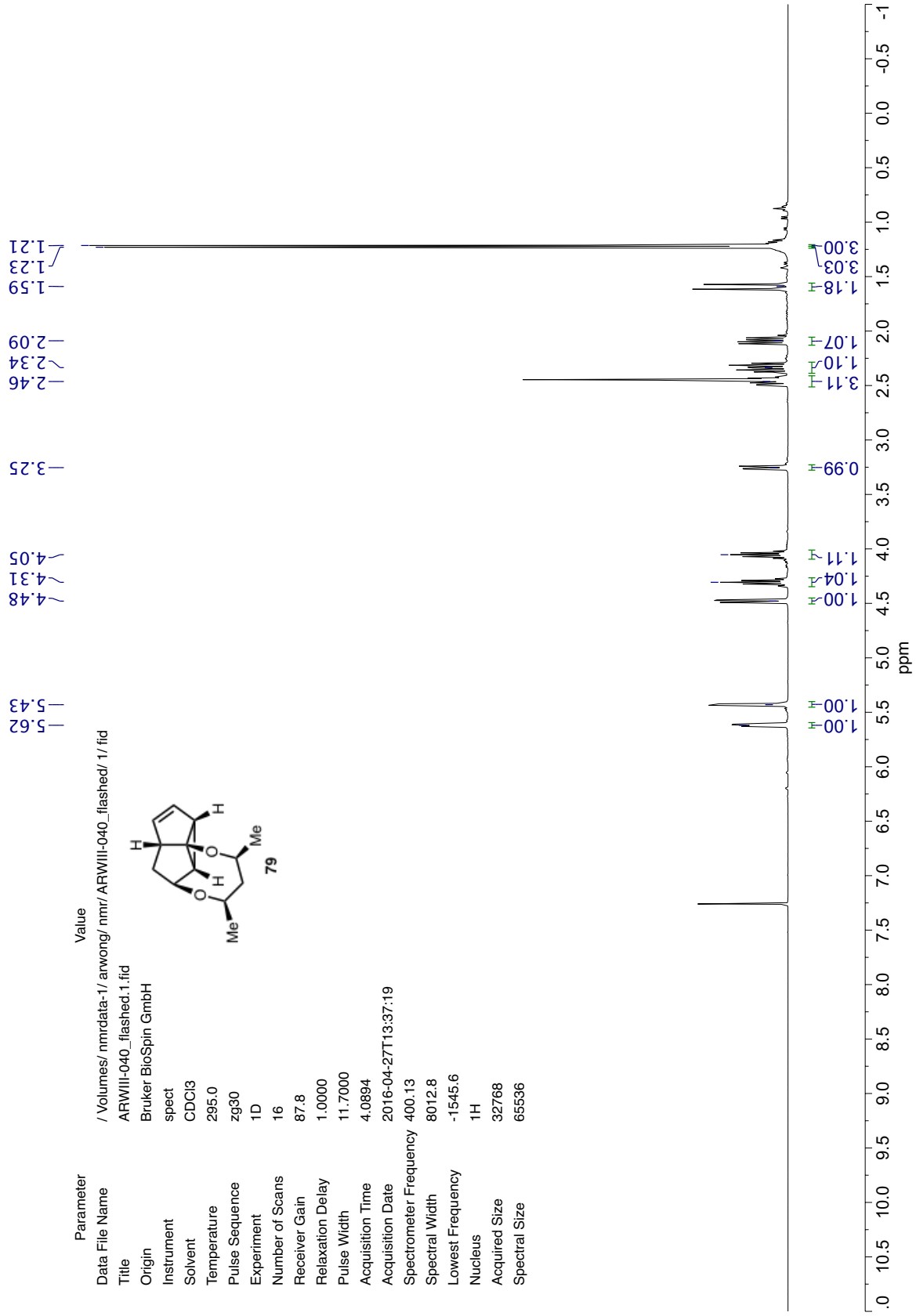
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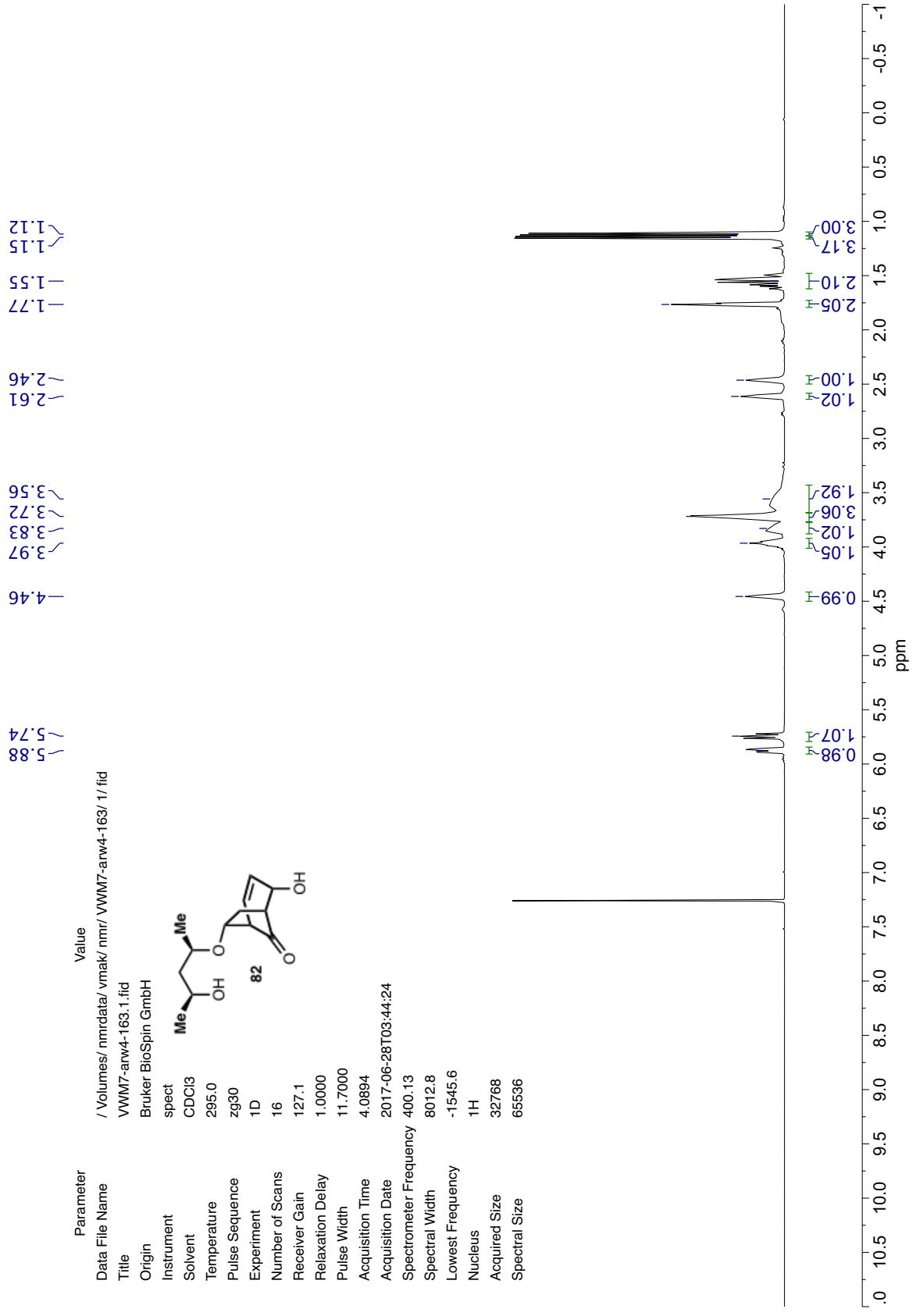
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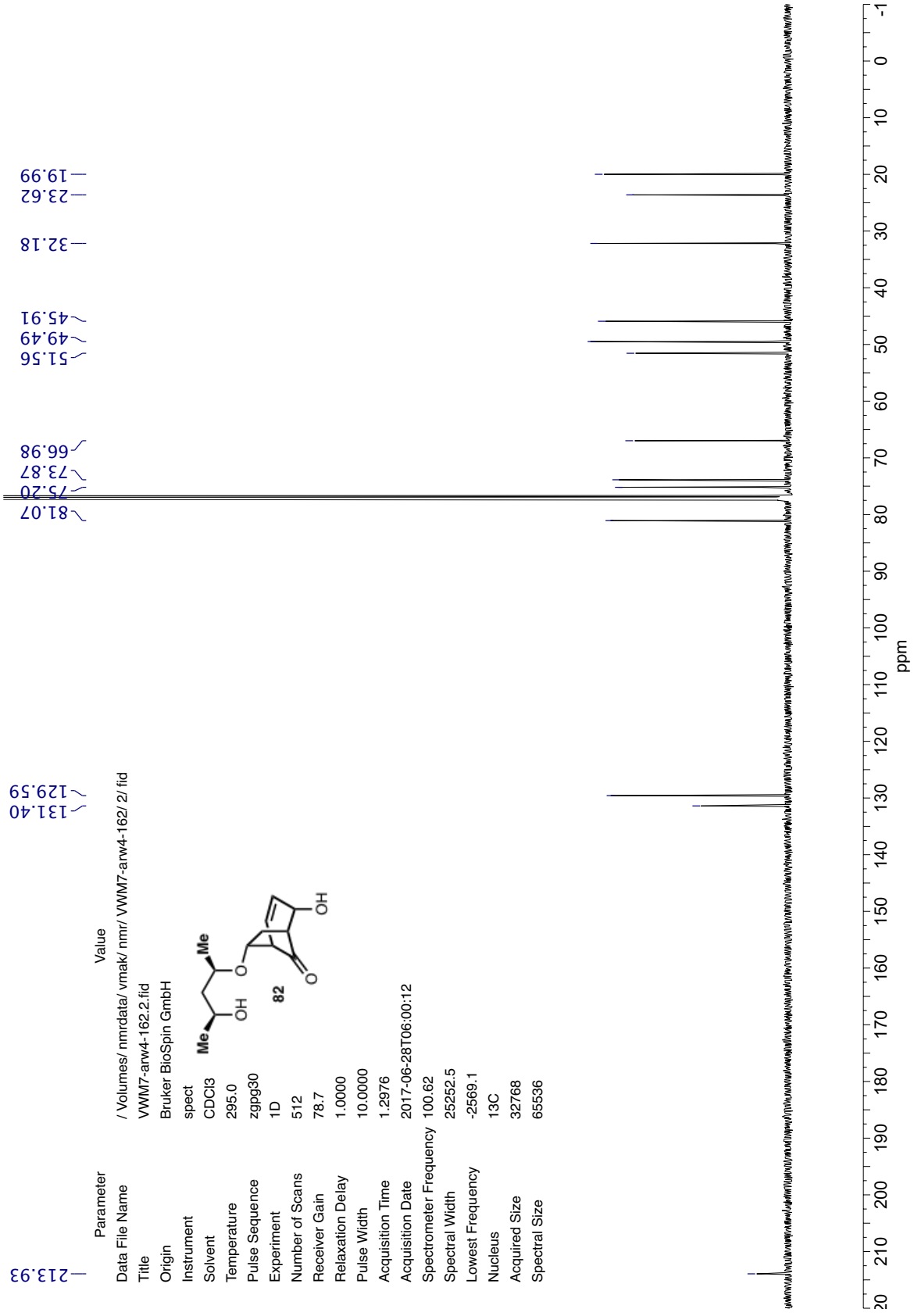
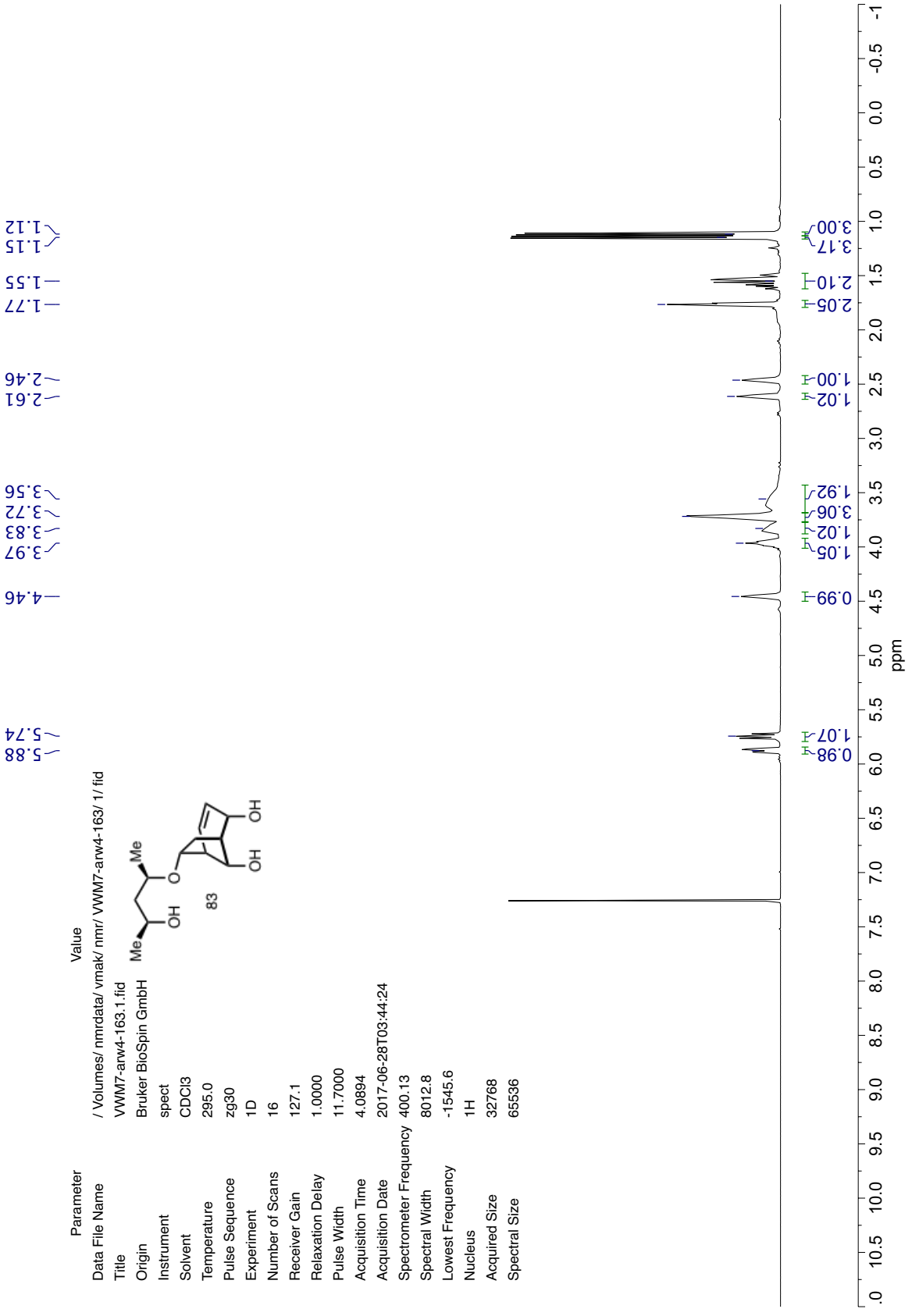
3.56
2.61
2.46
1.77
1.55
1.15
1.12
0.98
1.07
0.99
1.05
1.02
3.06
1.92
1.02
2.05
2.10
3.17
3.00
ppm


213.93
131.40
129.59
81.07
75.20
73.87
66.98
51.56
49.49
45.91
32.18
23.62
19.99
Parameter
Value
Data File Name / Volumes/ nmrdata/ vmak/ nmr/ VWM7-arw4-162/ 2/ fid
Title VWM7-arw4-162.2.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.0
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 512
Receiver Gain 78.7
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.2976
Acquisition Date 2017-06-28T06:00:12
Spectrometer Frequency 100.62
Spectral Width 25252.5
Lowest Frequency -2569.1
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
Me
OH
O
82
OH
O
Me
ppm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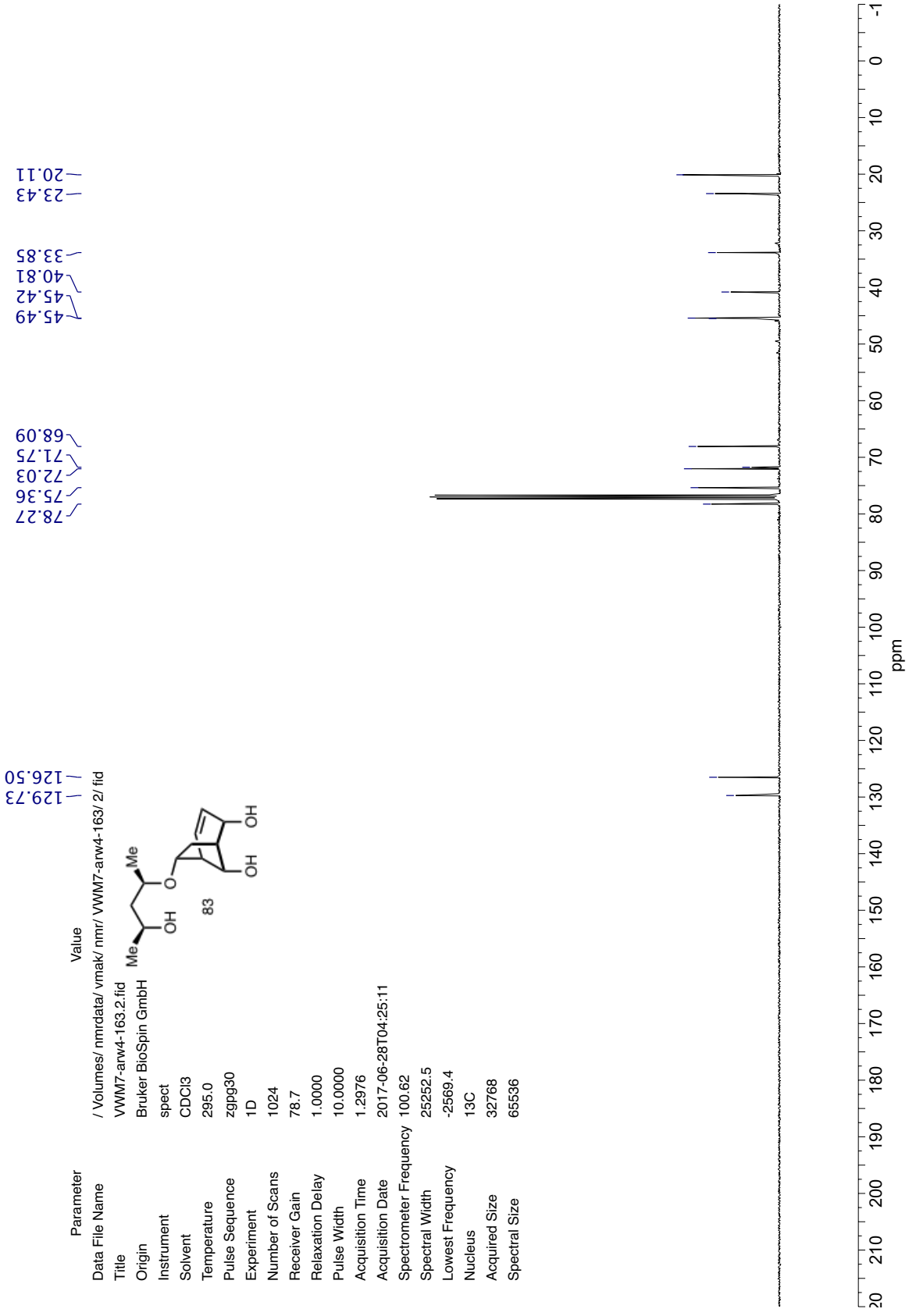
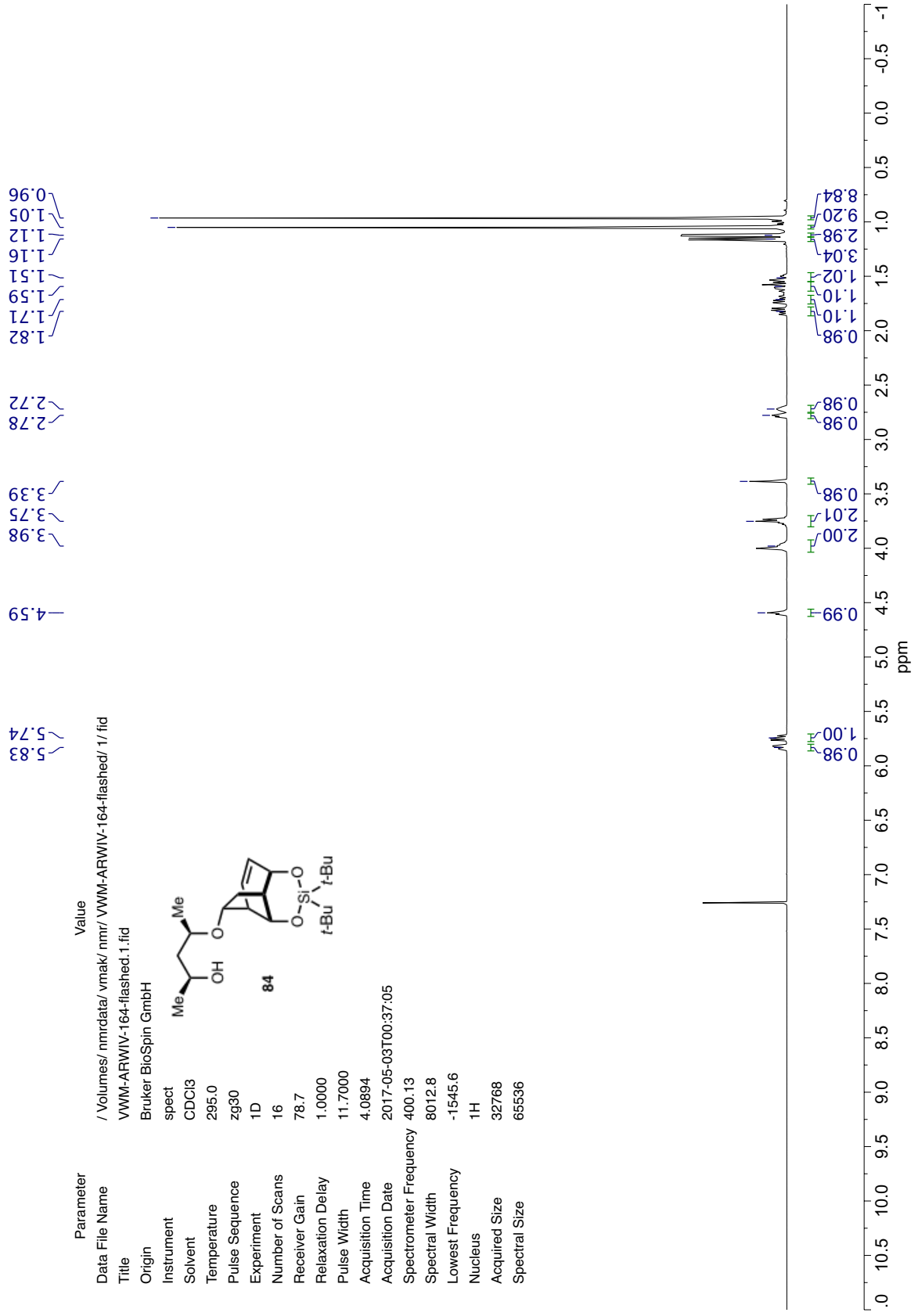
Value
Data File Name
/ Volumes/ nmrdata/ vmak/ nmr/ VWM7-arw4-163/ 1/ fid
Title
VWM7-arw4-163.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.0
Pulse Sequence
zg30
Experiment
1D
Number of Scans
16
Receiver Gain
127.1
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2017-06-28T03:44:24
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.6
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
Me
OH
O
Me
83
OH
OH
5.88
5.74
4.46
3.97
3.83
3.72
3.56
2.61
2.46
1.77
1.55
1.15
1.12
0.98
1.07
0.99
1.05
1.02
3.06
1.92
1.02
1.00
2.05
2.10
3.17
3.00
ppm


20.11
23.43
33.85
40.81
45.42
45.49
68.09
71.75
72.03
75.36
78.27
126.50
129.73
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ vmak/ nmr/ VWM7-arw4-163/ 2/ fid
Title
VWM7-arw4-163.2.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.0
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
1024
Receiver Gain
78.7
Relaxation Delay
1.0000
Pulse Width
10.0000
Acquisition Time
1.2976
Acquisition Date
2017-06-28T04:25:11
Spectrometer Frequency
100.62
Spectral Width
25252.5
Lowest Frequency
-2569.4
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
Me
OH
O
Me
83
OH
OH
ppm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Value
Data File Name
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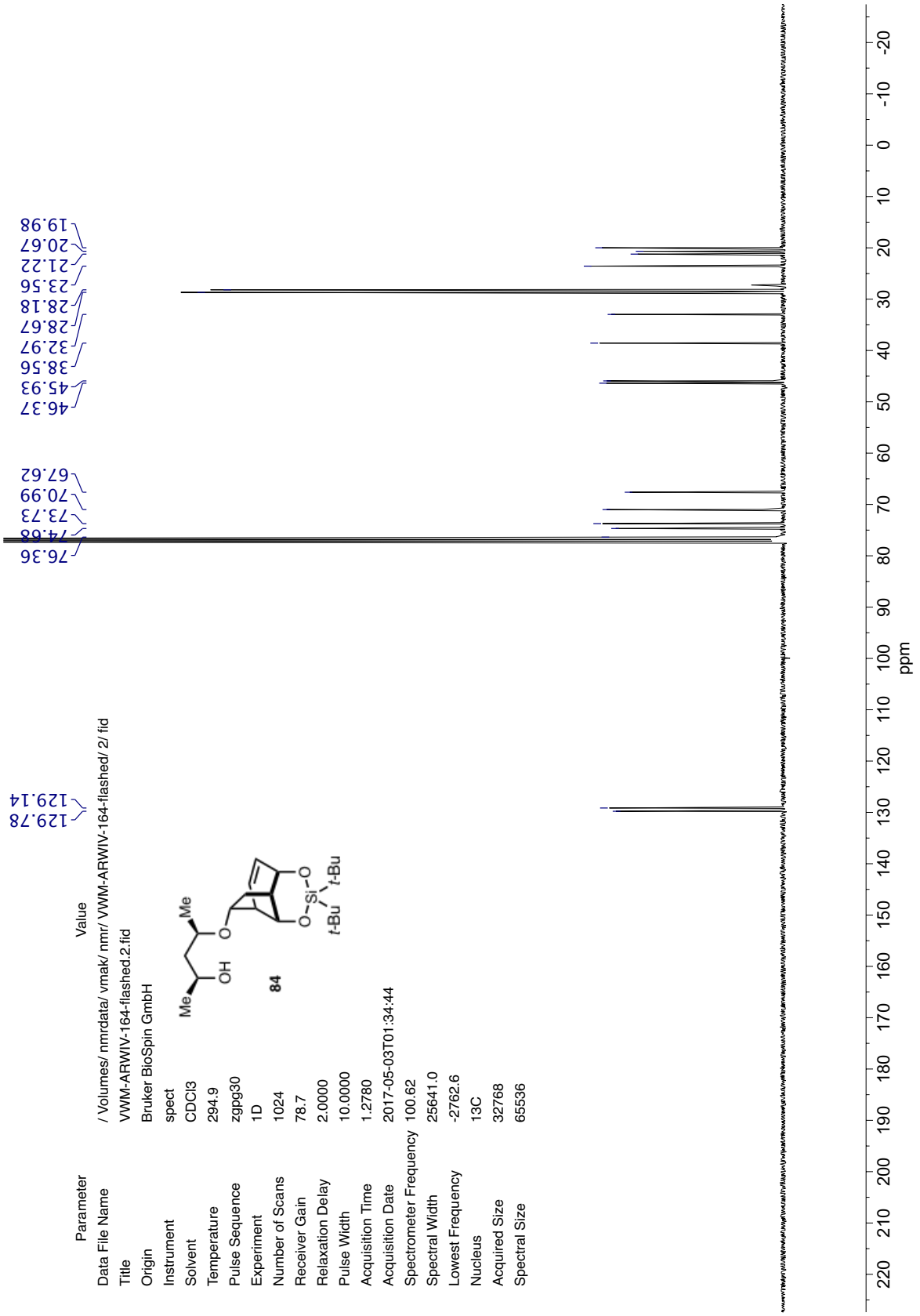
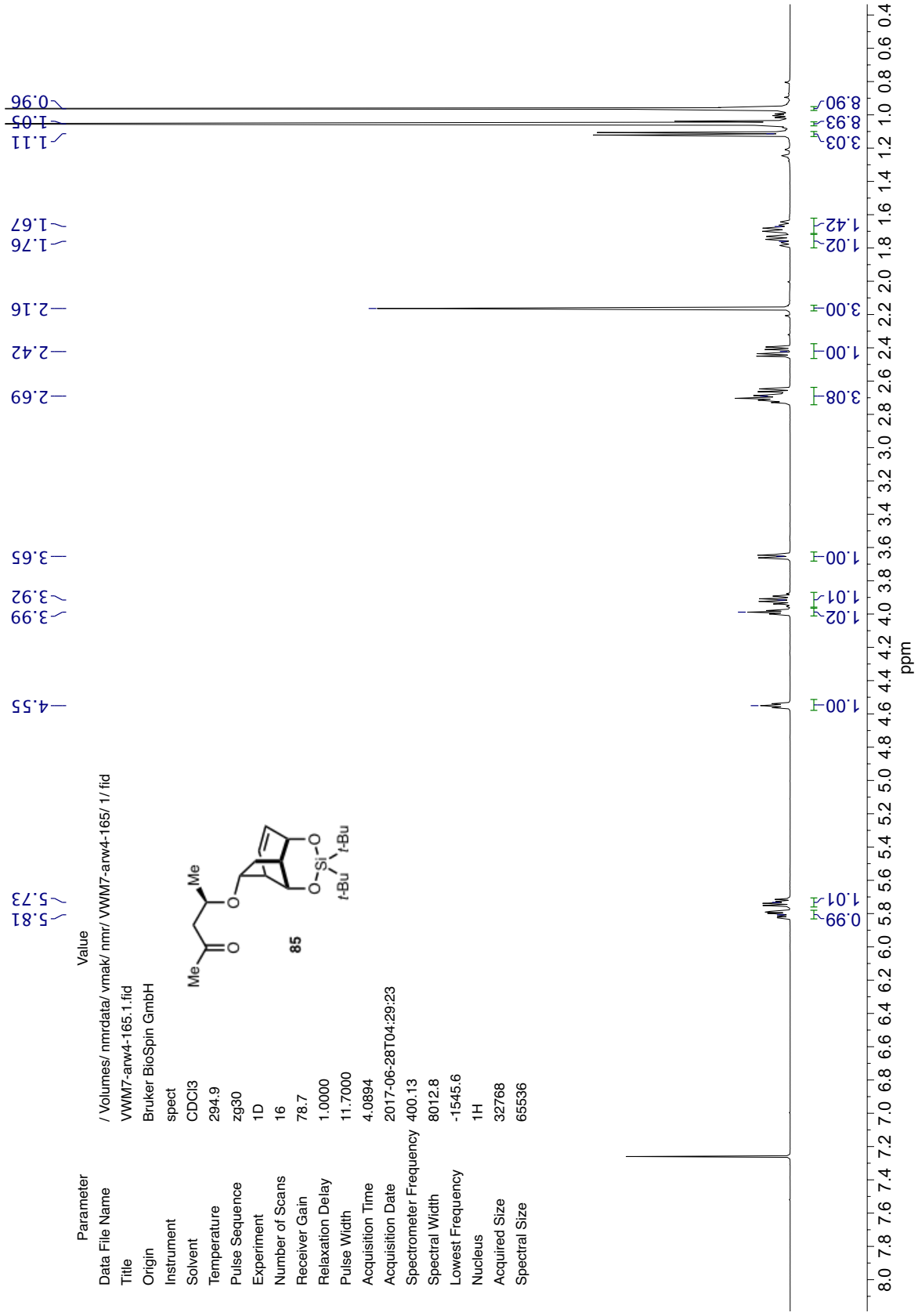
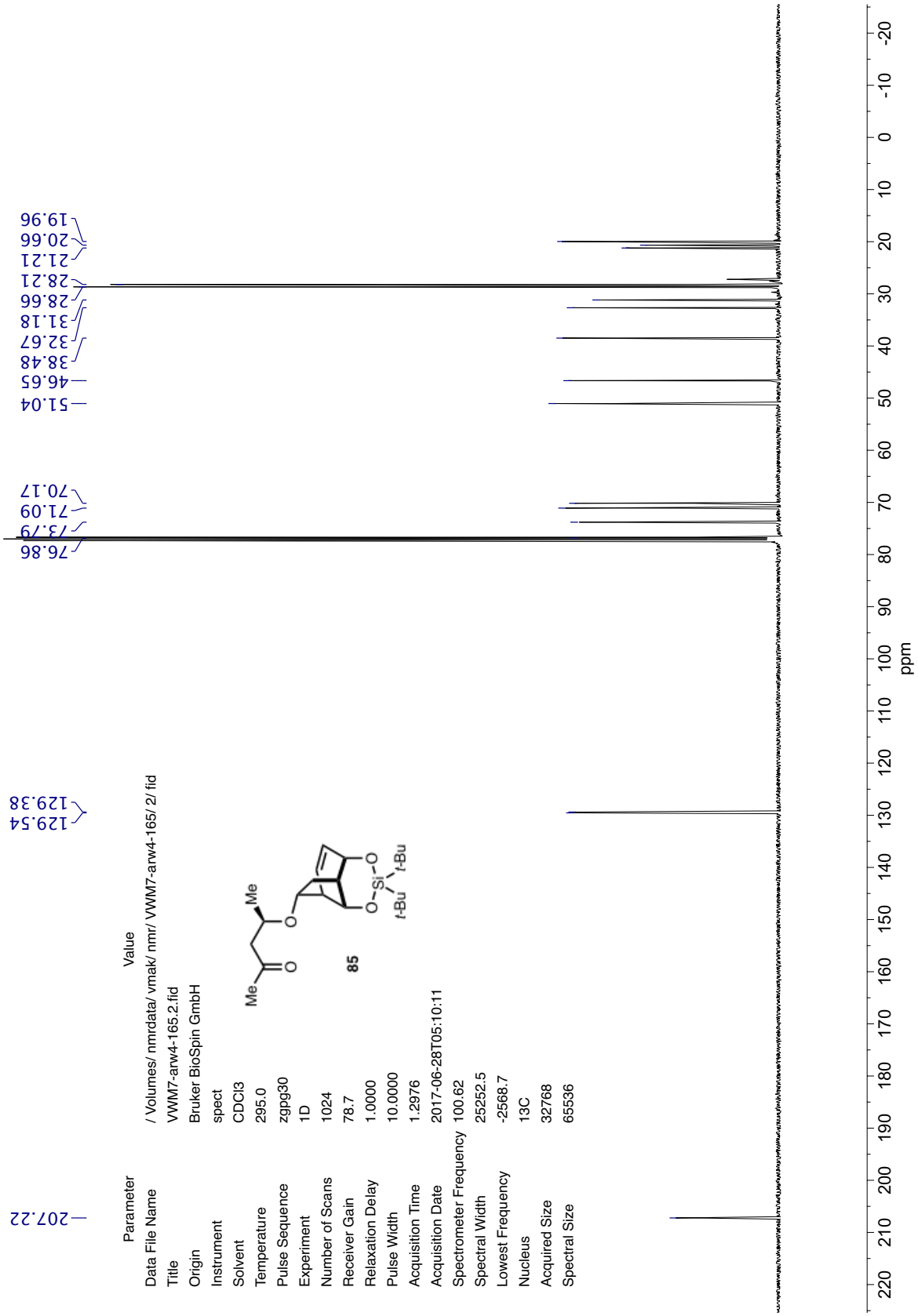
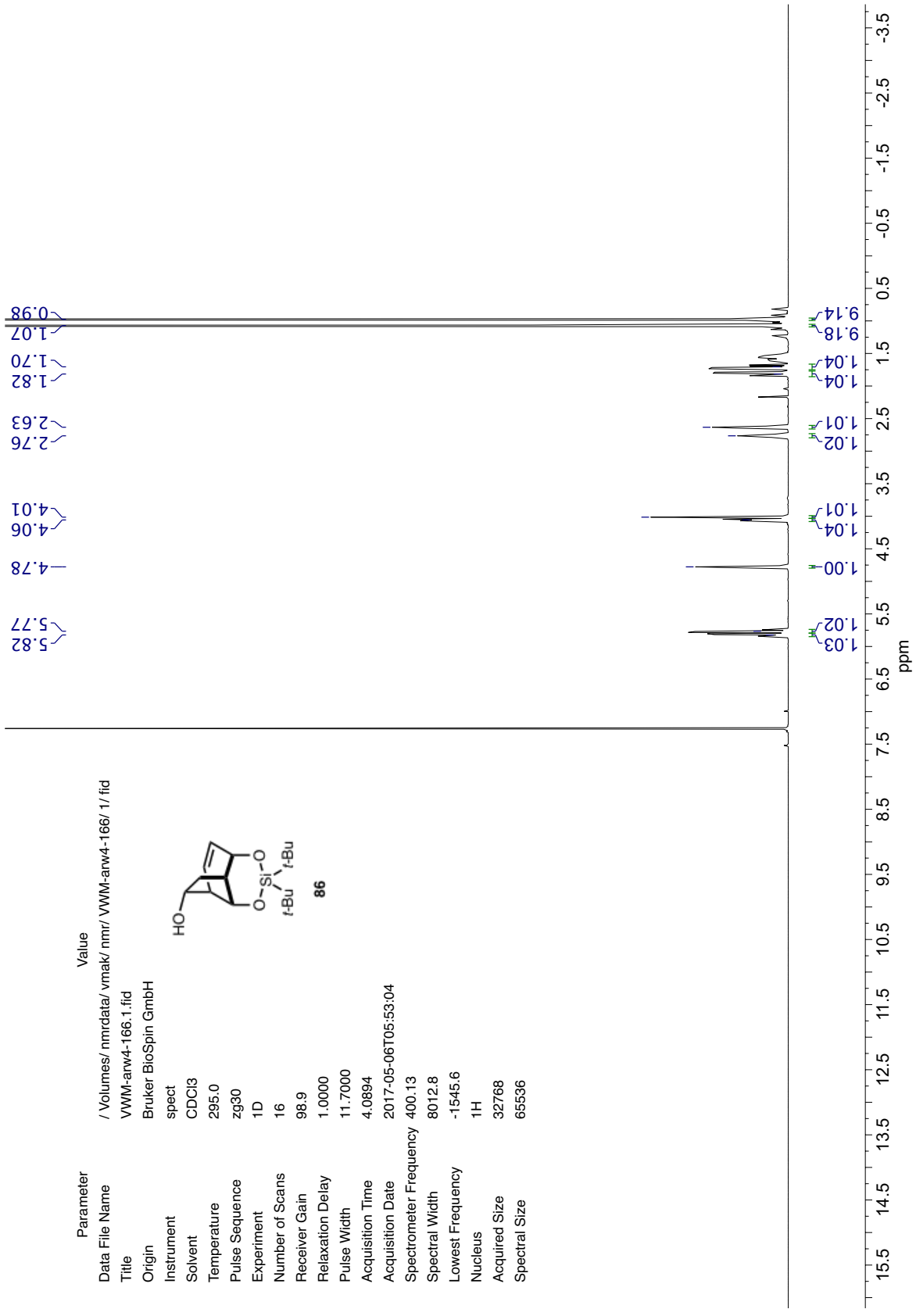
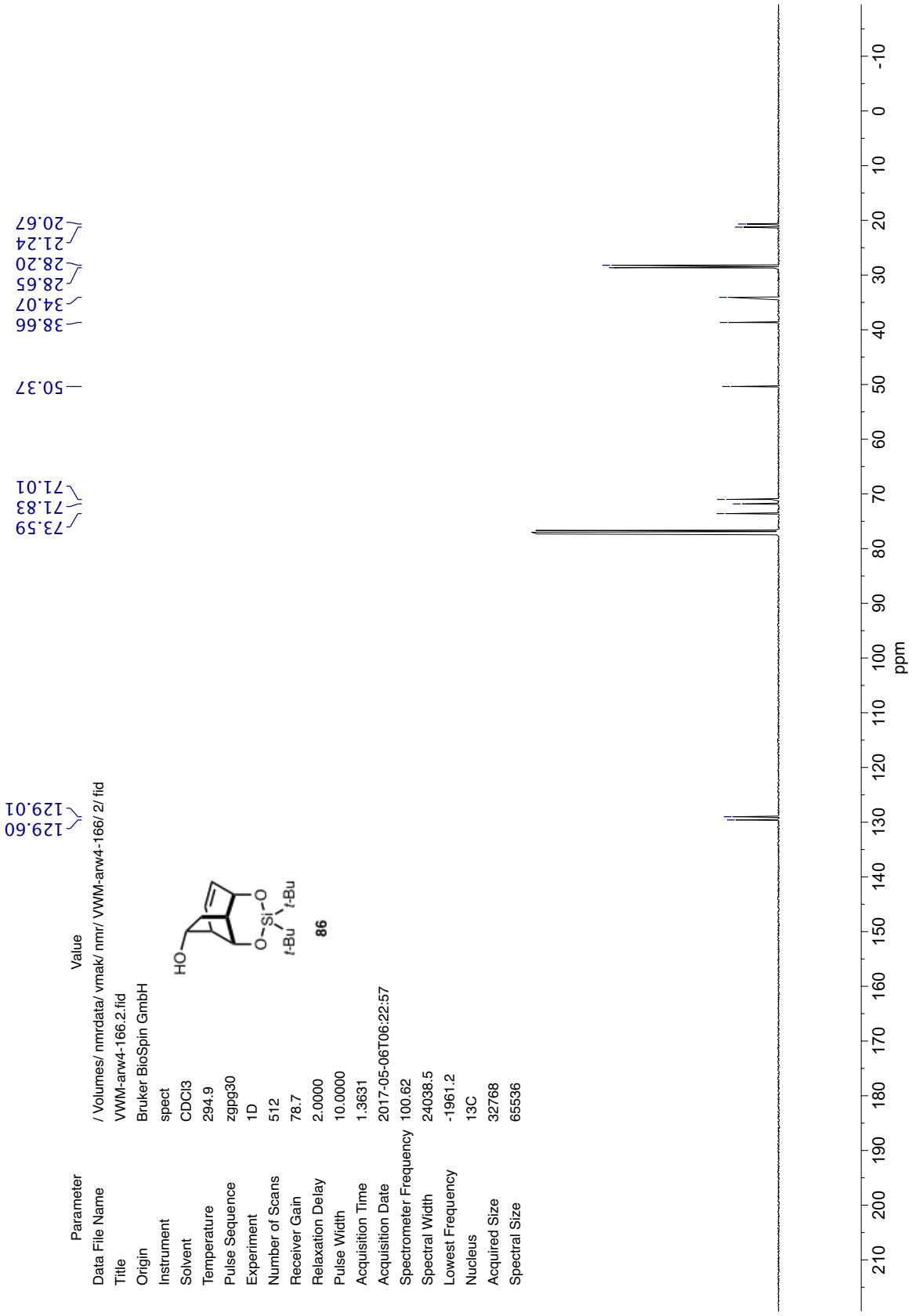
Title
VWM-ARWIV-164-flashed.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.0
Pulse Sequence
zg30
Experiment
1D
Number of Scans
16
Receiver Gain
78.7
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2017-05-03T00:37:05
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.6
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
Me
OH
Me
O
O
Si
t-Bu
t-Bu
84
5.83
5.74
4.59
3.98
3.75
3.39
2.78
2.72
1.82
1.71
1.59
1.51
1.16
1.12
1.05
0.96
1.00
0.99
2.00
2.01
0.98
0.98
0.98
1.10
1.10
0.98
2.98
9.20
8.84
ppm

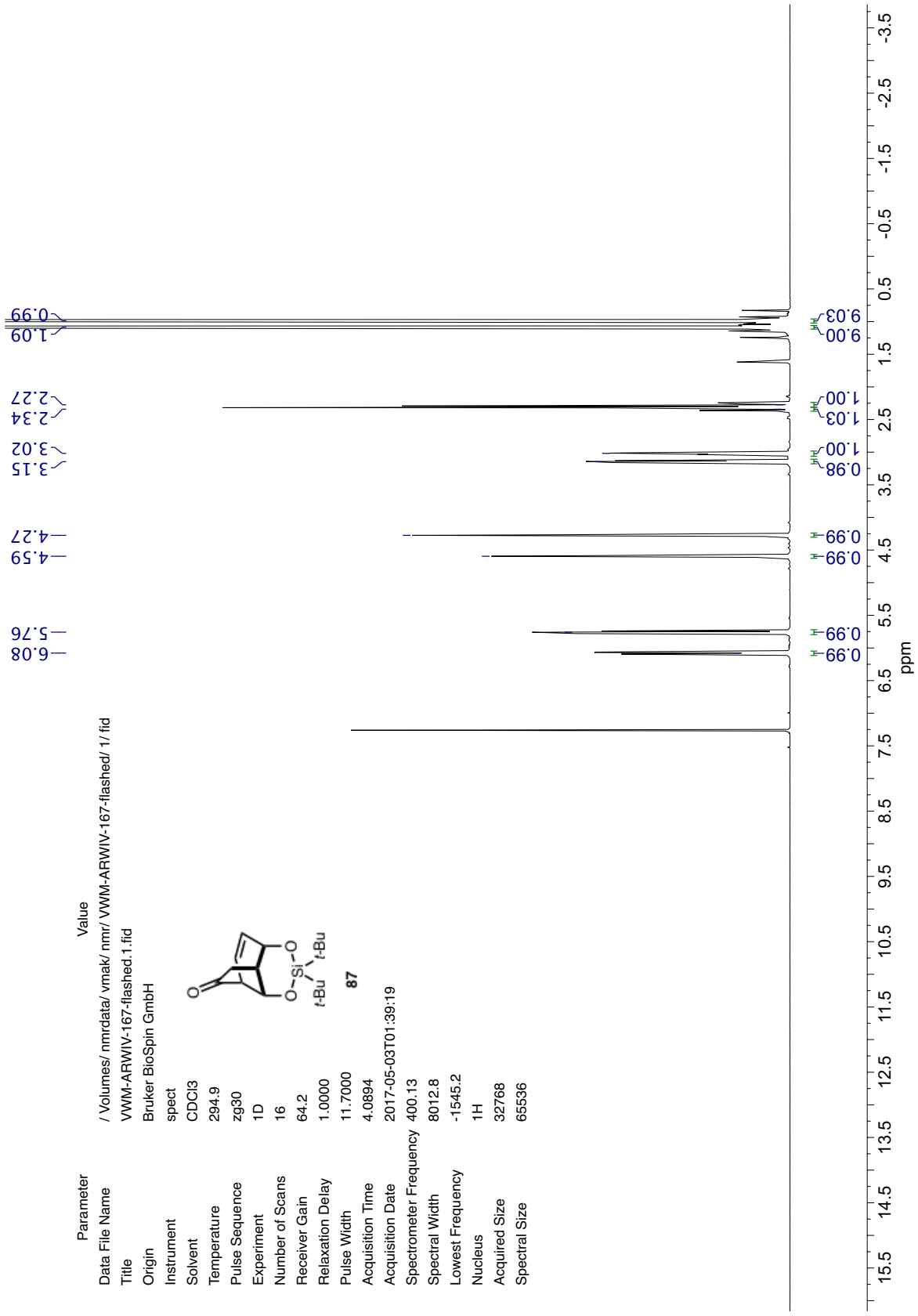

129.78
129.14
76.36
74.68
73.73
70.99
67.62
46.37
45.93
38.56
32.97
28.67
28.18
23.56
21.22
20.67
19.98
ppm
Parameter Value
Data File Name / Volumes/ nmrdata/ vmak/ nmr/ VWM-ARWIV-164-flashed/ 2/ fid
Title VWM-ARWIV-164-flashed.2.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 294.9
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 1024
Receiver Gain 78.7
Relaxation Delay 2.0000
Pulse Width 10.0000
Acquisition Time 1.2780
Acquisition Date 2017-05-03T01:34:44
Spectrometer Frequency 100.62
Spectral Width 25641.0
Lowest Frequency -2762.6
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
Me
OH
Me
O
O
Si
t-Bu
t-Bu
84

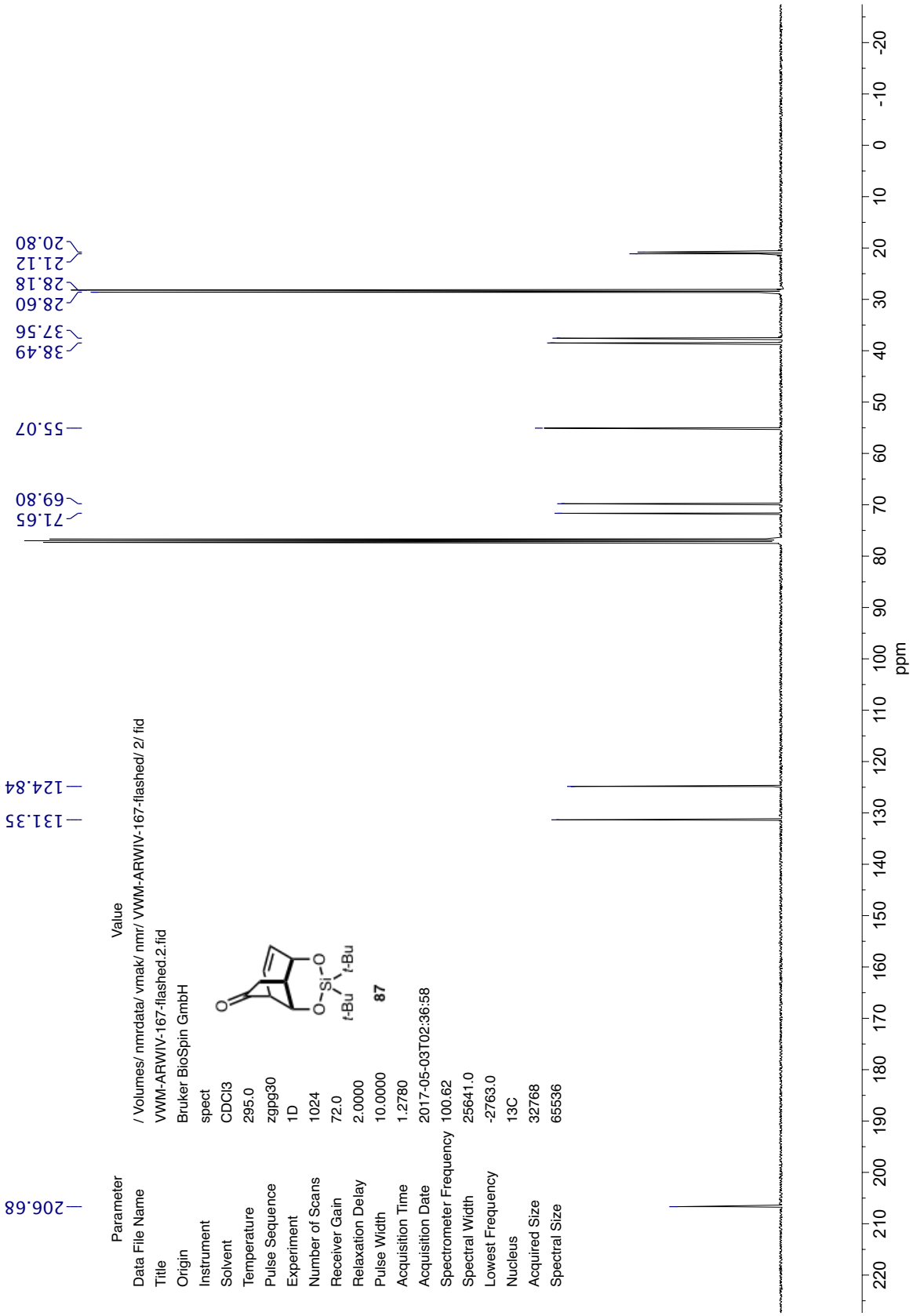

Parameter Value
Data File Name / Volumes/ nmrdata/ vmak/ nmr/ VWM7-arw4-165/ 1/ fid
Title VWM7-arw4-165.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 294.9
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 78.7
Relaxation Delay 1.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Acquisition Date 2017-06-28T04:29:23
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.6
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
85
ppm

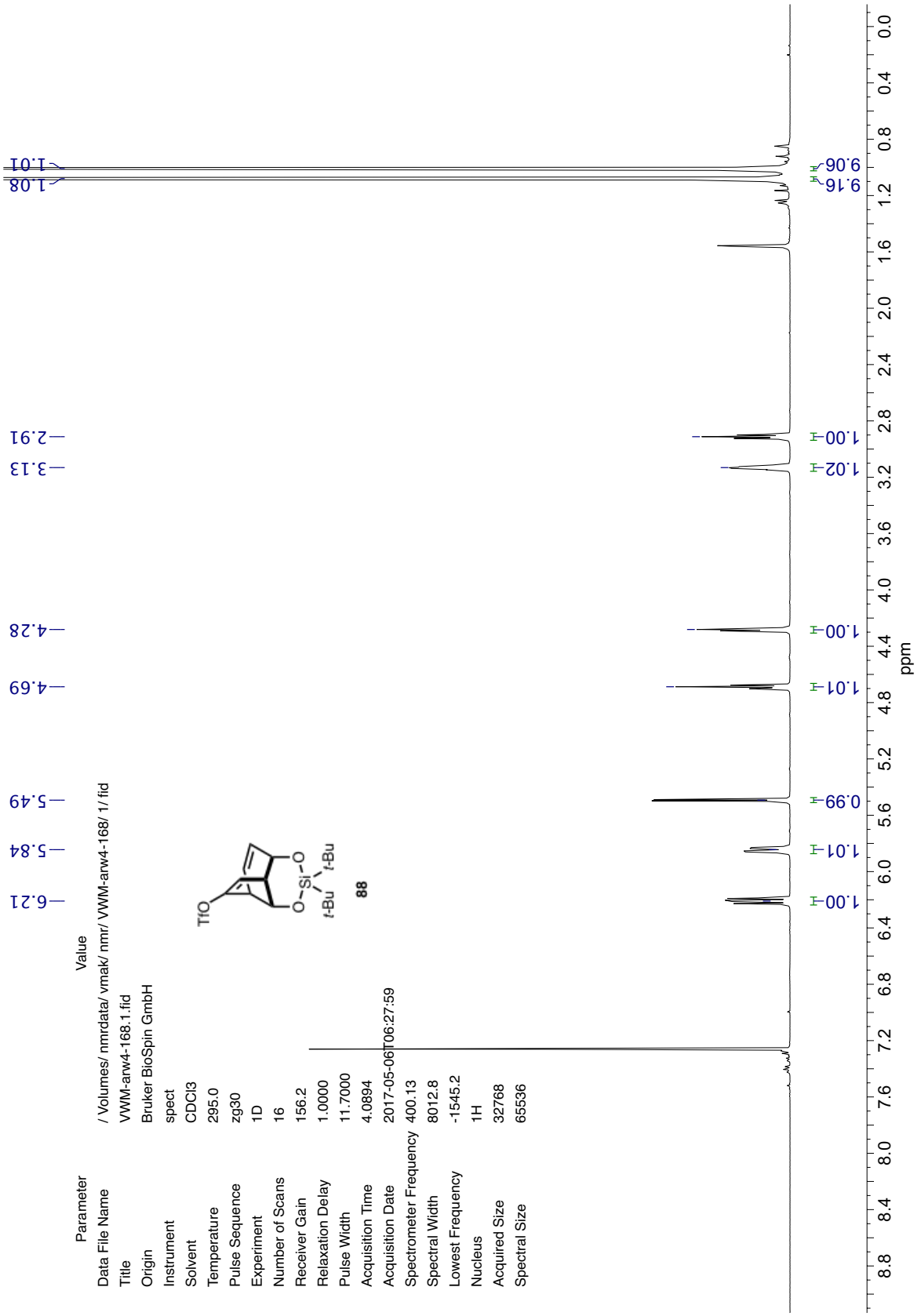

207.22
129.54
129.38
76.86
73.79
71.09
70.17
51.04
46.65
38.48
32.67
31.18
28.66
28.21
21.21
20.66
19.96
Me
Me
O
O
O
Si
O
t-Bu
t-Bu
85
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ vmak/ nmr/ VWM7-arw4-165/ 2/ fid
Title
VWM7-arw4-165.2.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.0
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
1024
Receiver Gain
78.7
Relaxation Delay
1.0000
Pulse Width
10.0000
Acquisition Time
1.2976
Acquisition Date
2017-06-28T05:10:11
Spectrometer Frequency
100.62
Spectral Width
25252.5
Lowest Frequency
-2568.7
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
ppm


Parameter
Value
Data File Name / Volumes/ nmrdata/ vmak/ nmr/ VWM-arw4-166/ 1/ fid
Title VWM-arw4-166.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.0
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 98.9
Relaxation Delay 1.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Acquisition Date 2017-05-06T05:53:04
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.6
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
HO
O
Si
O
t-Bu
t-Bu
86
0.98
1.07
1.70
1.82
2.63
2.76
4.01
4.06
4.78
5.77
5.82
9.14
9.18
1.04
1.04
1.01
1.02
1.01
1.04
1.00
1.02
1.03
15.5
14.5
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
-2.5
-3.5
ppm

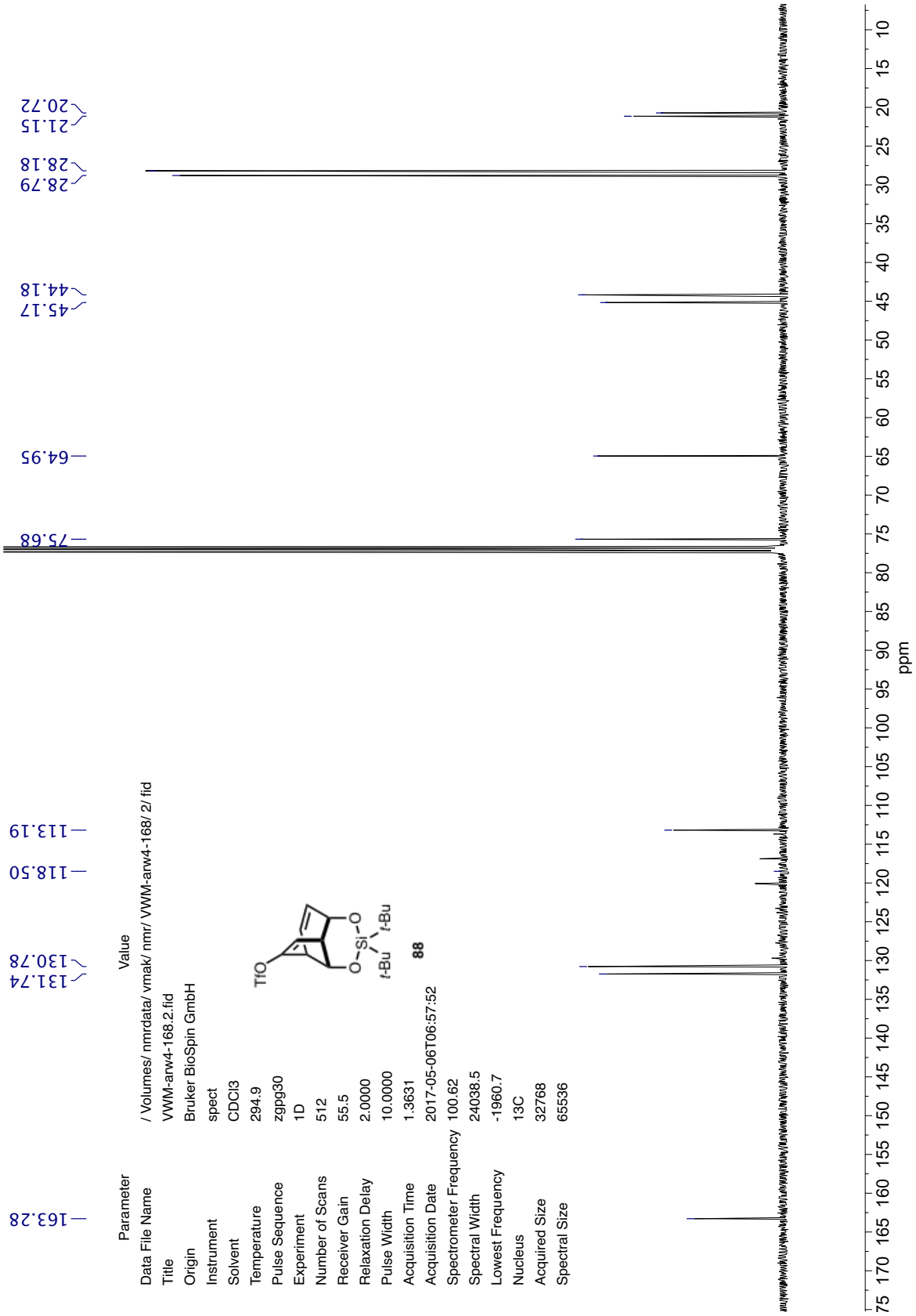

129.60
129.01
73.59
71.83
71.01
50.37
38.66
34.07
28.65
28.20
21.24
20.67
HO
O
Si
O
t-Bu
t-Bu
86
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ vmak/ nmr/ VWM-arw4-166/ 2/ fid
Title
VWM-arw4-166.2.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
294.9
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
512
Receiver Gain
78.7
Relaxation Delay
2.0000
Pulse Width
10.0000
Acquisition Time
1.3631
Acquisition Date
2017-05-06T06:22:57
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1961.2
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

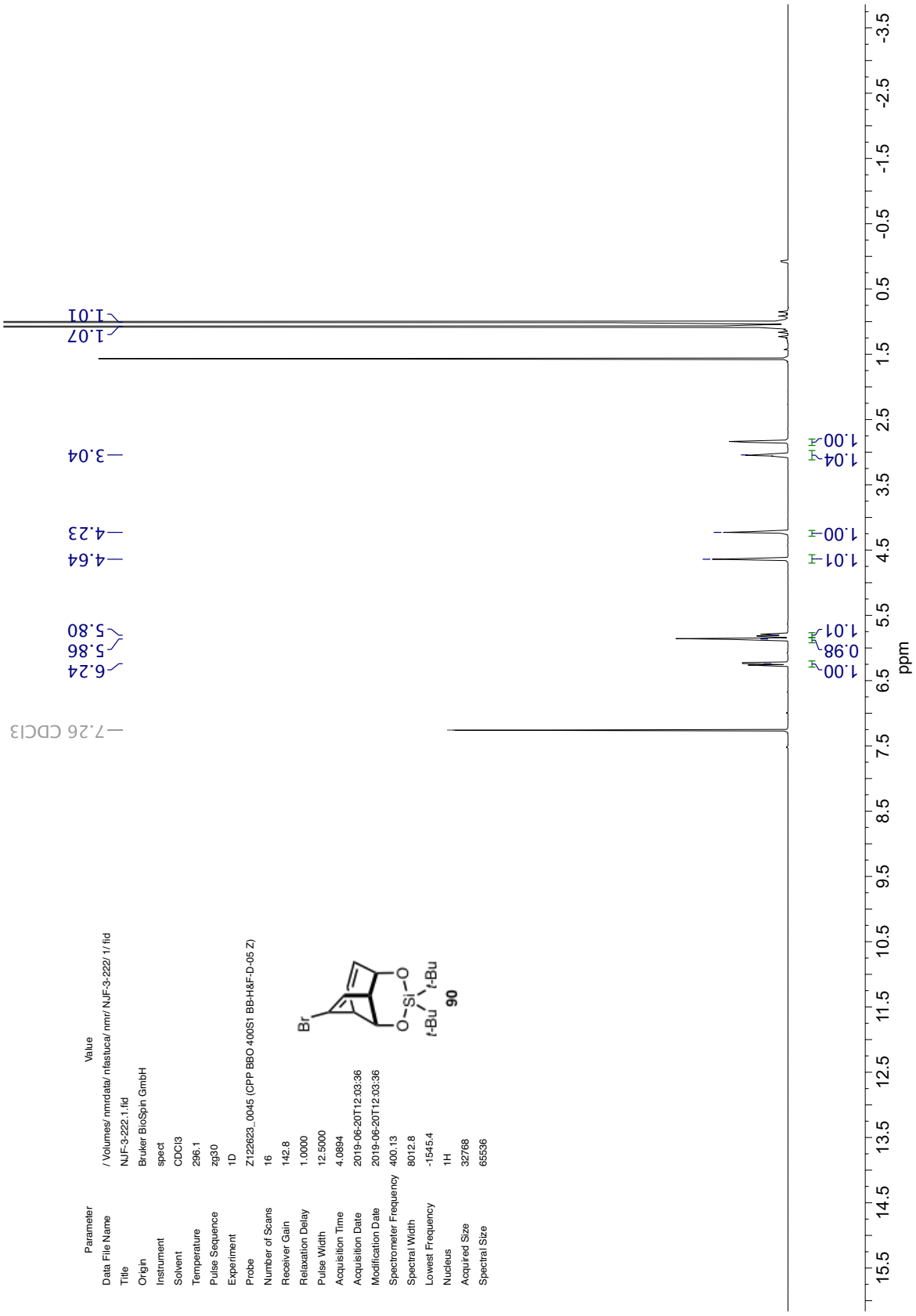

0.99
1.09
2.27
2.34
3.02
3.15
4.27
4.59
5.76
6.08
9.03
9.00
1.03
1.00
1.00
0.98
0.99
0.99
0.99
0.99
ppm
15.5
14.5
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
-2.5
-3.5
Parameter
Value
Data File Name / Volumes/ nmrdata/ vmak/ nmr/ VWM-ARWIV-167-flashed/ 1/ fid
Title VWM-ARWIV-167-flashed.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 294.9
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 64.2
Relaxation Delay 1.0000
Pulse Width 11.7000
87
Acquisition Time 4.0894
Acquisition Date 2017-05-03T01:39:19
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.2
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
O
O
Si
O
t-Bu
t-Bu

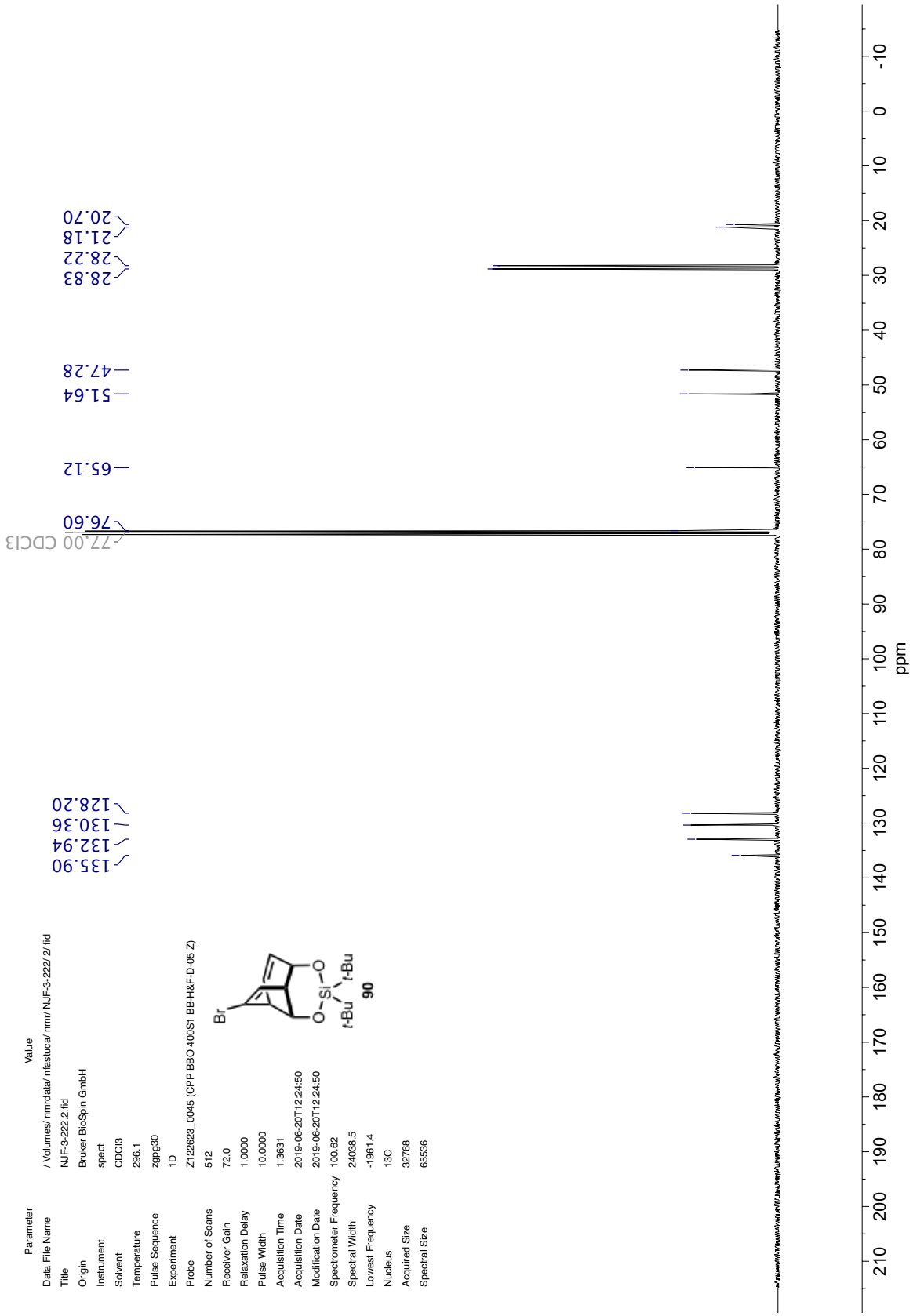

206.68
131.35
124.84
71.65
69.80
55.07
38.49
37.56
28.60
28.18
21.12
20.80
ppm
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
Parameter
Value
Data File Name / Volumes/ nmrdata/ vmak/ nmr/ VWM-ARWIV-167-flashed/ 2/ fid
Title VWM-ARWIV-167-flashed.2.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.0
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 1024
Receiver Gain 72.0
Relaxation Delay 2.0000
Pulse Width 10.0000
Acquisition Time 1.2780
Acquisition Date 2017-05-03T02:36:58
Spectrometer Frequency 100.62
Spectral Width 25641.0
Lowest Frequency -2763.0
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
O
O
Si
O
t-Bu
t-Bu
87

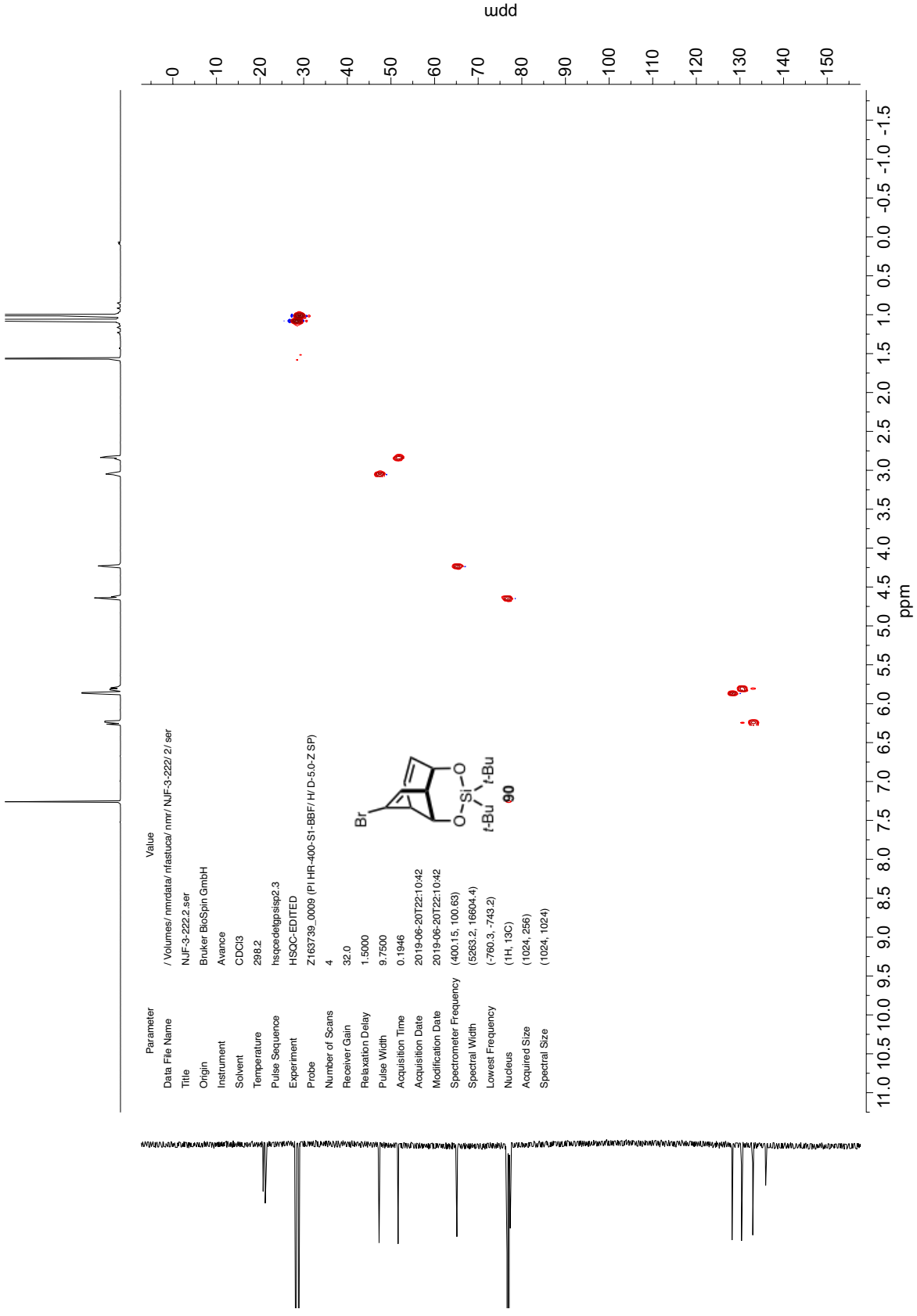


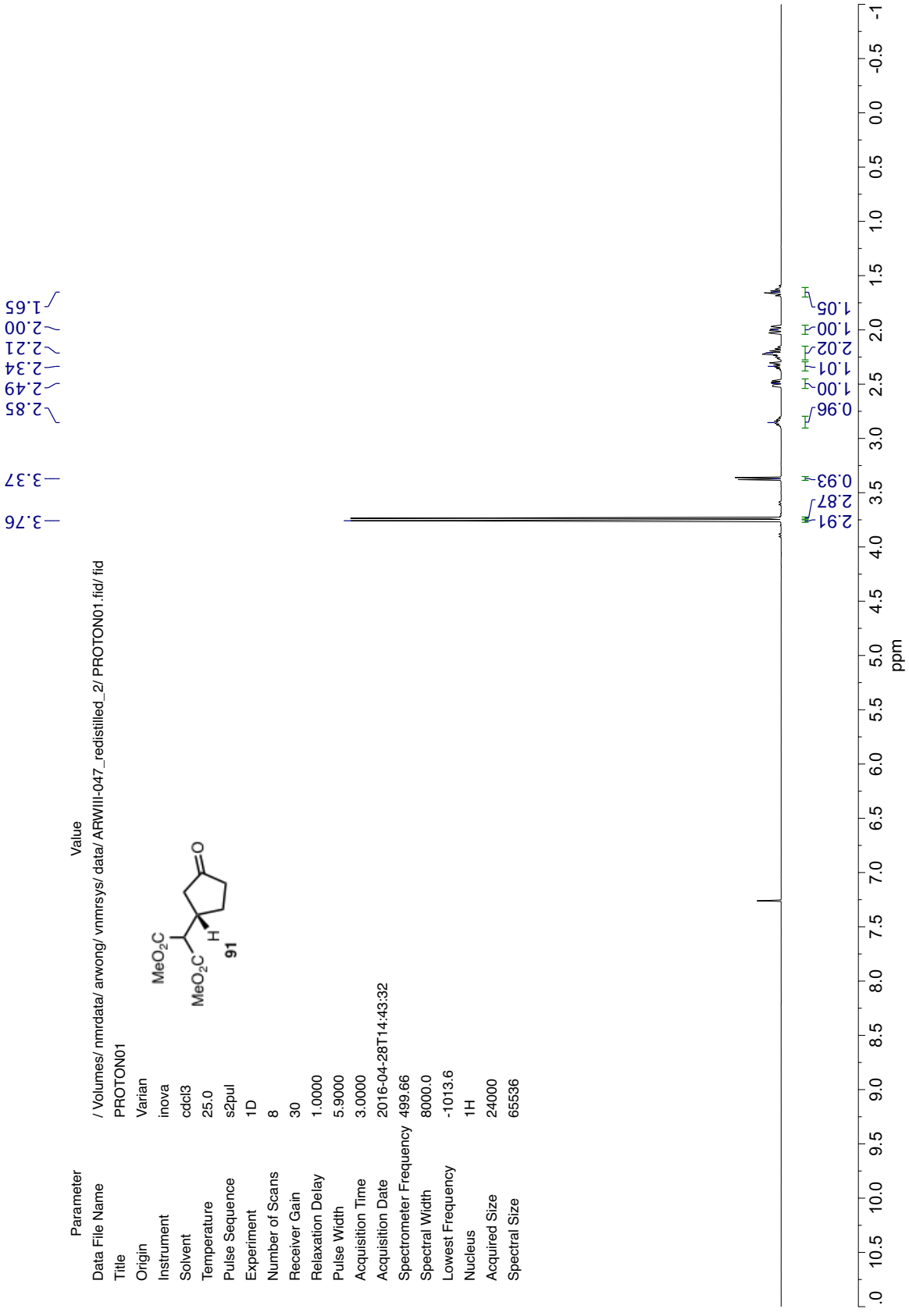
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ vmak/ nmr/ VWM-arw4-168/ 1/ fid
Title	VWM-arw4-168.1.fid
Origin	Bruker BioSpin GmbH
Instrument	spect
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-05-06T06:27:59
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.2
Nucleus	1H
Acquired Size	32768
Spectral Size	65536


163.28
131.74
130.78
118.50
113.19
75.68
64.95
45.17
44.18
28.79
28.18
21.15
20.72
TfO
O
Si
O
t-Bu
t-Bu
88
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ vmak/ nmr/ VWM-arw4-168/ 2/ fid
Title
VWM-arw4-168.2.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
294.9
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
512
Receiver Gain
55.5
Relaxation Delay
2.0000
Pulse Width
10.0000
Acquisition Time
1.3631
Acquisition Date
2017-05-06T06:57:52
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1960.7
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
ppm


Parameter Value
Data File Name /Volumes/nmrdata/nfastuca/nmr/NJF-3-222/1/fid
Title NJF-3-222.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 296.1
Pulse Sequence zg30
Experiment 1D
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 16
Receiver Gain 142.8
Relaxation Delay 1.0000
Pulse Width 12.5000
Acquisition Time 4.0894
Acquisition Date 2019-06-20T12:03:36
Modification Date 2019-06-20T12:03:36
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.4
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
Br
O
Si
O
t-Bu
t-Bu
90
7.26 CDCl3
6.24
5.86
5.80
4.64
4.23
3.04
1.07
1.01
1.00
0.98
1.01
1.00
1.01
1.00
1.04
1.00
ppm


Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-3-222/ 2/ fid
Title NJF-3-222-2.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 296.1
Pulse Sequence zgpg30
Experiment 1D
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 512
Receiver Gain 72.0
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2019-06-20T12:24:50
Modification Date 2019-06-20T12:24:50
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1961.4
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
Br
O
Si
O
t-Bu
t-Bu
90
135.90
132.94
130.36
128.20
77.00 CDCl3
76.60
65.12
51.64
47.28
28.83
28.22
21.18
20.70
ppm


ppm
ppm
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-3-222/ 2/ ser
Title NJF-3-222.2.ser
Origin Bruker BioSpin GmbH
Instrument Avance
Solvent CDCl3
Temperature 298.2
Pulse Sequence hsqcedetgpsisp2.3
Experiment HSQC-EDITED
Probe Z163739_0009 (PI HR-400-S1-BBF/ H/ D-5.0-Z SP)
Number of Scans 4
Receiver Gain 32.0
Relaxation Delay 1.5000
Pulse Width 9.7500
Acquisition Time 0.1946
Acquisition Date 2019-06-20T22:10:42
Modification Date 2019-06-20T22:10:42
Spectrometer Frequency (400.15, 100.63)
Spectral Width (5263.2, 16604.4)
Lowest Frequency (-760.3, -743.2)
Nucleus (1H, 13C)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
Br
O
Si
O
t-Bu
t-Bu
90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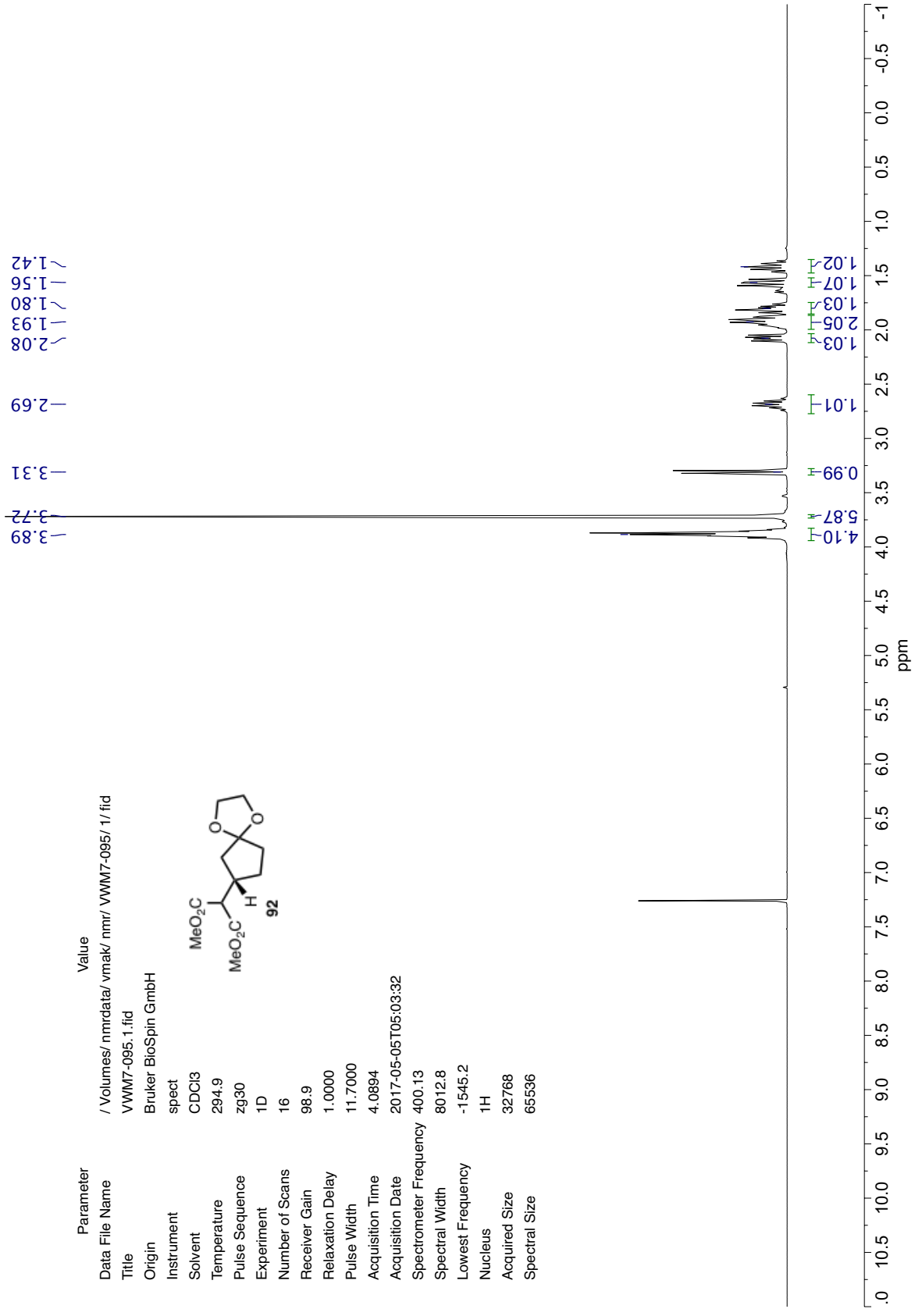
Title PROTON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 8
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 5.9000
Acquisition Time 3.0000
Acquisition Date 2016-04-28T14:43:32
Spectrometer Frequency 499.66
Spectral Width 8000.0
Lowest Frequency -1013.6
Nucleus 1H
Acquired Size 24000
Spectral Size 65536
MeO2C
MeO2C
H
O
91
3.76
3.37
2.85
2.49
2.34
2.21
2.00
1.65
2.91
2.87
0.93
0.96
1.00
1.01
2.02
1.00
1.05
ppm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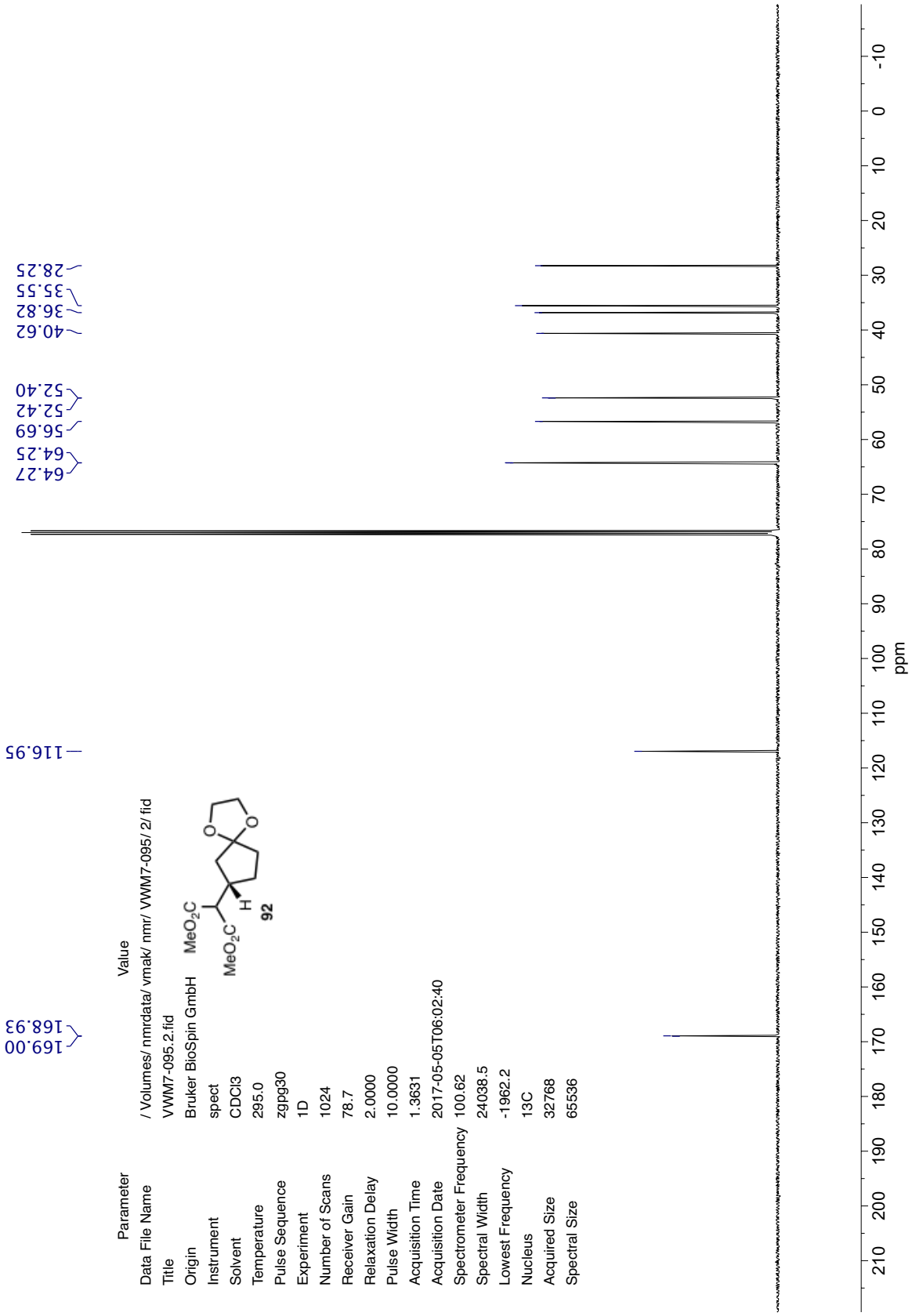
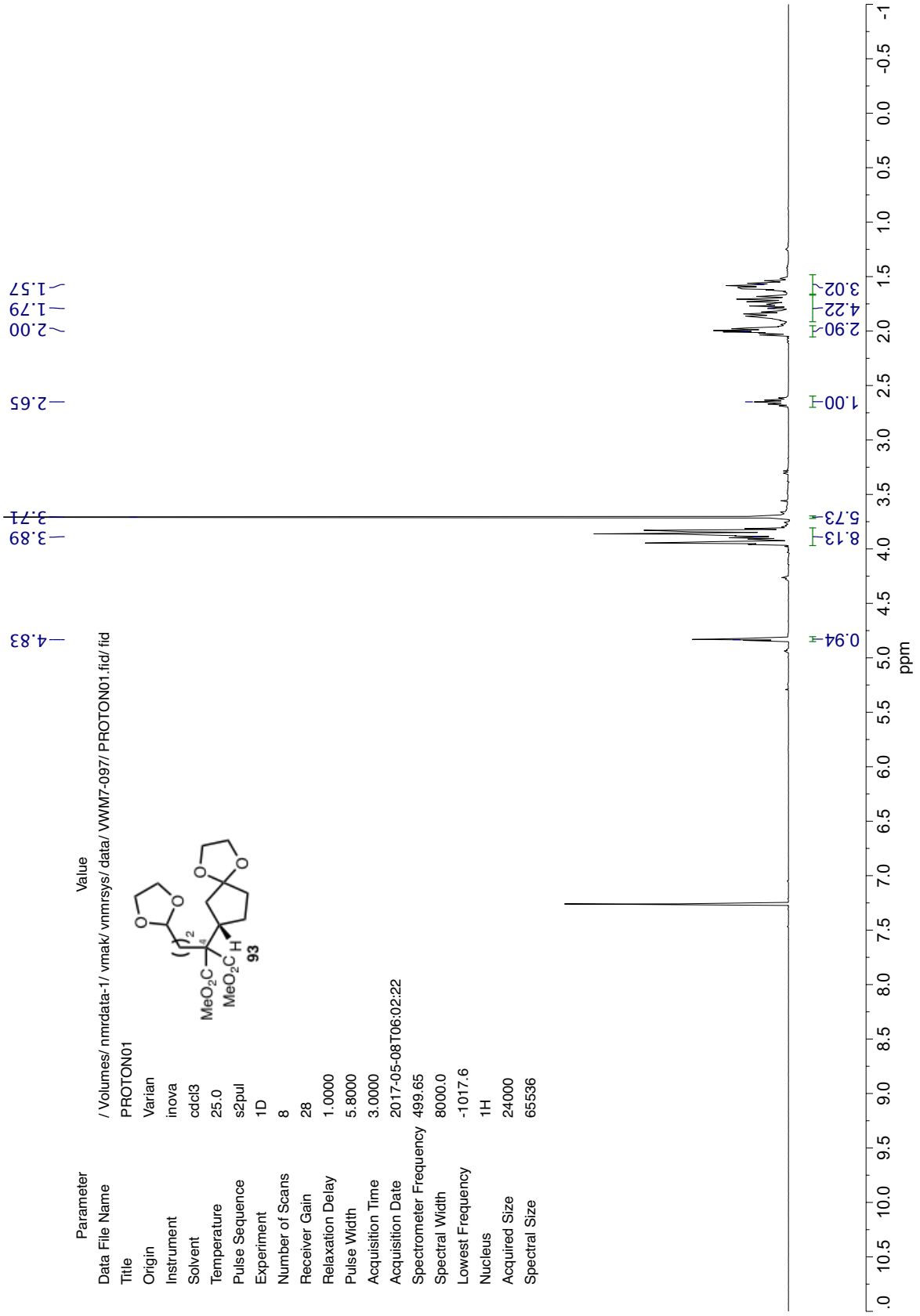
Title
VWM7-095.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
294.9
Pulse Sequence
zg30
Experiment
1D
Number of Scans
16
Receiver Gain
98.9
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2017-05-05T05:03:32
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.2
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
MeO2C
MeO2C
H
92
3.89
3.72
3.31
2.69
2.08
1.93
1.80
1.56
1.42
4.10
5.87
0.99
1.01
1.03
2.05
1.03
1.07
1.02
ppm


169.00
168.93
116.95
64.27
64.25
56.69
52.42
52.40
40.62
36.82
35.55
28.25
MeO2C
MeO2C
H
92
Parameter
Value
Data File Name / Volumes/ nmrdata/ vmak/ nmr/ VWM7-095/ 2/ fid
Title VWM7-095.2.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.0
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 1024
Receiver Gain 78.7
Relaxation Delay 2.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2017-05-05T06:02:40
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1962.2
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



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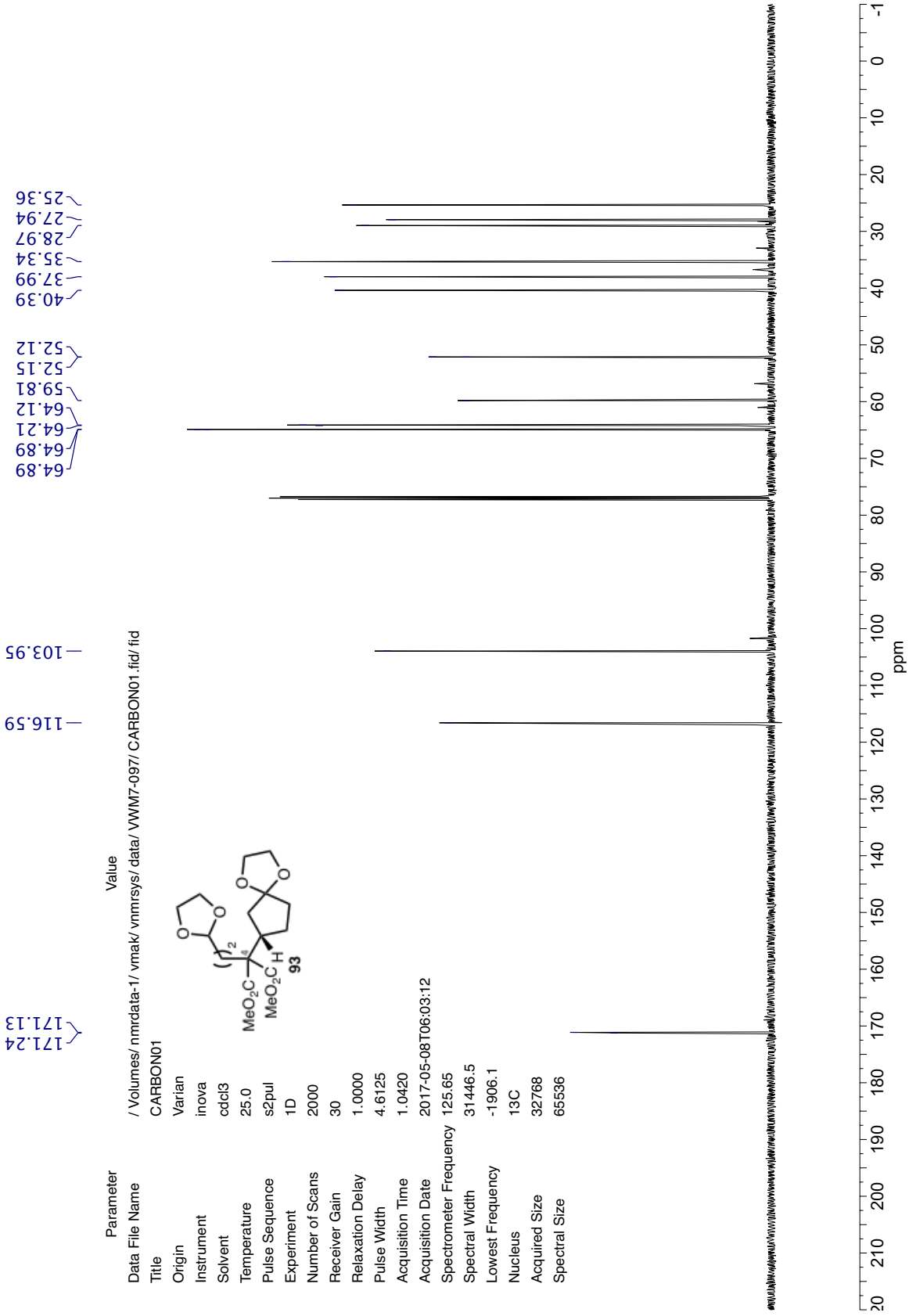
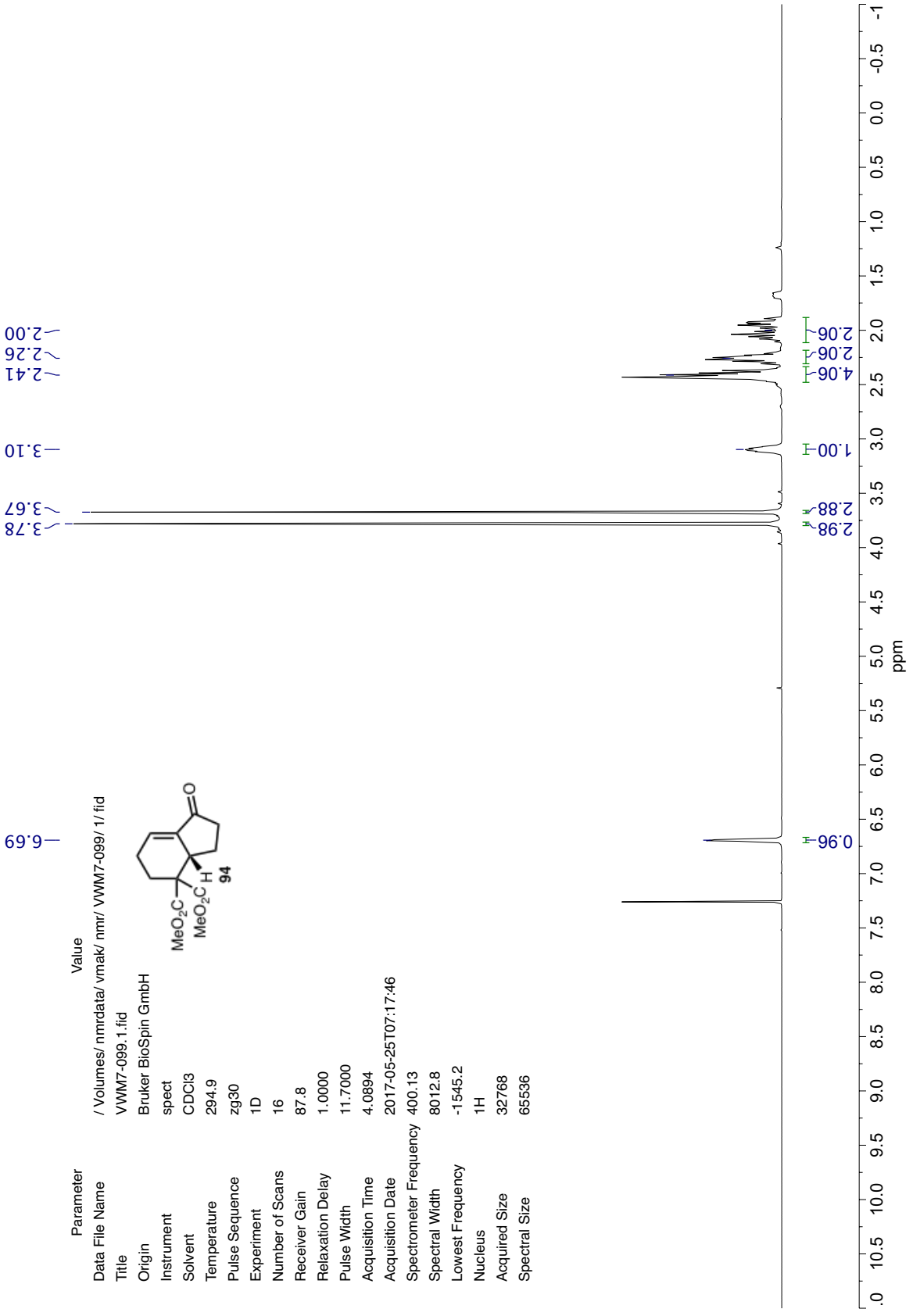
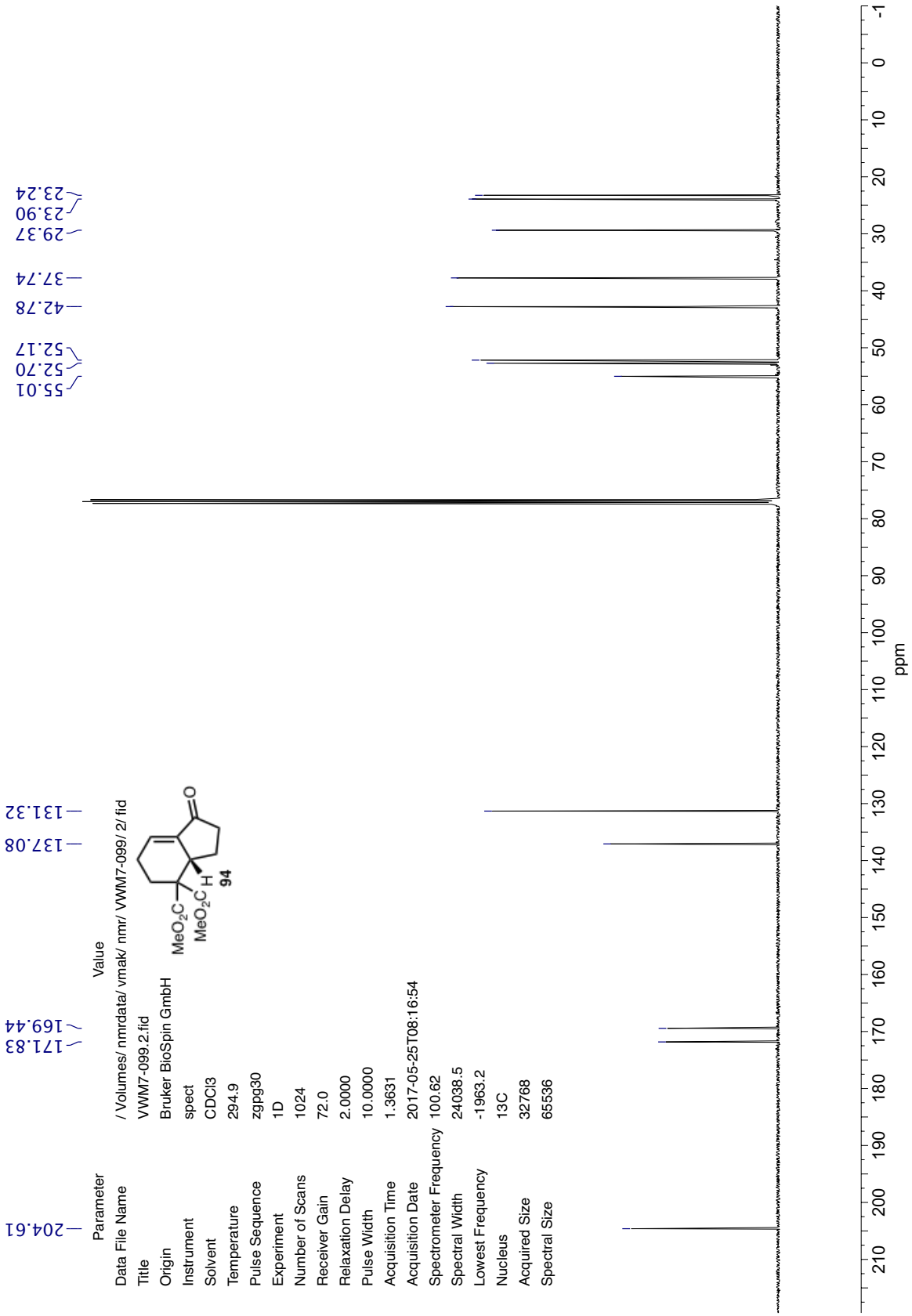
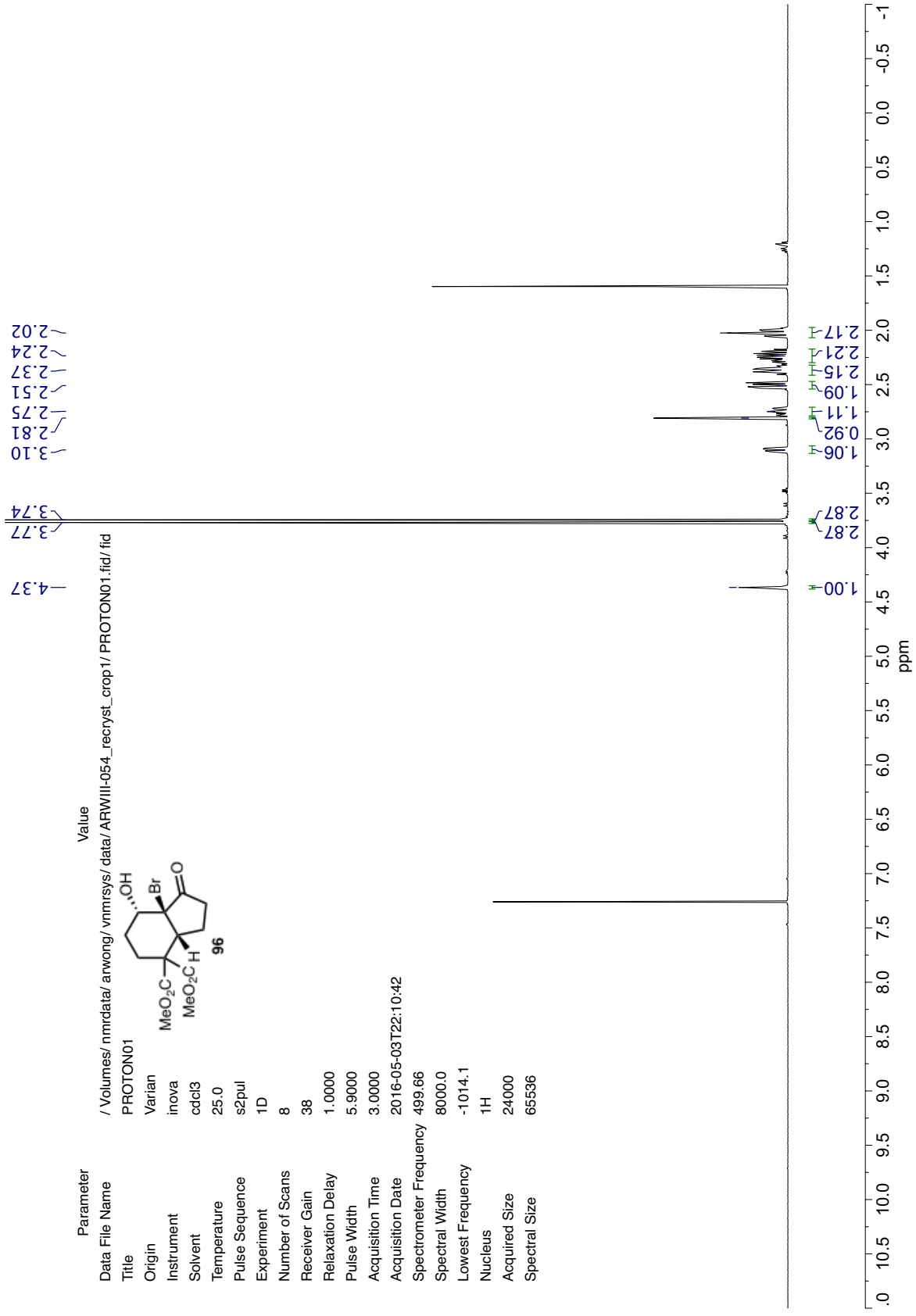
Title	PROTON01
Origin	Varian
Instrument	inova
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	8
Receiver Gain	28
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Acquisition Date	2017-05-08T06:02:22
Spectrometer Frequency	499.65
Spectral Width	8000.0
Lowest Frequency	-1017.6
Nucleus	1H
Acquired Size	24000
Spectral Size	65536


171.24
171.13
116.59
103.95
64.89
64.89
64.21
64.12
59.81
52.15
52.12
40.39
37.99
35.34
28.97
27.94
25.36
MeO2C
MeO2C
H
93
Parameter
Value
Data File Name / Volumes/ nmrdata-1/ vmak/ vnmrsys/ data/ VWM7-097/ CARBON01.fid/ fid
Title CARBON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 2000
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 4.6125
Acquisition Time 1.0420
Acquisition Date 2017-05-08T06:03:12
Spectrometer Frequency 125.65
Spectral Width 31446.5
Lowest Frequency -1906.1
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
ppm


6.69
3.78
3.67
3.10
2.41
2.26
2.00
0.96
2.98
2.88
1.00
4.06
2.06
2.06
2.00
MeO2C
MeO2C
H
94
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ vmak/ nmr/ VWM7-099/ 1/ fid
Title
VWM7-099.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
294.9
Pulse Sequence
zg30
Experiment
1D
Number of Scans
16
Receiver Gain
87.8
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2017-05-25T07:17:46
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.2
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
ppm


204.61
171.83
169.44
137.08
131.32
55.01
52.70
52.17
42.78
37.74
29.37
23.90
23.24
MeO2C
MeO2C
H
94
Parameter
Value
Data File Name / Volumes/ nmrdata/ vmak/ nmr/ VWM7-099/ 2/ fid
Title VWM7-099.2.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 294.9
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 1024
Receiver Gain 72.0
Relaxation Delay 2.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2017-05-25T08:16:54
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1963.2
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
ppm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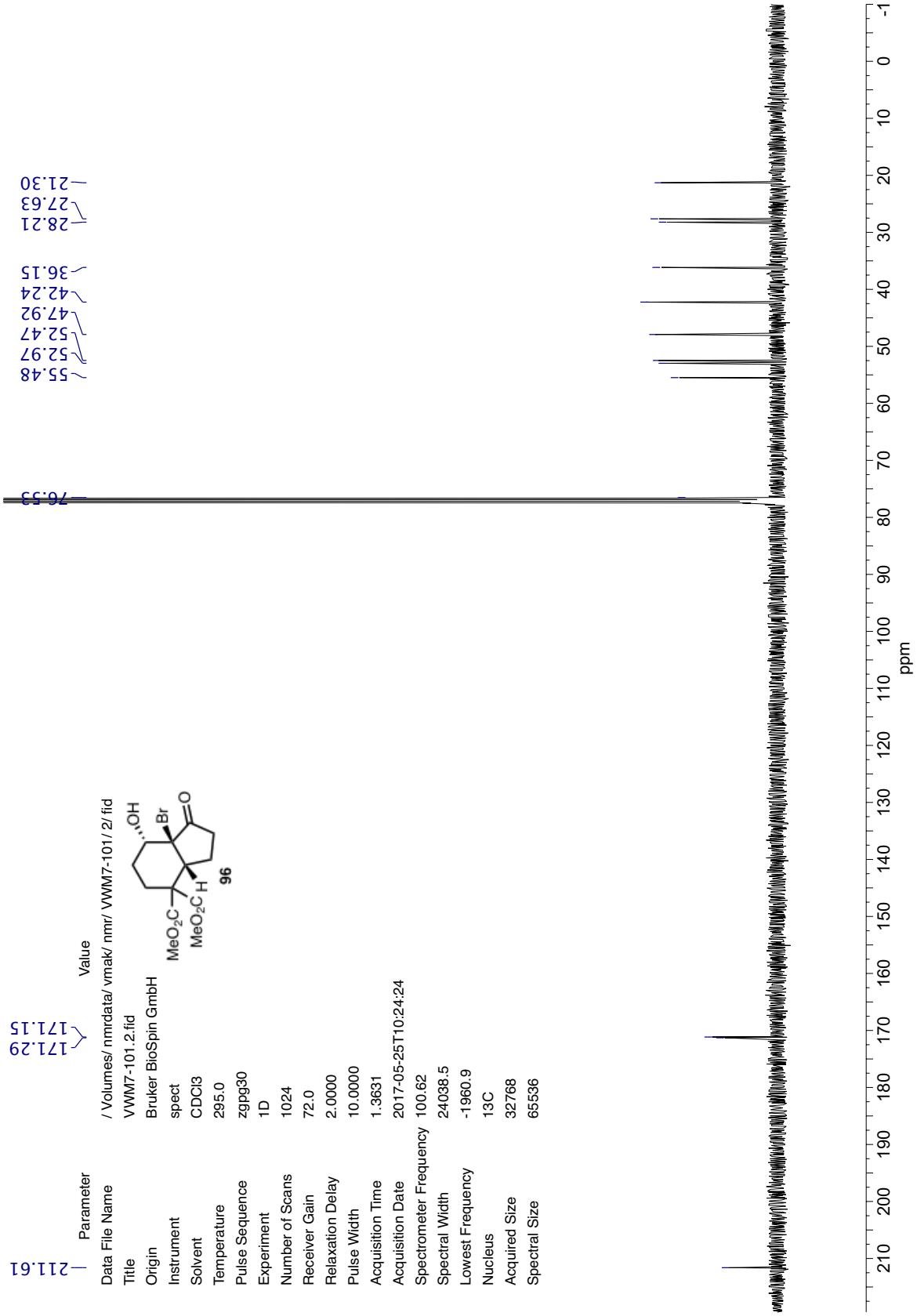
Title PROTON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 8
Receiver Gain 38
Relaxation Delay 1.0000
Pulse Width 5.9000
Acquisition Time 3.0000
Acquisition Date 2016-05-03T22:10:42
Spectrometer Frequency 499.66
Spectral Width 8000.0
Lowest Frequency -1014.1
Nucleus 1H
Acquired Size 24000
Spectral Size 65536
OH
Br
O
MeO2C
MeO2C
H
96
4.37
3.77
3.74
3.10
2.81
2.75
2.51
2.37
2.24
2.02
1.00
2.87
2.87
1.06
0.92
1.11
1.09
2.15
2.21
2.17
ppm


211.61
171.29
171.15
76.53
55.48
52.97
52.47
47.92
42.24
36.15
28.21
27.63
21.30
MeO2C
MeO2C
OH
Br
O
H
96
Parameter
Value
Data File Name / Volumes/ nmrdata/ vmak/ nmr/ VWM7-101/ 2/ fid
Title VWM7-101.2.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.0
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 1024
Receiver Gain 72.0
Relaxation Delay 2.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2017-05-25T10:24:24
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1960.9
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
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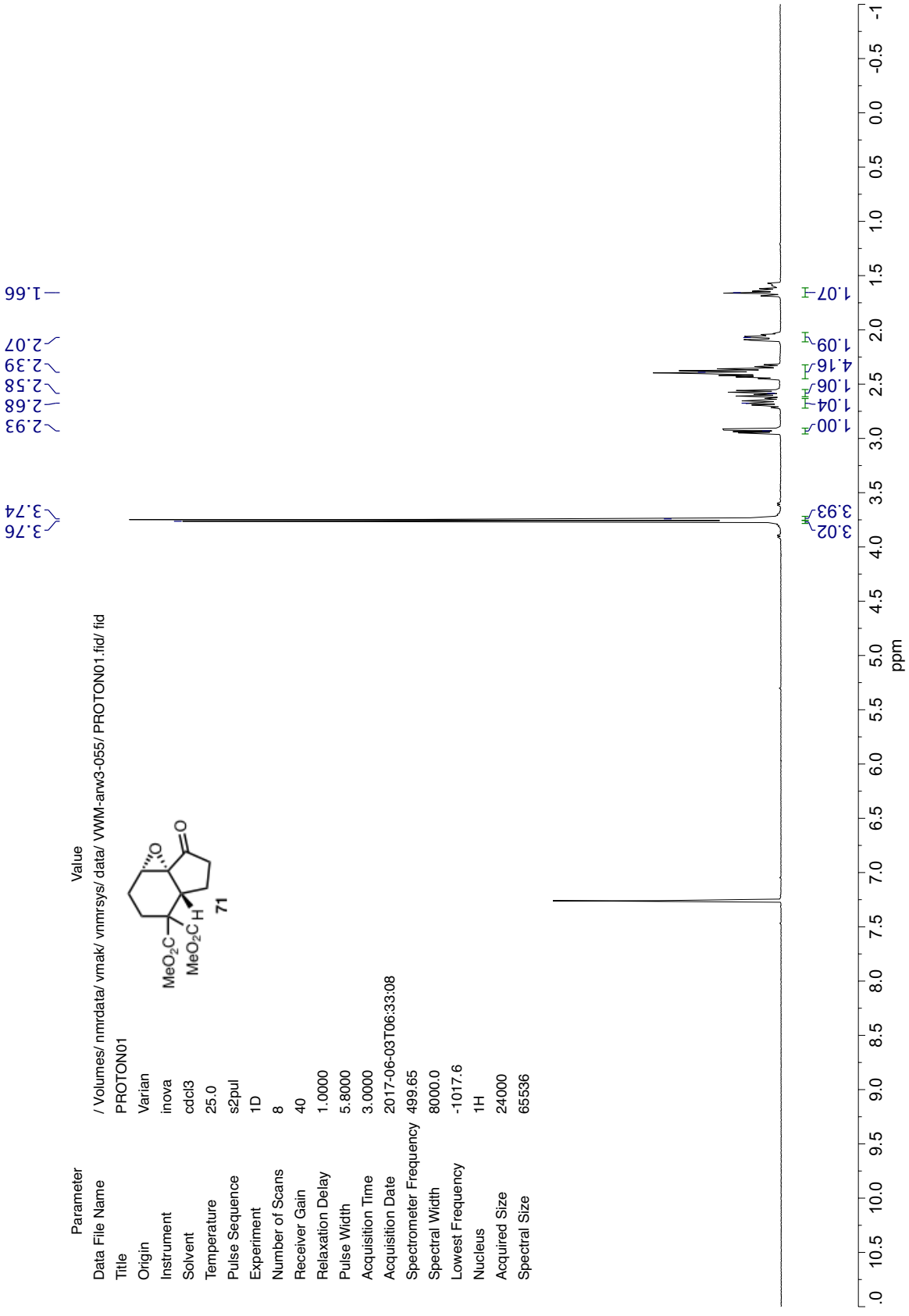
ppm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Value
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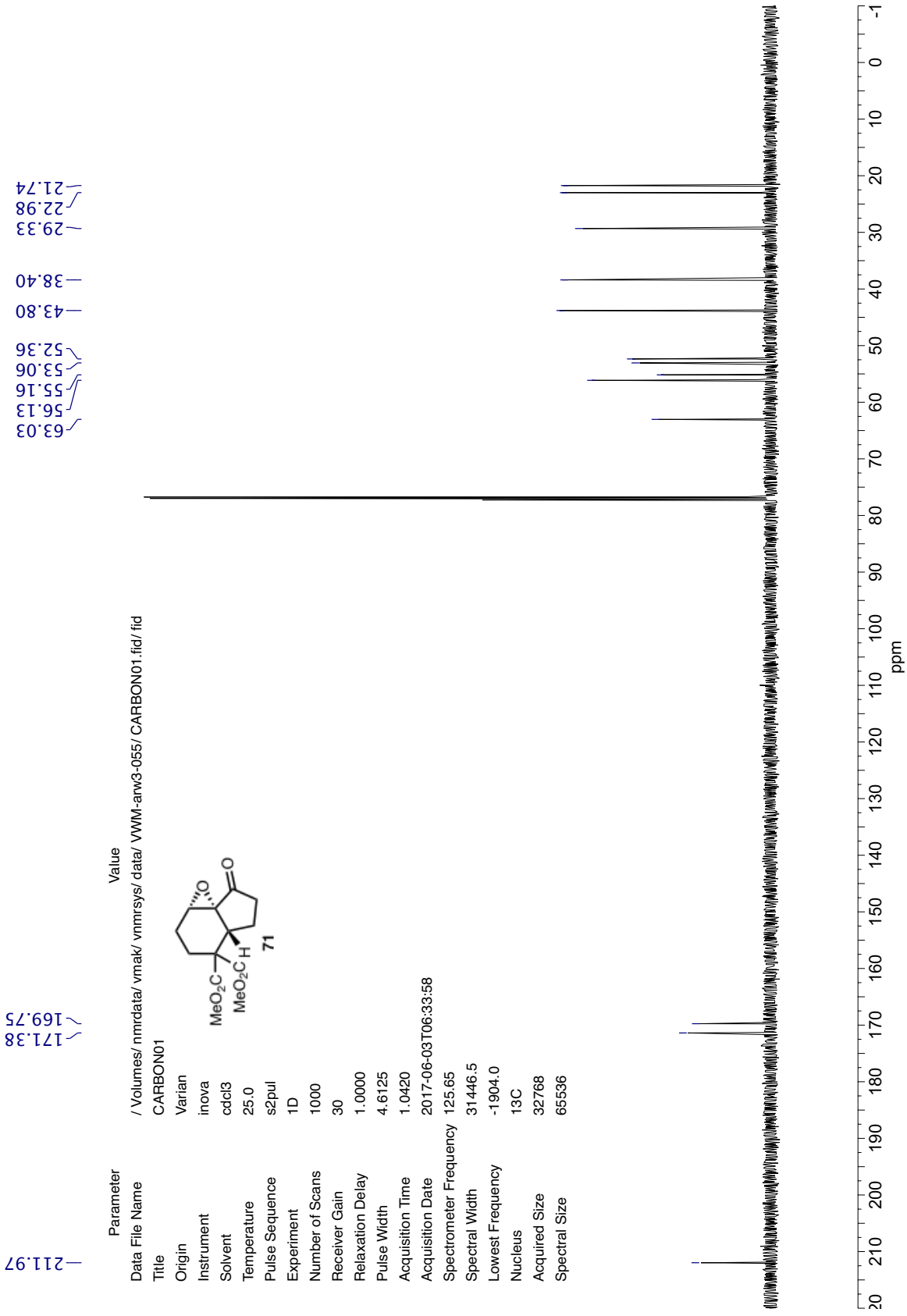
/ Volumes/ nmrdata/ vmak/ vnmrsys/ data/ VWM-arw3-055/ PROTON01.fid/ fid
Title
PROTON01
Origin
Varian
Instrument
inova
Solvent
cdcl3
Temperature
25.0
Pulse Sequence
s2pul
Experiment
1D
Number of Scans
8
Receiver Gain
40
Relaxation Delay
1.0000
Pulse Width
5.8000
Acquisition Time
3.0000
Acquisition Date
2017-06-03T06:33:08
Spectrometer Frequency
499.65
Spectral Width
8000.0
Lowest Frequency
-1017.6
Nucleus
1H
Acquired Size
24000
Spectral Size
65536
MeO2C
MeO2C
71
3.76
3.74
2.93
2.68
2.58
2.39
2.07
1.66
3.02
3.93
1.00
1.04
1.06
4.16
1.09
1.07
ppm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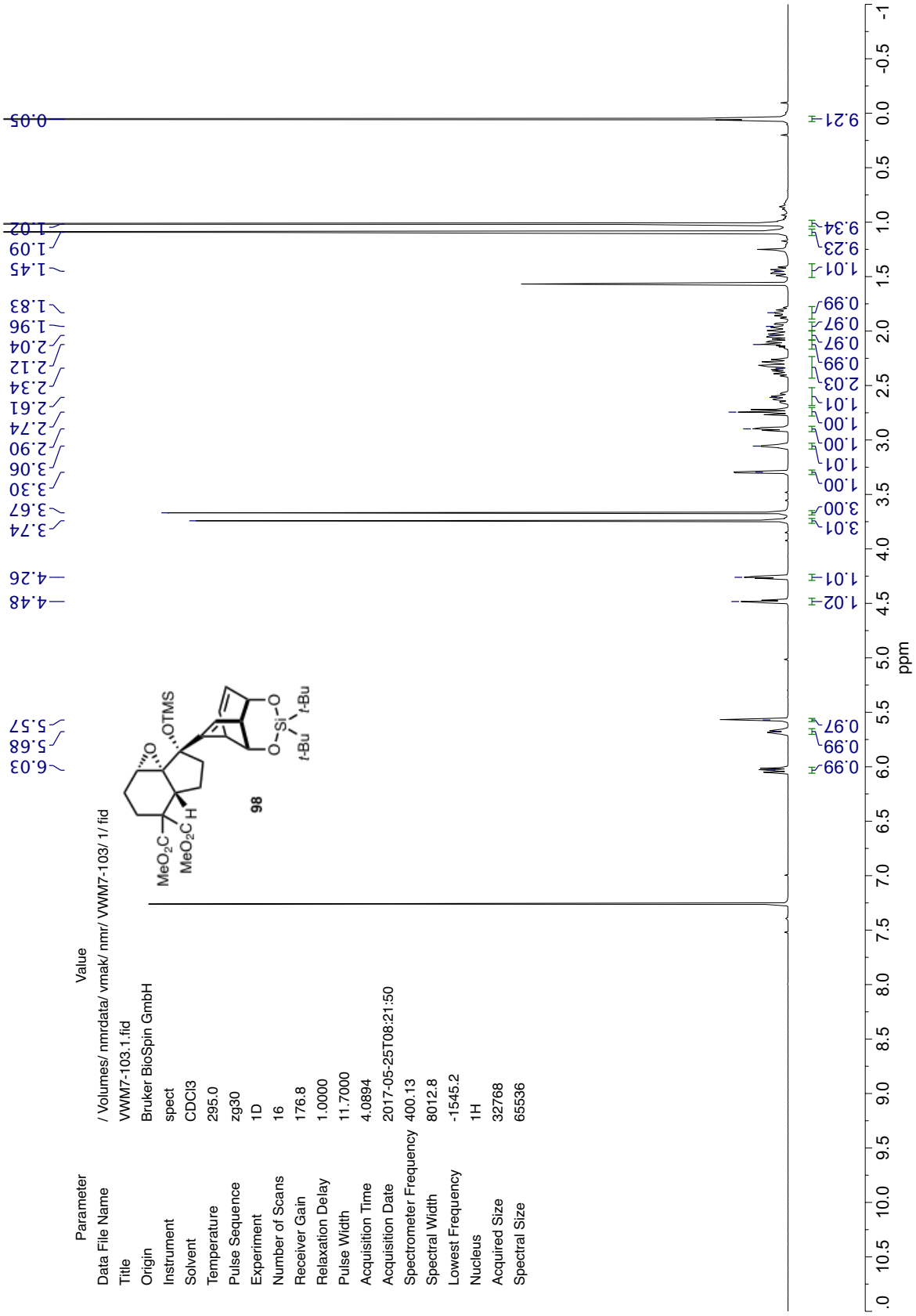
171.38
169.75
63.03
56.13
55.16
53.06
52.36
43.80
38.40
29.33
22.98
21.74
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ vmak/ vnmrsys/ data/ VWM-arw3-055/ CARBON01.fid/ fid
Title
CARBON01
Origin
Varian
Instrument
inova
Solvent
cdcl3
Temperature
25.0
Pulse Sequence
s2pul
Experiment
1D
Number of Scans
1000
Receiver Gain
30
Relaxation Delay
1.0000
Pulse Width
4.6125
Acquisition Time
1.0420
Acquisition Date
2017-06-03T06:33:58
Spectrometer Frequency
125.65
Spectral Width
31446.5
Lowest Frequency
-1904.0
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
MeO2C
MeO2C
H
O
O
71
ppm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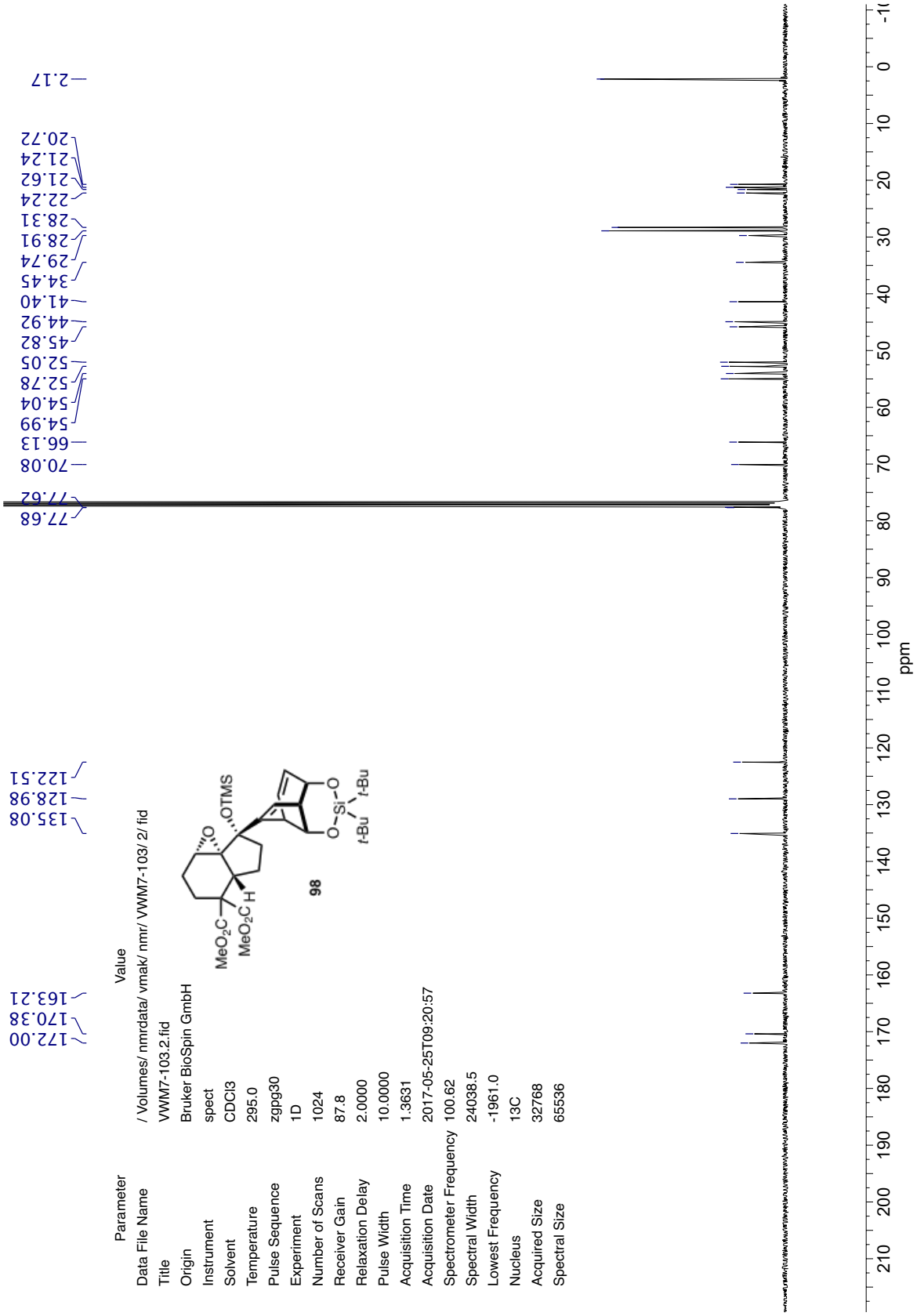
Data File Name / Volumes/ nmrdata/ vmak/ nmr/ VWM7-103/ 1/ fid
Title VWM7-103.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.0
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 176.8
Relaxation Delay 1.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Acquisition Date 2017-05-25T08:21:50
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.2
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
MeO2C
MeO2C
OTMS
O
O
Si
O
t-Bu
t-Bu
98
ppm



Parameter	Value
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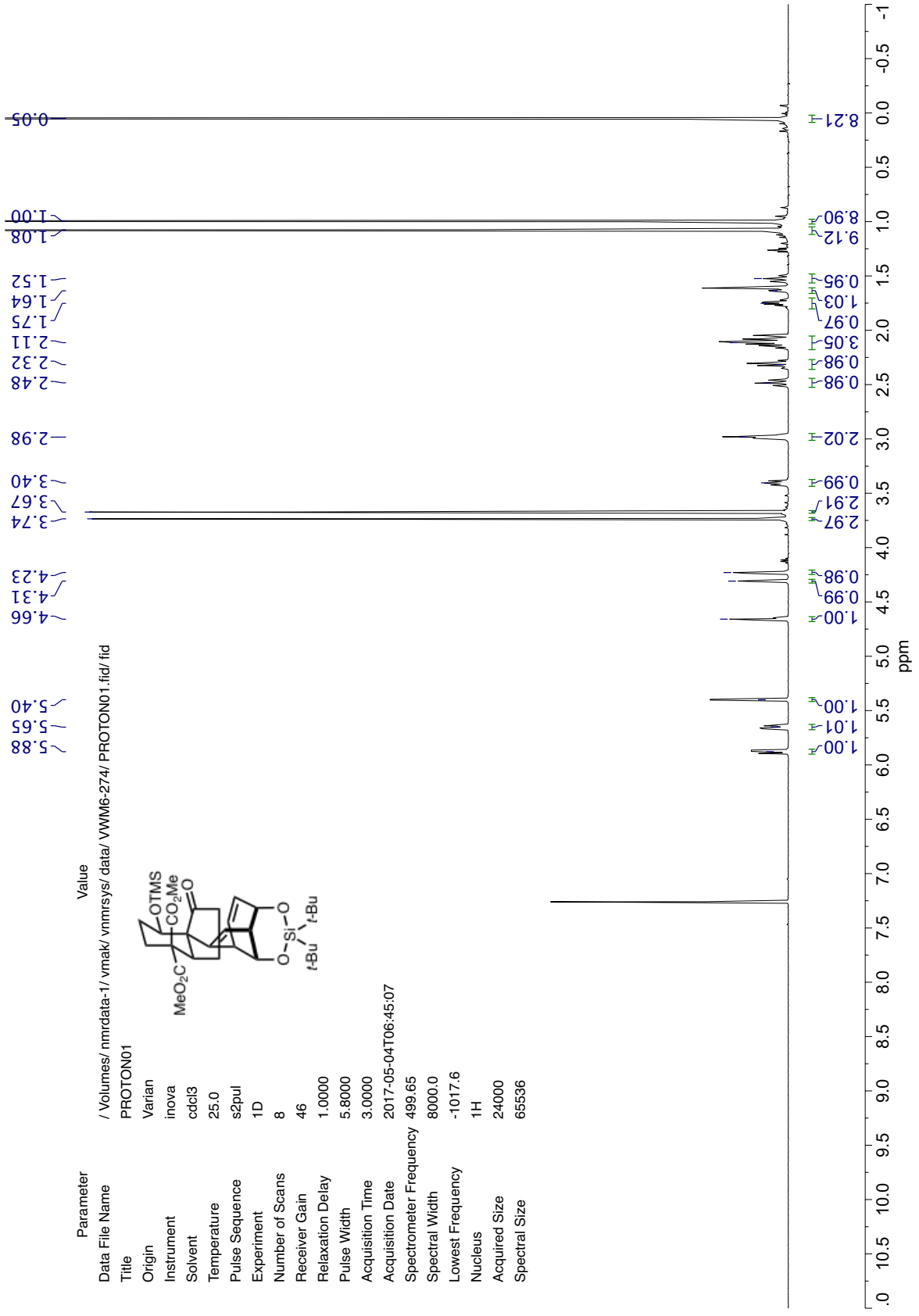
Title	VWM7-103.2.fid
Origin	Bruker BioSpin GmbH
Instrument	spect
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	1024
Receiver Gain	87.8
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-05-25T09:20:57
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536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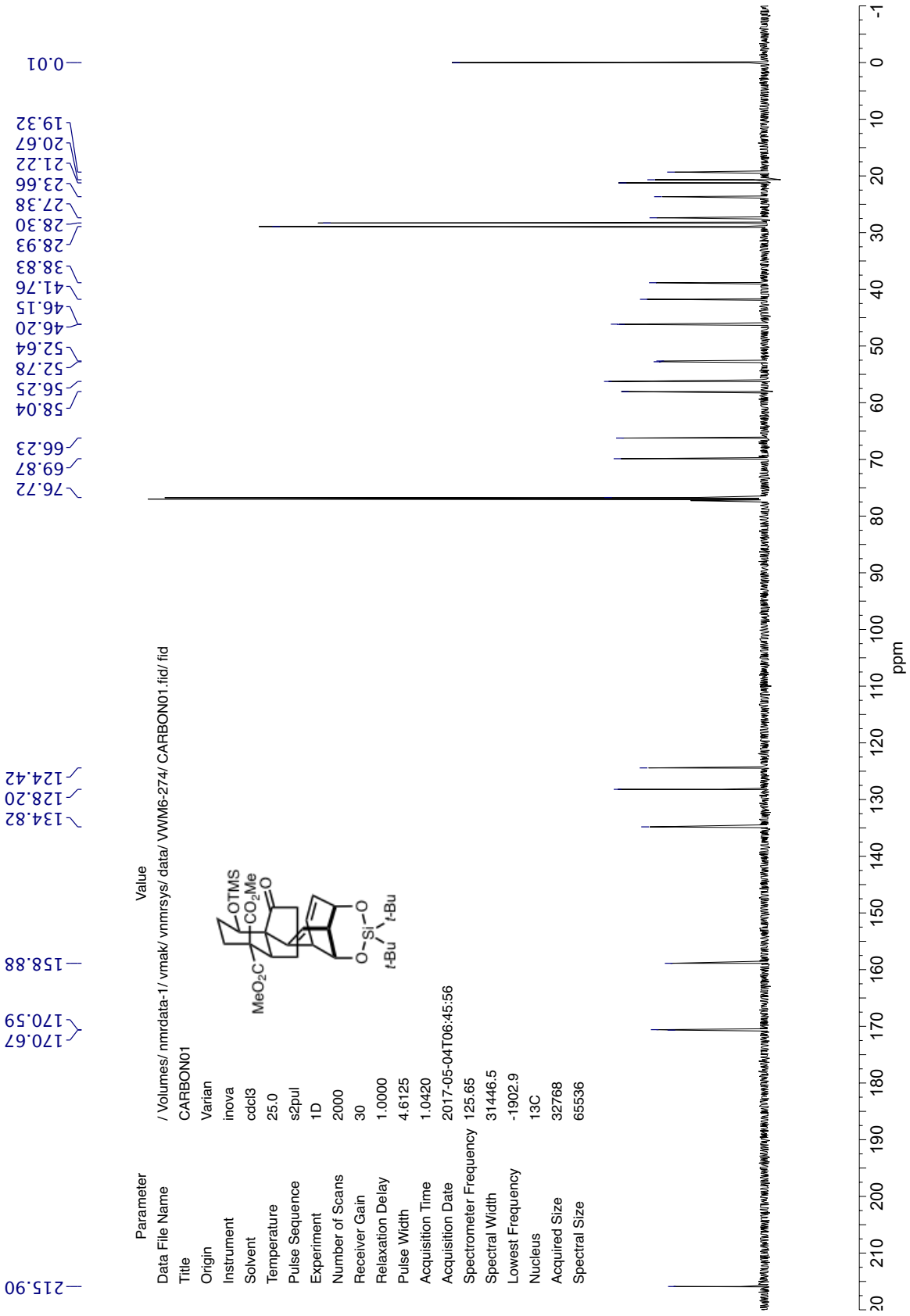
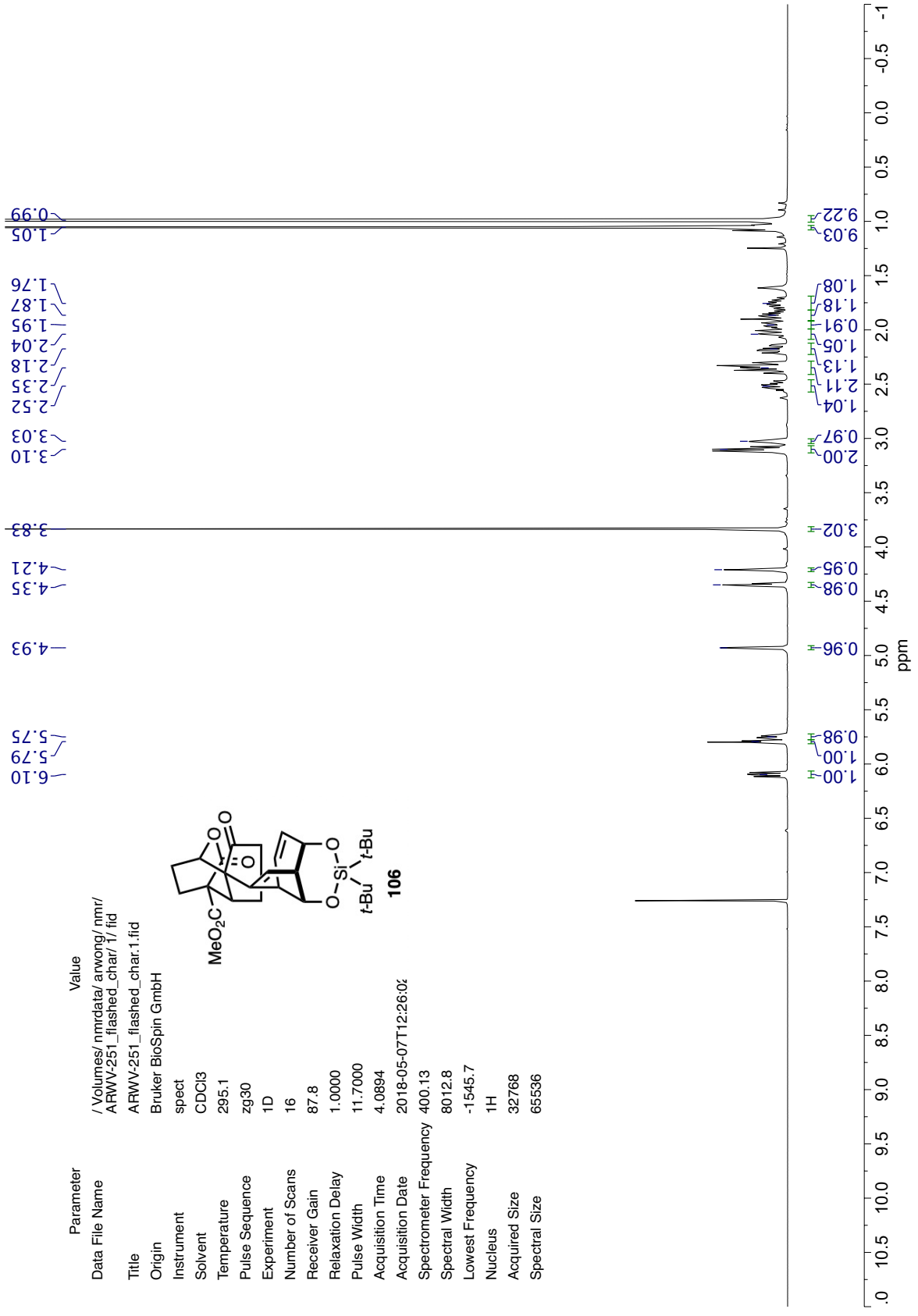
Value
Data File Name / Volumes/ nmrdata-1/ vmak/ vnmrsys/ data/ VWM6-274/ PROTON01.fid/ fid
Title PROTON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 8
Receiver Gain 46
Relaxation Delay 1.0000
Pulse Width 5.8000
Acquisition Time 3.0000
Acquisition Date 2017-05-04T06:45:07
Spectrometer Frequency 499.65
Spectral Width 8000.0
Lowest Frequency -1017.6
Nucleus 1H
Acquired Size 24000
Spectral Size 65536
OTMS
CO2Me
MeO2C
O
Si
t-Bu
t-Bu
ppm

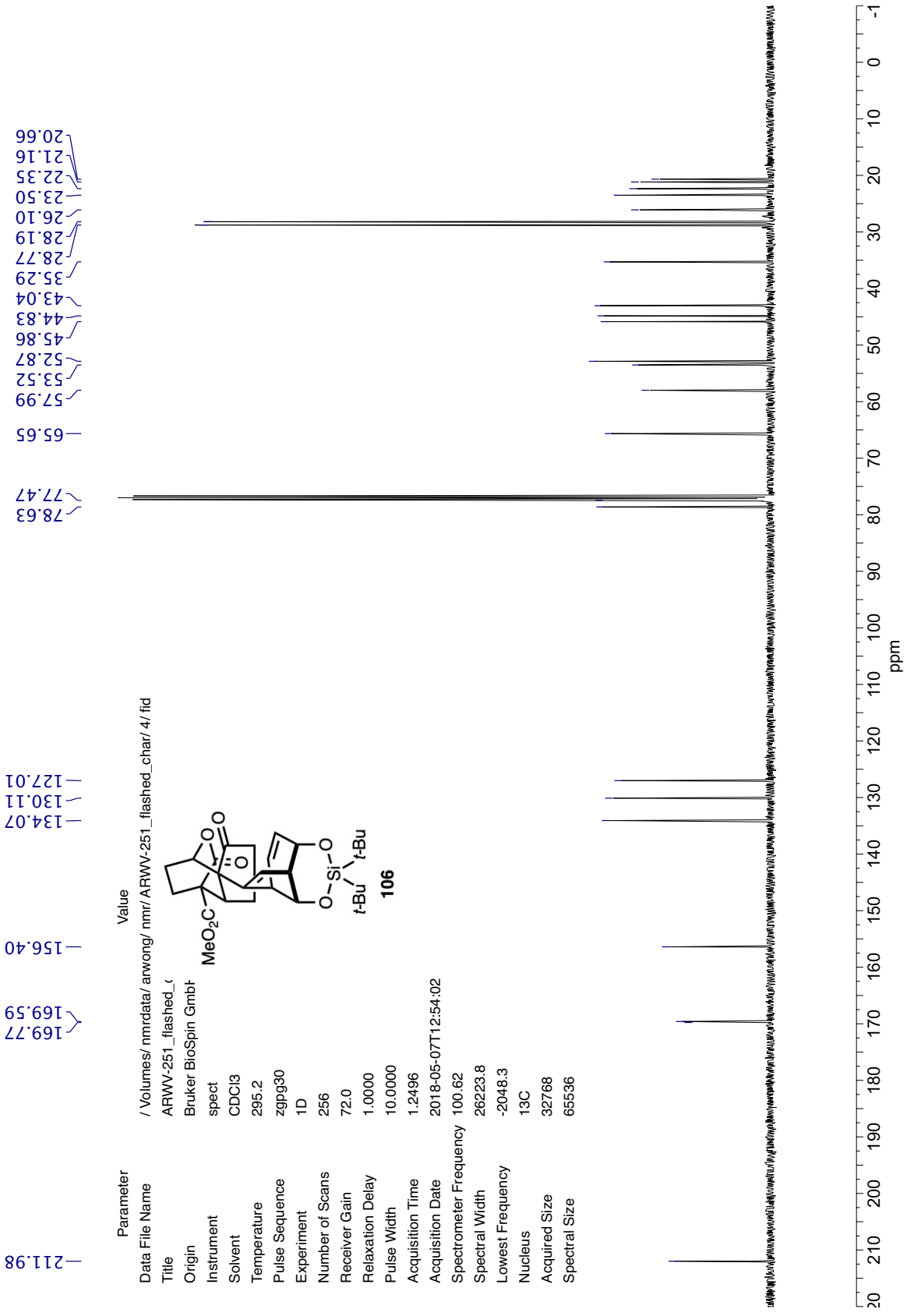

215.90
170.67
170.59
158.88
134.82
128.20
124.42
76.72
69.87
66.23
58.04
56.25
52.78
52.64
46.20
46.15
41.76
38.83
28.93
28.30
27.38
23.66
21.22
20.67
19.32
0.01
OTMS
CO2Me
O
MeO2C
O
Si
O
t-Bu
t-Bu
Value
Parameter
Data File Name / Volumes/ nmrdata-1/ vmak/ vnmrsys/ data/ VWM6-274/ CARBON01.fid/ fid
Title CARBON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 2000
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 4.6125
Acquisition Time 1.0420
Acquisition Date 2017-05-04T06:45:56
Spectrometer Frequency 125.65
Spectral Width 31446.5
Lowest Frequency -1902.9
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
ppm

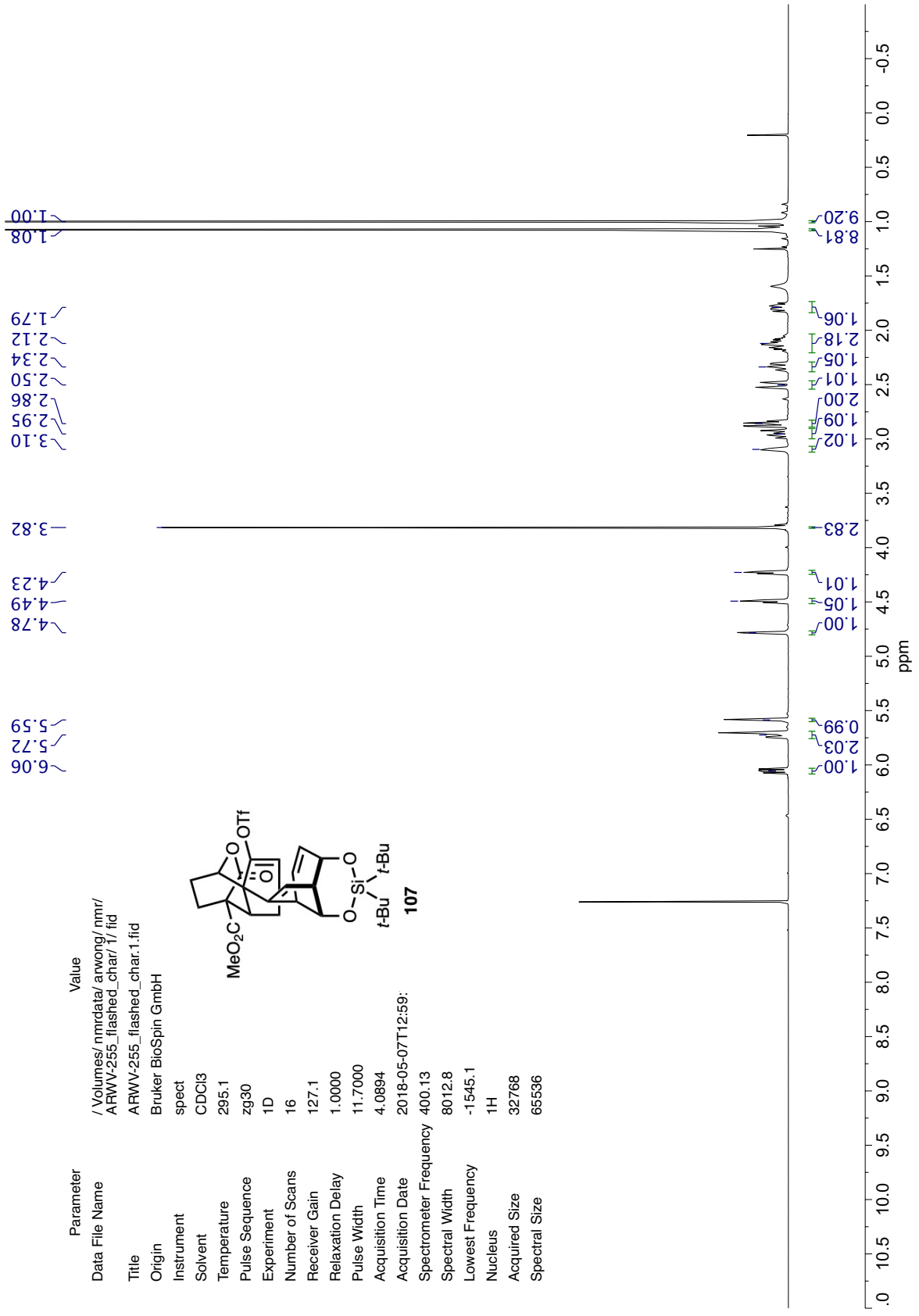
Appendix 2

Spectra Relevant to Chapter 3:

Towards C_{19}-Diterpenoid Alkaloids: Approaches to the C4 Chiral Quaternary Center


Parameter
Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWV-251_flashed_char/ 1/ fid
Title
ARWV-251_flashed_char.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zg30
Experiment
1D
Number of Scans
16
Receiver Gain
87.8
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2018-05-07T12:26:0
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.7
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
MeO2C
t-Bu
t-Bu
106
ppm


211.98
169.77
169.59
156.40
134.07
130.11
127.01
78.63
77.47
65.65
57.99
53.52
52.87
45.86
44.83
43.04
35.29
28.77
28.19
26.10
23.50
22.35
21.16
20.66
MeO2C
O
O
O
O
Si
O
t-Bu
t-Bu
106
Parameter
Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWV-251_flashed_char/ 4/ fid
Title ARWV-251_flashed_c
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.2
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 256
Receiver Gain 72.0
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.2496
Acquisition Date 2018-05-07T12:54:02
Spectrometer Frequency 100.62
Spectral Width 26223.8
Lowest Frequency -2048.3
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
ppm


Parameter
Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWV-255_flashed_char/ 1/ fid
Title
ARWV-255_flashed_char.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zg30
Experiment
1D
Number of Scans
16
Receiver Gain
127.1
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2018-05-07T12:59:
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.1
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
MeO2C
OTf
Si
t-Bu
t-Bu
107
6.06
5.72
5.59
4.78
4.49
4.23
3.82
3.10
2.95
2.86
2.50
2.34
2.12
1.79
1.08
1.00
1.00
2.03
0.99
1.00
1.05
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1.02
1.09
2.00
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1.05
2.18
1.06
8.81
9.20
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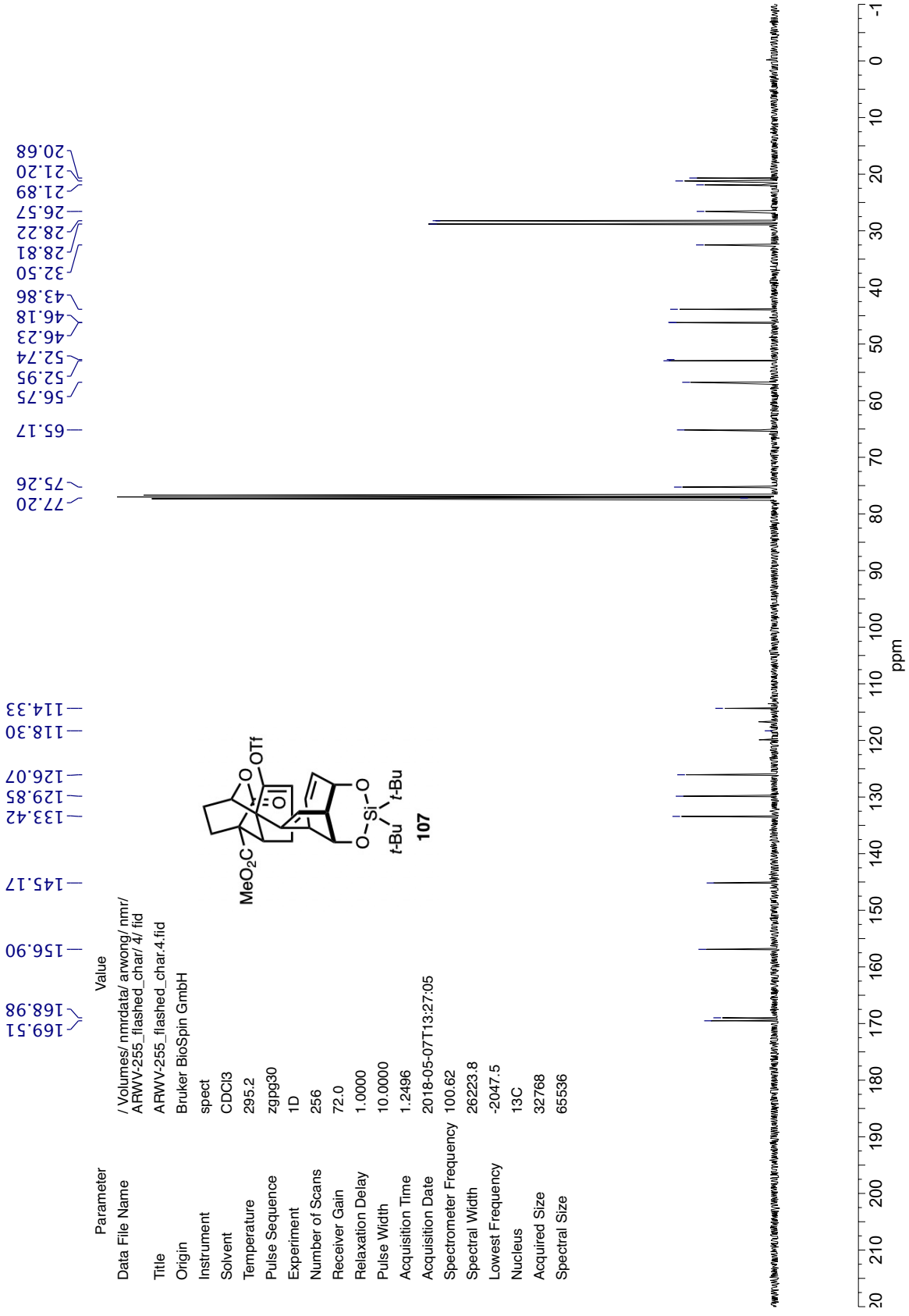
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168.98
156.90
145.17
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129.85
126.07
118.30
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77.20
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56.75
52.95
52.74
46.23
46.18
43.86
32.50
28.81
28.22
26.57
21.89
21.20
20.68
MeO2C
OTf
O
O
O
Si
O
t-Bu
t-Bu
107
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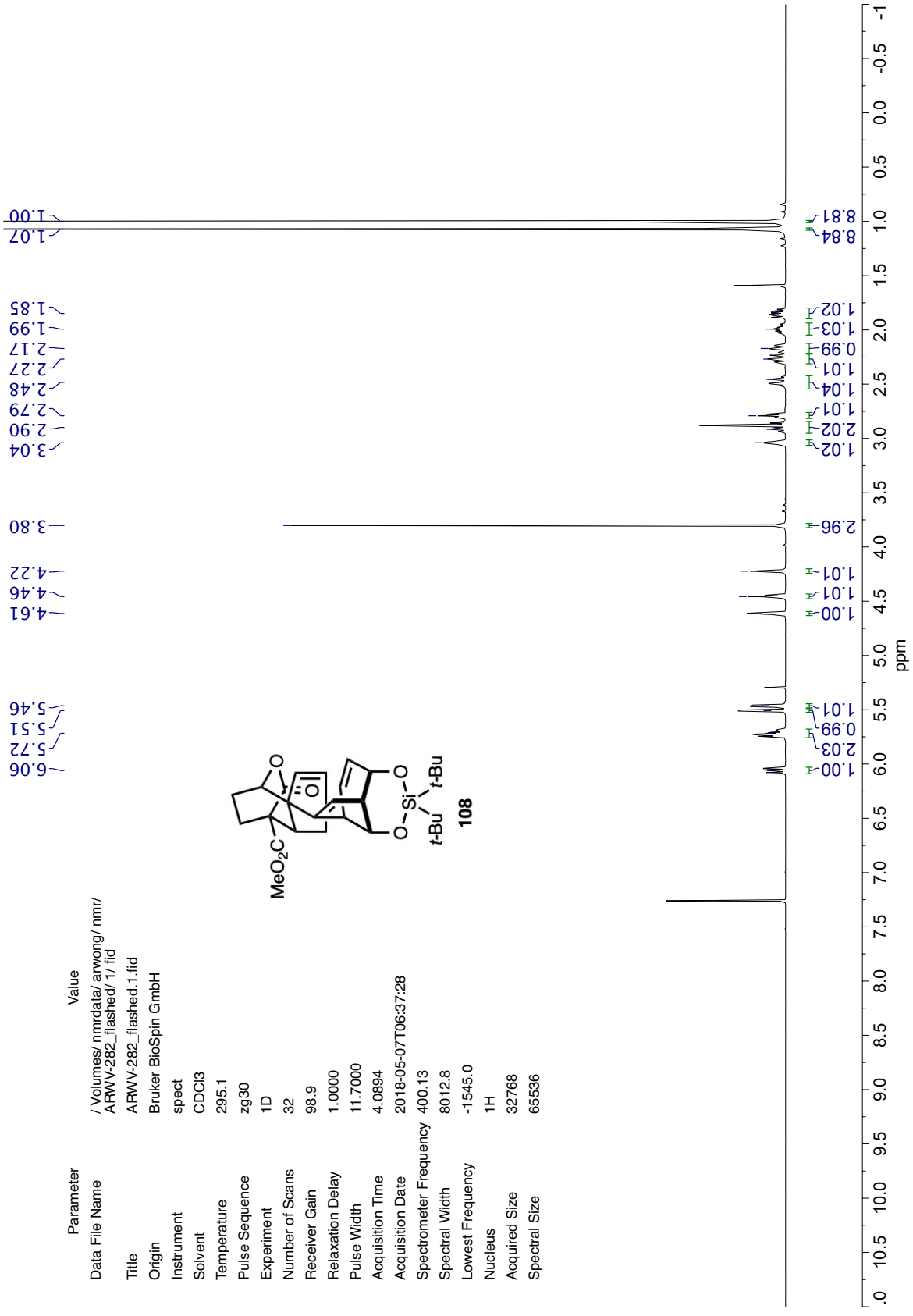
Title
ARWV-255_flashed_char.4.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.2
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
256
Receiver Gain
72.0
Relaxation Delay
1.0000
Pulse Width
10.0000
Acquisition Time
1.2496
Acquisition Date
2018-05-07T13:27:05
Spectrometer Frequency
100.62
Spectral Width
26223.8
Lowest Frequency
-2047.5
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
ppm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Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zg30
Experiment
1D
Number of Scans
32
Receiver Gain
98.9
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2018-05-07T06:37:28
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.0
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
MeO2C
O
O
O
Si
t-Bu
t-Bu
108
6.06
5.72
5.51
5.46
4.61
4.46
4.22
3.80
3.04
2.90
2.79
2.48
2.27
2.17
1.99
1.85
1.07
1.00
1.00
2.03
0.99
1.01
1.00
1.01
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1.04
1.01
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1.03
1.02
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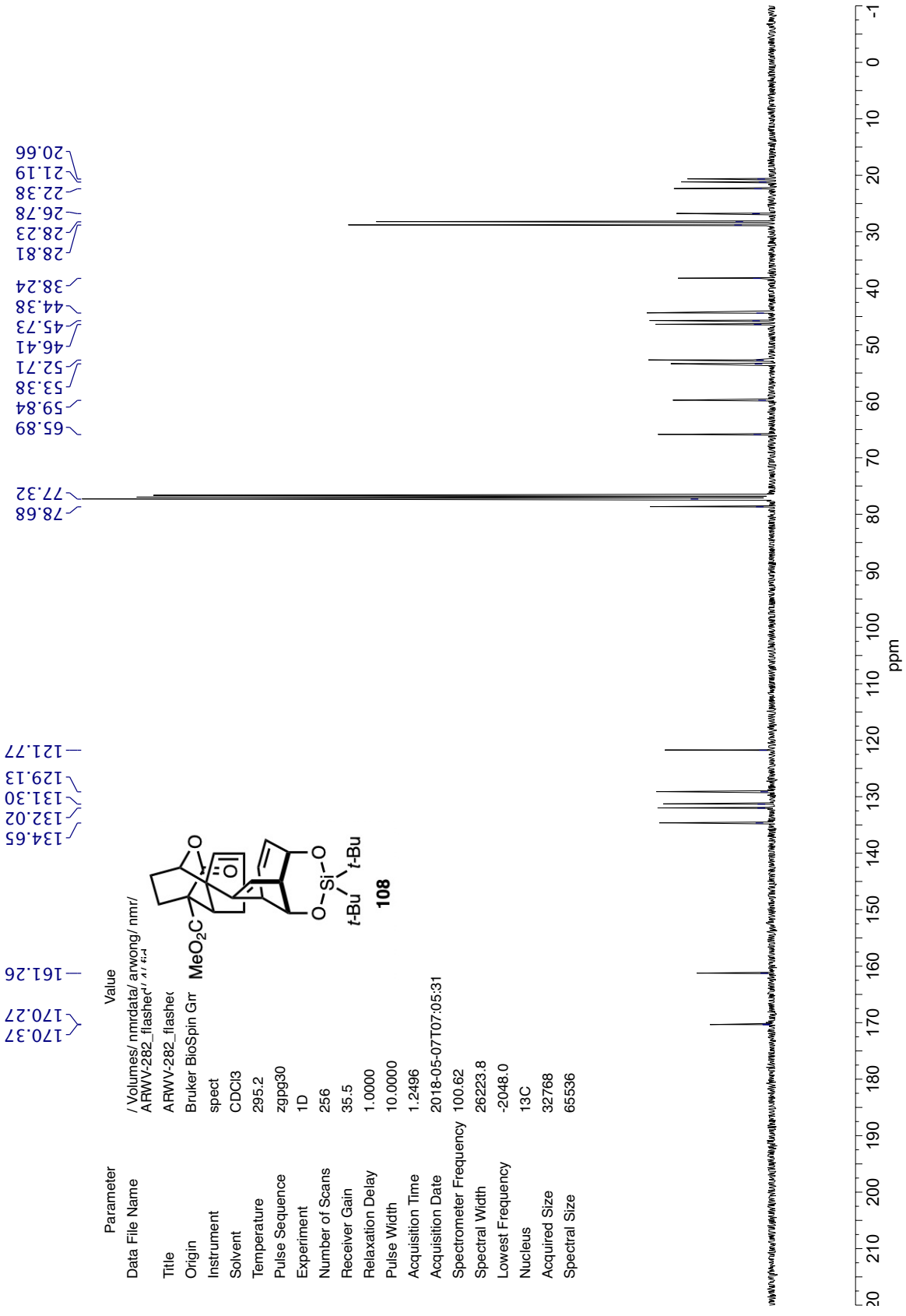
ppm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Data File Name
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Title
ARWV-282_flashed
Origin
Bruker BioSpin Gr
Instrument
spect
Solvent
CDCl3
Temperature
295.2
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
256
Receiver Gain
35.5
Relaxation Delay
1.0000
Pulse Width
10.0000
Acquisition Time
1.2496
Acquisition Date
2018-05-07T07:05:31
Spectrometer Frequency
100.62
Spectral Width
26223.8
Lowest Frequency
-2048.0
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
MeO2C
O
Si
t-Bu
t-Bu
108
170.37
170.27
161.26
134.65
132.02
131.30
129.13
121.77
78.68
77.32
65.89
59.84
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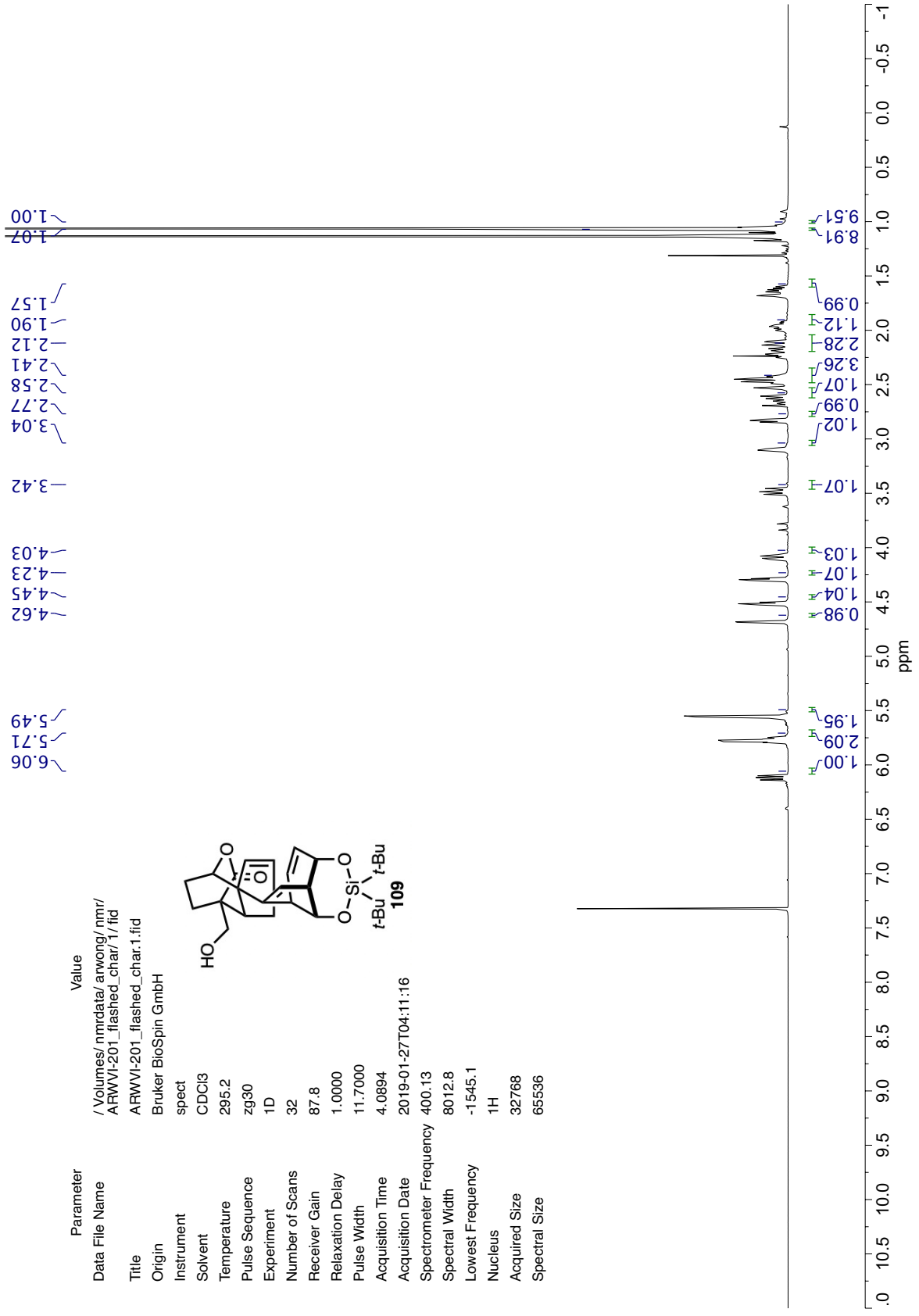
ppm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ARWVI-201_flashed_char.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.2
Pulse Sequence
zg30
Experiment
1D
Number of Scans
32
Receiver Gain
87.8
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2019-01-27T04:11:16
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.1
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
HO
O
O
O
Si
O
t-Bu
t-Bu
109
6.06
5.71
5.49
4.62
4.45
4.23
4.03
3.42
3.04
2.77
2.58
2.41
2.12
1.90
1.57
1.00
1.07
9.51
8.91
0.99
1.12
2.28
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1.02
1.07
1.03
1.07
1.04
0.98
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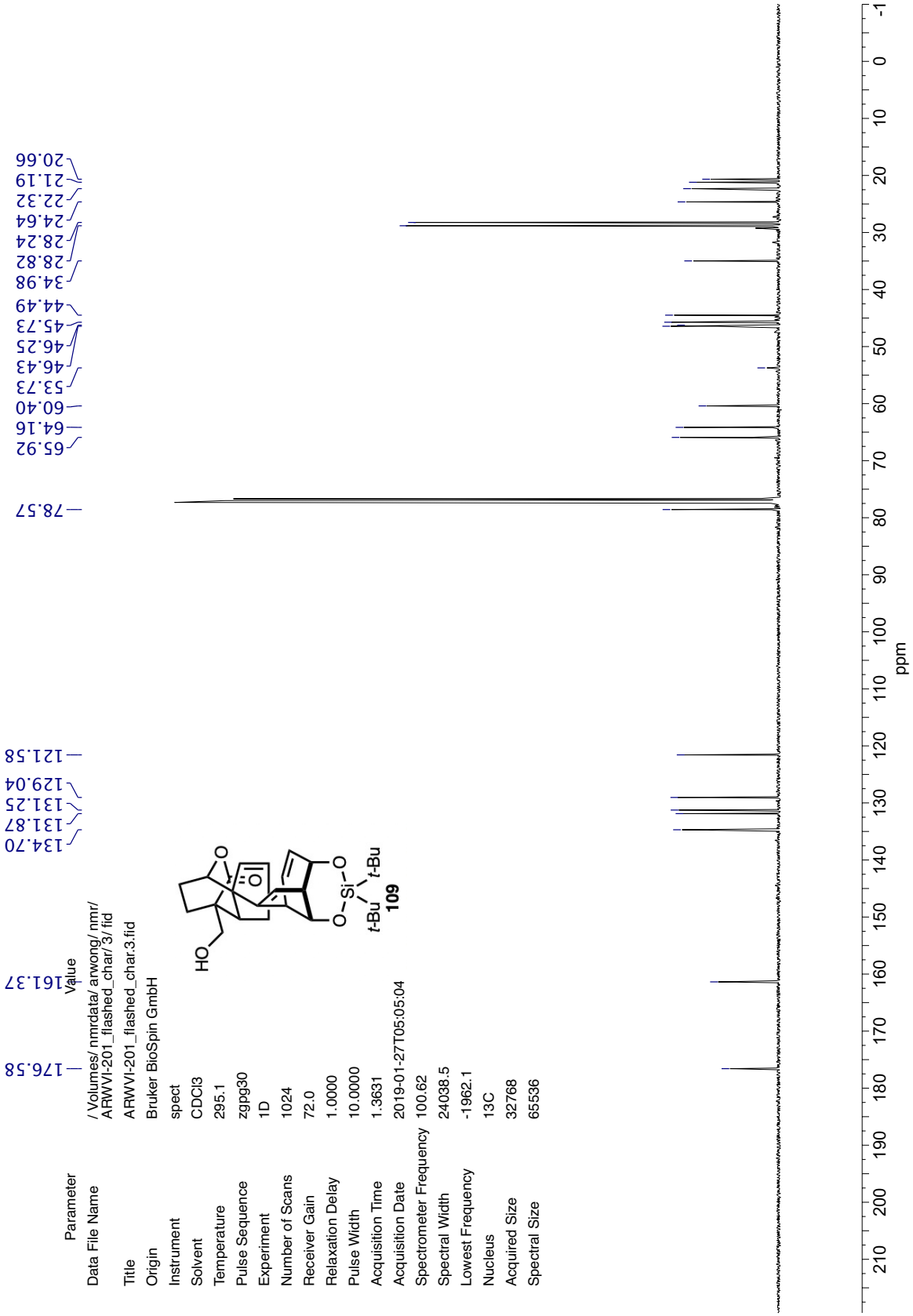
2.09
1.95
ppm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Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWVI-201_flashed_char/ 3/ fid
Title
ARWVI-201_flashed_char.3.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
1024
Receiver Gain
72.0
Relaxation Delay
1.0000
Pulse Width
10.0000
Acquisition Time
1.3631
Acquisition Date
2019-01-27T05:05:04
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1962.1
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
HO
O
O
O
Si
O
t-Bu
t-Bu
109
176.58
161.37
134.70
131.87
131.25
129.04
121.58
78.57
65.92
64.16
60.40
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45.73
44.49
34.98
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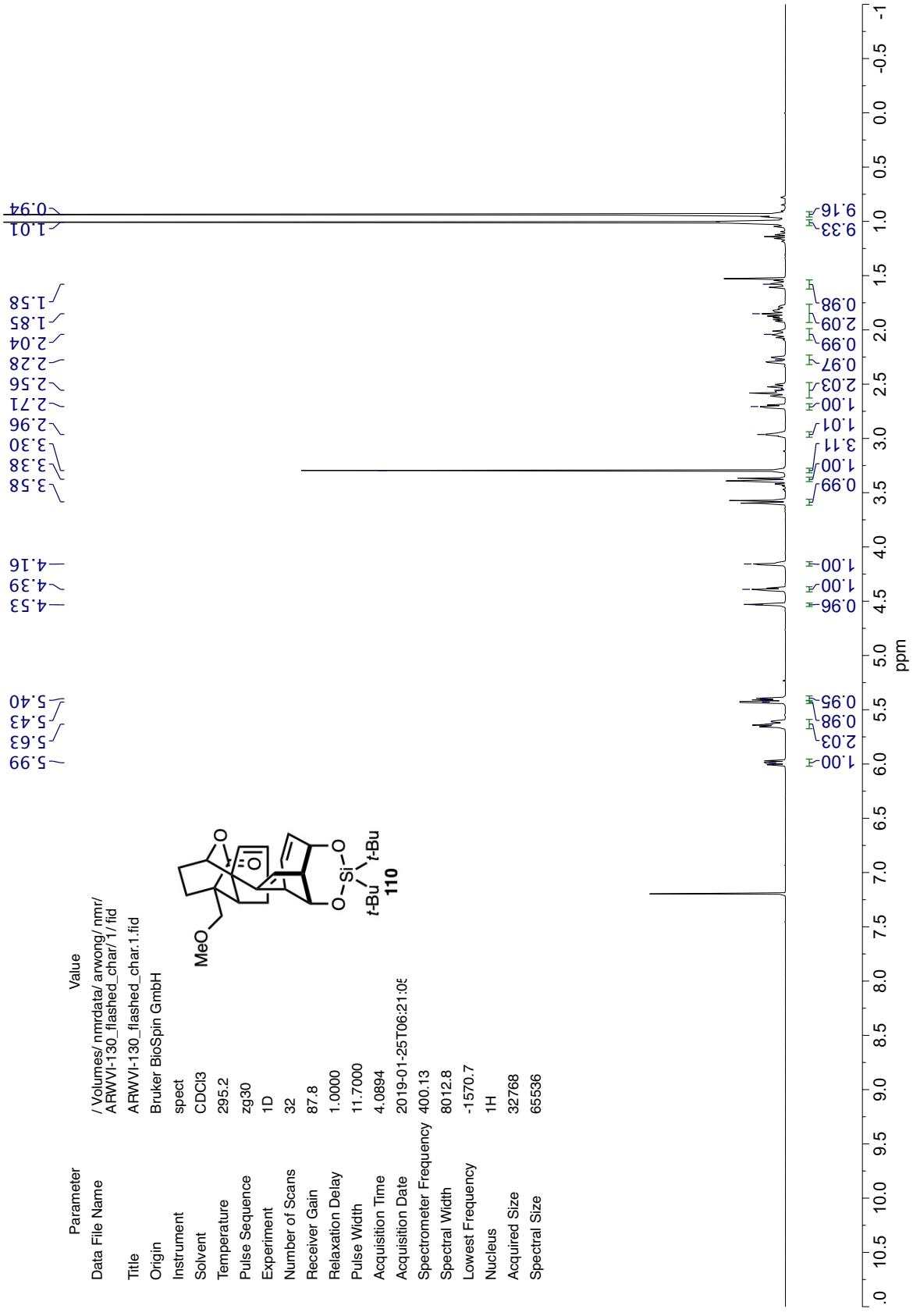
24.64
22.32
21.19
20.66
ppm


Parameter
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Data File Name
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Title
ARWVI-130_flashed_char.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.2
Pulse Sequence
zg30
Experiment
1D
Number of Scans
32
Receiver Gain
87.8
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2019-01-25T06:21:0
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1570.7
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
MeO
O
O
O
Si
O
t-Bu
t-Bu
110
5.99
5.63
5.43
5.40
4.53
4.39
4.16
3.58
3.38
3.30
2.96
2.71
2.56
2.28
2.04
1.85
1.58
1.01
0.94
1.00
2.03
0.98
0.95
0.96
1.00
1.00
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0.99
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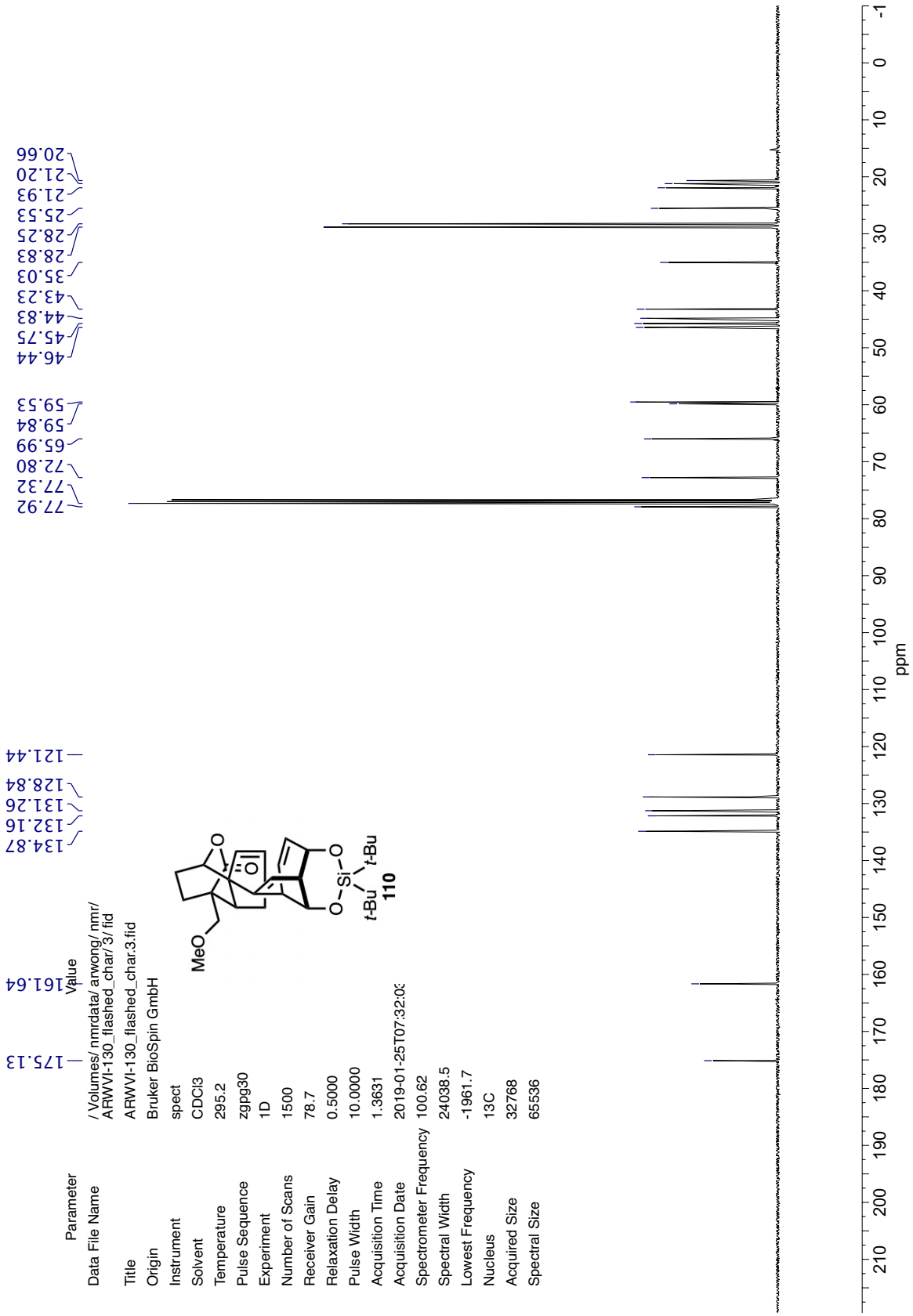
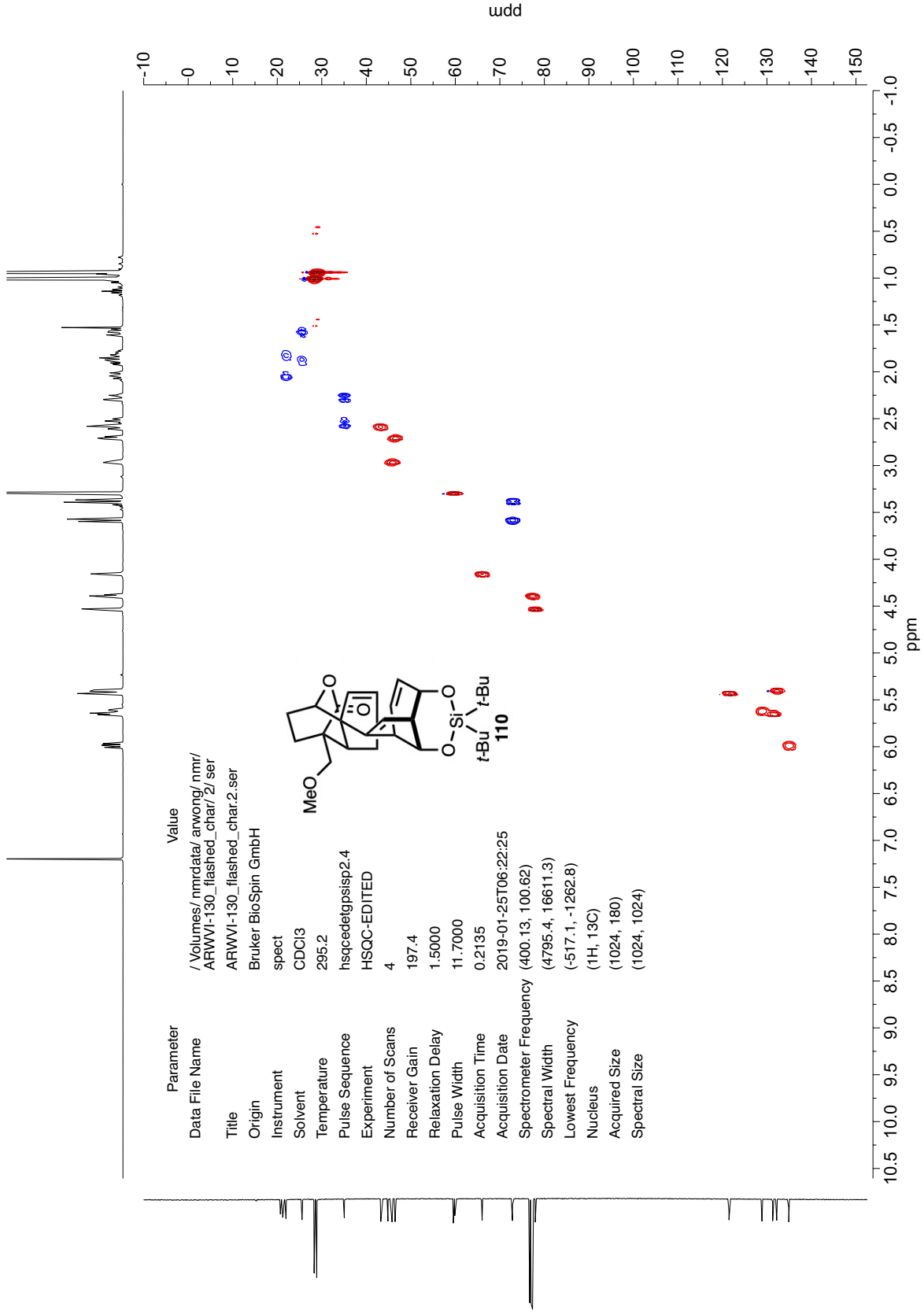
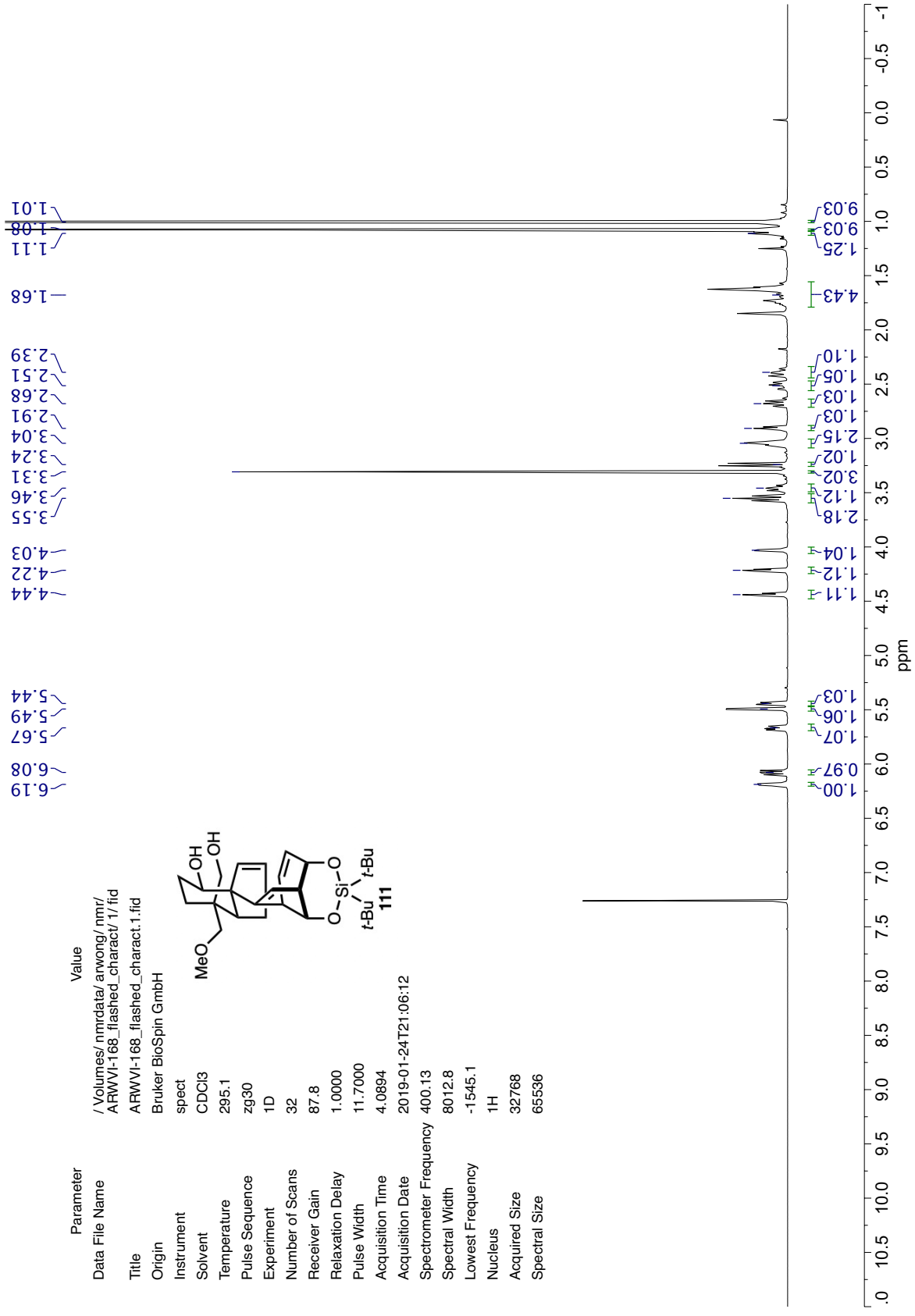
9.16
ppm



Parameter	Value
Data File Name	/ Volumes/ nmrdata/ arwong/ nmr/ ARWVI-130_flashed_char/ 3/ fid
Title	ARWVI-130_flashed_char.3.fid
Origin	Bruker BioSpin GmbH
Instrument	spect
Solvent	CDCl3
Temperature	295.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	1500
Receiver Gain	78.7
Relaxation Delay	0.5000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2019-01-25T07:32:0
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536


ppm
ppm
MeO
O
O
O
O
Si
t-Bu
t-Bu
110
Parameter Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-130_flashed_char/ 2/ ser
Title ARWVI-130_flashed_char.2.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.2
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 11.7000
Acquisition Time 0.2135
Acquisition Date 2019-01-25T06:22:25
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-517.1, -1262.8)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)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Data File Name
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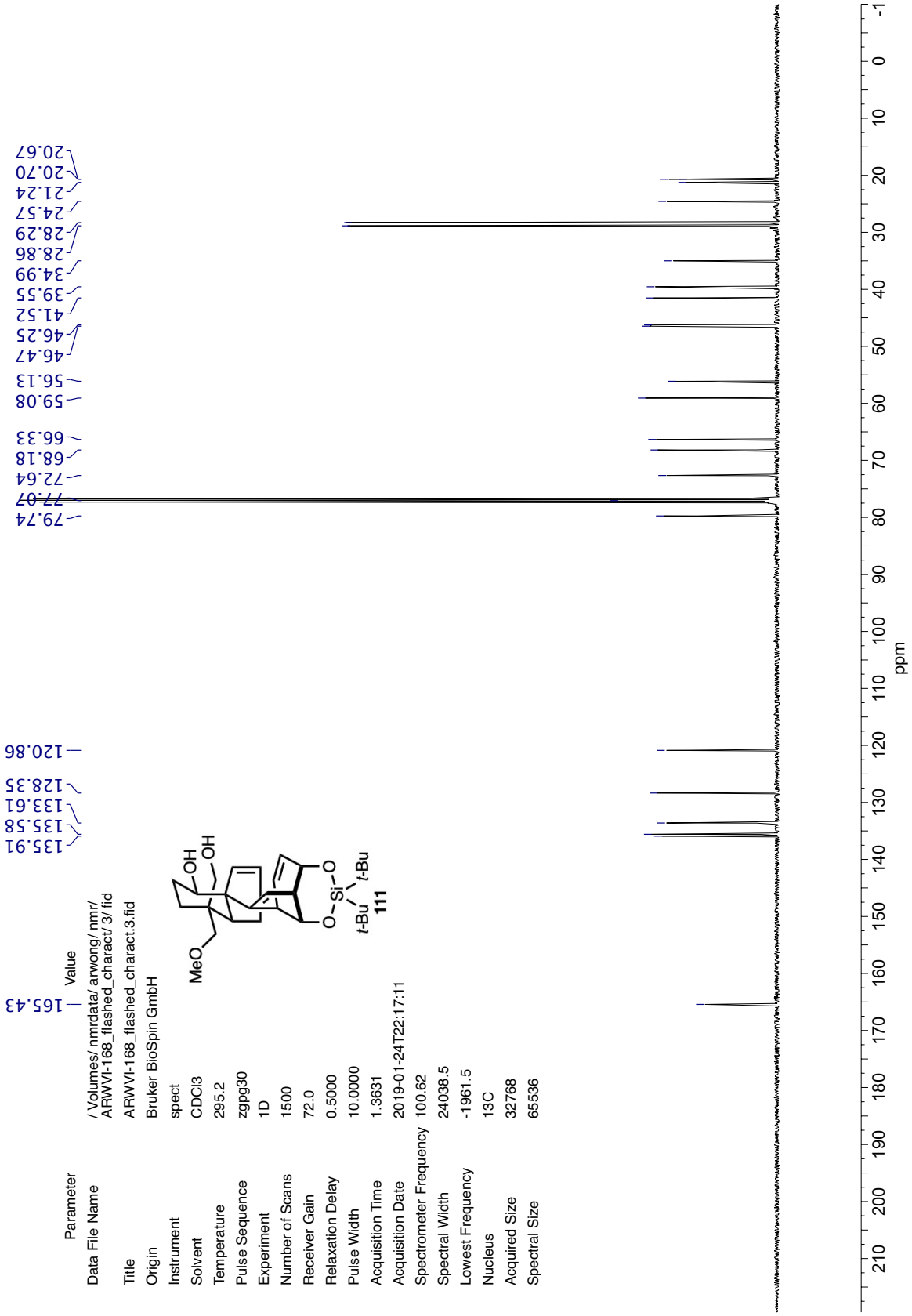
Title
ARWVI-168_flashed_charact.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zg30
Experiment
1D
Number of Scans
32
Receiver Gain
87.8
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2019-01-24T21:06:12
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.1
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
MeO
OH
OH
O
Si
O
t-Bu
t-Bu
111
ppm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Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-168_flashed_charact/ 3/ fid
Title ARWVI-168_flashed_charact.3.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.2
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 1500
Receiver Gain 72.0
Relaxation Delay 0.5000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2019-01-24T22:17:11
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1961.5
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
MeO
OH
OH
O
Si
O
t-Bu
t-Bu
111
165.43
135.91
135.58
133.61
128.35
120.86
79.74
77.07
72.64
68.18
66.33
59.08
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46.25
41.52
39.55
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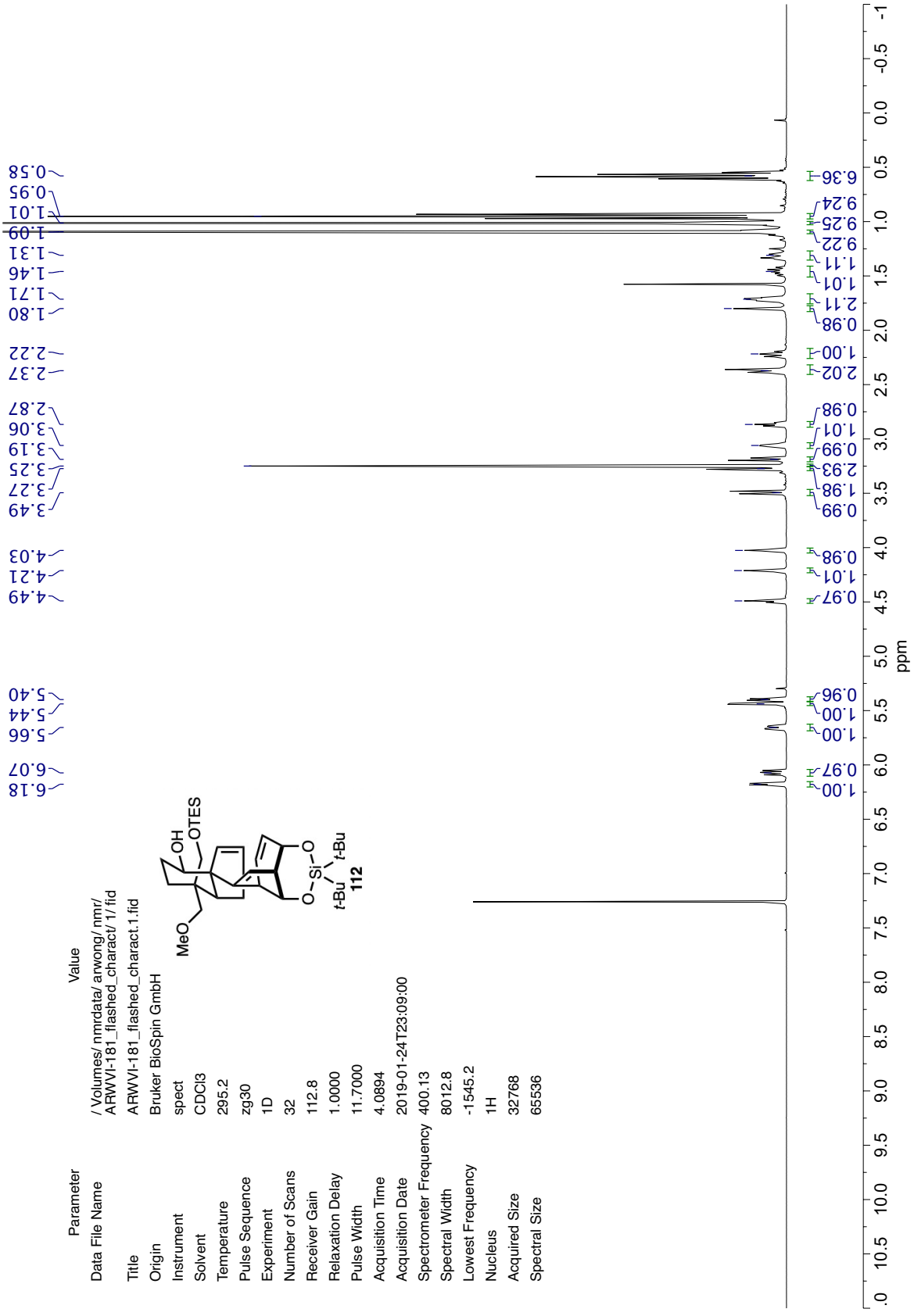
24.57
21.24
20.70
20.67
ppm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Data File Name
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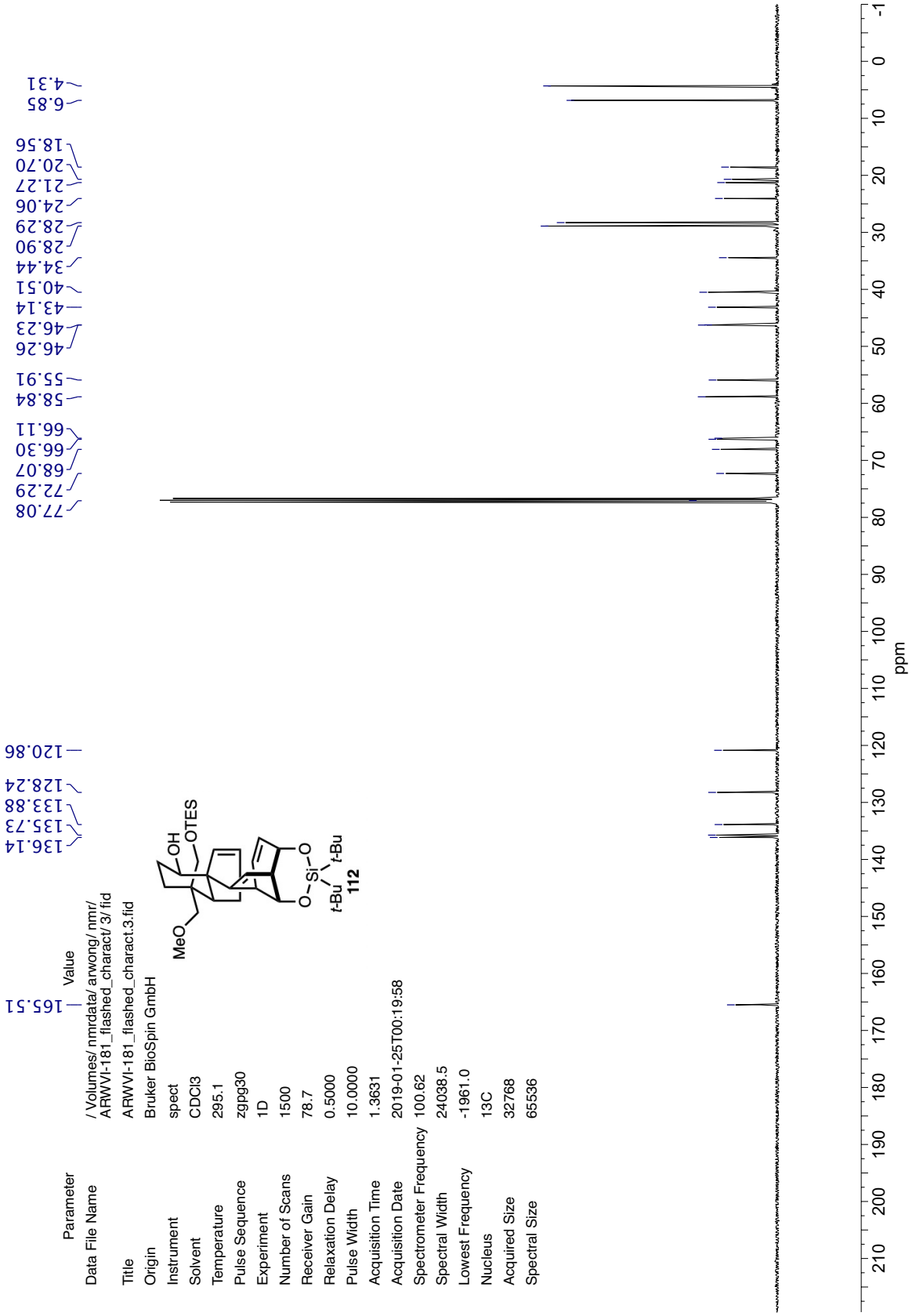
Title
ARWVI-181_flashed_charact.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.2
Pulse Sequence
zg30
Experiment
1D
Number of Scans
32
Receiver Gain
112.8
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2019-01-24T23:09:00
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.2
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
MeO
OH
OTES
O
Si
O
t-Bu
t-Bu
112
ppm


Parameter
Value
Data File Name
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Title
ARWVI-181_flashed_charact.3.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
1500
Receiver Gain
78.7
Relaxation Delay
0.5000
Pulse Width
10.0000
Acquisition Time
1.3631
Acquisition Date
2019-01-25T00:19:58
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1961.0
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
MeO
OH
OTES
O
Si
O
t-Bu
t-Bu
112
165.51
136.14
135.73
133.88
128.24
120.86
77.08
72.29
68.07
66.30
66.11
58.84
55.91
46.26
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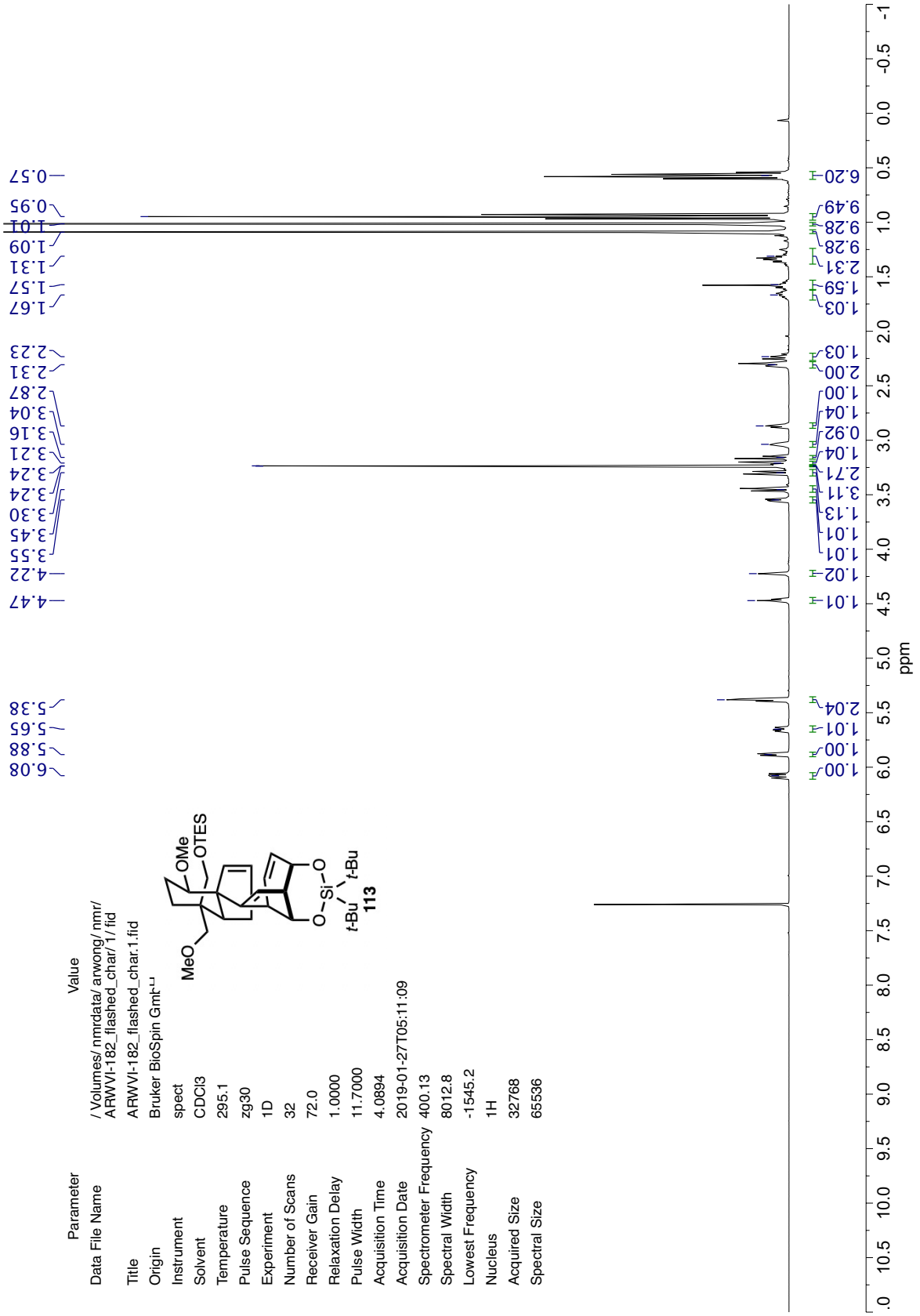
ppm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Value
Data File Name
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Title
ARWVI-182_flashed_char.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zg30
Experiment
1D
Number of Scans
32
Receiver Gain
72.0
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2019-01-27T05:11:09
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.2
Nucleus
1H
Acquired Size
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Spectral Size
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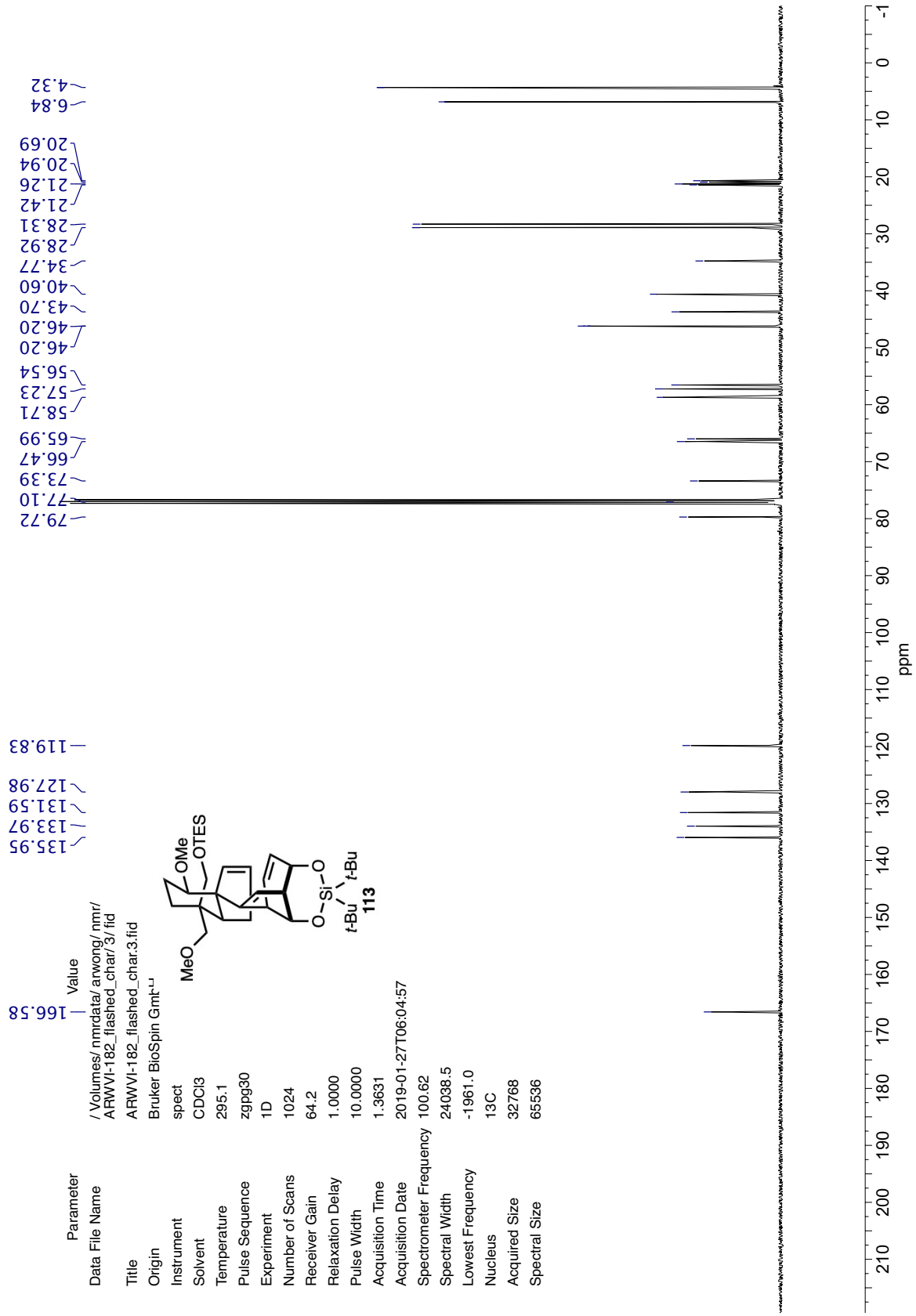
MeO
OMe
OTES
O
Si
O
t-Bu
t-Bu
113
ppm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Data File Name
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Title
ARWVI-182_flashed_char.3.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
1024
Receiver Gain
64.2
Relaxation Delay
1.0000
Pulse Width
10.0000
Acquisition Time
1.3631
Acquisition Date
2019-01-27T06:04:57
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1961.0
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
MeO
OMe
OTES
O
Si
O
t-Bu
t-Bu
113
166.58
135.95
133.97
131.59
127.98
119.83
79.72
77.10
73.39
66.47
65.99
58.71
57.23
56.54
46.20
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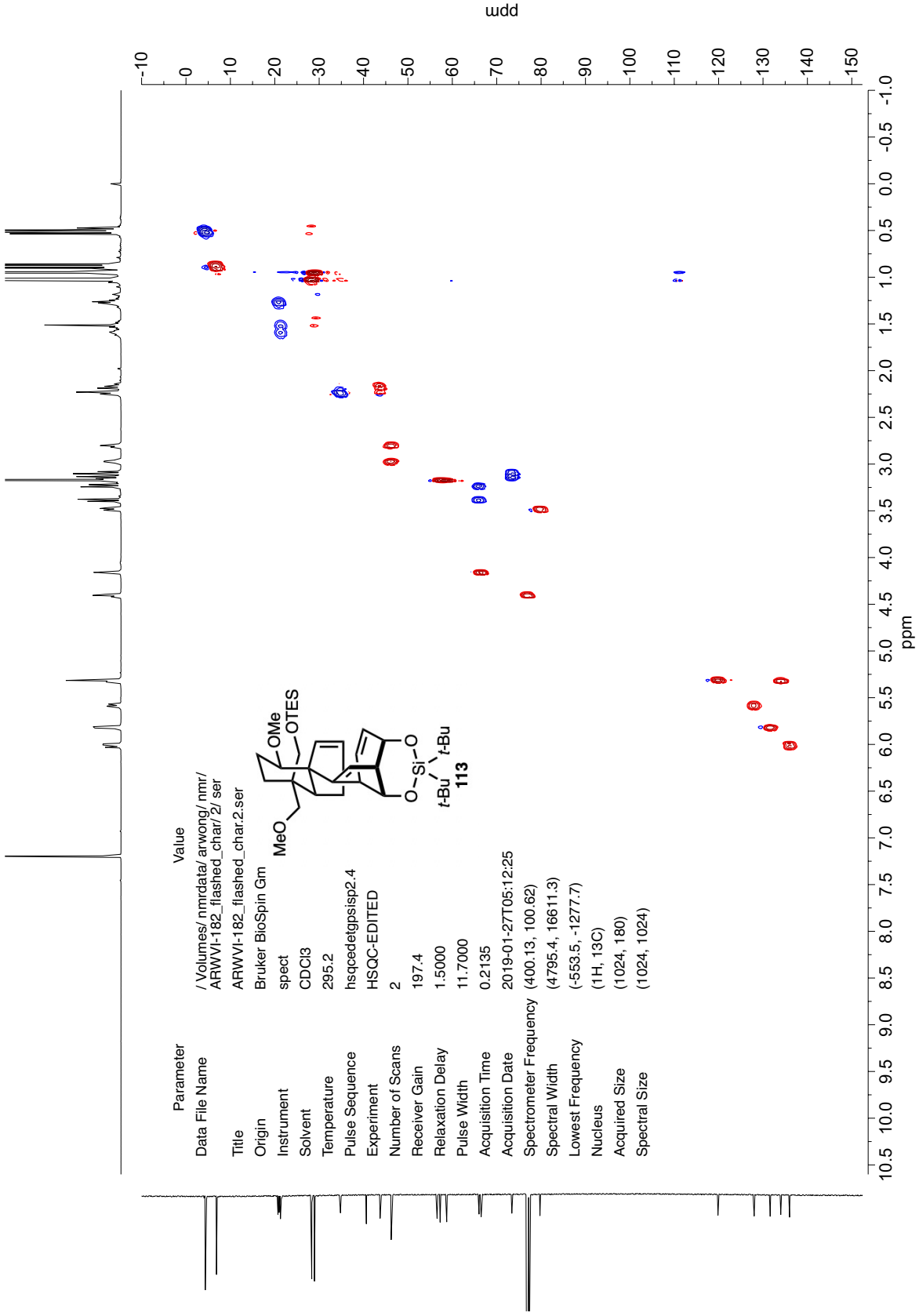
20.94
20.69
6.84
4.32
ppm


ppm
ppm
MeO
OMe
OTES
O
Si
O
t-Bu
t-Bu
113
Parameter
Value
Data File Name
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Title
ARWVI-182_flashed_char.2.ser
Origin
Bruker BioSpin Gm
Instrument
spect
Solvent
CDCl3
Temperature
295.2
Pulse Sequence
hsqcedetgpsisp2.4
Experiment
HSQC-EDITED
Number of Scans
2
Receiver Gain
197.4
Relaxation Delay
1.5000
Pulse Width
11.7000
Acquisition Time
0.2135
Acquisition Date
2019-01-27T05:12:25
Spectrometer Frequency
(400.13, 100.62)
Spectral Width
(4795.4, 16611.3)
Lowest Frequency
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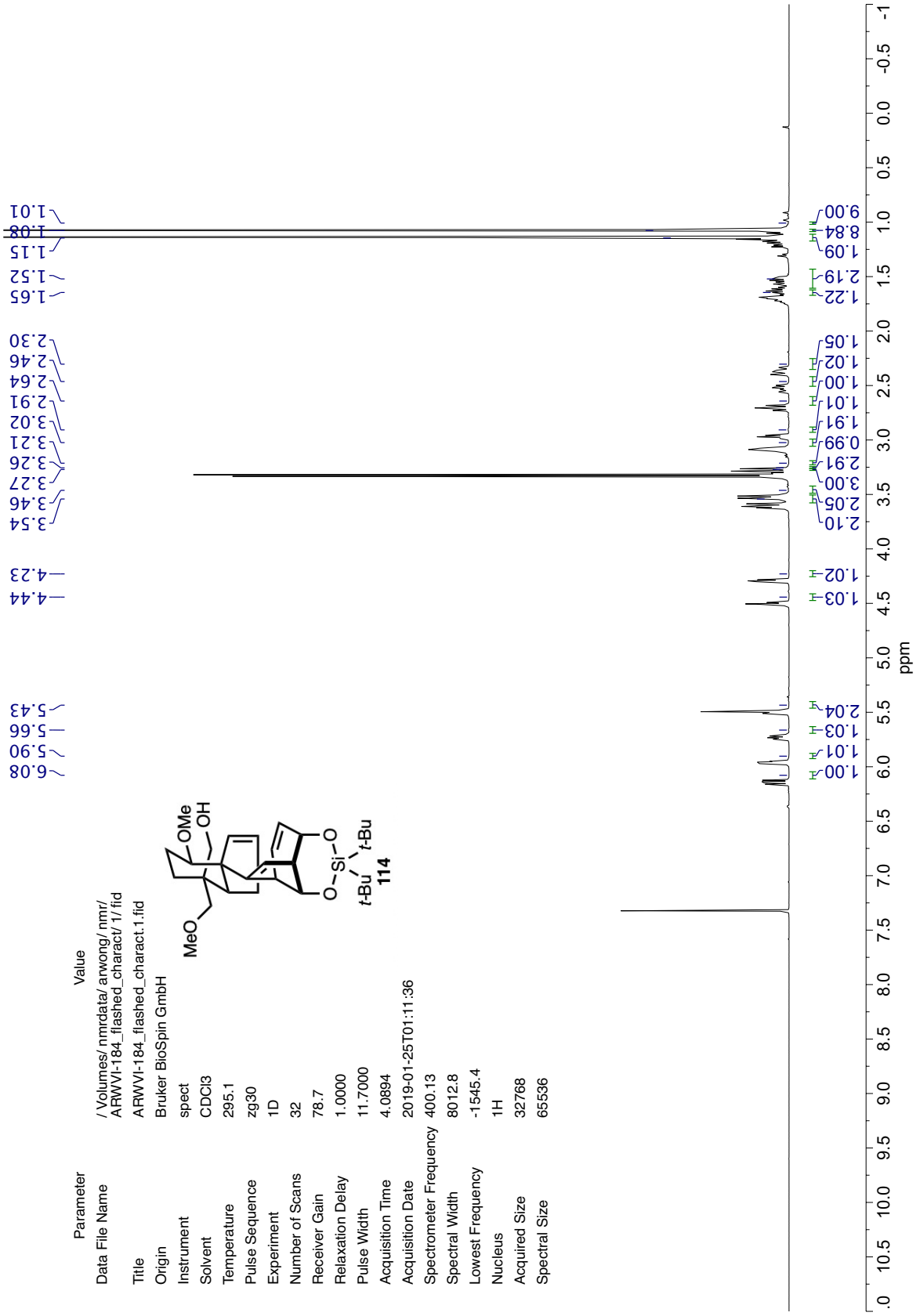
Nucleus
(1H, 13C)
Acquired Size
(1024, 180)
Spectral Size
(1024, 1024)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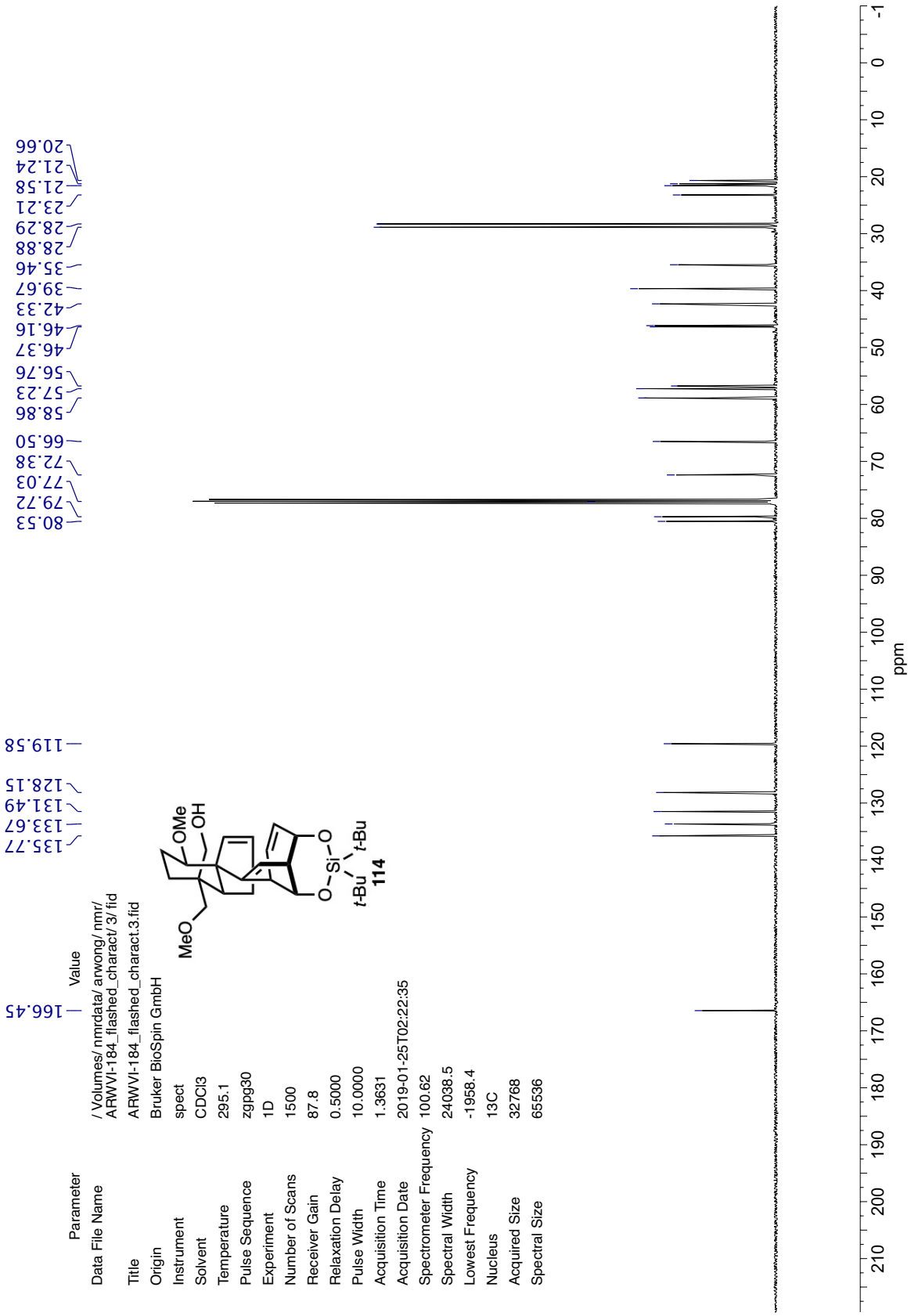
Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWVI-184_flashed_charact/ 1/ fid
Title
ARWVI-184_flashed_charact.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zg30
Experiment
1D
Number of Scans
32
Receiver Gain
78.7
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2019-01-25T01:11:36
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.4
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
MeO
OMe
OH
O
Si
O
t-Bu
t-Bu
114
ppm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Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWVI-184_flashed_charact/ 3/ fid
Title
ARWVI-184_flashed_charact.3.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
1500
Receiver Gain
87.8
Relaxation Delay
0.5000
Pulse Width
10.0000
Acquisition Time
1.3631
Acquisition Date
2019-01-25T02:22:35
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1958.4
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
MeO
OMe
OH
O
Si
O
t-Bu
t-Bu
114
166.45
135.77
133.67
131.49
128.15
119.58
80.53
79.72
77.03
72.38
66.50
58.86
57.23
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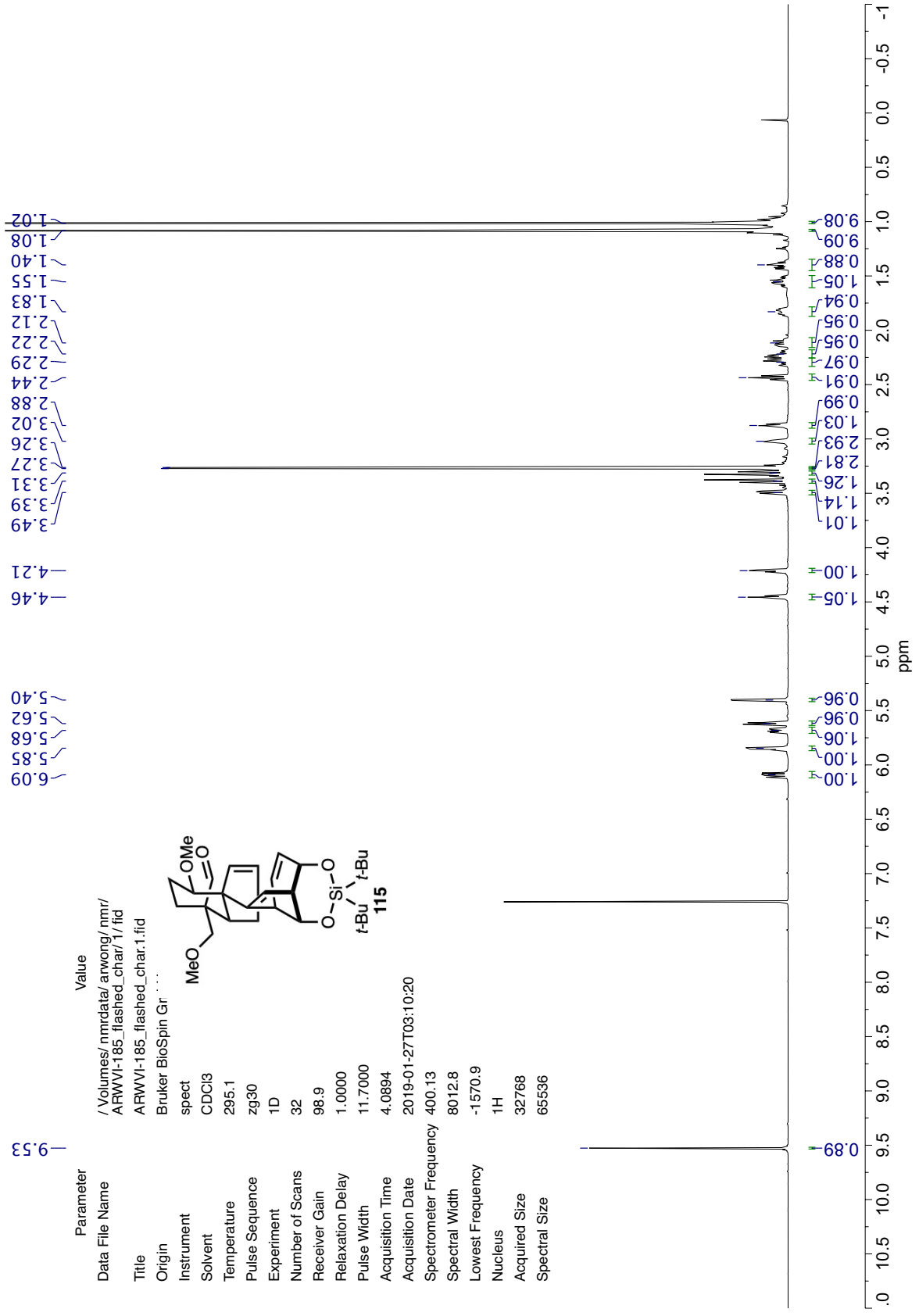
ppm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Data File Name
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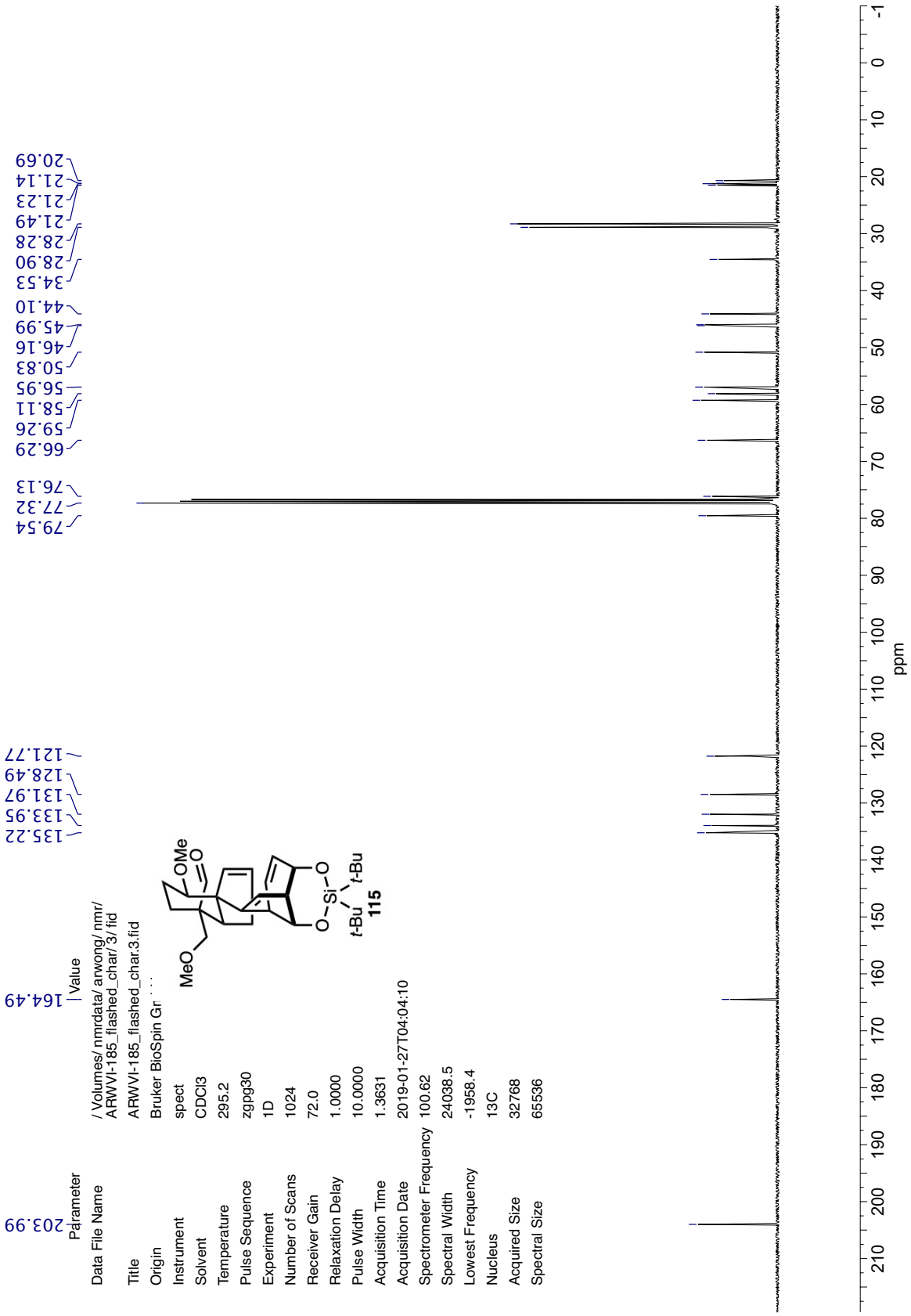
Title
ARWVI-185_flashed_char.1.fid
Origin
Bruker BioSpin Gr
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zg30
Experiment
1D
Number of Scans
32
Receiver Gain
98.9
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2019-01-27T03:10:20
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1570.9
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
MeO
OMe
O
O
Si
O
t-Bu
t-Bu
115
ppm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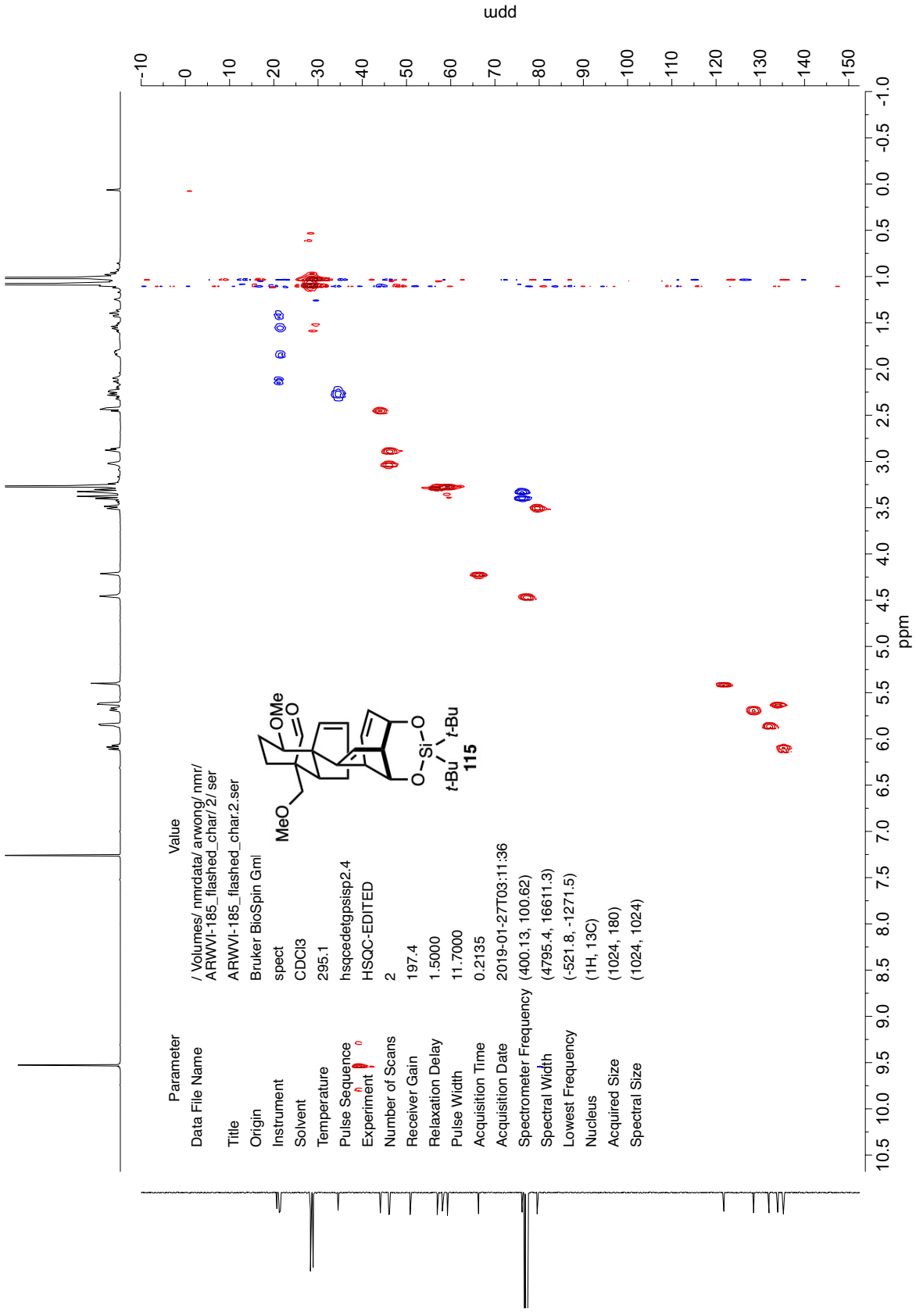
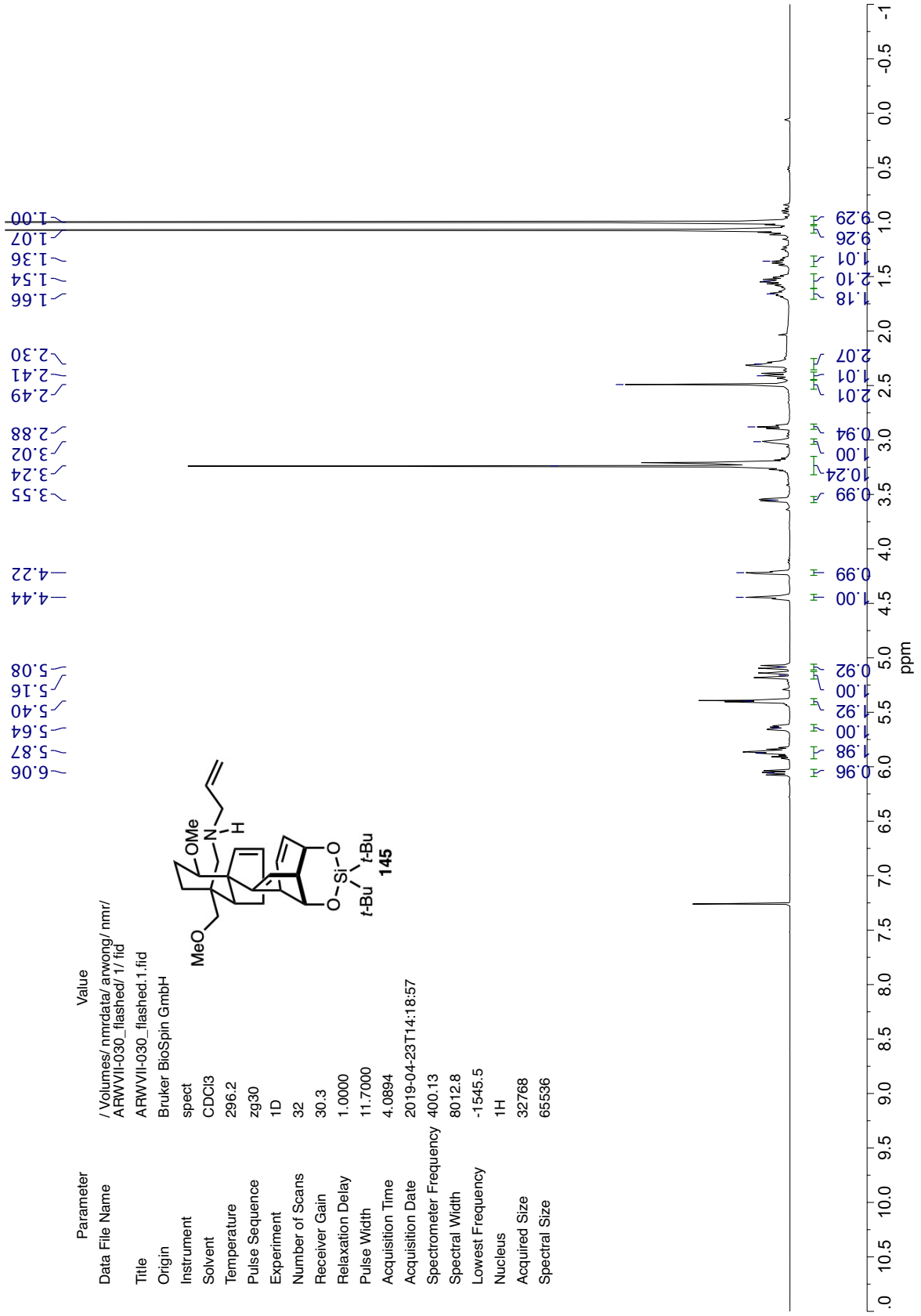
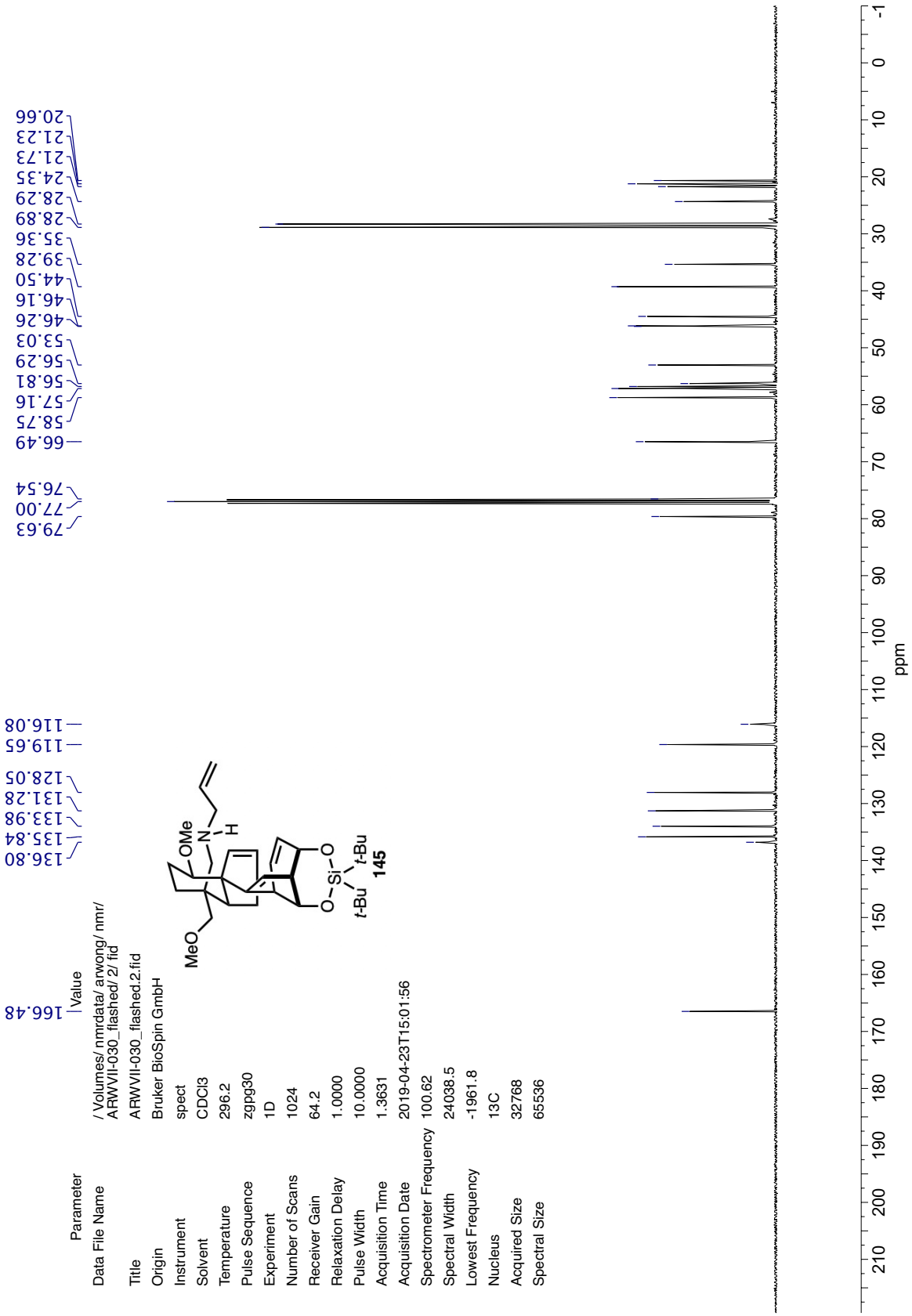
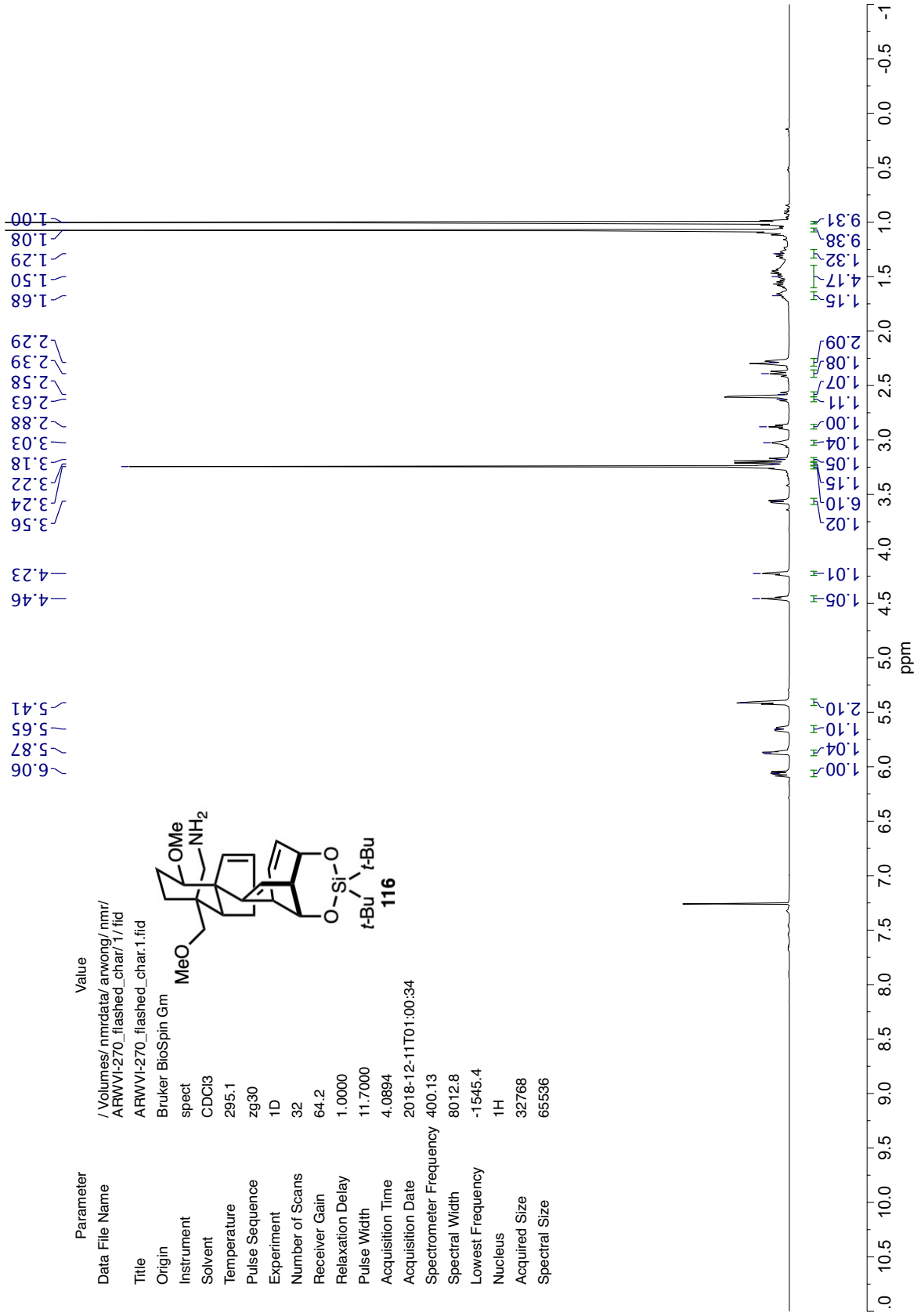
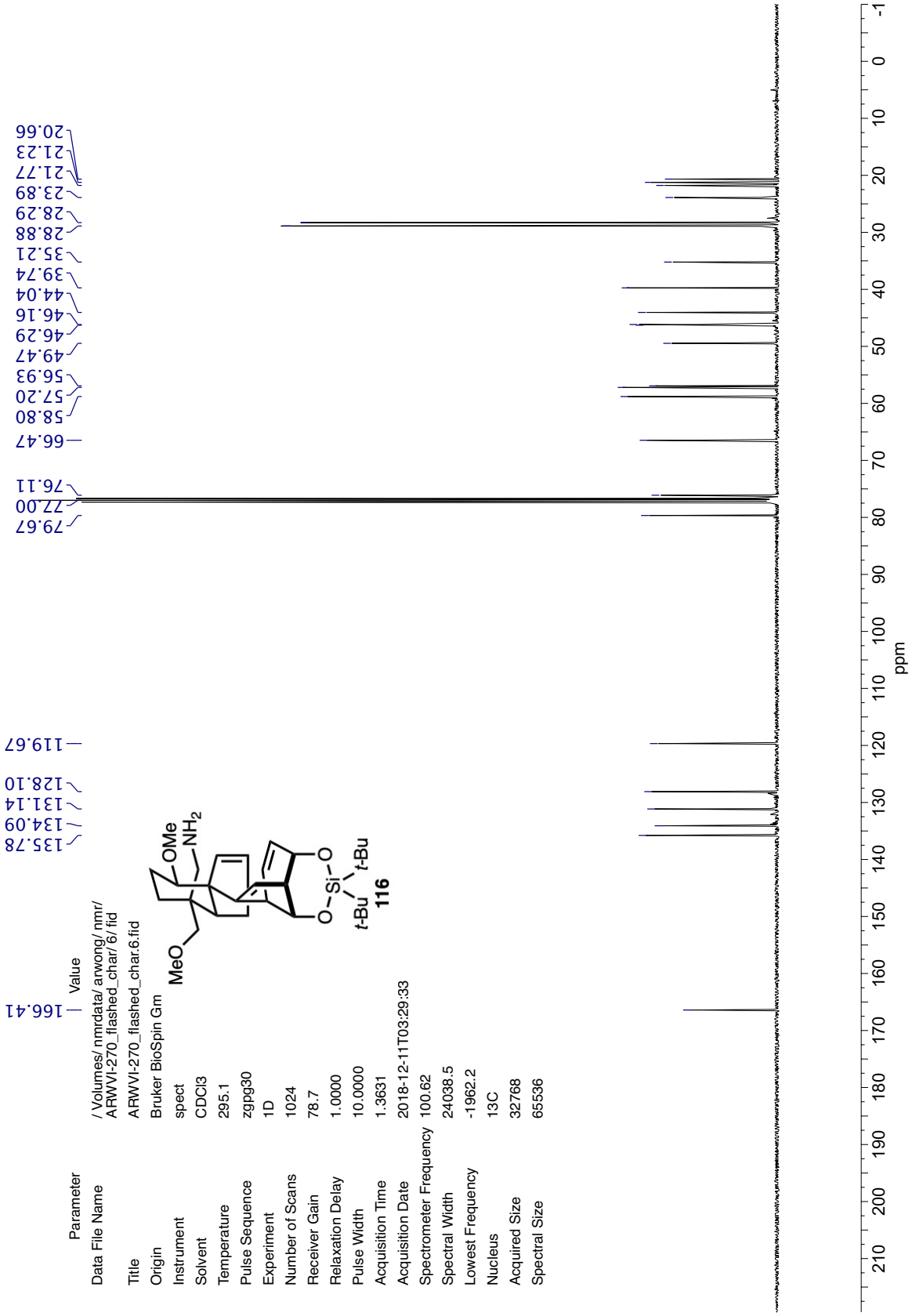
164.49
135.22
133.95
131.97
128.49
121.77
79.54
77.32
76.13
66.29
59.26
58.11
56.95
50.83
46.16
45.99
44.10
34.53
28.90
28.28
21.49
21.23
21.14
20.69
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWVI-185_flashed_char/3/ fid
Title
ARWVI-185_flashed_char.3.fid
Origin
Bruker BioSpin Gr
Instrument
spect
Solvent
CDCl3
Temperature
295.2
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
1024
Receiver Gain
72.0
Relaxation Delay
1.0000
Pulse Width
10.0000
Acquisition Time
1.3631
Acquisition Date
2019-01-27T04:04:10
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1958.4
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
MeO
OMe
O
O
Si
O
t-Bu
t-Bu
115
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
ppm

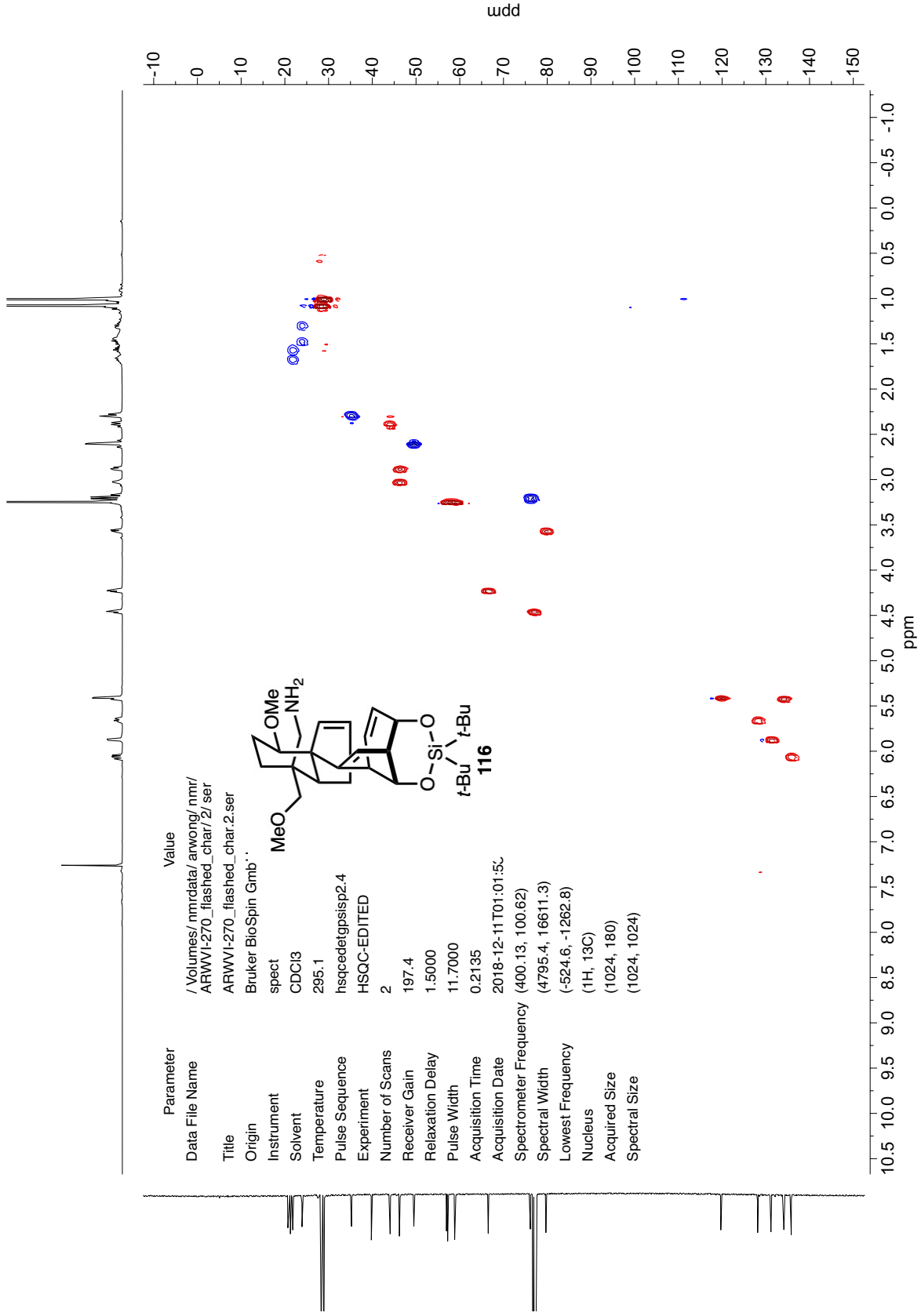

ppm
ppm
MeO
OMe
O
O
Si
O
t-Bu
t-Bu
115
Parameter Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-185_flashed_char/ 2/ ser
Title ARWVI-185_flashed_char:2.ser
Origin Bruker BioSpin Gml
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 11.7000
Acquisition Time 0.2135
Acquisition Date 2019-01-27T03:11:36
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-521.8, -1271.5)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)

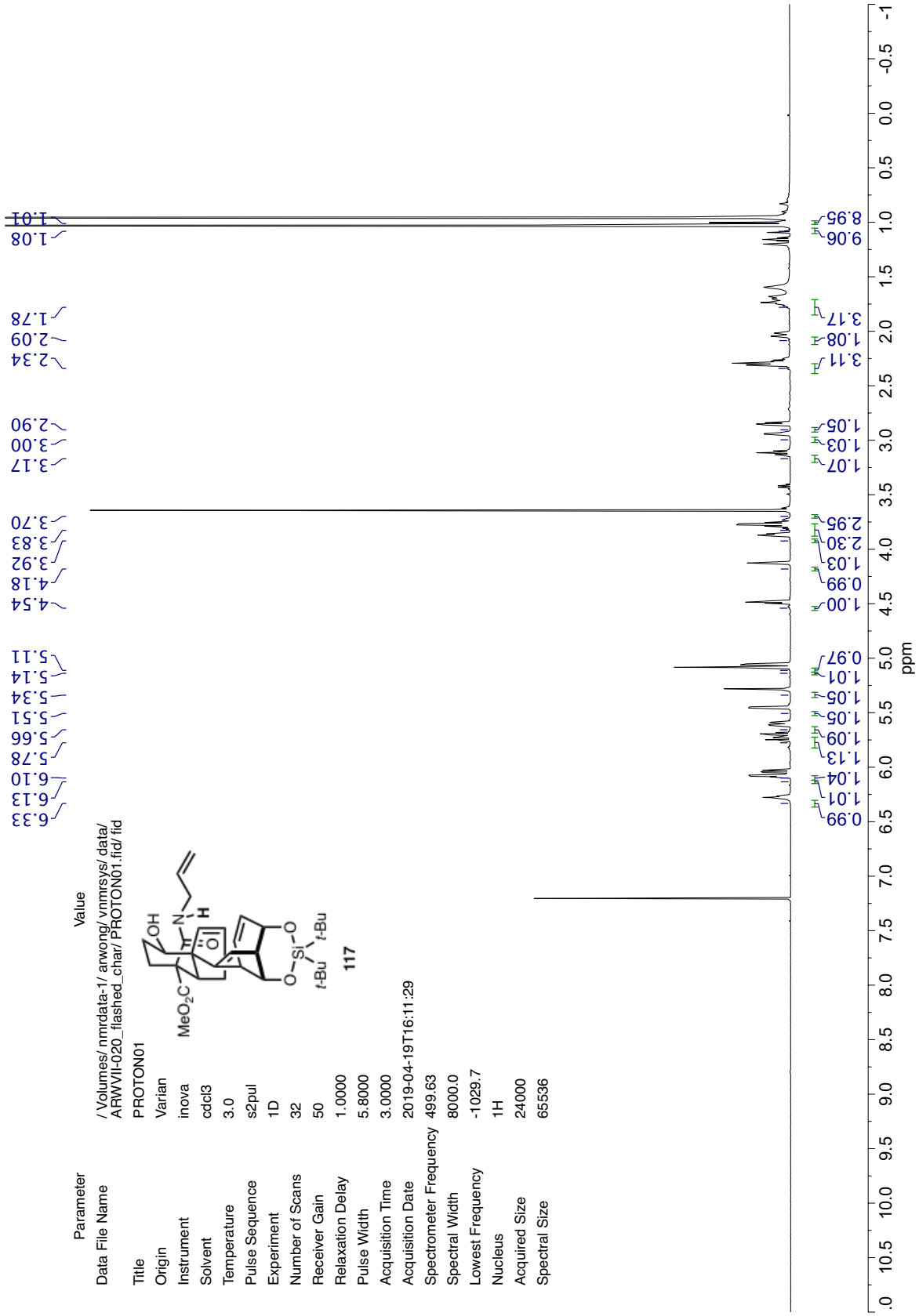

Parameter
Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWVII-030_flashed/ 1/ fid
Title
ARWVII-030_flashed.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
296.2
Pulse Sequence
zg30
Experiment
1D
Number of Scans
32
Receiver Gain
30.3
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2019-04-23T14:18:57
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.5
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
MeO
OMe
N
H
O
Si
O
t-Bu
t-Bu
145
6.06
5.87
5.64
5.40
5.16
5.08
4.44
4.22
3.55
3.24
3.02
2.88
2.49
2.41
2.30
1.66
1.54
1.36
1.07
1.00
0.96
1.98
1.00
1.92
1.00
1.00
0.92
1.00
0.99
10.24
1.00
0.94
2.01
1.01
2.07
1.18
2.10
1.01
9.26
9.29
ppm


Parameter | Value
Data File Name | / Volumes/ nmrdata/ arwong/ nmr/ ARWVII-030_flashed/ 2/ fid
Title | ARWVII-030_flashed.2.fid
Origin | Bruker BioSpin GmbH
Instrument | spect
Solvent | CDCl3
Temperature | 296.2
Pulse Sequence | zgpg30
Experiment | 1D
Number of Scans | 1024
Receiver Gain | 64.2
Relaxation Delay | 1.0000
Pulse Width | 10.0000
Acquisition Time | 1.3631
Acquisition Date | 2019-04-23T15:01:56
Spectrometer Frequency | 100.62
Spectral Width | 24038.5
Lowest Frequency | -1961.8
Nucleus | 13C
Acquired Size | 32768
Spectral Size | 65536
166.48
136.80
135.84
133.98
131.28
128.05
119.65
116.08
79.63
77.00
76.54
66.49
58.75
57.16
56.81
56.29
53.03
46.26
46.16
44.50
39.28
35.36
28.89
28.29
24.35
21.73
21.23
20.66
MeO
OMe
N
H
O
Si
O
t-Bu
t-Bu
145
ppm


Parameter
Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWVI-270_flashed_char/1 / fid
Title
ARWVI-270_flashed_char.1.fid
Origin
Bruker BioSpin Gm
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zg30
Experiment
1D
Number of Scans
32
Receiver Gain
64.2
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2018-12-11T01:00:34
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.4
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
OMe
NH2
MeO
O
Si
O
t-Bu
t-Bu
116
ppm


Parameter
Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWVI-270_flashed_char/ 6/ fid
Title
ARWVI-270_flashed_char.6.fid
Origin
Bruker BioSpin Gm
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
1024
Receiver Gain
78.7
Relaxation Delay
1.0000
Pulse Width
10.0000
Acquisition Time
1.3631
Acquisition Date
2018-12-11T03:29:33
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1962.2
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
MeO
OMe
NH2
O
Si
O
t-Bu
t-Bu
116
166.41
135.78
134.09
131.14
128.10
119.67
79.67
77.00
76.11
66.47
58.80
57.20
56.93
49.47
46.29
46.16
44.04
39.74
35.21
28.88
28.29
23.89
21.77
21.23
20.66
ppm


ppm
ppm
MeO
OMe
NH2
O
Si
O
t-Bu
t-Bu
116
Parameter Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-270_flashed_char/2/ ser
Title ARWVI-270_flashed_char.2.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 11.7000
Acquisition Time 0.2135
Acquisition Date 2018-12-11T01:01:5
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-524.6, -1262.8)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)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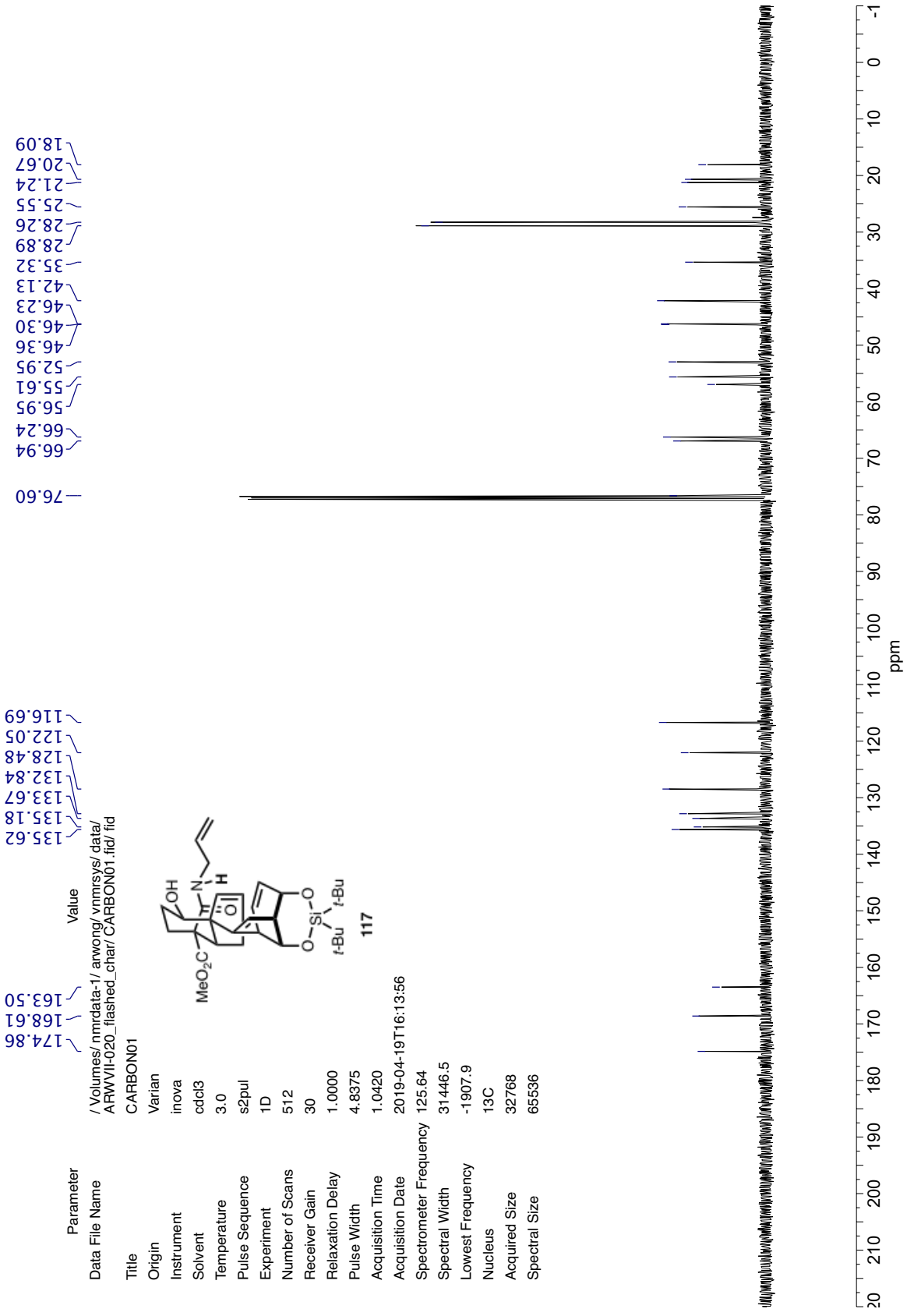
Data File Name
/ Volumes/ nmrdata-1/ arwong/ vnmrsys/ data/ ARWVII-020_flashed_char/ PROTON01.fid/ fid
Title
PROTON01
Origin
Varian
Instrument
inova
Solvent
cdcl3
Temperature
3.0
Pulse Sequence
s2pul
Experiment
1D
Number of Scans
32
Receiver Gain
50
Relaxation Delay
1.0000
Pulse Width
5.8000
Acquisition Time
3.0000
Acquisition Date
2019-04-19T16:11:29
Spectrometer Frequency
499.63
Spectral Width
8000.0
Lowest Frequency
-1029.7
Nucleus
1H
Acquired Size
24000
Spectral Size
65536
117
ppm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Value
Data File Name
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Title
CARBON01
Origin
Varian
Instrument
inova
Solvent
cdcl3
Temperature
3.0
Pulse Sequence
s2pul
Experiment
1D
Number of Scans
512
Receiver Gain
30
Relaxation Delay
1.0000
Pulse Width
4.8375
Acquisition Time
1.0420
Acquisition Date
2019-04-19T16:13:56
Spectrometer Frequency
125.64
Spectral Width
31446.5
Lowest Frequency
-1907.9
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
117
174.86
168.61
163.50
135.62
135.18
133.67
132.84
128.48
122.05
116.69
76.60
66.94
66.24
56.95
55.61
52.95
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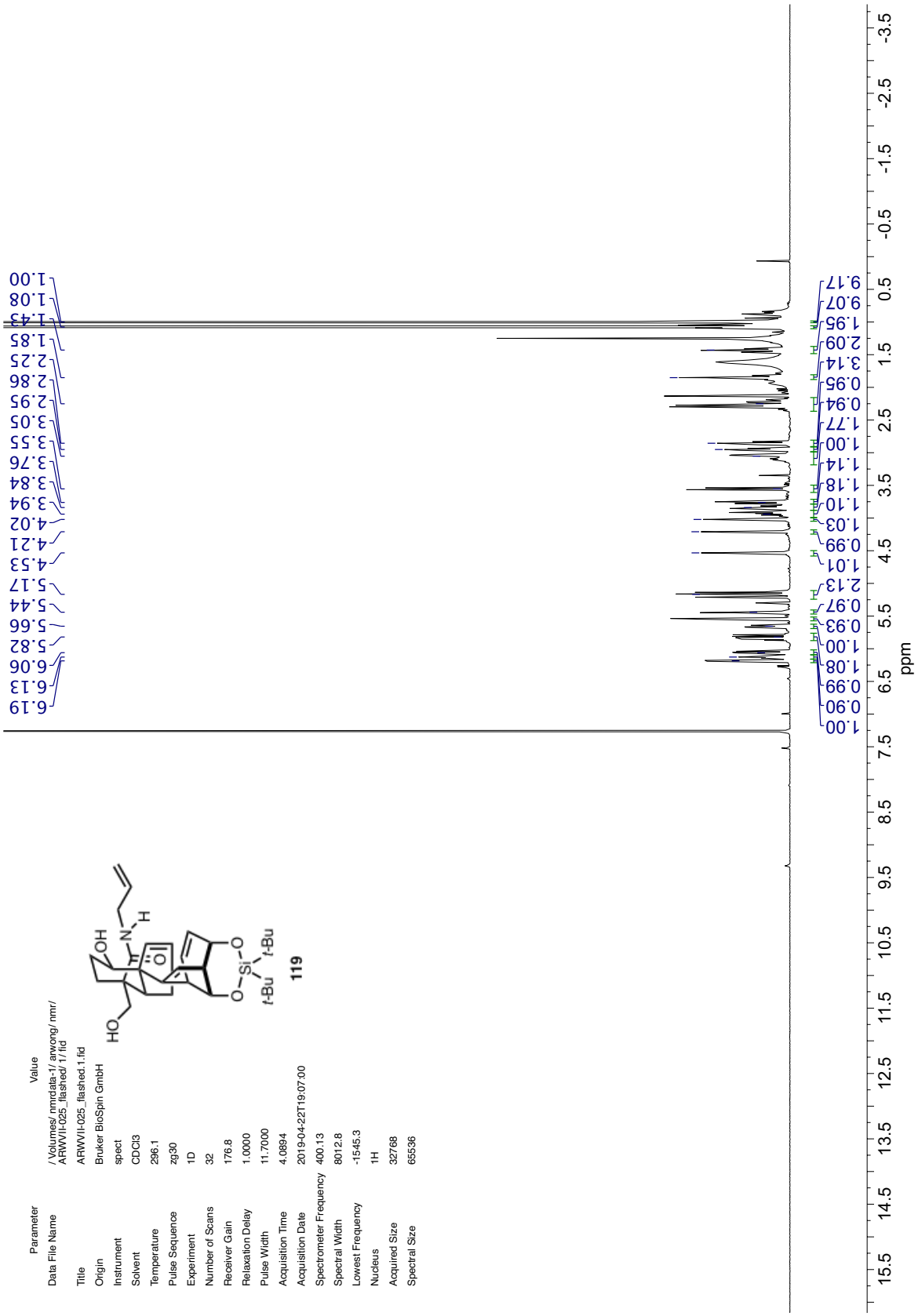
46.23
42.13
35.32
28.89
28.26
25.55
21.24
20.67
18.09
ppm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Value
Data File Name
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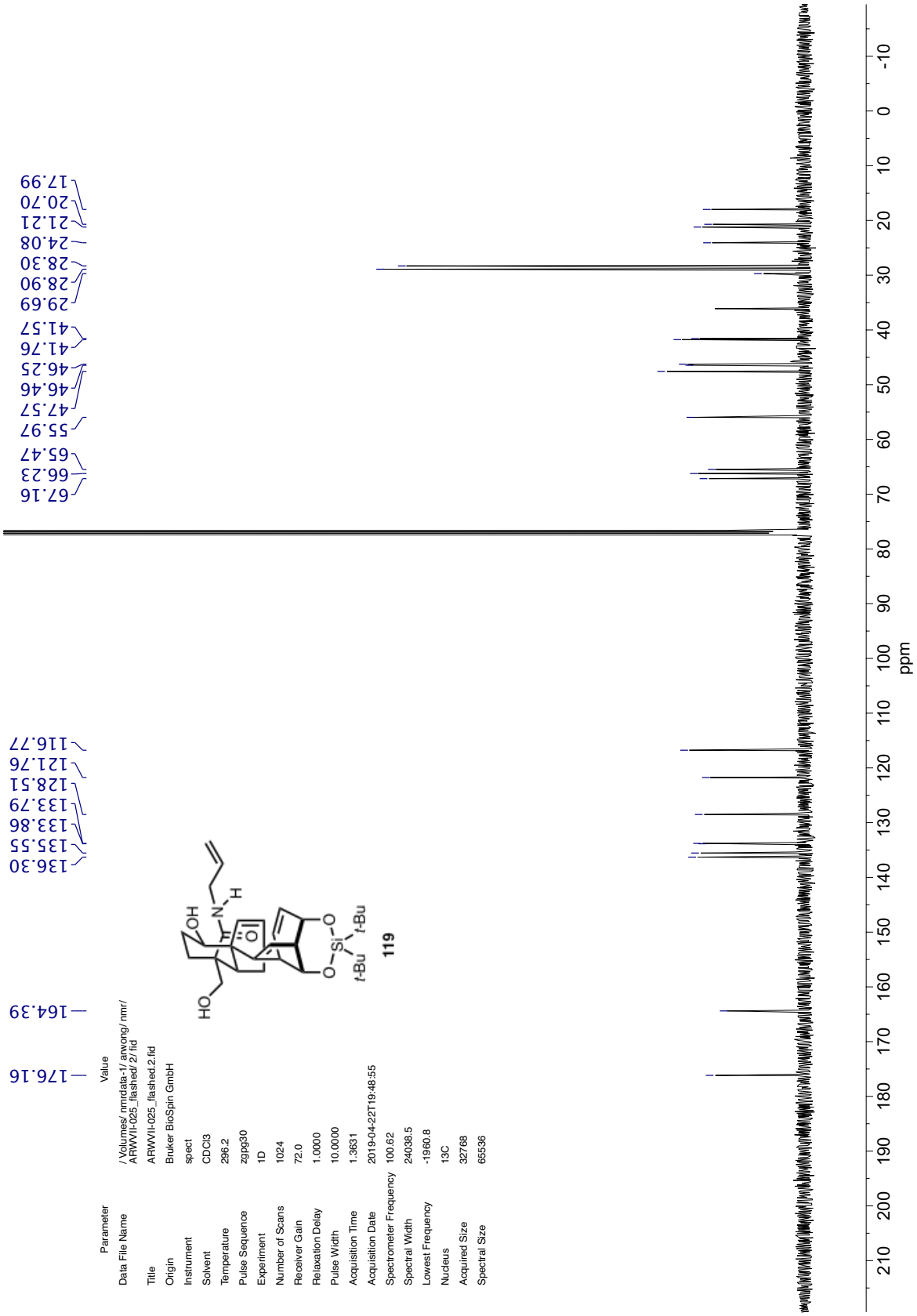
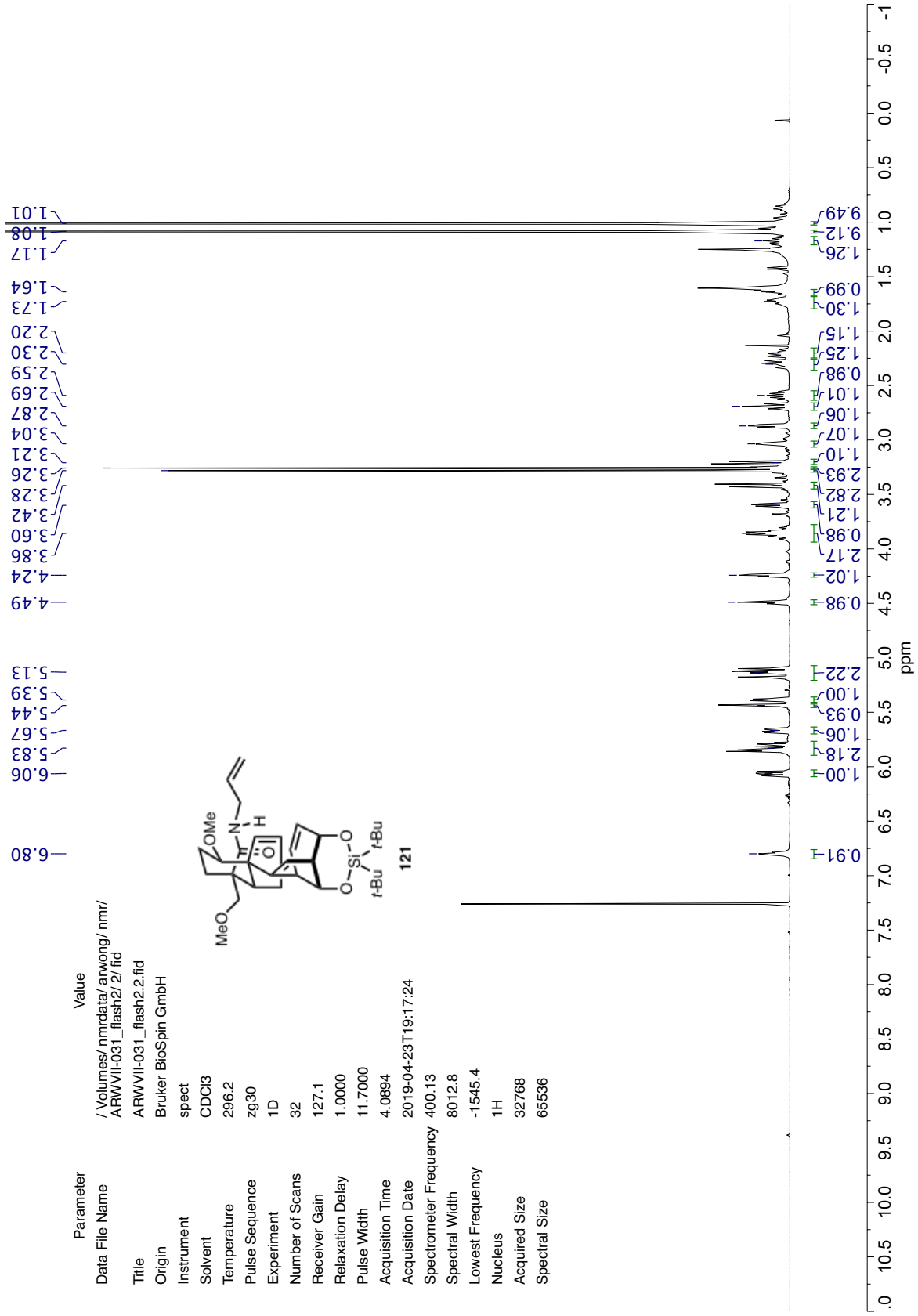
Title
ARWVII-025_flashed.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
296.1
Pulse Sequence
zg30
Experiment
1D
Number of Scans
32
Receiver Gain
176.8
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2019-04-22T19:07:00
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.3
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
119
ppm



Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ anwong/ nmr/ ARWVII-025_flashed/ 2/ fid
Title	ARWVII-025_flashed.2.fid
Origin	Bruker BioSpin GmbH
Instrument	spect
Solvent	CDCl3
Temperature	296.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	1024
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2019-04-22T19:48:55
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536


Parameter
Value
Data File Name
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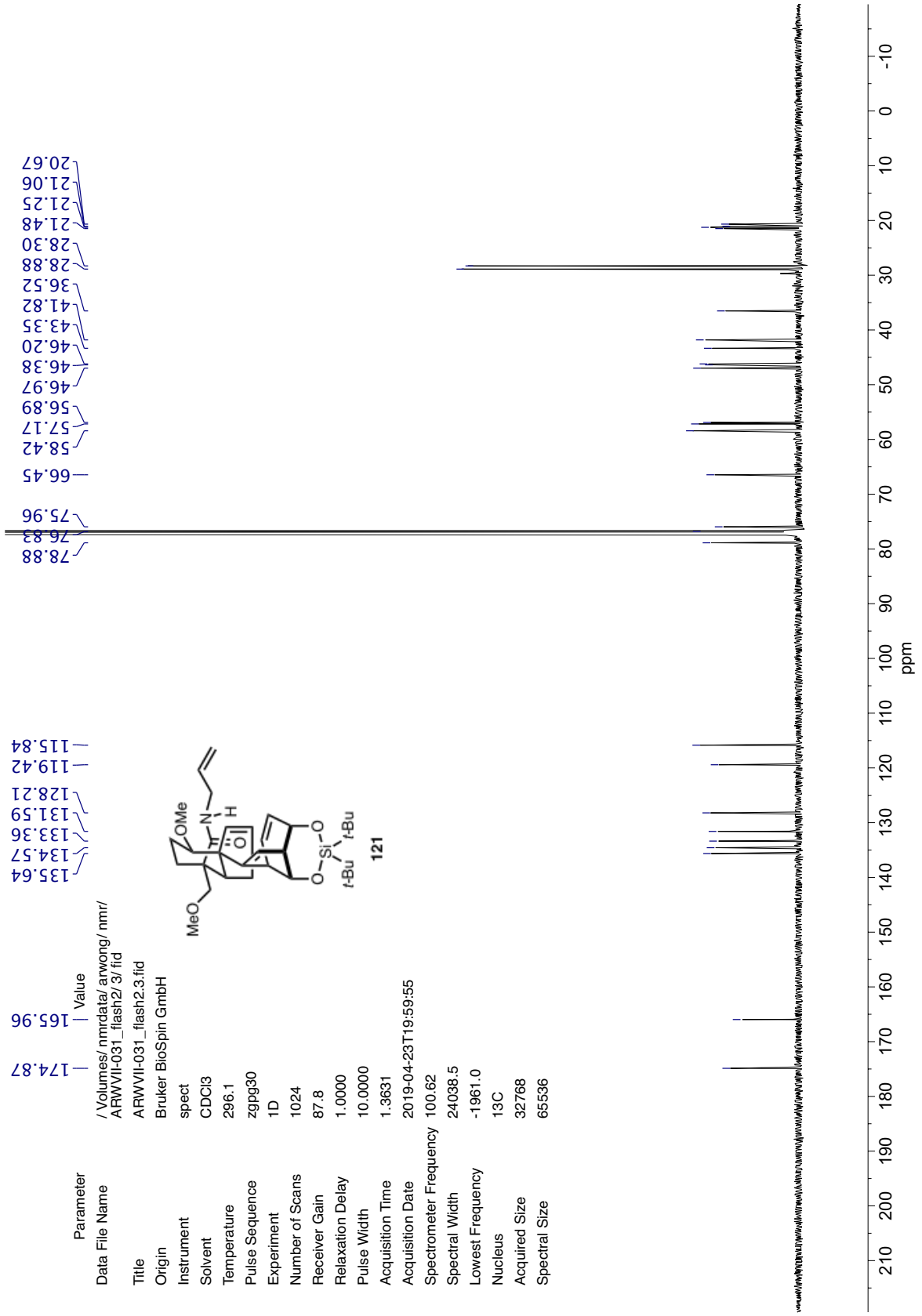
Title
ARWVII-031_flash2.2.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
296.2
Pulse Sequence
zg30
Experiment
1D
Number of Scans
32
Receiver Gain
127.1
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2019-04-23T19:17:24
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.4
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
121
ppm


Parameter
Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWVII-031_flash2/ 3/ fid
Title
ARWVII-031_flash2.3.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
296.1
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
1024
Receiver Gain
87.8
Relaxation Delay
1.0000
Pulse Width
10.0000
Acquisition Time
1.3631
Acquisition Date
2019-04-23T19:59:55
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1961.0
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
MeO
OMe
H
N
O
O
Si
O
t-Bu
t-Bu
121
174.87
165.96
135.64
134.57
133.36
131.59
128.21
119.42
115.84
78.88
76.83
75.96
66.45
58.42
57.17
56.89
46.97
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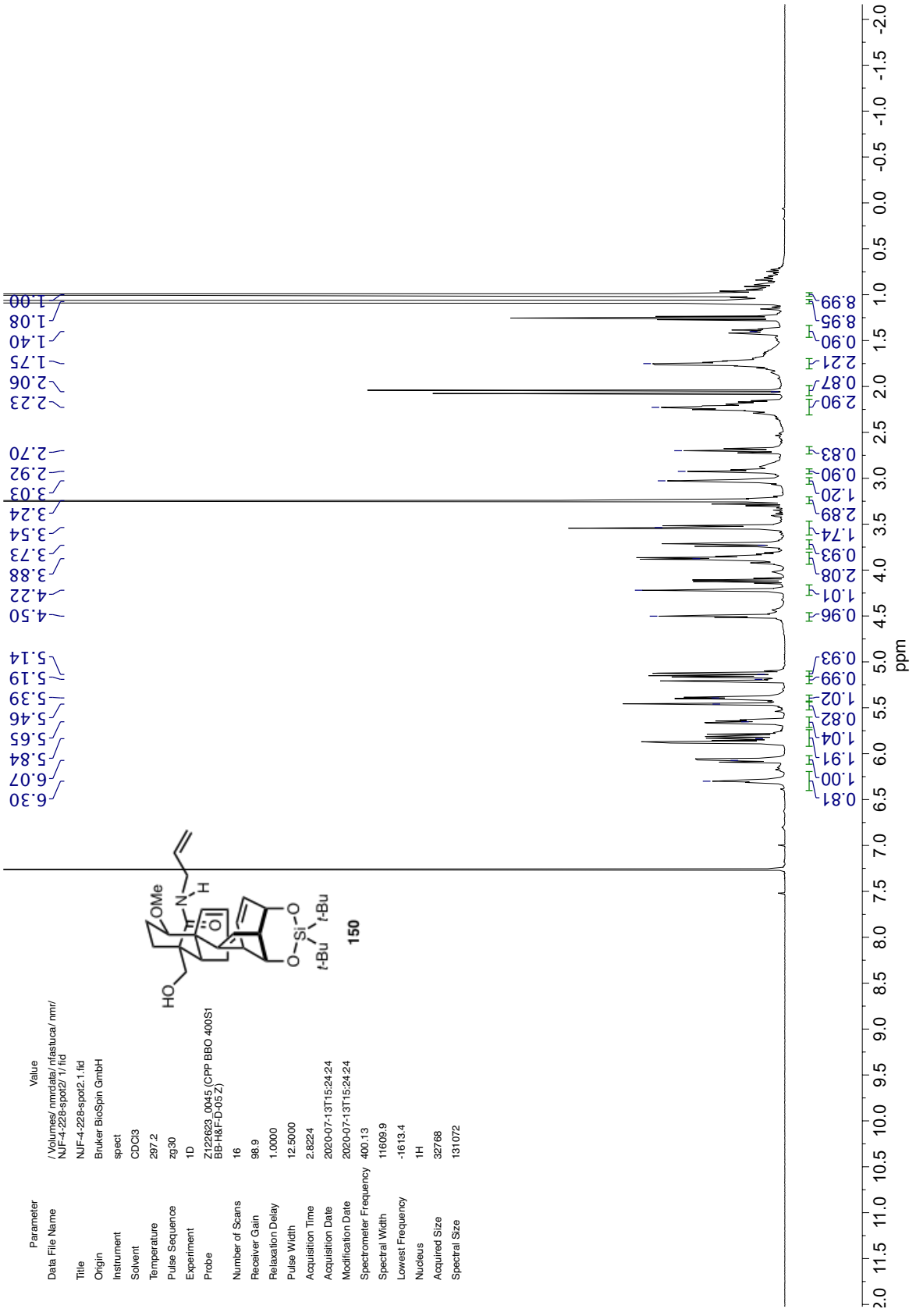
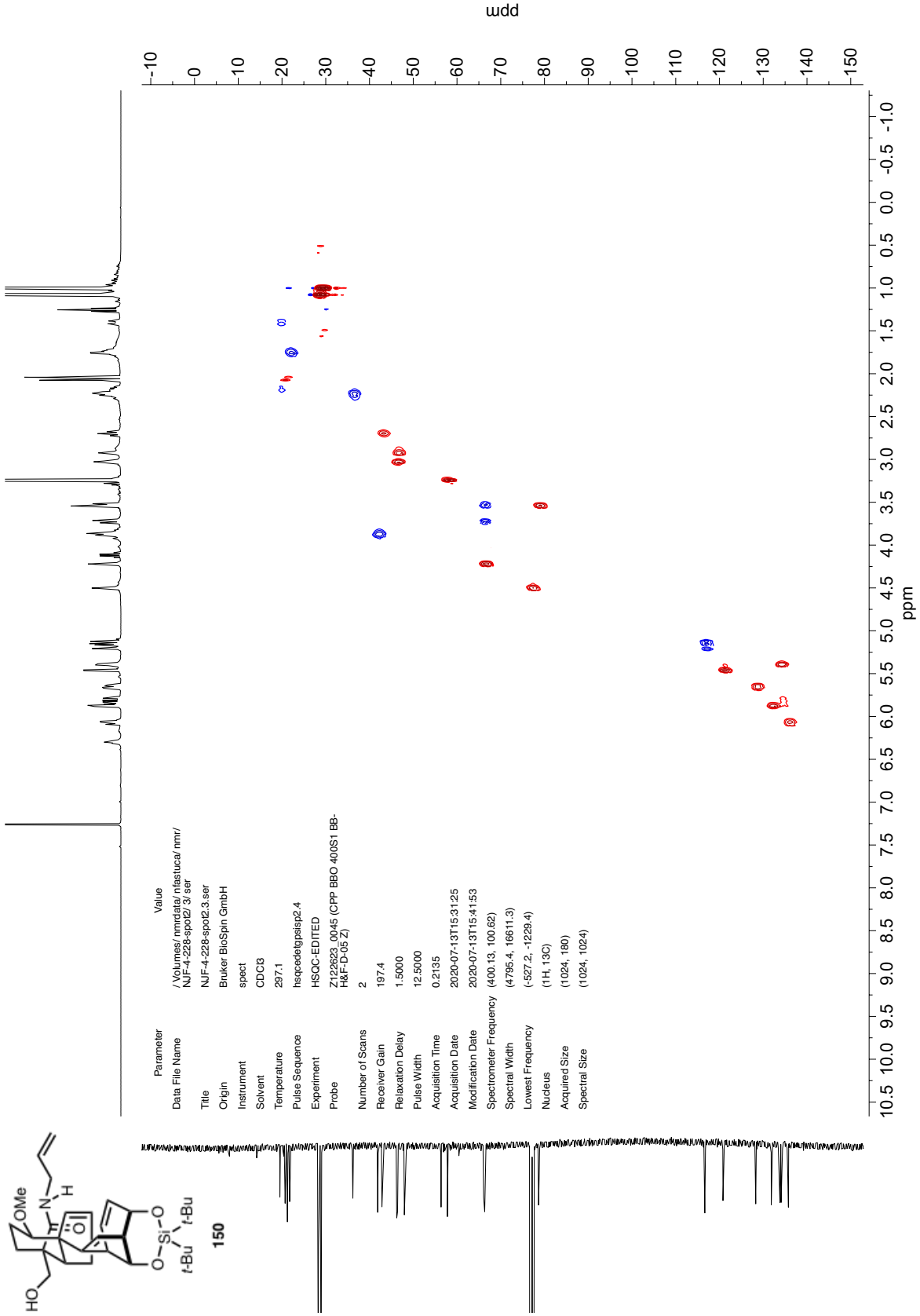
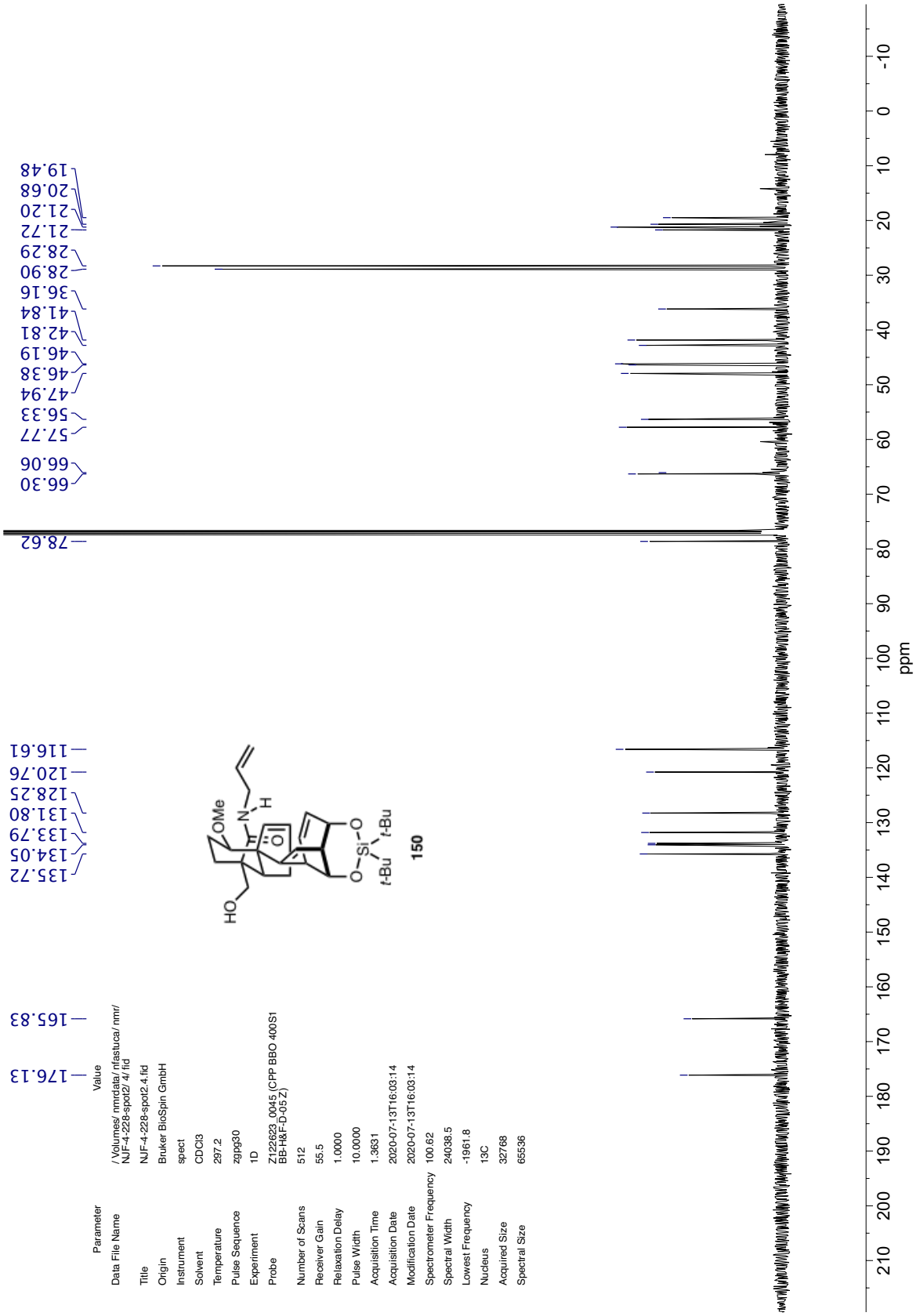
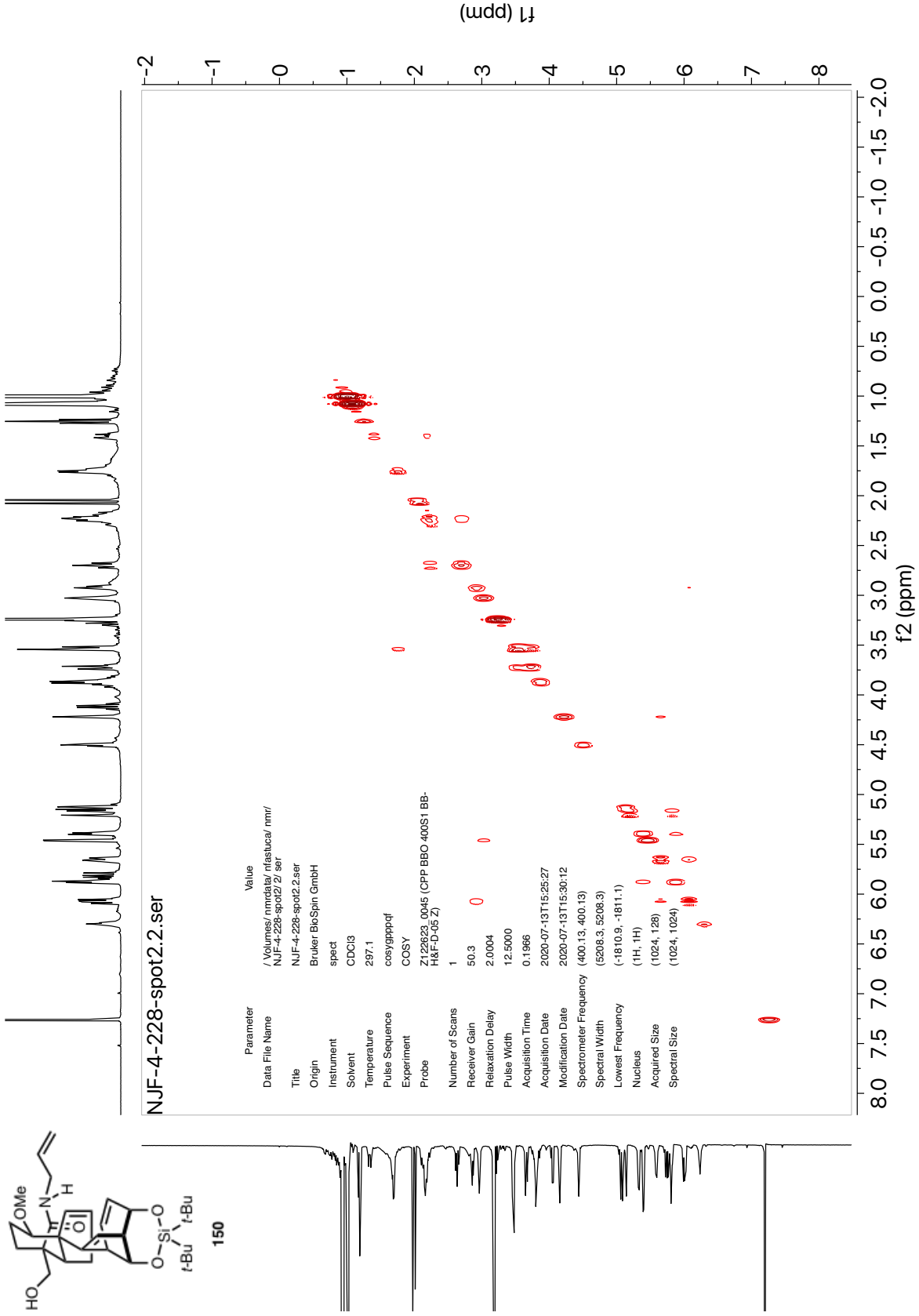
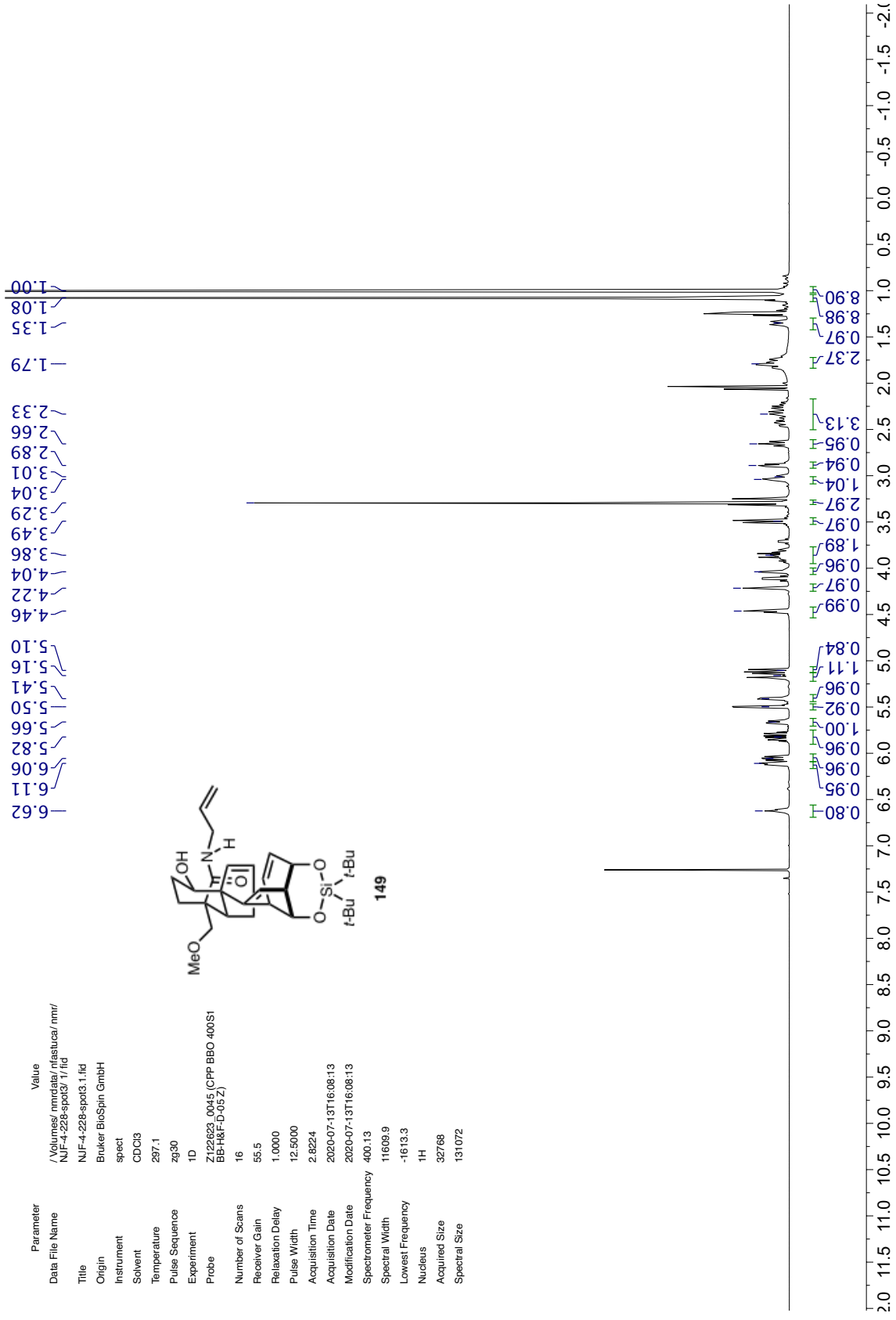
43.35
41.82
36.52
28.88
28.30
21.48
21.25
21.06
20.67
ppm

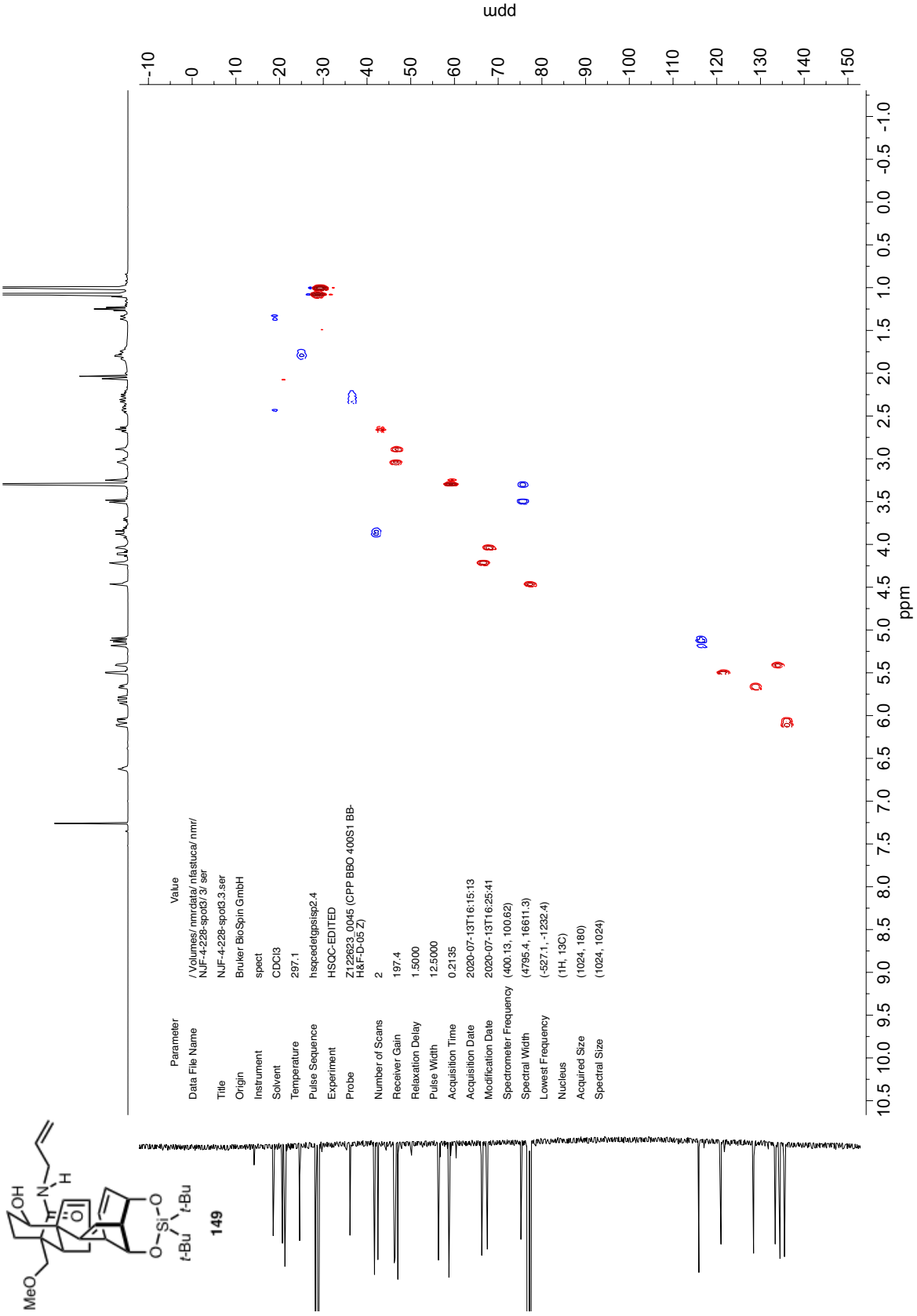

Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-228-spot2/ 1/ fid
Title
NJF-4-228-spot2.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
zg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
16
Receiver Gain
98.9
Relaxation Delay
1.0000
Pulse Width
12.5000
Acquisition Time
2.8224
Acquisition Date
2020-07-13T15:24:24
Modification Date
2020-07-13T15:24:24
Spectrometer Frequency
400.13
Spectral Width
11609.9
Lowest Frequency
-1613.4
Nucleus
1H
Acquired Size
32768
Spectral Size
131072
HO
OMe
N
H
OH
O
Si
t-Bu
t-Bu
150
6.30
6.07
5.84
5.65
5.46
5.39
5.19
5.14
4.50
4.22
3.88
3.73
3.54
3.24
3.03
2.92
2.70
2.23
2.06
1.75
1.40
1.08
1.00
8.99
8.95
0.90
2.21
0.87
2.90
0.83
0.90
1.20
2.89
1.74
0.93
2.08
1.01
0.96
0.93
0.99
1.02
0.82
1.04
1.91
1.00
0.81
ppm

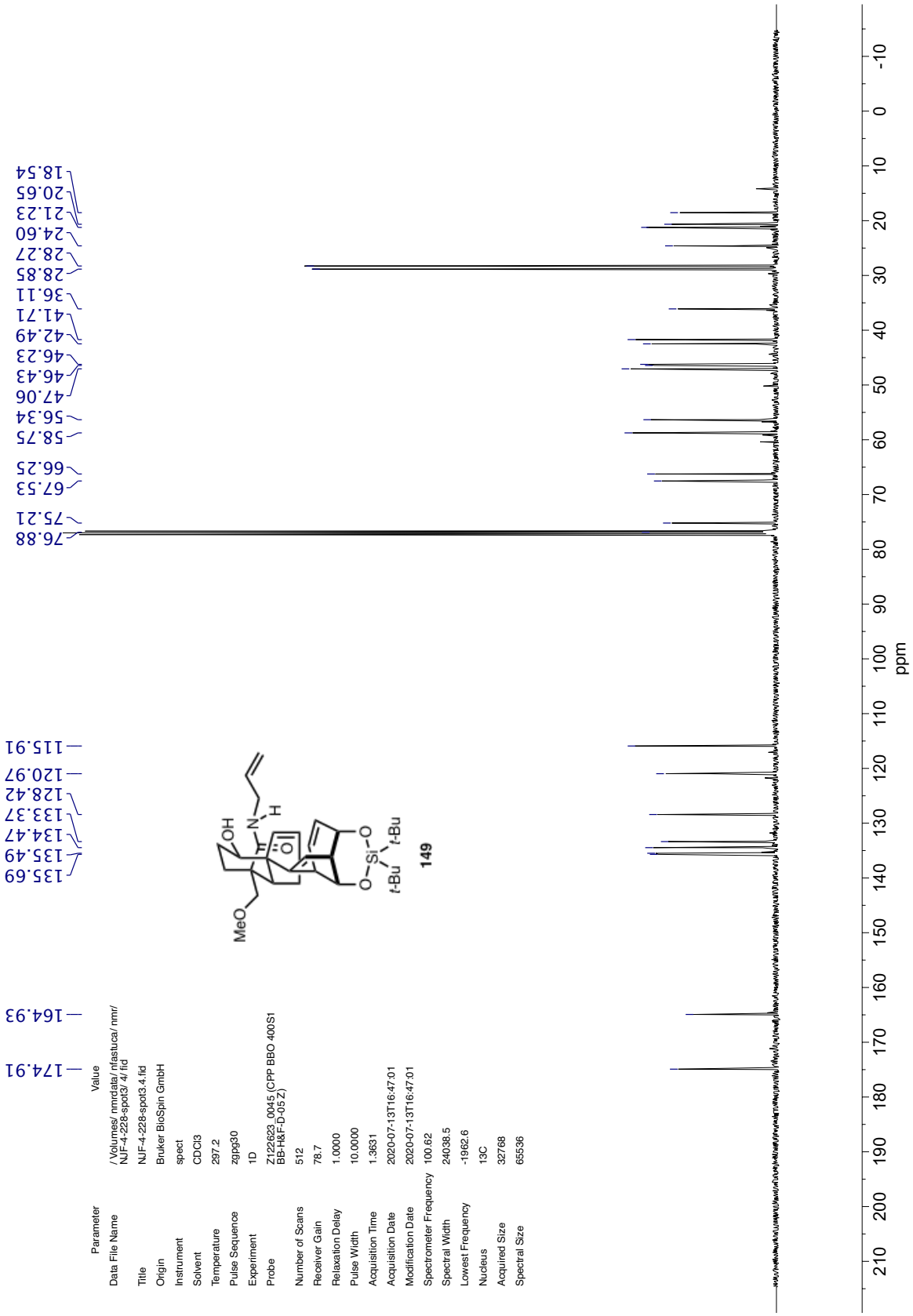

ppm
ppm
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-228-spot2/ 3/ ser
Title NJF-4-228-spot2.3.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-07-13T15:31:25
Modification Date 2020-07-13T15:41:53
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-527.2, -1229.4)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
OMe
HO
t-Bu
t-Bu
150

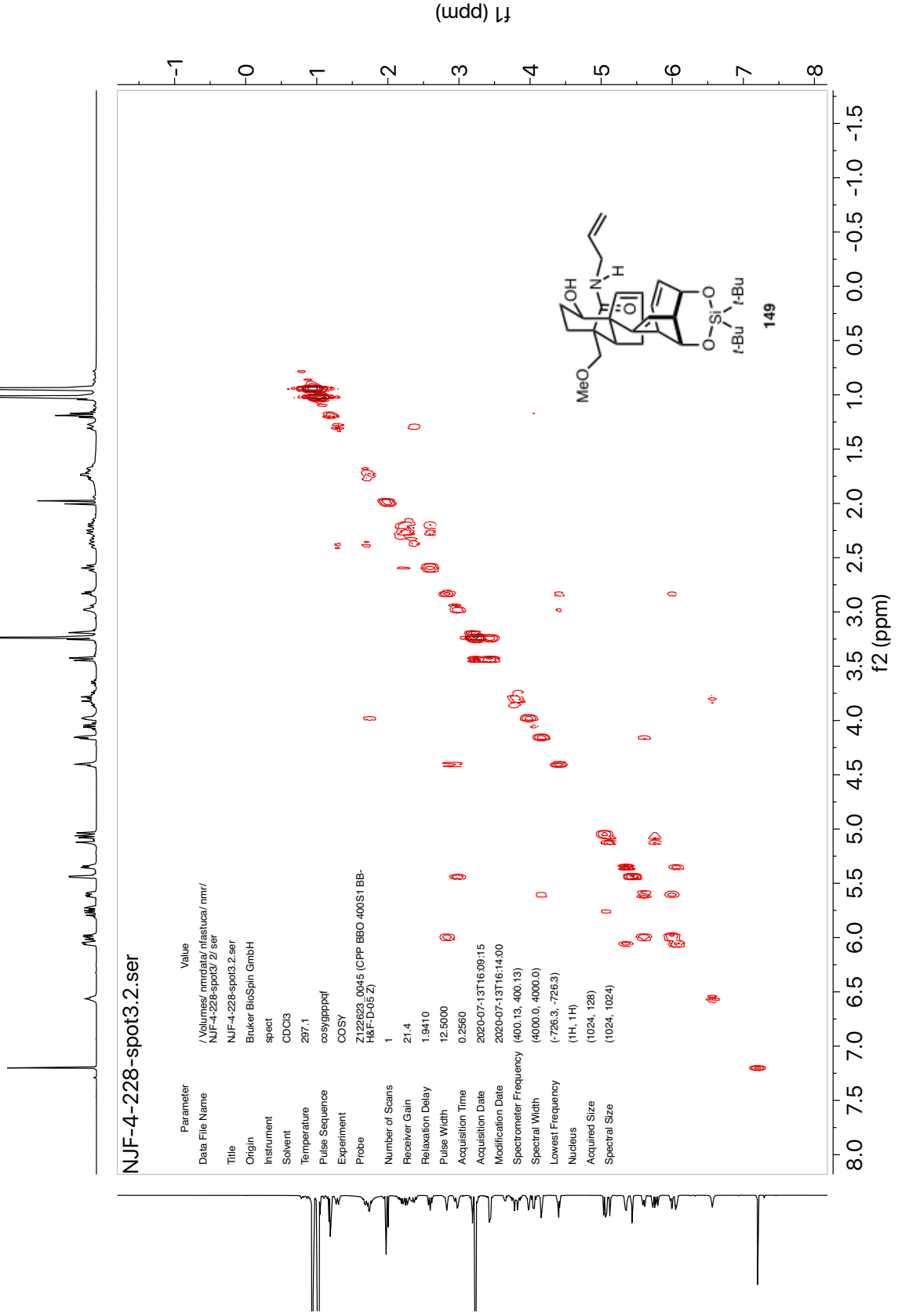

19.48
20.68
21.20
21.72
28.29
28.90
36.16
41.84
42.81
46.19
46.38
47.94
56.33
57.77
66.06
66.30
78.62
116.61
120.76
128.25
131.80
133.79
134.05
135.72
165.83
176.13
OMe
N
H
HO
O
O
Si
O
t-Bu
t-Bu
150
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4 -228-spot2/ 4/ fid
Title
NJF-4-228-spot2.4.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
zgpg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
512
Receiver Gain
55.5
Relaxation Delay
1.0000
Pulse Width
10.0000
Acquisition Time
1.3631
Acquisition Date
2020-07-13T16:03:14
Modification Date
2020-07-13T16:03:14
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1961.8
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

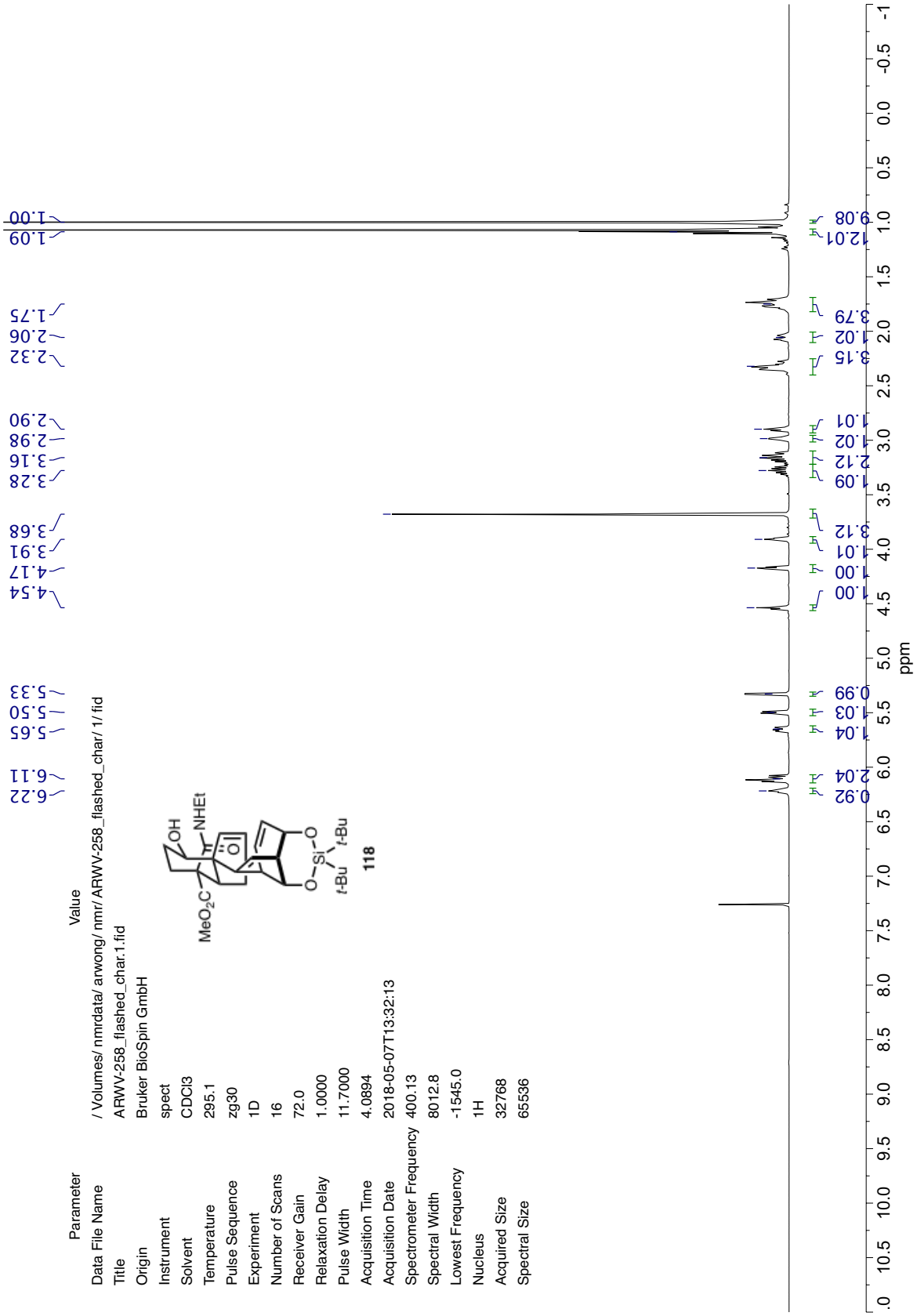

NJF-4-228-spot2.2.ser
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-228-spot2/ 2/ ser
Title NJF-4-228-spot2.2.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.1
Pulse Sequence cosygpppqf
Experiment COSY
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 1
Receiver Gain 50.3
Relaxation Delay 2.0004
Pulse Width 12.5000
Acquisition Time 0.1966
Acquisition Date 2020-07-13T15:25:27
Modification Date 2020-07-13T15:30:12
Spectrometer Frequency (400.13, 400.13)
Spectral Width (5208.3, 5208.3)
Lowest Frequency (-1810.9, -1811.1)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
f2 (ppm)
f1 (ppm)
OMe
HO
O-Si-O
t-Bu t-Bu
150

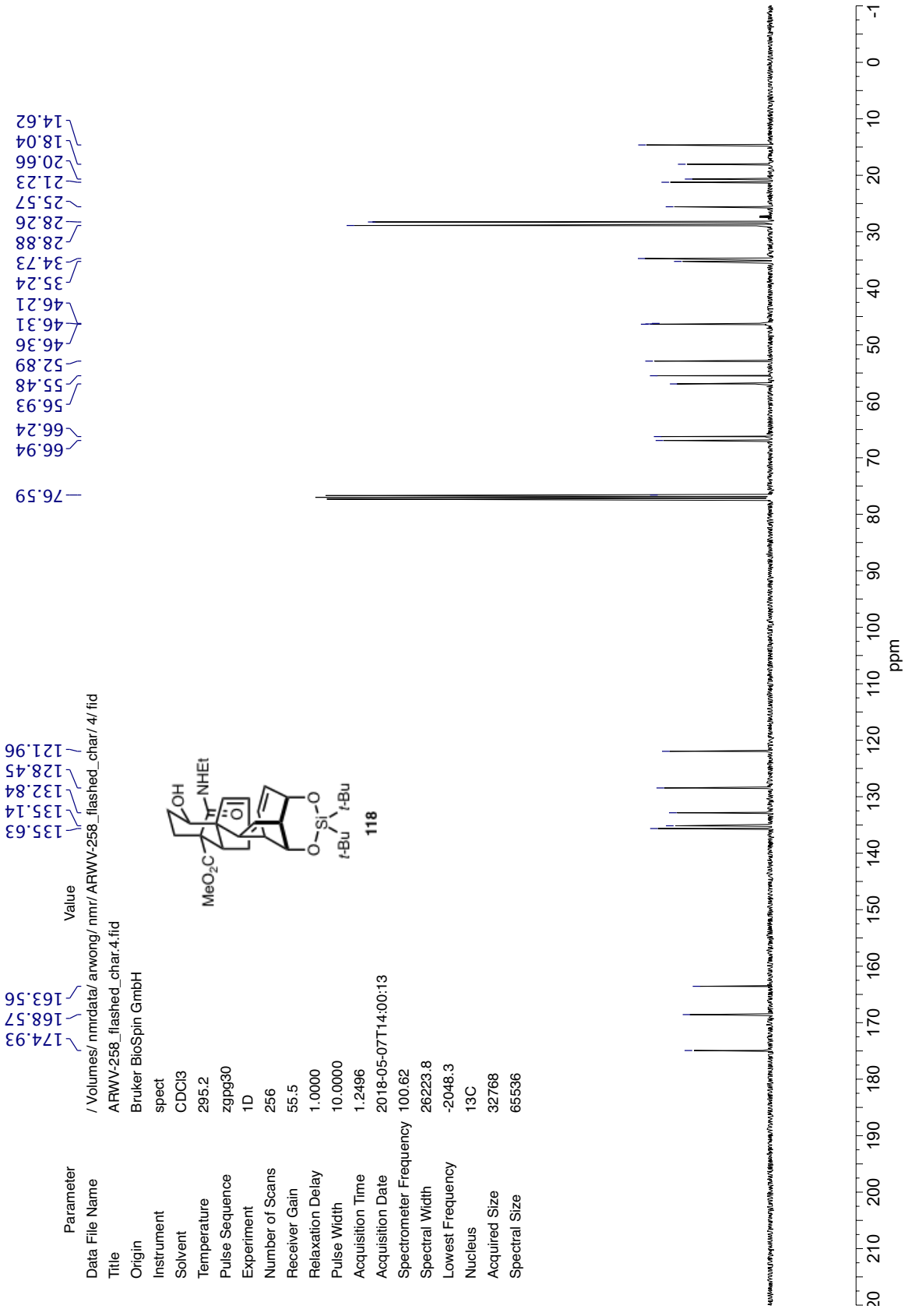

Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-228-spot3/ 1/ fid
Title
NJF-4-228-spot3.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.1
Pulse Sequence
zg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
16
Receiver Gain
55.5
Relaxation Delay
1.0000
Pulse Width
12.5000
Acquisition Time
2.8224
Acquisition Date
2020-07-13T16:08:13
Modification Date
2020-07-13T16:08:13
Spectrometer Frequency
400.13
Spectral Width
11609.9
Lowest Frequency
-1613.3
Nucleus
1H
Acquired Size
32768
Spectral Size
131072
MeO
OH
H
N
H
O
O
Si
O
t-Bu
t-Bu
149
6.62
6.11
6.06
5.82
5.66
5.50
5.41
5.16
5.10
4.46
4.22
4.04
3.86
3.49
3.29
3.04
3.01
2.89
2.66
2.33
1.79
1.35
1.08
1.00
0.80
0.95
0.96
0.96
1.00
0.92
0.96
1.11
0.84
0.99
0.97
0.96
1.89
0.97
2.97
1.04
0.94
0.95
3.13
2.37
0.97
8.98
8.90
ppm

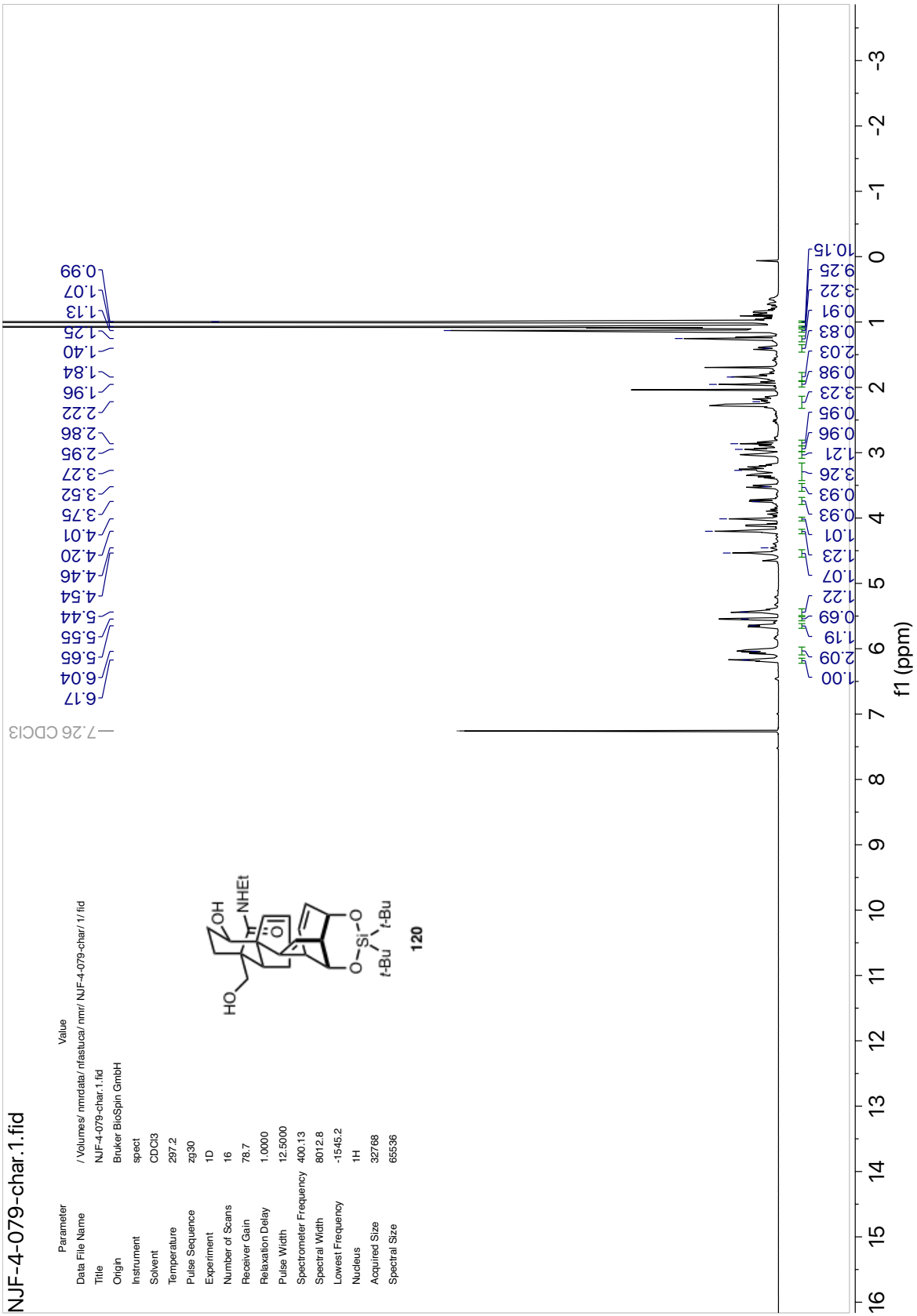

149
MeO
OH
N
H
O
O
Si
t-Bu
t-Bu
ppm
Parameter Value
Data File Name /Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-228-spot3/ 3/ ser
Title NJF-4-228-spot3.3.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-07-13T16:15:13
Modification Date 2020-07-13T16:25:41
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-527.1, -1232.4)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)

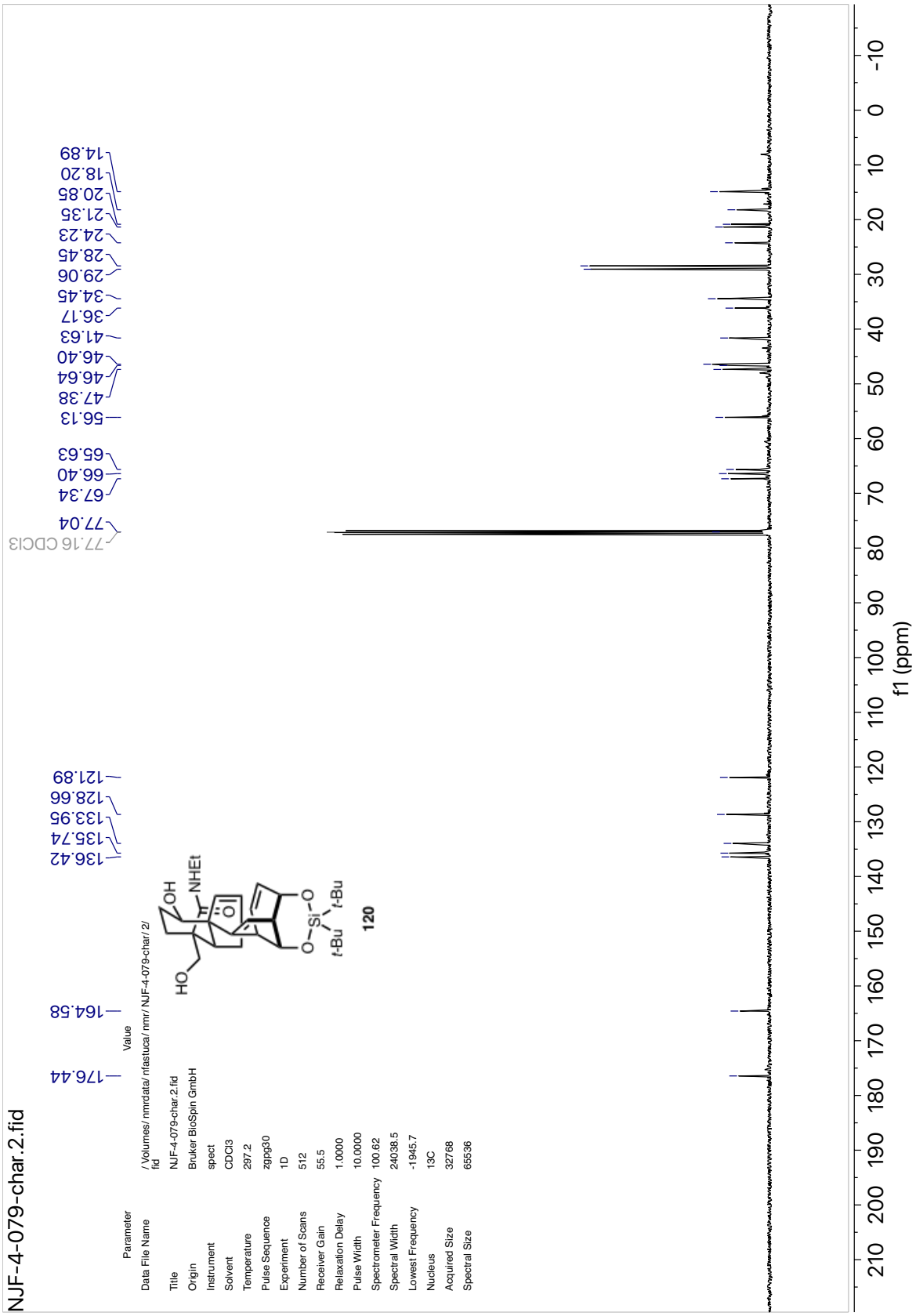

Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-228-spot3/ 4/ fid
Title
NJF-4-228-spot3.4.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
zgpg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
512
Receiver Gain
78.7
Relaxation Delay
1.0000
Pulse Width
10.0000
Acquisition Time
1.3631
Acquisition Date
2020-07-13T16:47:01
Modification Date
2020-07-13T16:47:01
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1962.6
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
174.91
164.93
135.69
135.49
134.47
133.37
128.42
120.97
115.91
76.88
75.21
67.53
66.25
58.75
56.34
47.06
46.43
46.23
42.49
41.71
36.11
28.85
28.27
24.60
21.23
20.65
18.54
MeO
OH
N
H
O
O
Si
O
t-Bu
t-Bu
149
ppm

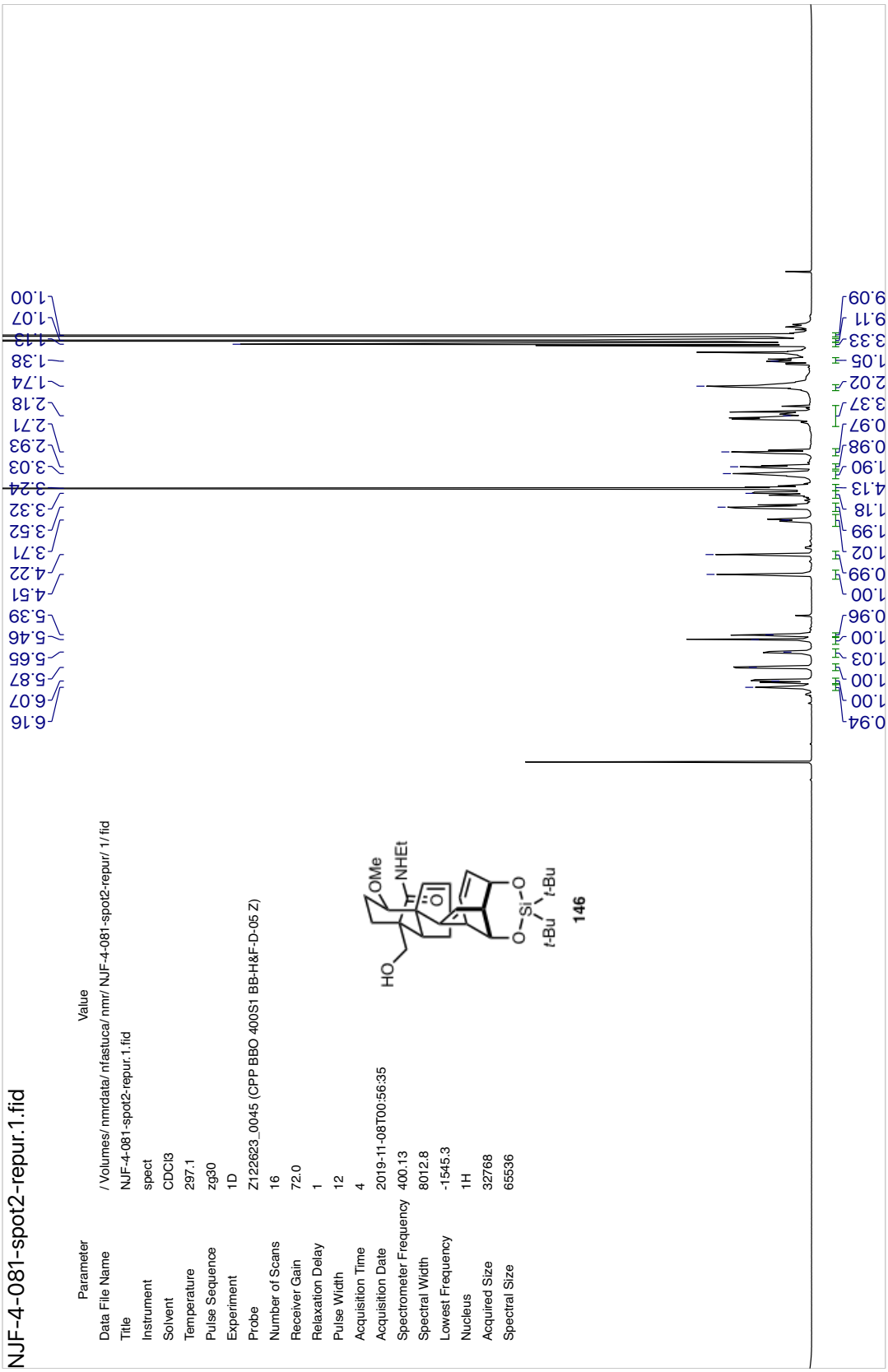

NJF-4-228-spot3.2.ser
Parameter Value
Data File Name /Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-228-spot3/ 2/ ser
Title NJF-4-228-spot3.2.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.1
Pulse Sequence cosygpppqf
Experiment COSY
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 1
Receiver Gain 21.4
Relaxation Delay 1.9410
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-07-13T16:09:15
Modification Date 2020-07-13T16:14:00
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-726.3, -726.3)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
MeO
OH
H
N
O
O
Si
t-Bu
t-Bu
149
f2 (ppm)
f1 (ppm)

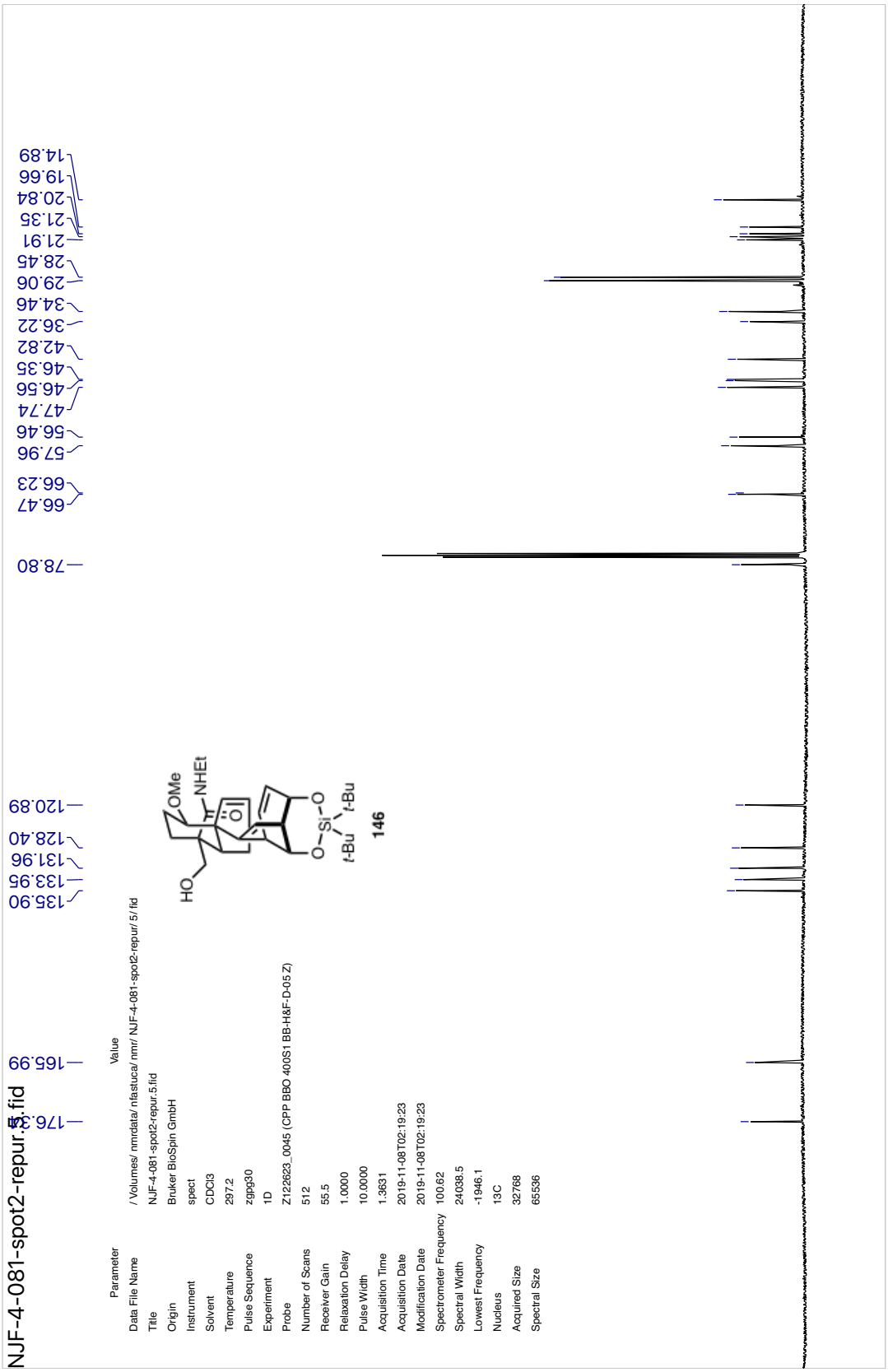

Parameter
Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWV-258_flashed_char/ 1/ fid
Title ARWV-258_flashed_char.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 72.0
Relaxation Delay 1.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Acquisition Date 2018-05-07T13:32:13
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.0
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
OH
NHEt
MeO2C
O
O
Si
O
t-Bu
t-Bu
118
ppm

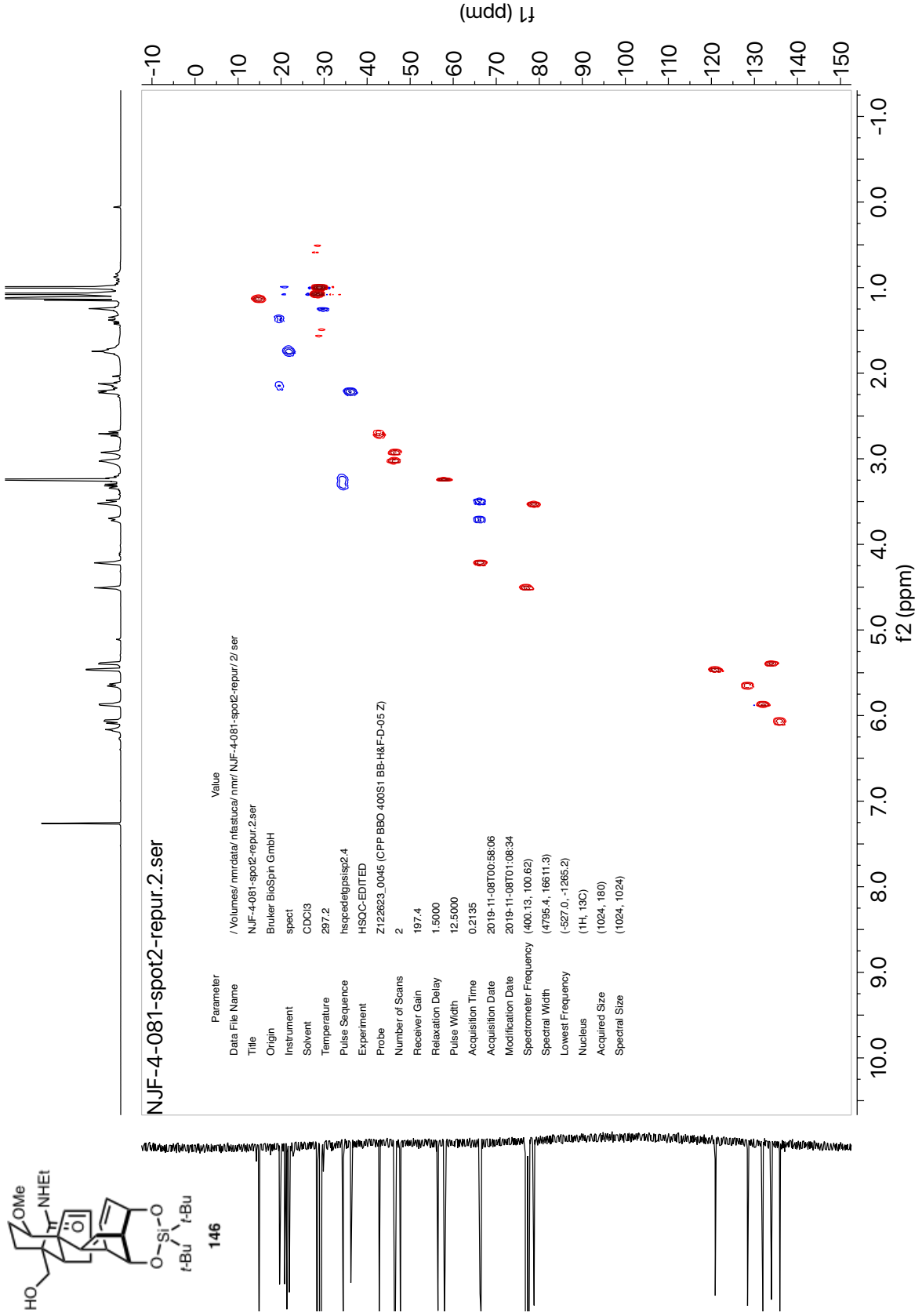

174.93
168.57
163.56
135.63
135.14
132.84
128.45
121.96
76.59
66.94
66.24
56.93
55.48
52.89
46.36
46.31
46.21
35.24
34.73
28.88
28.26
25.57
21.23
20.66
18.04
14.62
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWV-258_flashed_char/ 4/ fid
Title
ARWV-258_flashed_char.4.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.2
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
256
Receiver Gain
55.5
Relaxation Delay
1.0000
Pulse Width
10.0000
Acquisition Time
1.2496
Acquisition Date
2018-05-07T14:00:13
Spectrometer Frequency
100.62
Spectral Width
26223.8
Lowest Frequency
-2048.3
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
OH
NHEt
MeO2C
O
O
Si
O
t-Bu
t-Bu
118
ppm

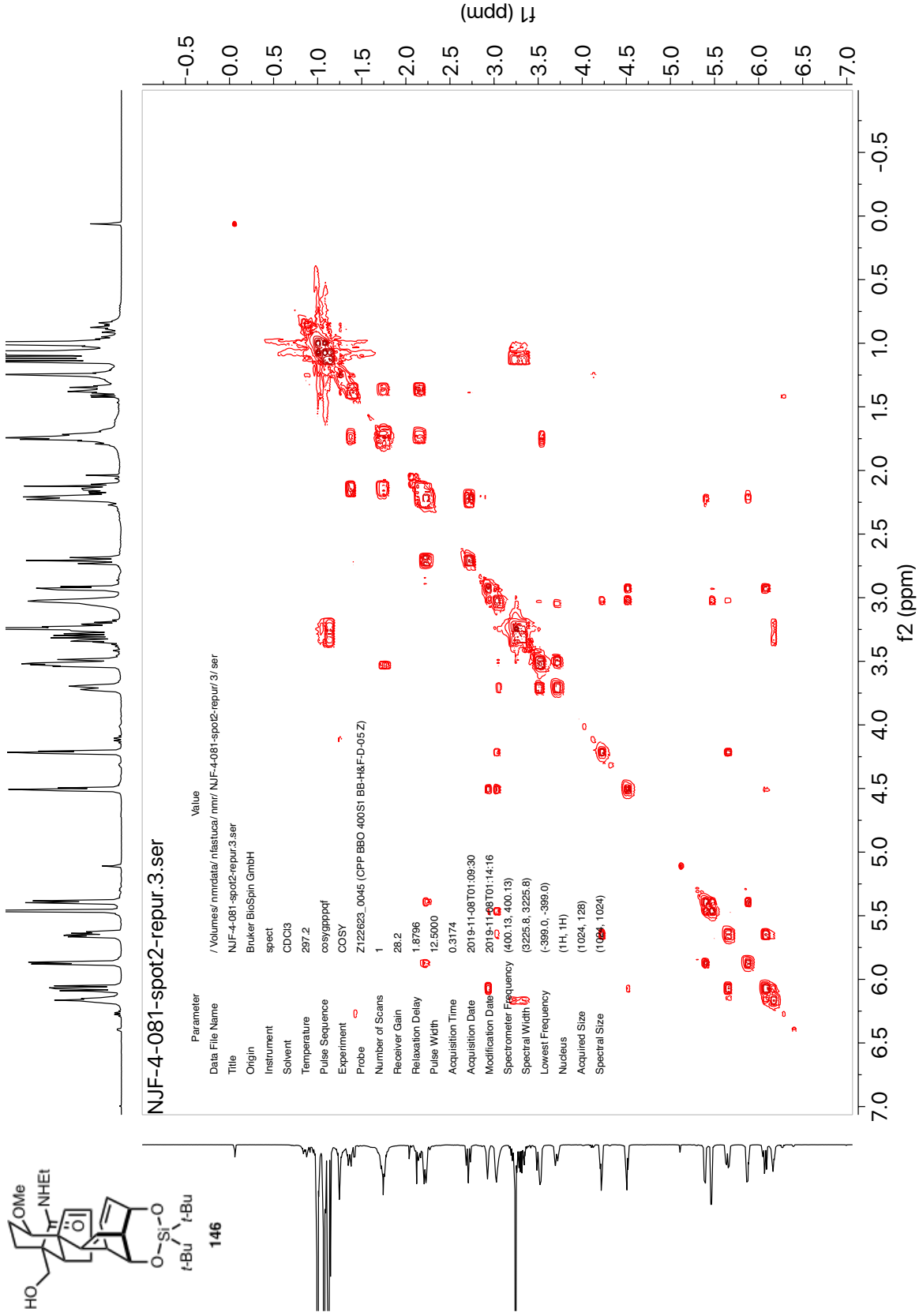

NJF-4-079-char.1.fid
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-079-char/ 1/ fid
Title
NJF-4-079-char.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
zg30
Experiment
1D
Number of Scans
16
Receiver Gain
78.7
Relaxation Delay
1.0000
Pulse Width
12.5000
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.2
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
OH
NHEt
HO
O
O
Si
t-Bu
t-Bu
120
7.26 CDCl3
6.17
6.04
5.65
5.55
5.44
4.54
4.46
4.20
4.01
3.75
3.52
3.27
2.95
2.86
2.22
1.96
1.84
1.40
1.25
1.13
1.07
0.99
1.00
2.09
1.19
0.69
1.22
1.07
1.23
1.01
0.93
0.93
3.26
1.21
0.96
0.95
3.23
0.98
2.03
0.83
0.91
3.22
9.25
10.15
f1 (ppm)

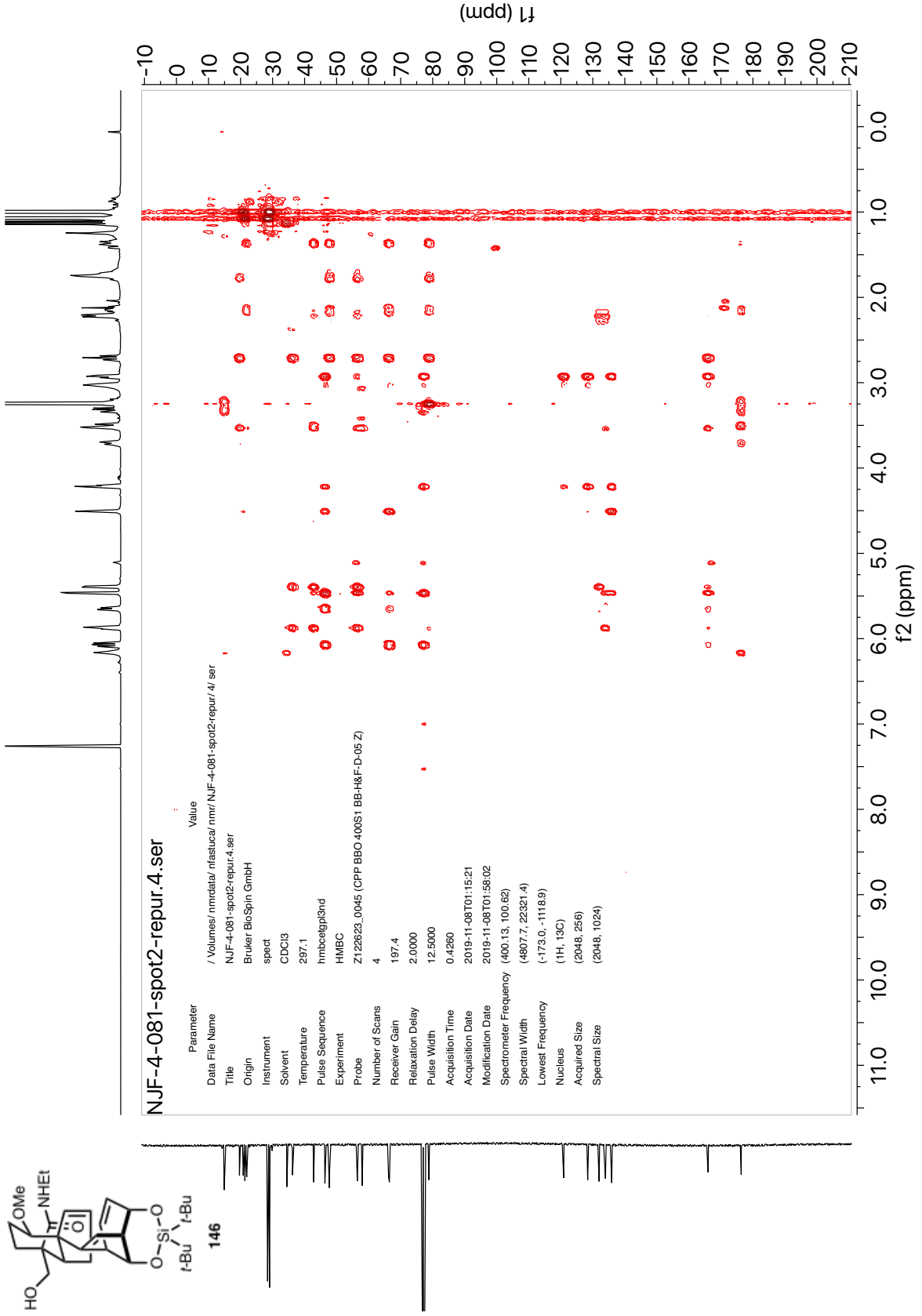

NJF-4-079-char.2.fid
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-079-char/ 2/ fid
Title
NJF-4-079-char.2.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
512
Receiver Gain
55.5
Relaxation Delay
1.0000
Pulse Width
10.0000
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1945.7
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
120
176.44
164.58
136.42
135.74
133.95
128.66
121.89
77.16 CDCl3
77.04
67.34
66.40
65.63
56.13
47.38
46.64
46.40
41.63
36.17
34.45
29.06
28.45
24.23
21.35
20.85
18.20
14.89
f1 (ppm)

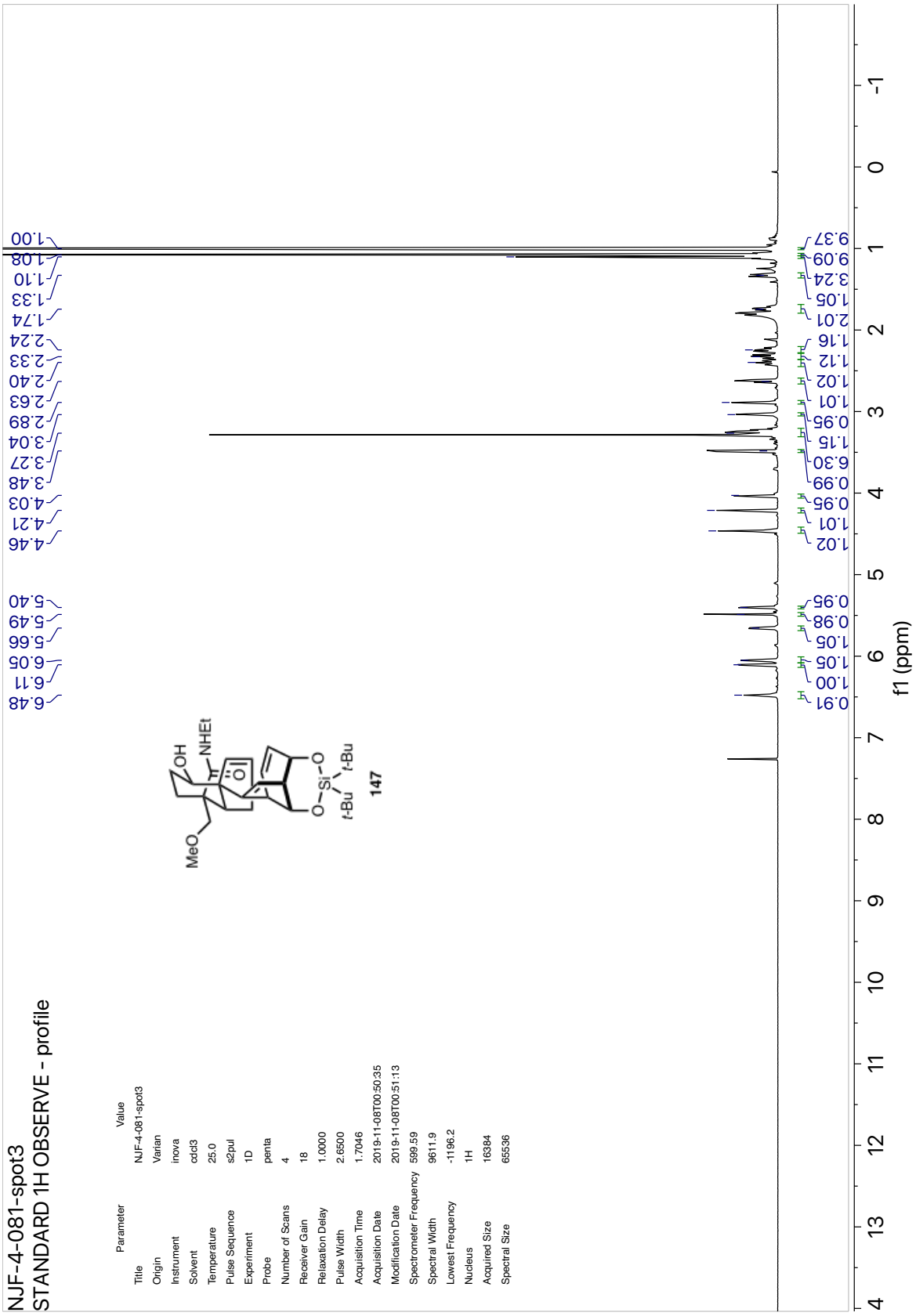

NJF-4-081-spot2-repur.1.fid
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-081-spot2-repur/ 1/ fid
Title
NJF-4-081-spot2-repur.1.fid
Instrument
spect
Solvent
CDCl3
Temperature
297.1
Pulse Sequence
zg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
16
Receiver Gain
72.0
Relaxation Delay
1
Pulse Width
12
Acquisition Time
4
Acquisition Date
2019-11-08T00:56:35
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.3
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
OMe
NHEt
HO
O
O
Si
O
t-Bu
t-Bu
146
6.16
6.07
5.87
5.65
5.46
5.39
4.51
4.22
3.71
3.52
3.32
3.24
3.03
2.93
2.71
2.18
1.74
1.38
1.13
1.07
1.00
0.94
1.00
1.00
1.03
1.00
0.96
1.00
0.99
1.02
1.99
1.18
4.13
1.90
0.98
0.97
3.37
2.02
1.05
3.33
9.11
9.09
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

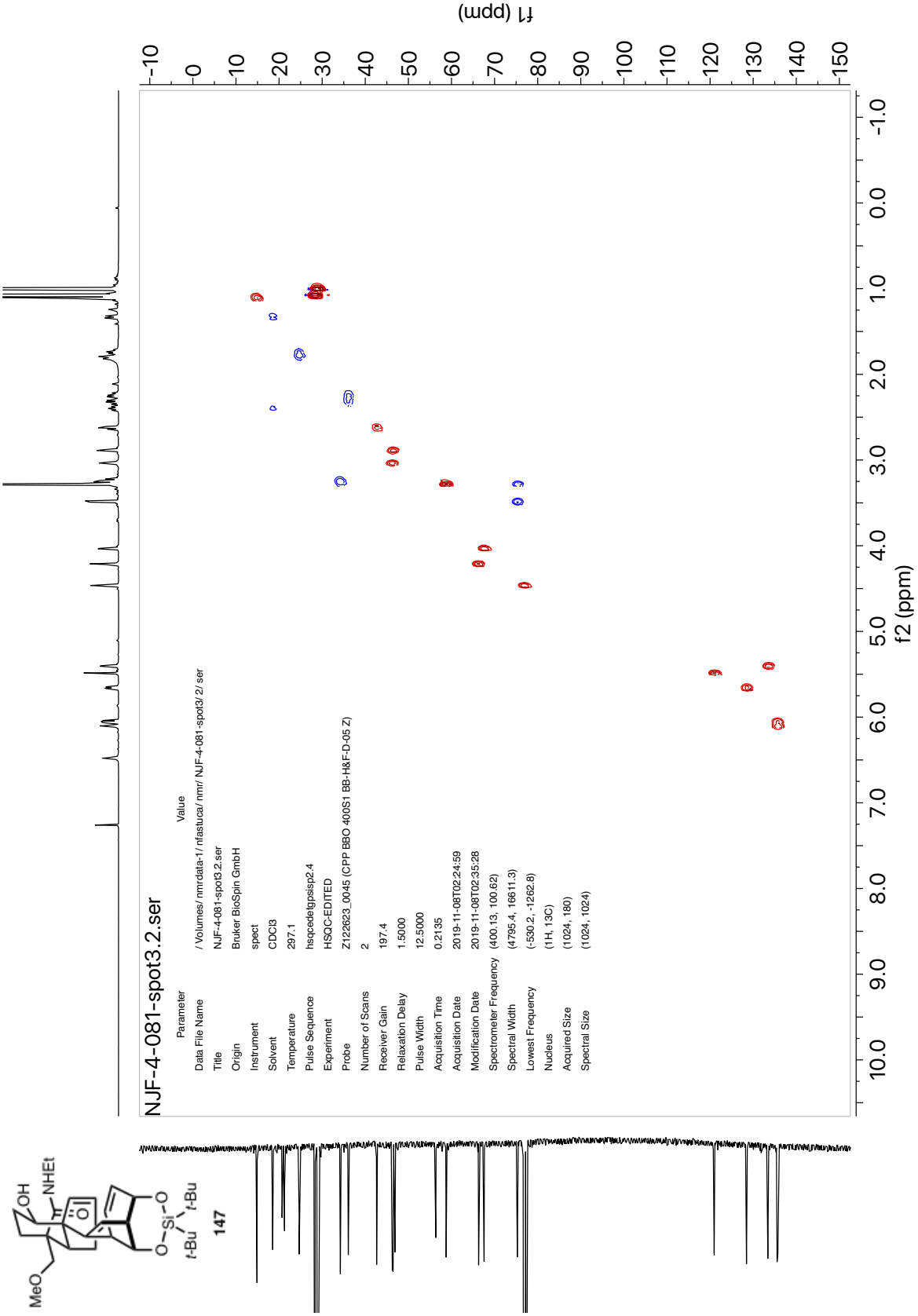

NJF-4-081-spot2-repur.5.fid
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-081-spot2-repur/ 5/ fid
Title NJF-4-081-spot2-repur.5.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence zgpg30
Experiment 1D
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 512
Receiver Gain 55.5
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2019-11-08T02:19:23
Modification Date 2019-11-08T02:19:23
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1946.1
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
HO
OMe
NHEt
O
O–Si–O
t-Bu
t-Bu
146
176.33
165.99
135.90
133.95
131.96
128.40
120.89
78.80
66.47
66.23
57.96
56.46
47.74
46.56
46.35
42.82
36.22
34.46
29.06
28.45
21.91
21.35
20.84
19.66
14.89
f1 (ppm)

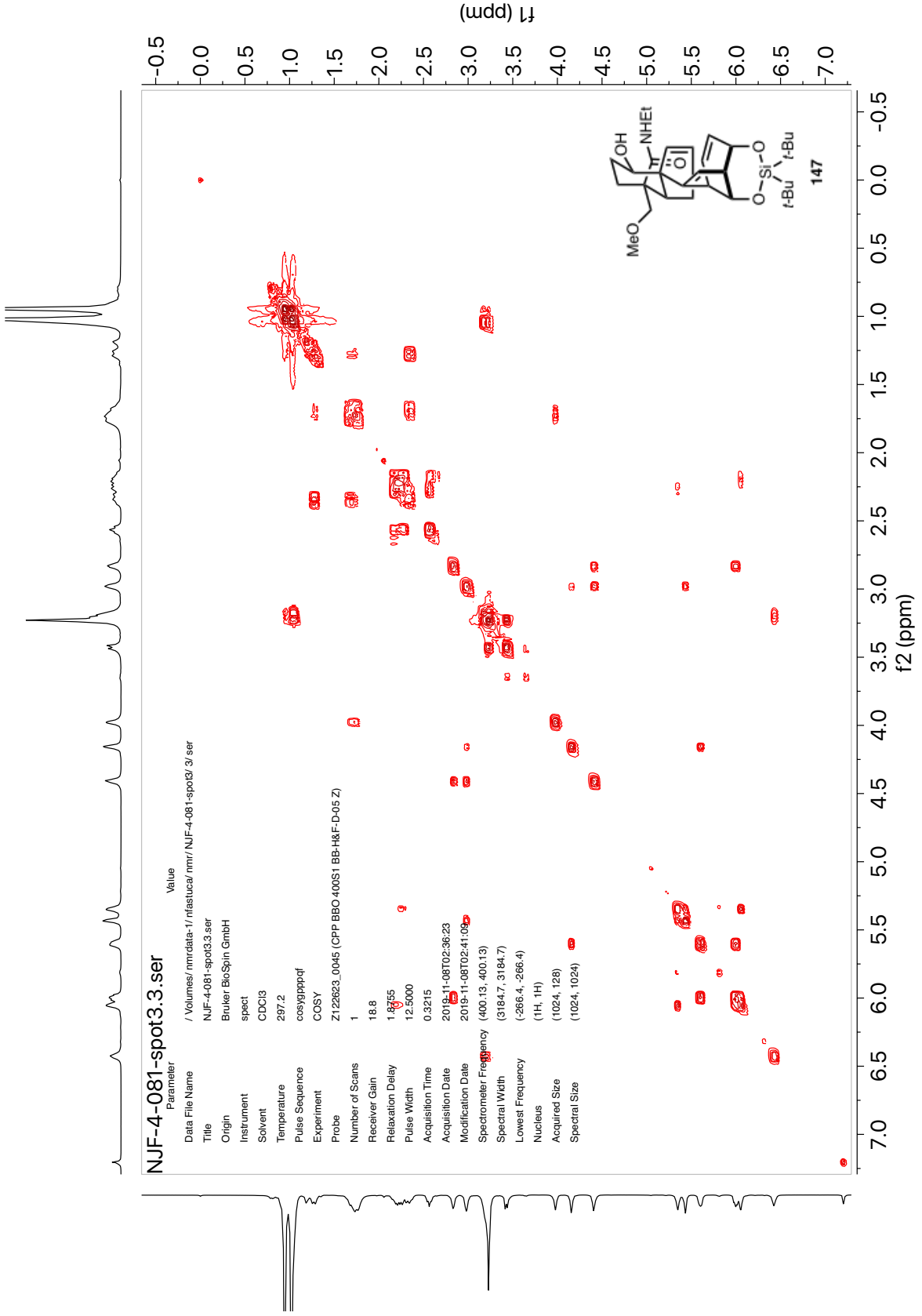

NJF-4-081-spot2-repur.2.ser
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-081-spot2-repur/ 2/ ser
Title NJF-4-081-spot2-repur.2.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2019-11-08T00:58:06
Modification Date 2019-11-08T01:08:34
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-527.0, -1265.2)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
f1 (ppm)
f2 (ppm)
HO
OMe
NHEt
O
O–Si–O
t-Bu
t-Bu
146

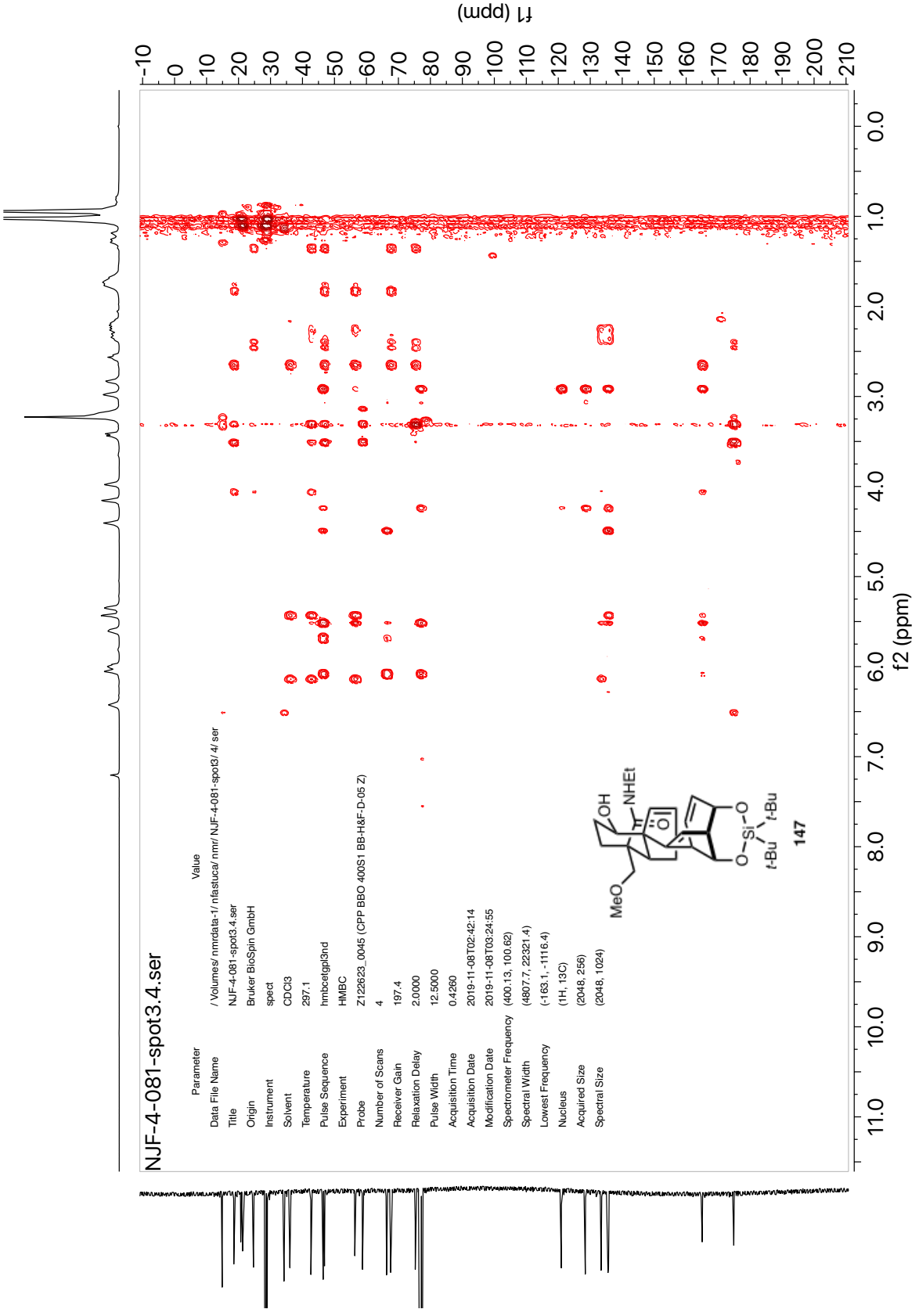

NJF-4-081-spot2-repur.3.ser
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-081-spot2-repur/ 3/ ser
Title
NJF-4-081-spot2-repur.3.ser
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
cosygpppqf
Experiment
COSY
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
1
Receiver Gain
28.2
Relaxation Delay
1.8796
Pulse Width
12.5000
Acquisition Time
0.3174
Acquisition Date
2019-11-08T01:09:30
Modification Date
2019-11-08T01:14:16
Spectrometer Frequency
(400.13, 400.13)
Spectral Width
(3225.8, 3225.8)
Lowest Frequency
(-399.0, -399.0)
Nucleus
(1H, 1H)
Acquired Size
(1024, 128)
Spectral Size
(1024, 1024)
f1 (ppm)
f2 (ppm)
HO
OMe
NHEt
O
O–Si–O
t-Bu
t-Bu
146

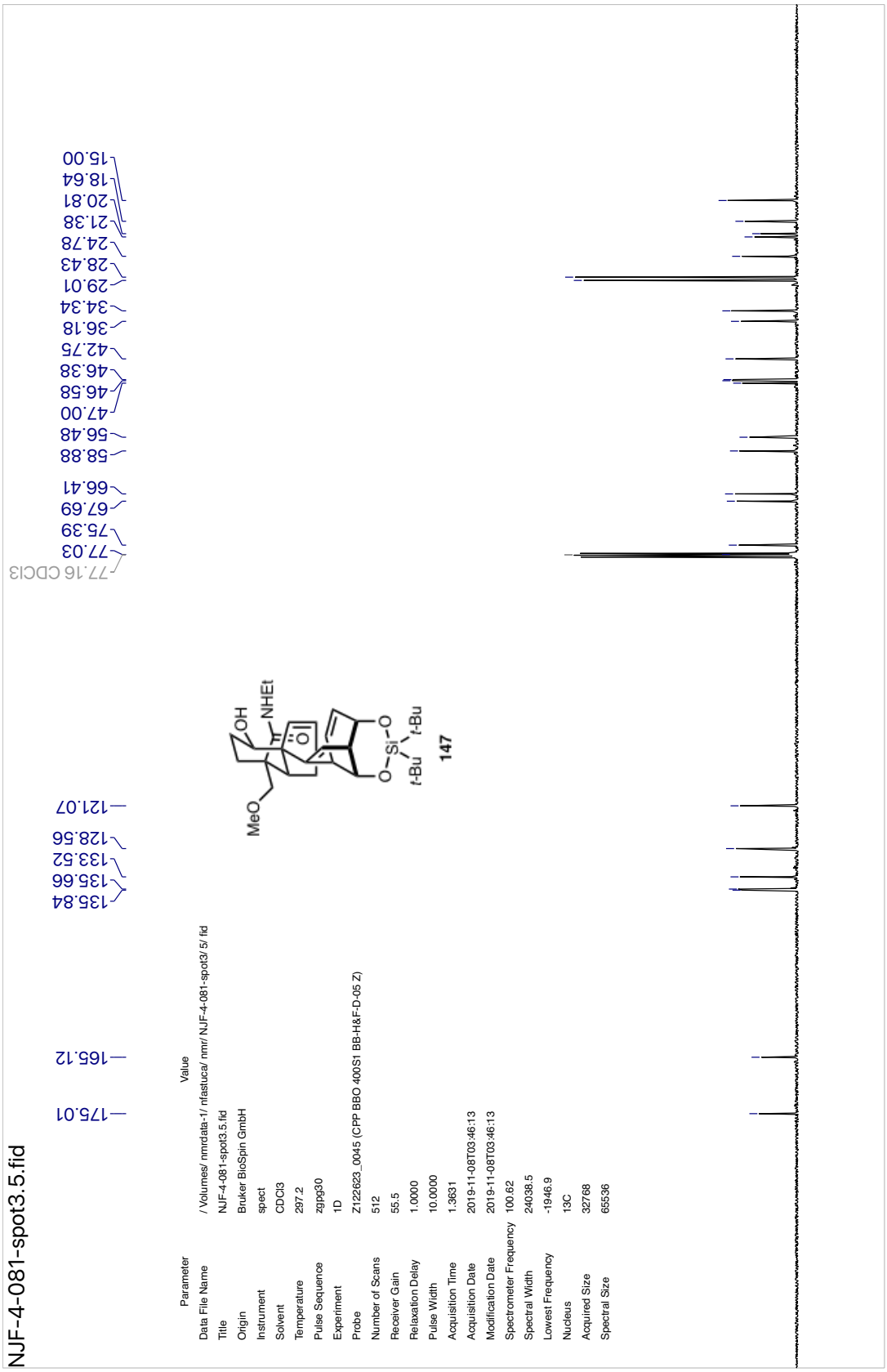

NJF-4-081-spot2-repur.4.ser
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-081-spot2-repur/ 4/ ser
Title NJF-4-081-spot2-repur.4.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.1
Pulse Sequence hmbcetgpl3nd
Experiment HMBC
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2019-11-08T01:15:21
Modification Date 2019-11-08T01:58:02
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-173.0, -1118.9)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
f1 (ppm)
f2 (ppm)
146
HO
OMe
NHEt
O
O–Si–O
t-Bu
t-Bu


NJF-4-081-spot3
STANDARD 1H OBSERVE - profile
Parameter Value
Title NJF-4-081-spot3
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe penta
Number of Scans 4
Receiver Gain 18
Relaxation Delay 1.0000
Pulse Width 2.6500
Acquisition Time 1.7046
Acquisition Date 2019-11-08T00:50:35
Modification Date 2019-11-08T00:51:13
Spectrometer Frequency 599.59
Spectral Width 9611.9
Lowest Frequency -1196.2
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
MeO
OH
NHEt
O
O
Si
t-Bu
t-Bu
147
f1 (ppm)

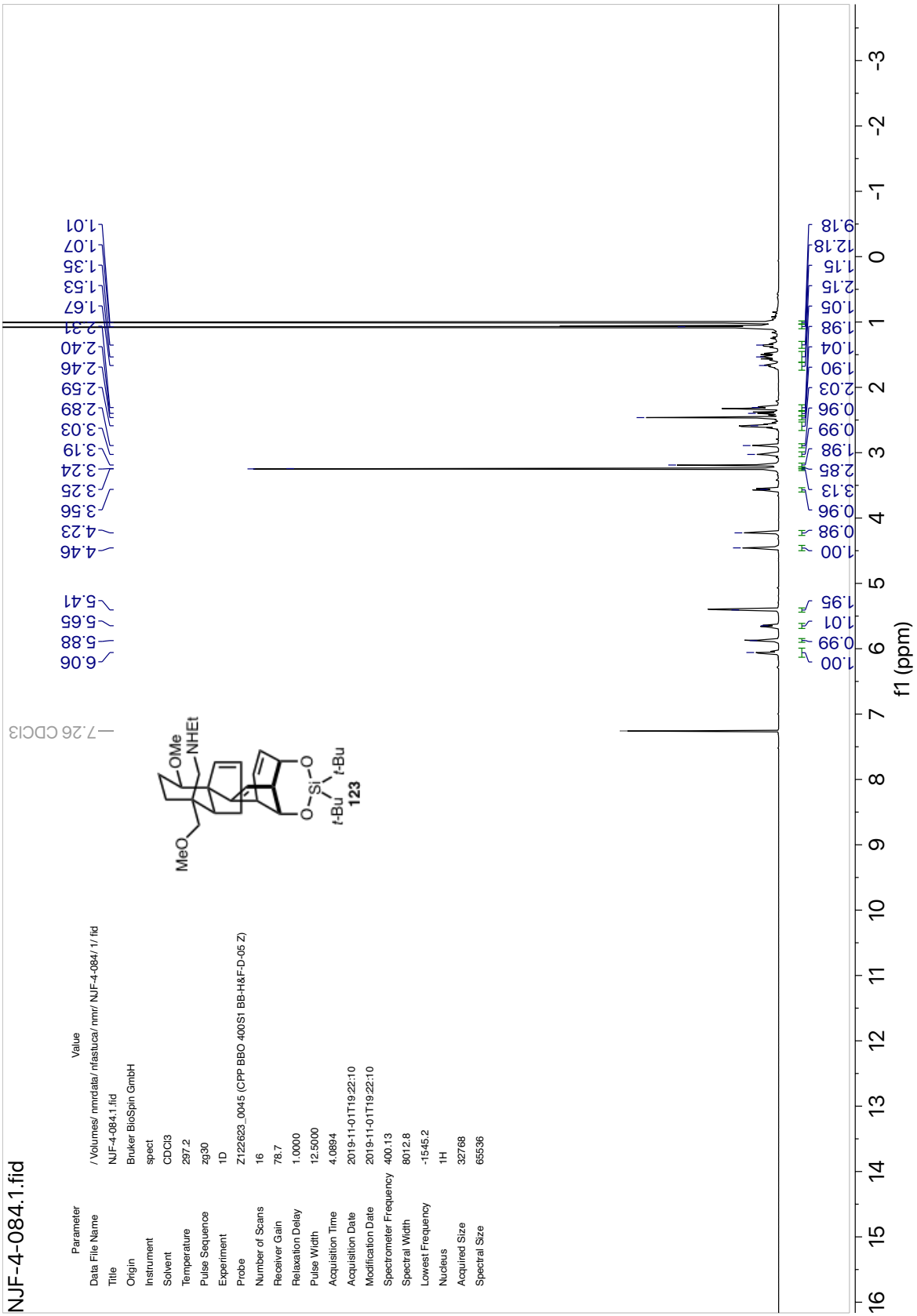

NJF-4-081-spot3.2.ser
Parameter Value
Data File Name / Volumes/ nmrdata-1/ nfastuca/ nmr/ NJF-4-081-spot3/ 2/ ser
Title NJF-4-081-spot3.2.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2019-11-08T02:24:59
Modification Date 2019-11-08T02:35:28
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-530.2, -1262.8)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
f1 (ppm)
f2 (ppm)
MeO
OH
NHEt
O
O
Si
t-Bu
t-Bu
147

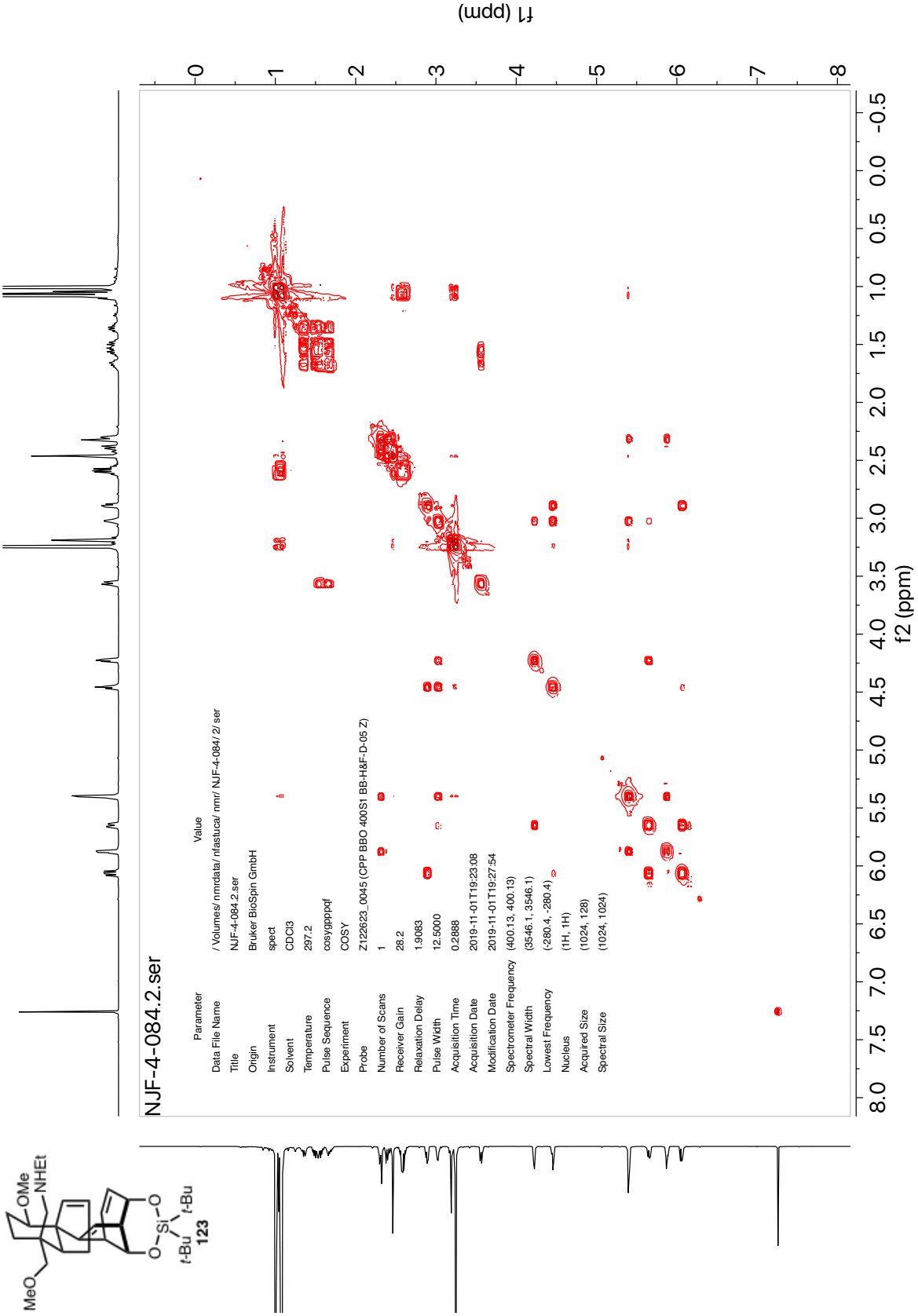

NJF-4-081-spot3.3.ser
Parameter Value
Data File Name / Volumes/ nmrdata-1/ nfastuca/ nmr/ NJF-4-081-spot3/ 3/ ser
Title NJF-4-081-spot3.3.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence cosygpppqf
Experiment COSY
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 1
Receiver Gain 18.8
Relaxation Delay 1.8755
Pulse Width 12.5000
Acquisition Time 0.3215
Acquisition Date 2019-11-08T02:36:23
Modification Date 2019-11-08T02:41:09
Spectrometer Frequency (400.13, 400.13)
Spectral Width (3184.7, 3184.7)
Lowest Frequency (-266.4, -266.4)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
MeO
OH
NHEt
O
O
Si
O
t-Bu
t-Bu
147
f1 (ppm)
f2 (ppm)

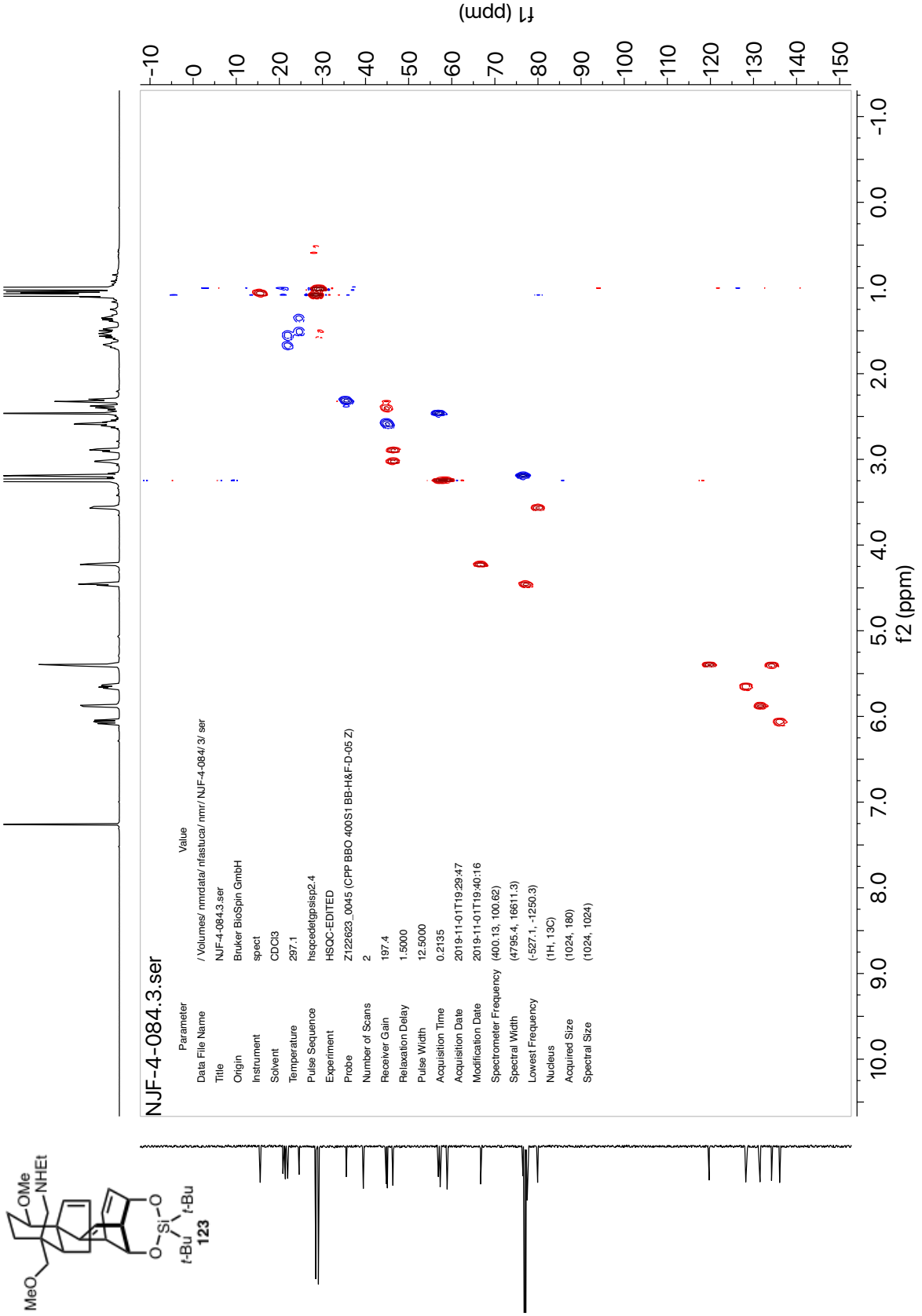

NJF-4-081-spot3.4.ser
Parameter
Value
Data File Name
/ Volumes/ nmrdata-1/ nfastuca/ nmr/ NJF-4-081-spot3/ 4/ ser
Title
NJF-4-081-spot3.4.ser
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.1
Pulse Sequence
hmbcetgpl3nd
Experiment
HMBC
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
4
Receiver Gain
197.4
Relaxation Delay
2.0000
Pulse Width
12.5000
Acquisition Time
0.4260
Acquisition Date
2019-11-08T02:42:14
Modification Date
2019-11-08T03:24:55
Spectrometer Frequency
(400.13, 100.62)
Spectral Width
(4807.7, 22321.4)
Lowest Frequency
(-163.1, -1116.4)
Nucleus
(1H, 13C)
Acquired Size
(2048, 256)
Spectral Size
(2048, 1024)
MeO
OH
NHEt
O
O
Si
O
t-Bu
t-Bu
147
f1 (ppm)
f2 (ppm)

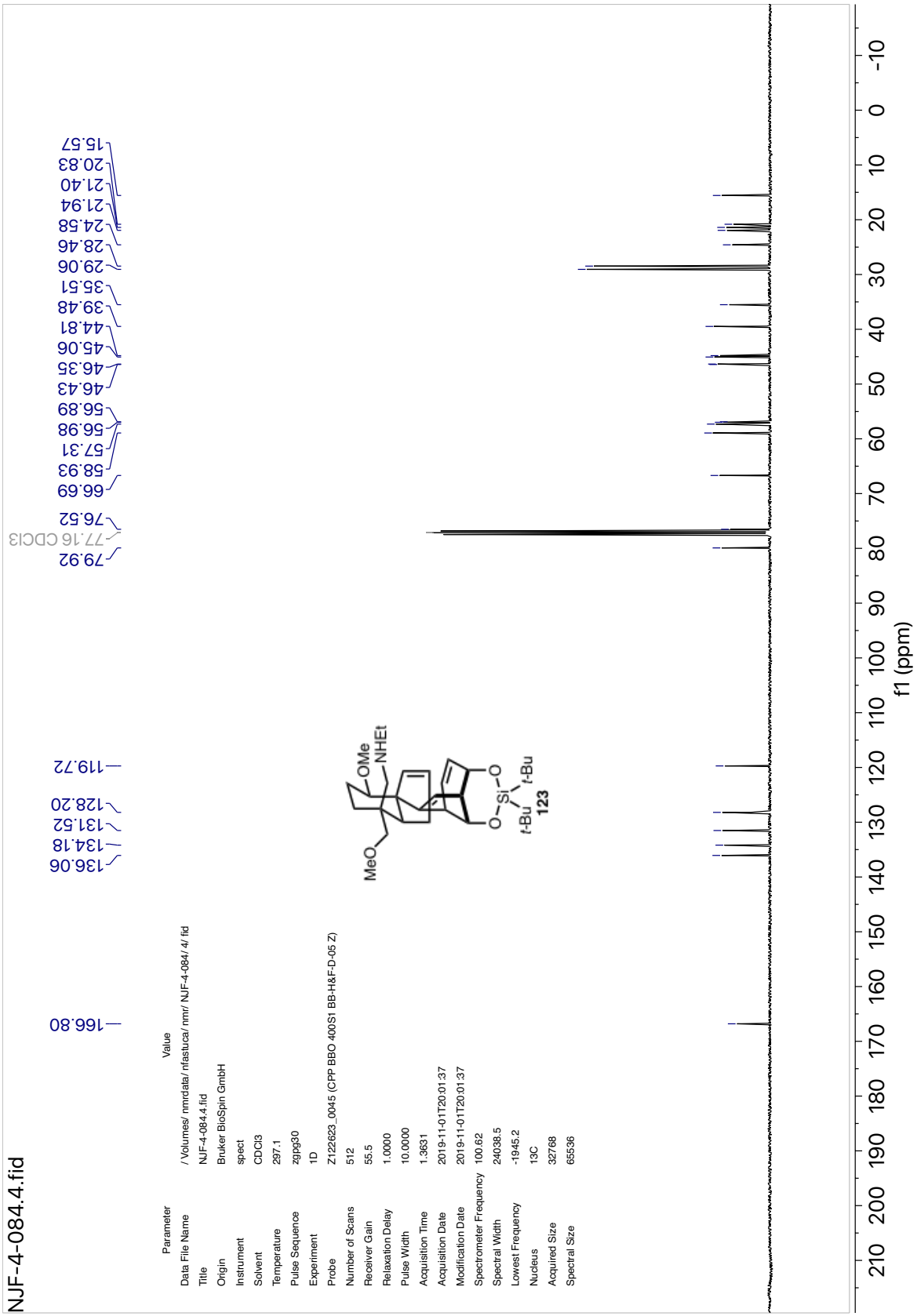


Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ nfastuca/ nmr/ NJF-4-081-spot3/ 5/ fid
Title	NJF-4-081-spot3.5.fid
Origin	Bruker BioSpin GmbH
Instrument	spect
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans	512
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2019-11-08T03:46:13
Modification Date	2019-11-08T03:46:13
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1946.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

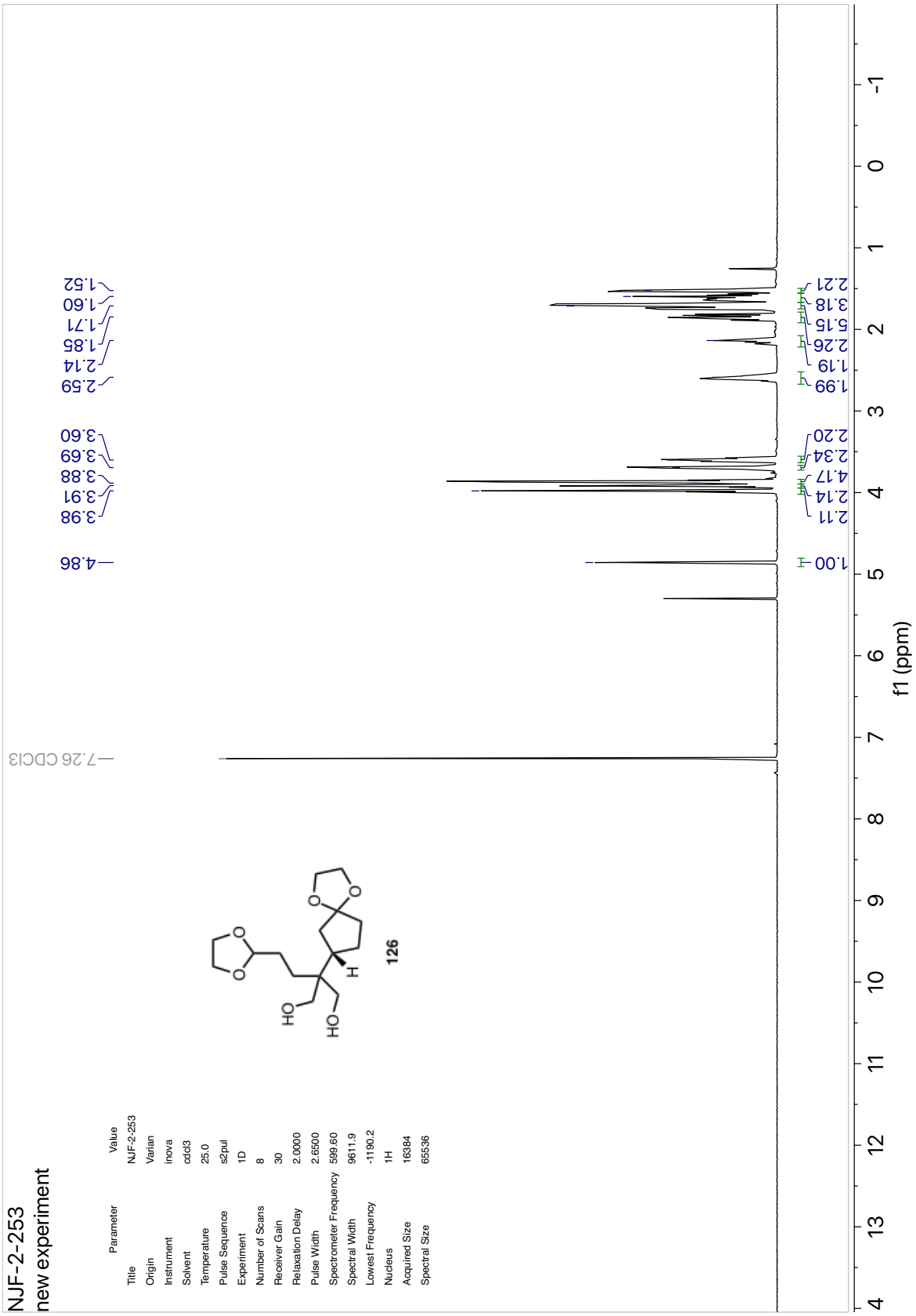

NJF-4-084.1.fid
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-084/ 1/ fid
Title NJF-4-084.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence zg30
Experiment 1D
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 16
Receiver Gain 78.7
Relaxation Delay 1.0000
Pulse Width 12.5000
Acquisition Time 4.0894
Acquisition Date 2019-11-01T19:22:10
Modification Date 2019-11-01T19:22:10
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.2
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
7.26 CDCl3
6.06
5.88
5.65
5.41
4.46
4.23
3.56
3.25
3.24
3.19
3.03
2.89
2.59
2.46
2.40
2.31
1.67
1.53
1.35
1.07
1.01
OMe
NHEt
MeO
O
Si
O
t-Bu
t-Bu
123
1.00
0.99
1.01
1.95
1.00
0.98
0.96
3.13
2.85
1.98
0.99
0.96
2.03
1.90
1.04
1.98
1.05
2.15
1.15
12.18
9.18
f1 (ppm)

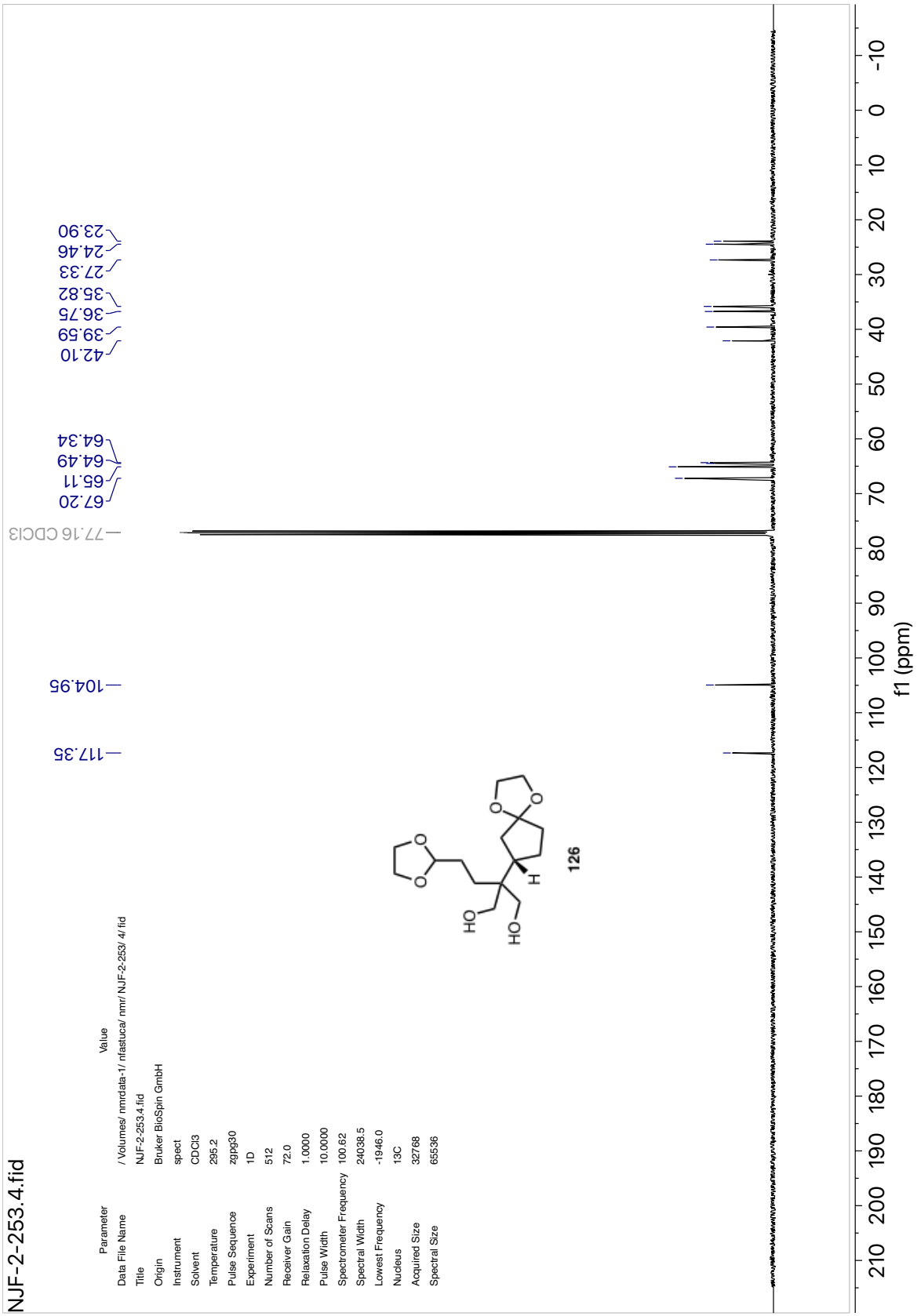

NJF-4-084.2.ser
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-084 / 2/ ser
Title NJF-4-084.2.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence cosygpppqf
Experiment COSY
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 1
Receiver Gain 28.2
Relaxation Delay 1.9083
Pulse Width 12.5000
Acquisition Time 0.2888
Acquisition Date 2019-11-01T19:23:08
Modification Date 2019-11-01T19:27:54
Spectrometer Frequency (400.13, 400.13)
Spectral Width (3546.1, 3546.1)
Lowest Frequency (-280.4, -280.4)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
f2 (ppm)
f1 (ppm)
OMe
NHEt
MeO
O
Si
t-Bu
t-Bu
123

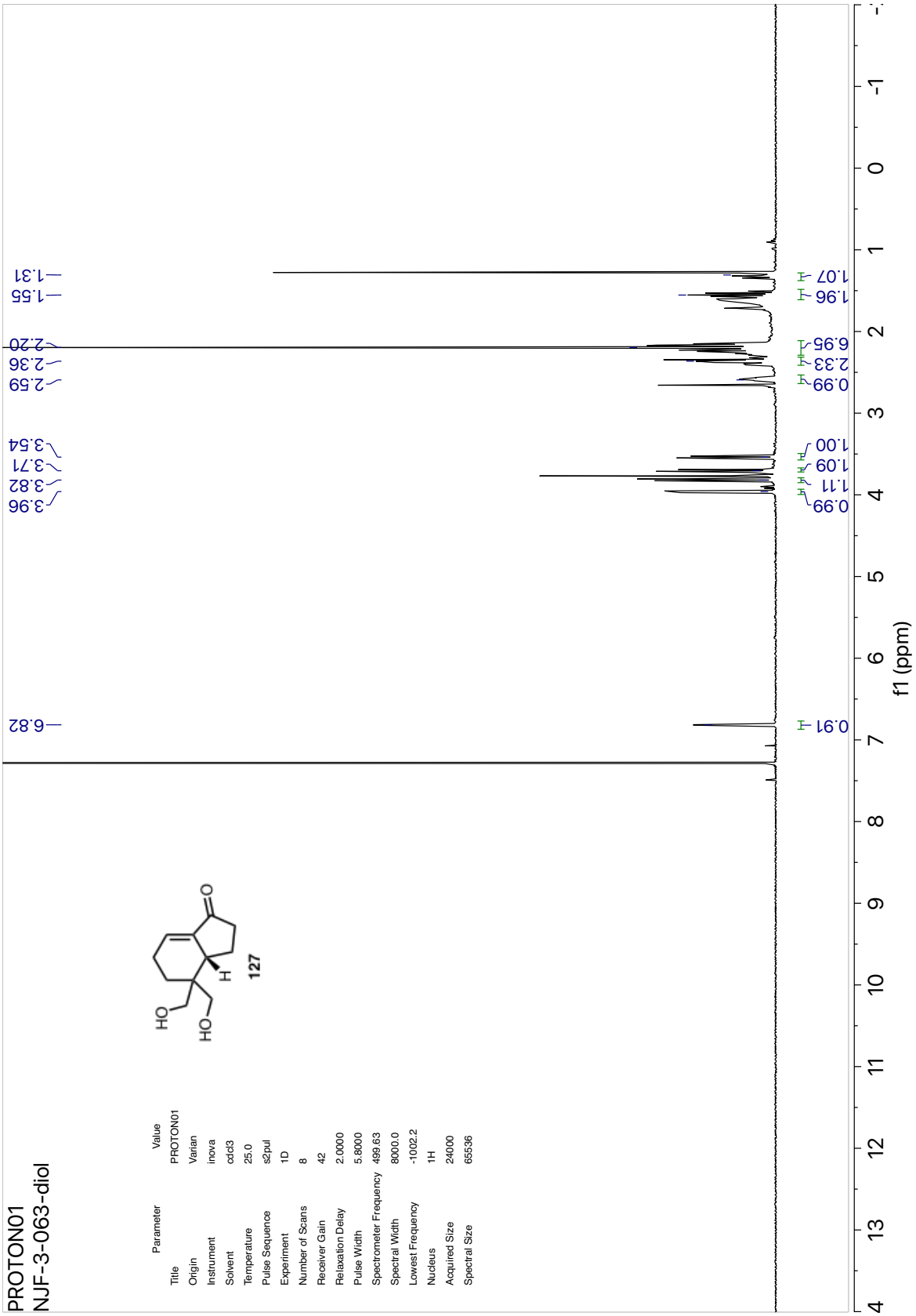

NJF-4-084.3.ser
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-084/ 3/ ser
Title NJF-4-084.3.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2019-11-01T19:29:47
Modification Date 2019-11-01T19:40:16
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-527.1, -1250.3)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
f1 (ppm)
f2 (ppm)
OMe
NHEt
MeO
O
Si
t-Bu
t-Bu
123

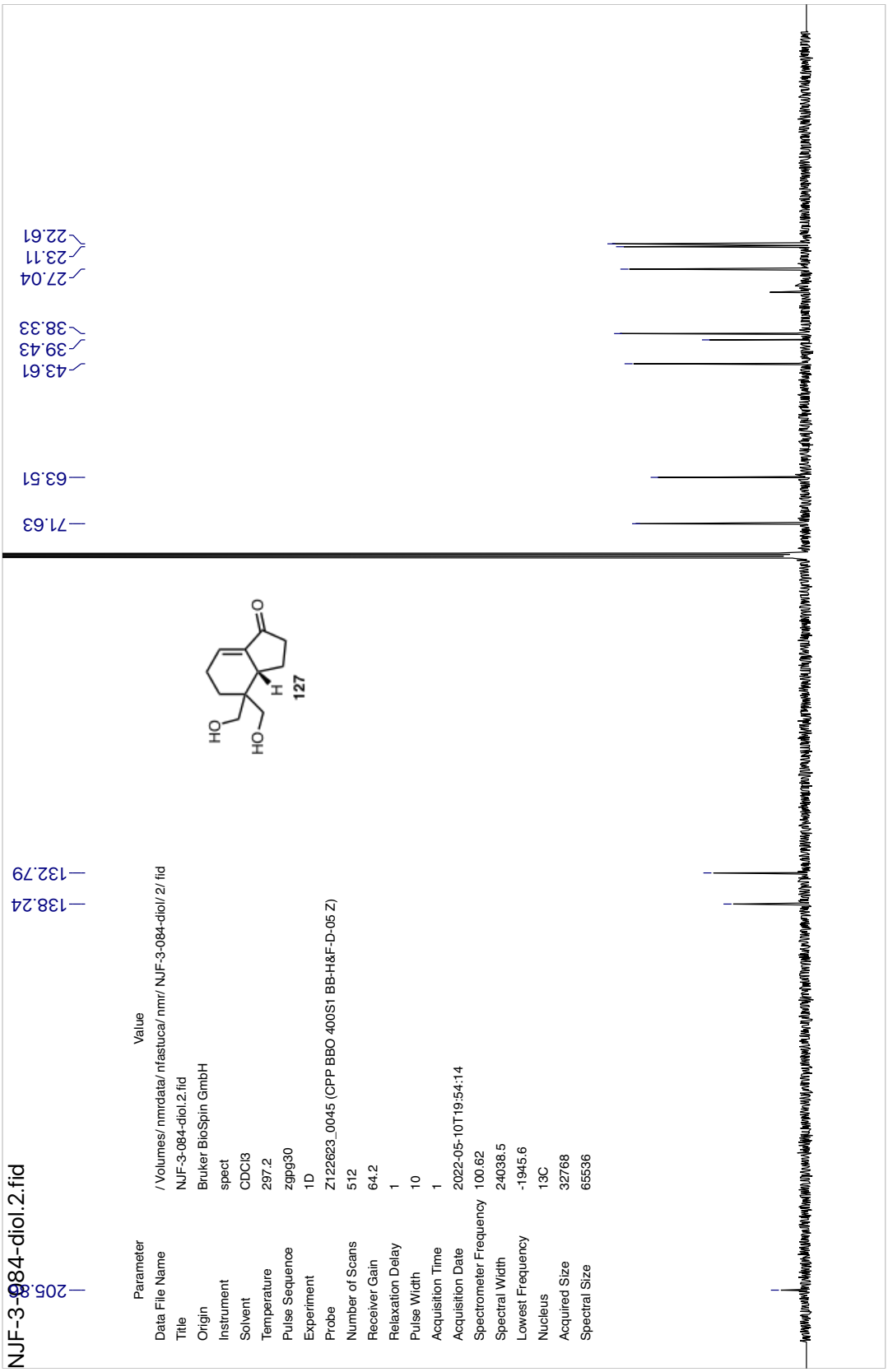


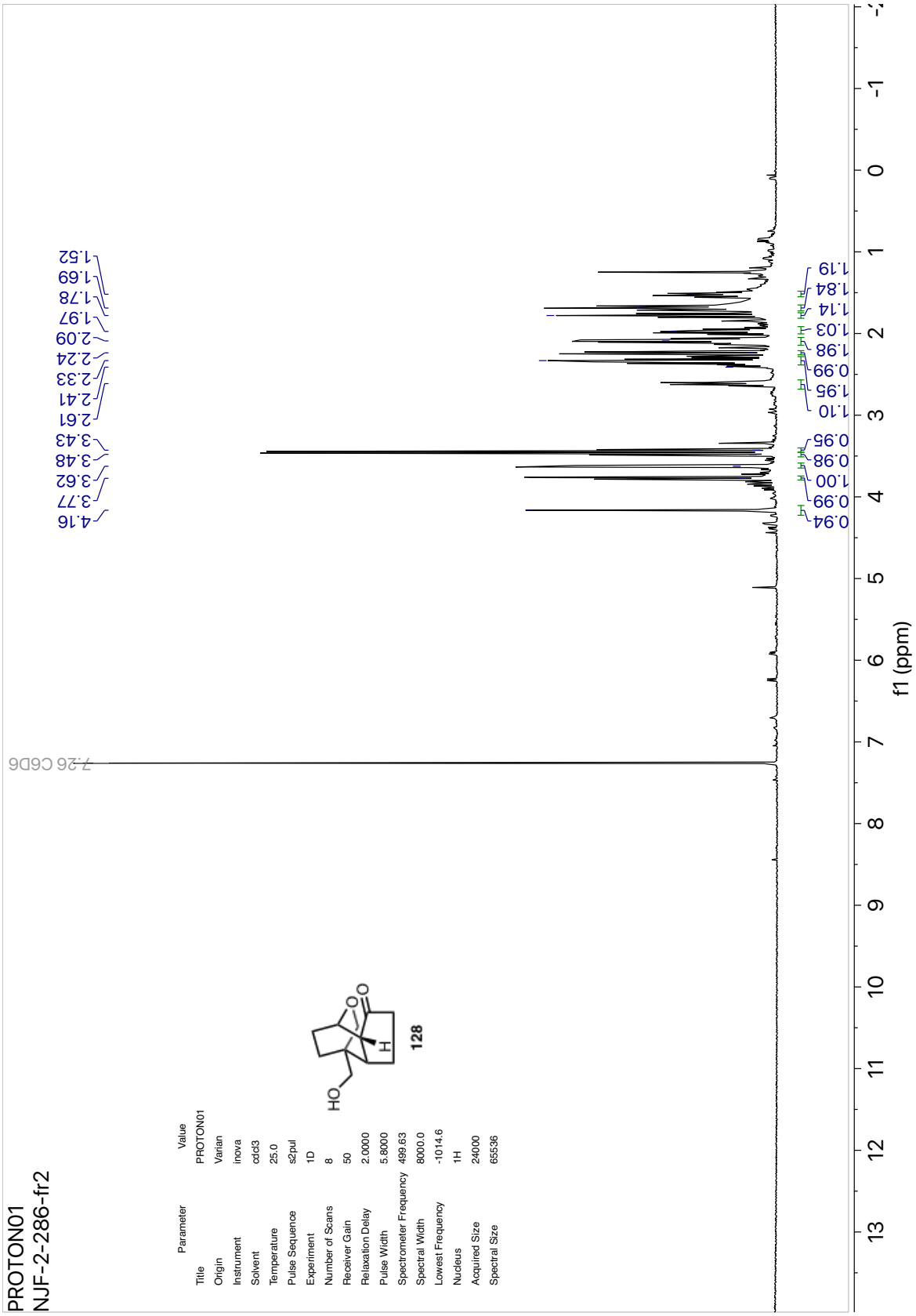
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-084/ 4/ fid
Title	NJF-4-084.4.fid
Origin	Bruker BioSpin GmbH
Instrument	spect
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Experiment	1D
Probe	Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans	512
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2019-11-01T20:01:37
Modification Date	2019-11-01T20:01:37
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

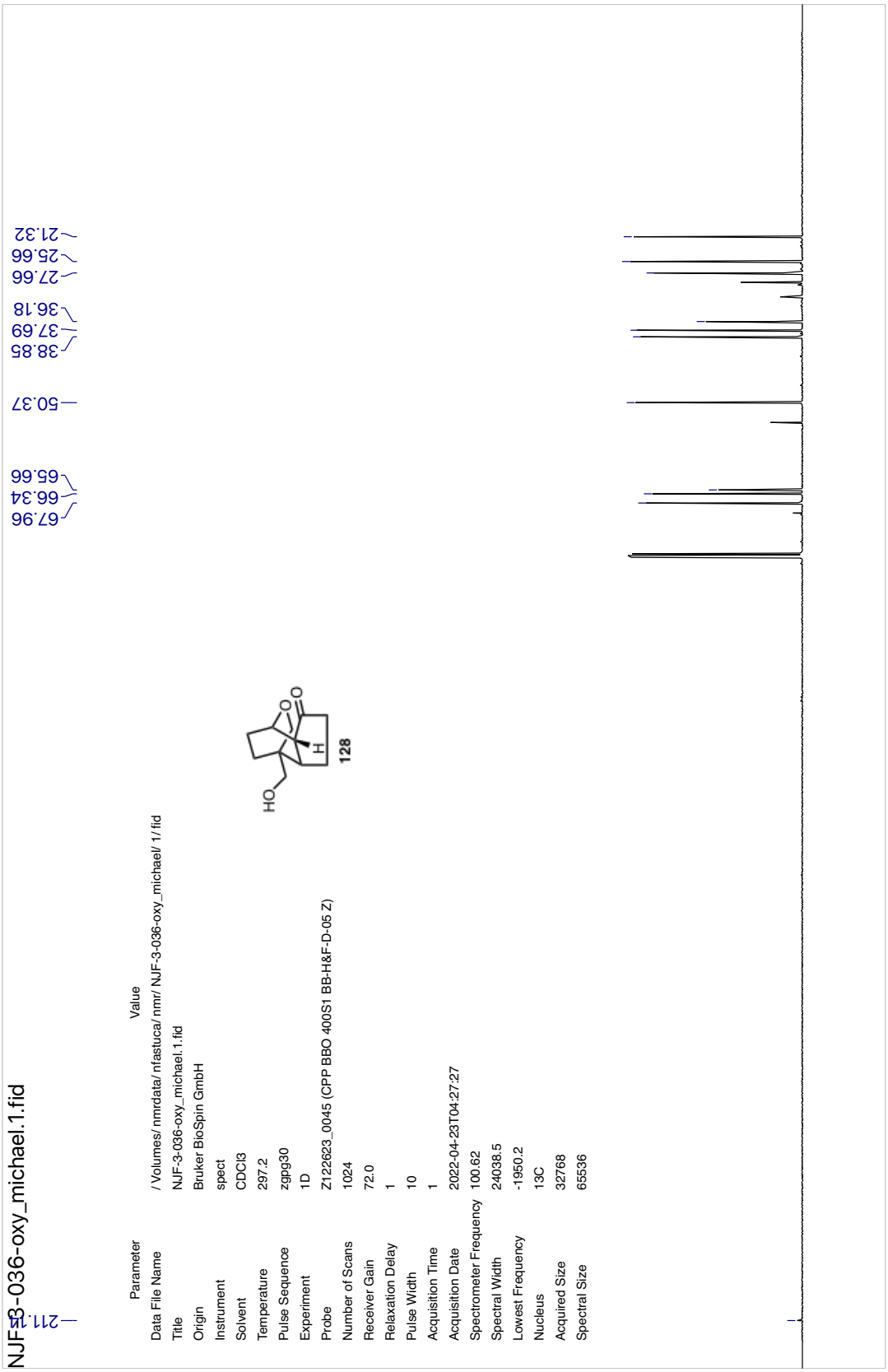

NJF-2-253
new experiment
Parameter Value
Title NJF-2-253
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 8
Receiver Gain 30
Relaxation Delay 2.0000
Pulse Width 2.6500
Spectrometer Frequency 599.60
Spectral Width 9611.9
Lowest Frequency -1190.2
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
126
7.26 CDCl3
4.86
3.98
3.91
3.88
3.69
3.60
2.59
2.14
1.85
1.71
1.60
1.52
1.00
2.11
2.14
4.17
2.34
2.20
1.99
1.19
2.26
5.15
3.18
2.21
f1 (ppm)

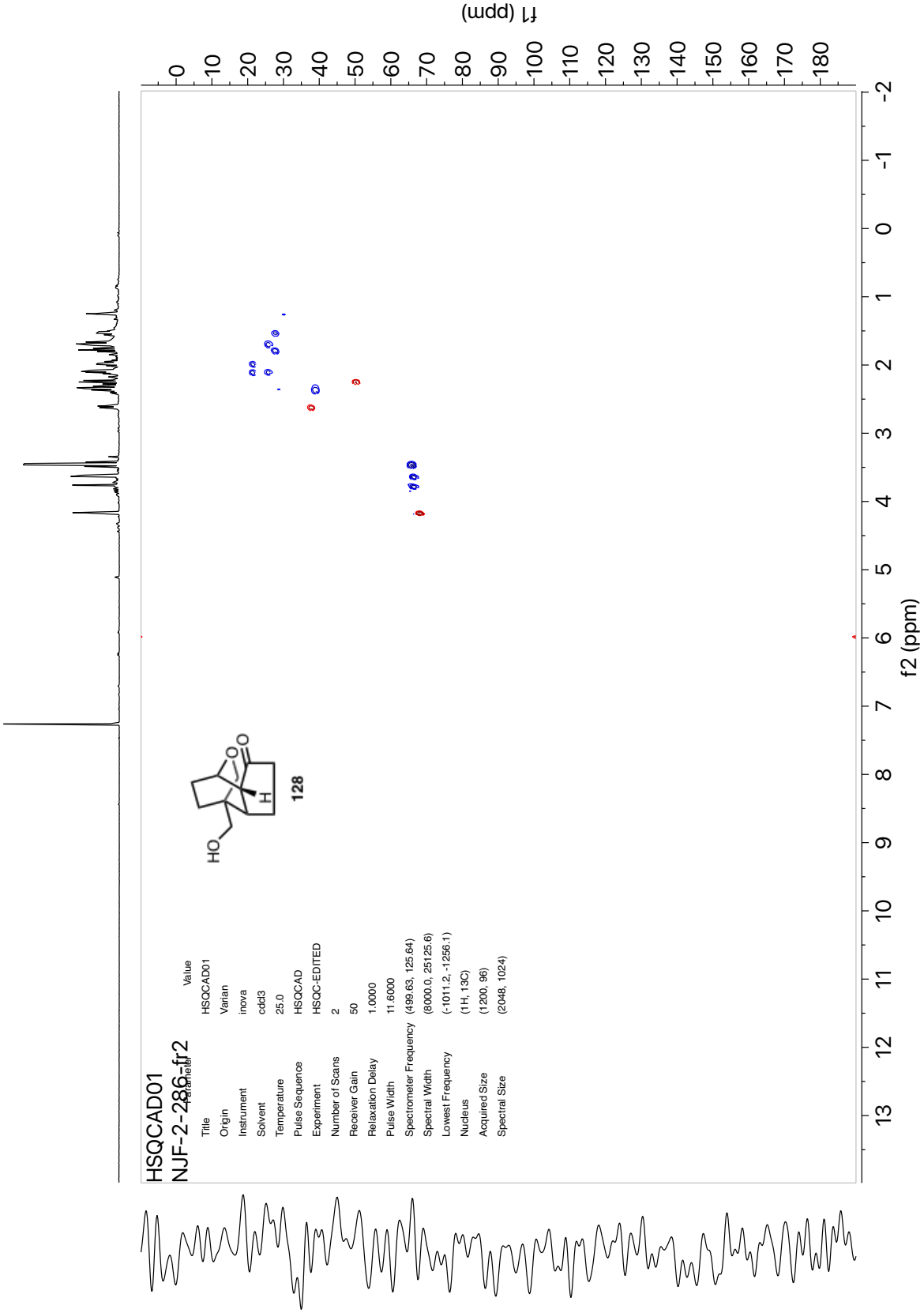

NJF-2-253.4.fid
Parameter Value
Data File Name / Volumes/ nmrdata-1/ nfastuca/ nmr/ NJF-2-253/ 4/ fid
Title NJF-2-253.4.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.2
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 512
Receiver Gain 72.0
Relaxation Delay 1.0000
Pulse Width 10.0000
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1946.0
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
117.35
104.95
77.16 CDCl3
67.20
65.11
64.49
64.34
42.10
39.59
36.75
35.82
27.33
24.46
23.90
HO
HO
H
126
f1 (ppm)

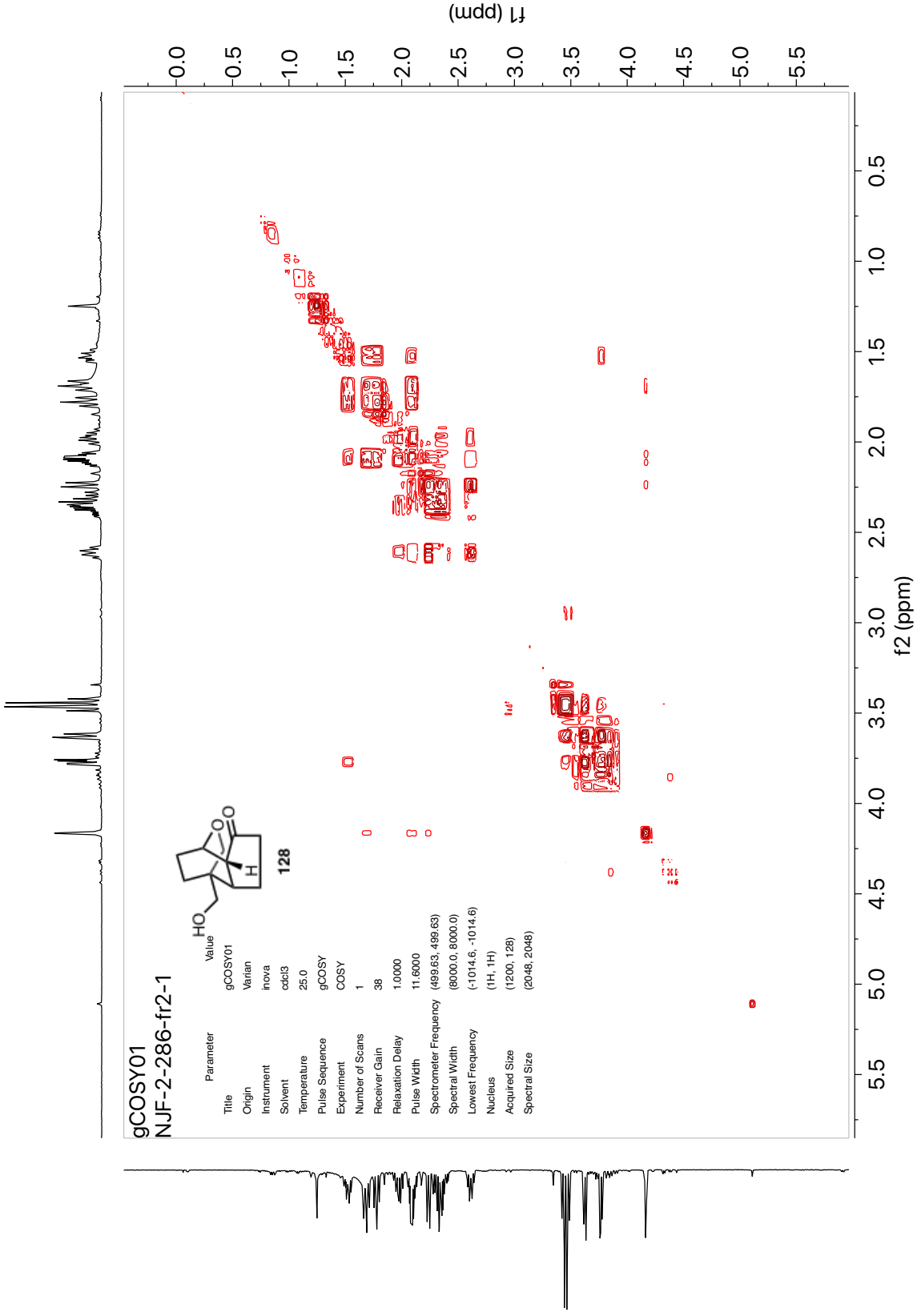

PROTON01
NJF-3-063-diol
Parameter Value
Title PROTON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 8
Receiver Gain 42
Relaxation Delay 2.0000
Pulse Width 5.8000
Spectrometer Frequency 499.63
Spectral Width 8000.0
Lowest Frequency -1002.2
Nucleus 1H
Acquired Size 24000
Spectral Size 65536
HO
HO
H
O
127
6.82
3.96
3.82
3.71
3.54
2.59
2.36
2.20
1.55
1.31
0.91
0.99
1.11
1.09
1.00
2.33
6.95
1.96
1.07
f1 (ppm)

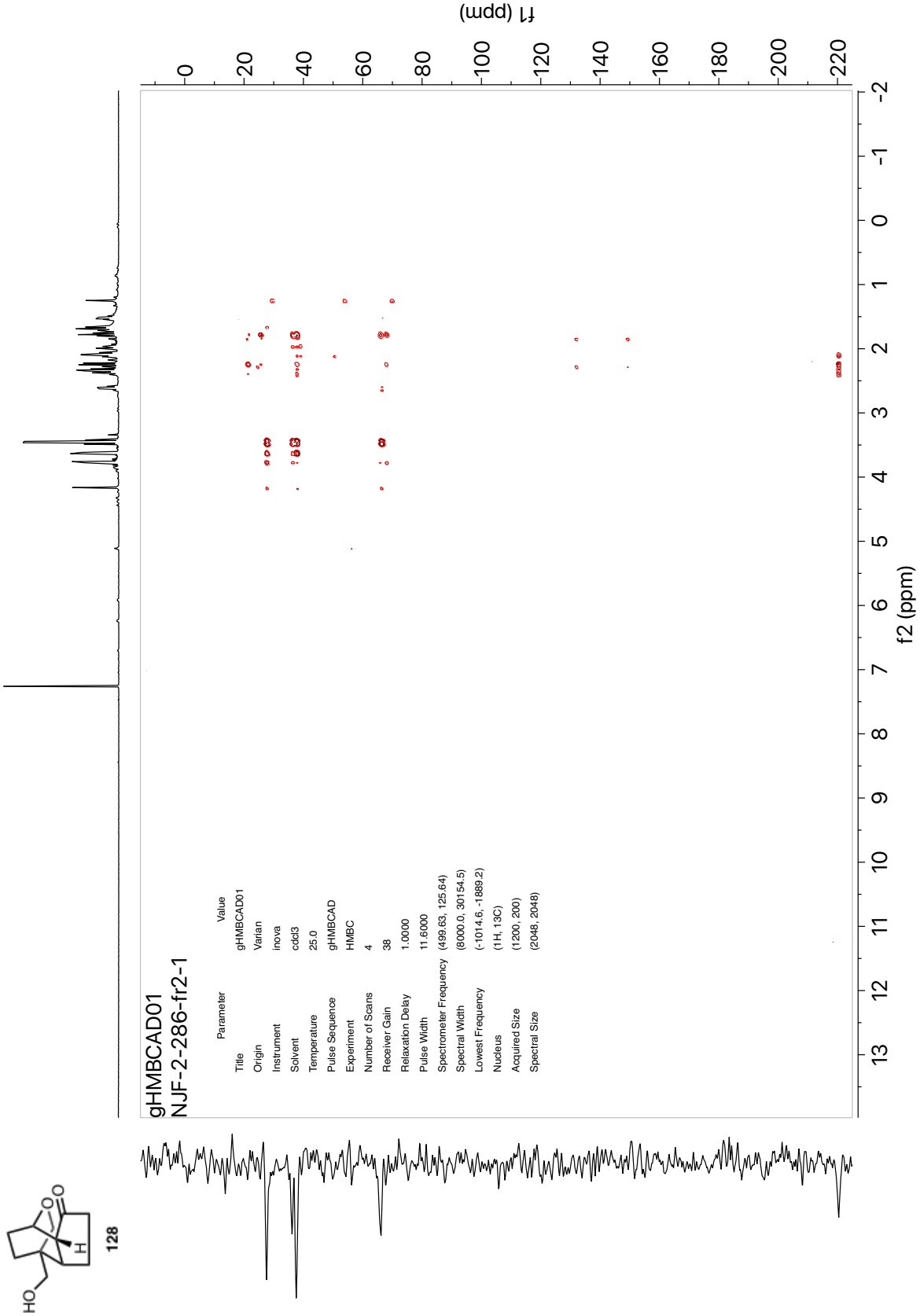

NJF-3-084-diol.2.fid
205.88
138.24
132.79
71.63
63.51
43.61
39.43
38.33
27.04
23.11
22.61
HO
HO
H
O
127
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-3-084-diol/ 2/ fid
Title
NJF-3-084-diol.2.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
zgpg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
512
Receiver Gain
64.2
Relaxation Delay
1
Pulse Width
10
Acquisition Time
1
Acquisition Date
2022-05-10T19:54:14
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1945.6
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

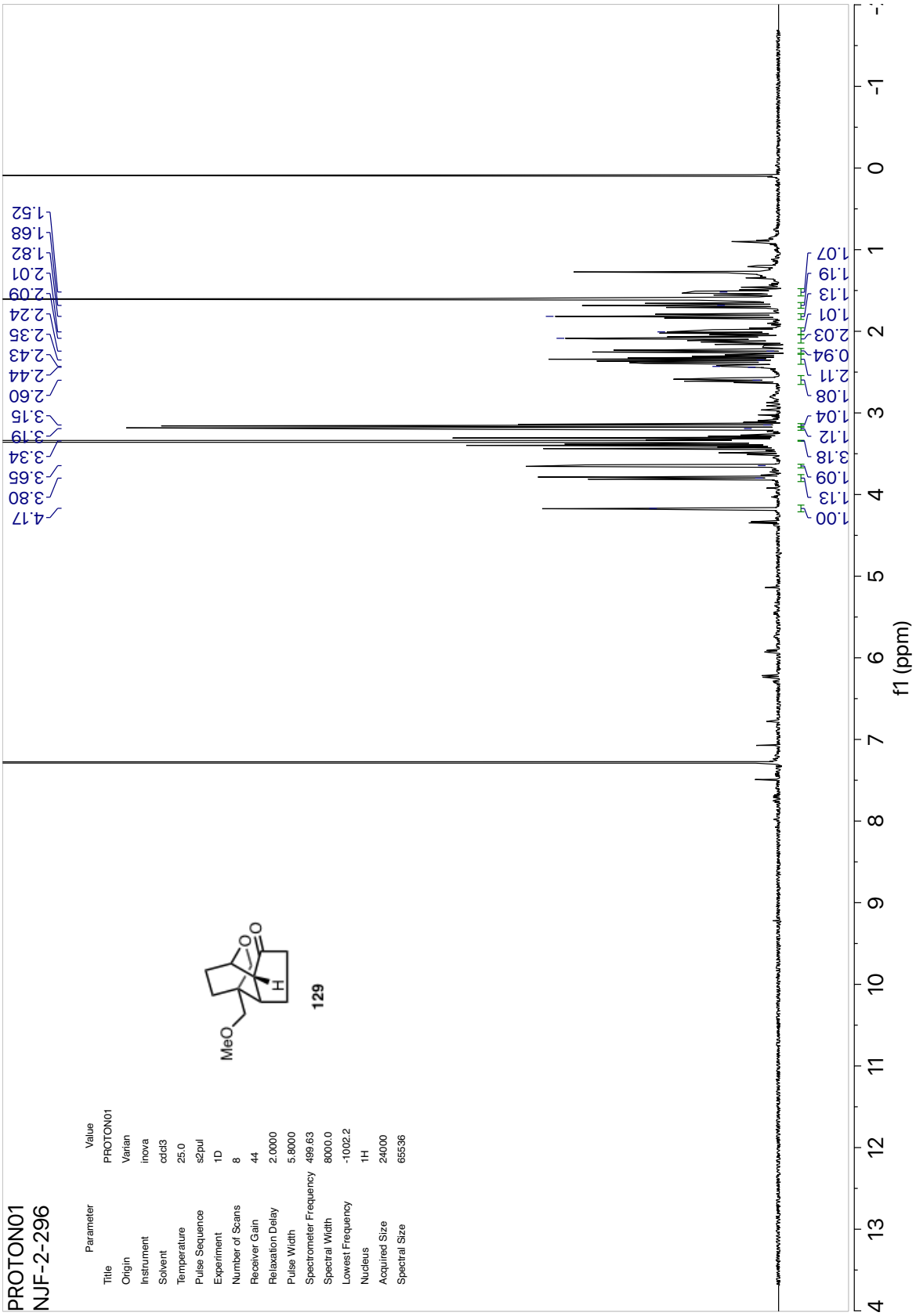

PROTON01
NJF-2-286-fr2
Parameter Value
Title PROTON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 8
Receiver Gain 50
Relaxation Delay 2.0000
Pulse Width 5.8000
Spectrometer Frequency 499.63
Spectral Width 8000.0
Lowest Frequency -1014.6
Nucleus 1H
Acquired Size 24000
Spectral Size 65536
HO
O
O
H
128
7.26 C6D6
4.16
3.77
3.62
3.48
3.43
2.61
2.41
2.33
2.24
2.09
1.97
1.78
1.69
1.52
0.94
0.99
1.00
0.98
0.95
1.10
1.95
0.99
1.98
1.03
1.14
1.84
1.19
f1 (ppm)

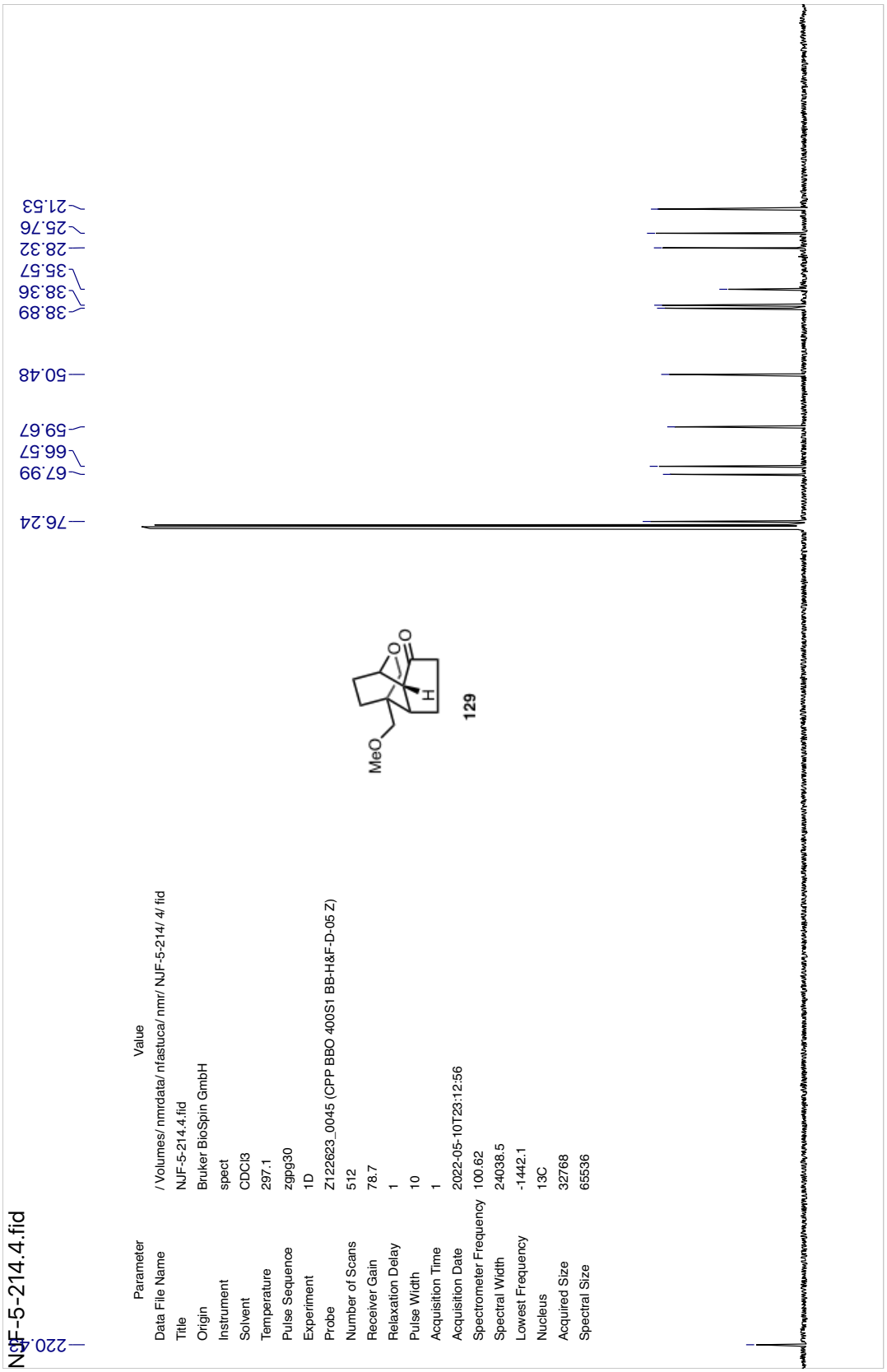

NJF-3-036-oxy_michael.1.fid
211.12
67.96
66.34
65.66
50.37
38.85
37.69
36.18
27.66
25.66
21.32
HO
O
O
H
128
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-3-036-oxy_michael/ 1/ fid
Title
NJF-3-036-oxy_michael.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
zgpg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
1024
Receiver Gain
72.0
Relaxation Delay
1
Pulse Width
10
Acquisition Time
1
Acquisition Date
2022-04-23T04:27:27
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1950.2
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


HSQCAD01
NJF-2-286-fr2
Parameter Value
Title HSQCAD01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence HSQCAD
Experiment HSQC-EDITED
Number of Scans 2
Receiver Gain 50
Relaxation Delay 1.0000
Pulse Width 11.6000
Spectrometer Frequency (499.63, 125.64)
Spectral Width (8000.0, 25125.6)
Lowest Frequency (-1011.2, -1256.1)
Nucleus (1H, 13C)
Acquired Size (1200, 96)
Spectral Size (2048, 1024)
HO
O
O
H
128
f1 (ppm)
f2 (ppm)


gCOSY01
NJF-2-286-fr2-1
Parameter Value
Title gCOSY01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence gCOSY
Experiment COSY
Number of Scans 1
Receiver Gain 38
Relaxation Delay 1.0000
Pulse Width 11.6000
Spectrometer Frequency (499.63, 499.63)
Spectral Width (8000.0, 8000.0)
Lowest Frequency (-1014.6, -1014.6)
Nucleus (1H, 1H)
Acquired Size (1200, 128)
Spectral Size (2048, 2048)
128
HO
O
O
H
f1 (ppm)
f2 (ppm)

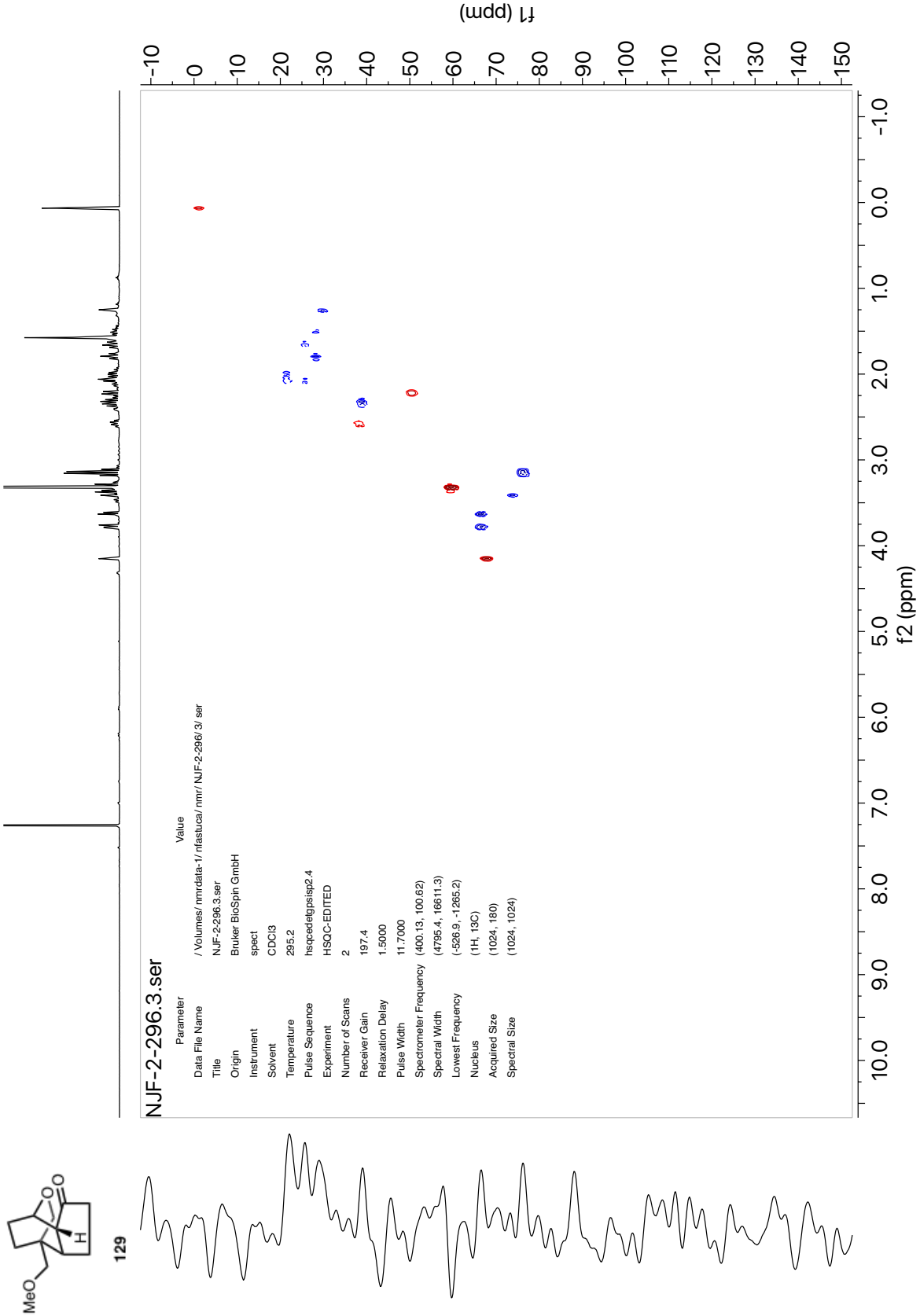

gHMBCAD01
NJF-2-286-fr2-1
Parameter Value
Title gHMBCAD01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence gHMBCAD
Experiment HMBC
Number of Scans 4
Receiver Gain 38
Relaxation Delay 1.0000
Pulse Width 11.6000
Spectrometer Frequency (499.63, 125.64)
Spectral Width (8000.0, 30154.5)
Lowest Frequency (-1014.6, -1889.2)
Nucleus (1H, 13C)
Acquired Size (1200, 200)
Spectral Size (2048, 2048)
f1 (ppm)
f2 (ppm)
HO
O
O
H
128

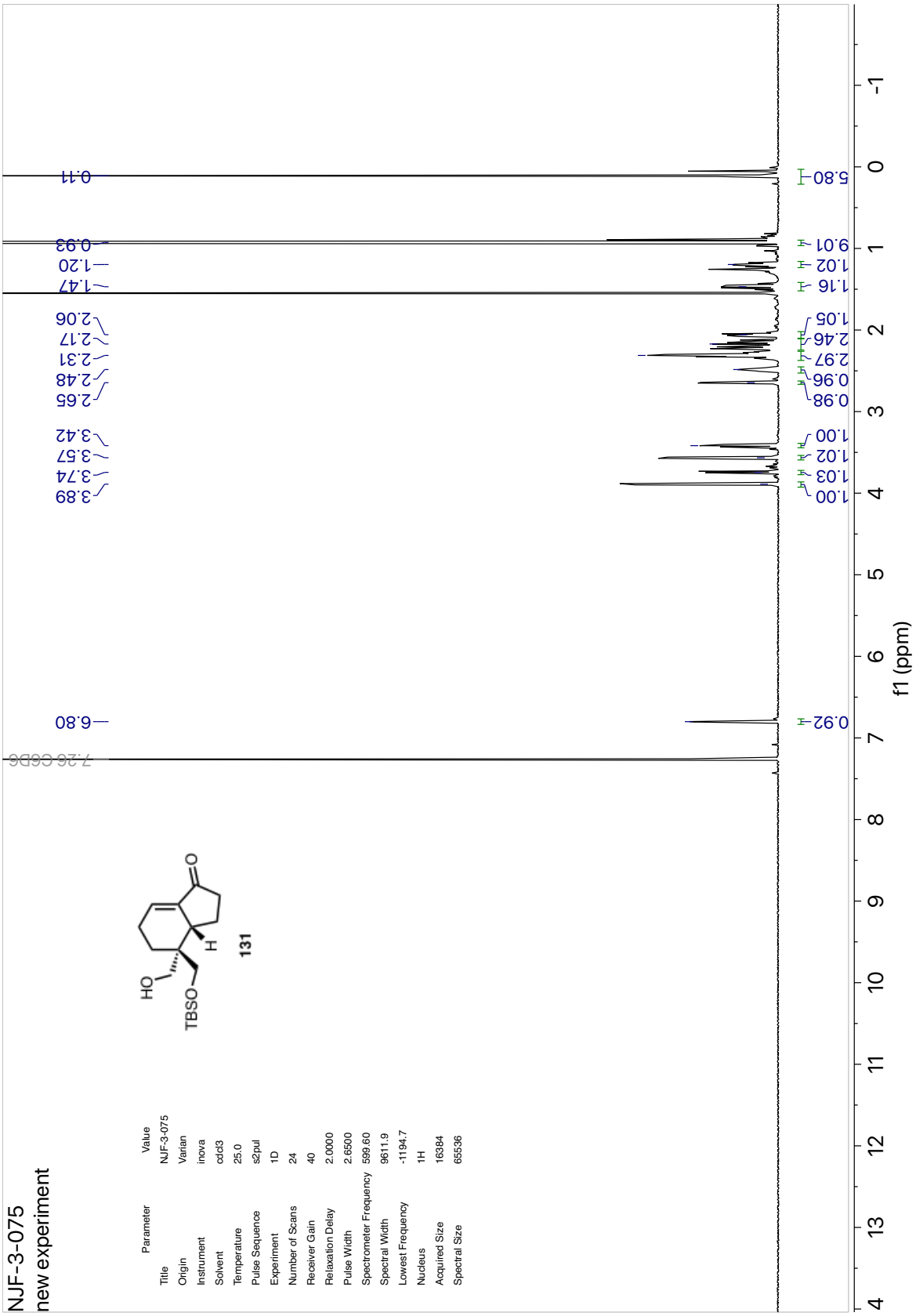

PROTON01
NJF-2-296
Parameter Value
Title PROTON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 8
Receiver Gain 44
Relaxation Delay 2.0000
Pulse Width 5.8000
Spectrometer Frequency 499.63
Spectral Width 8000.0
Lowest Frequency -1002.2
Nucleus 1H
Acquired Size 24000
Spectral Size 65536
MeO
H
129
4.17
3.80
3.65
3.34
3.19
3.15
2.60
2.44
2.43
2.35
2.24
2.09
2.01
1.82
1.68
1.52
1.00
1.13
1.09
3.18
1.12
1.04
1.08
2.11
0.94
2.03
1.01
1.13
1.19
1.07
f1 (ppm)

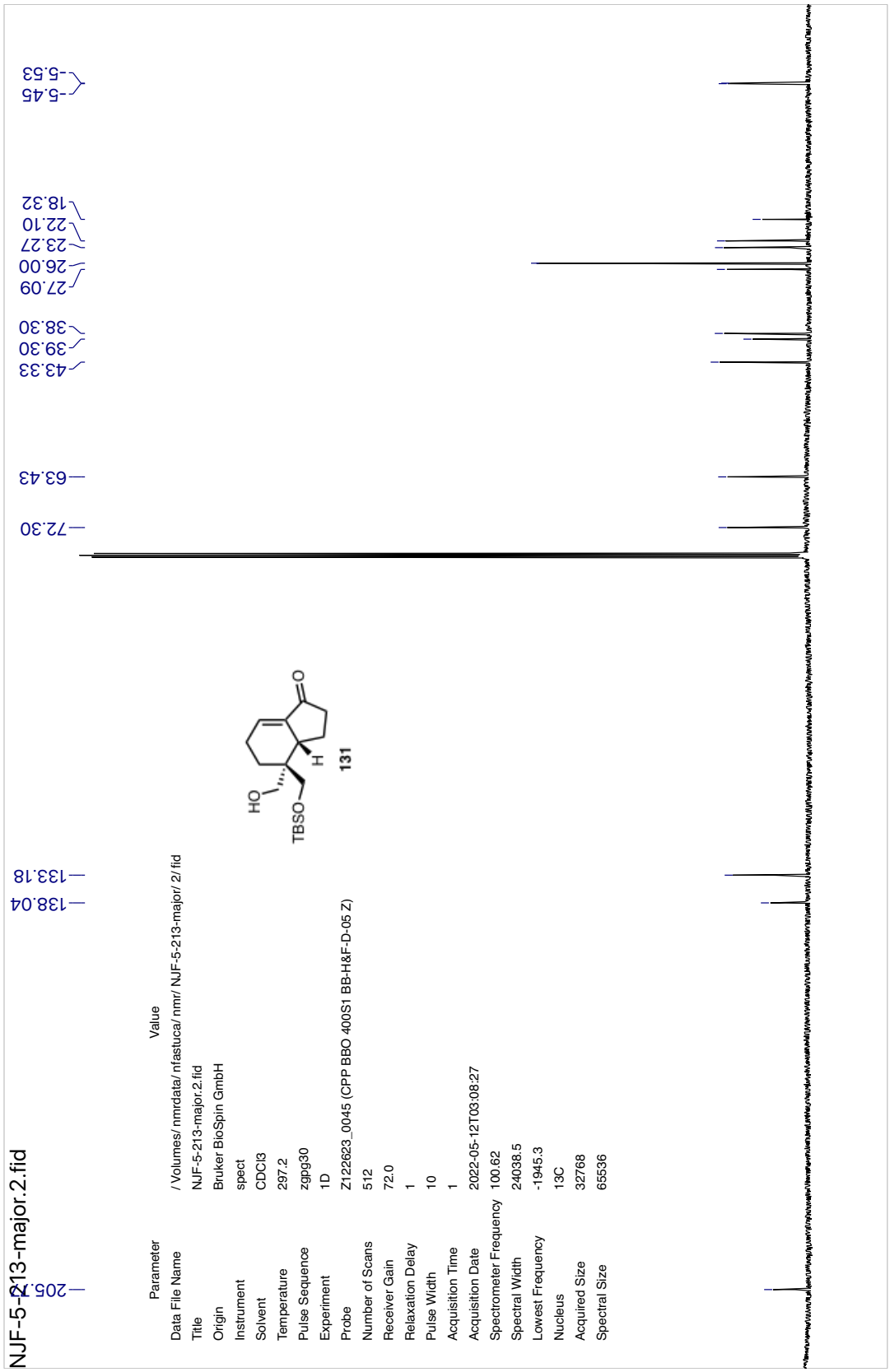


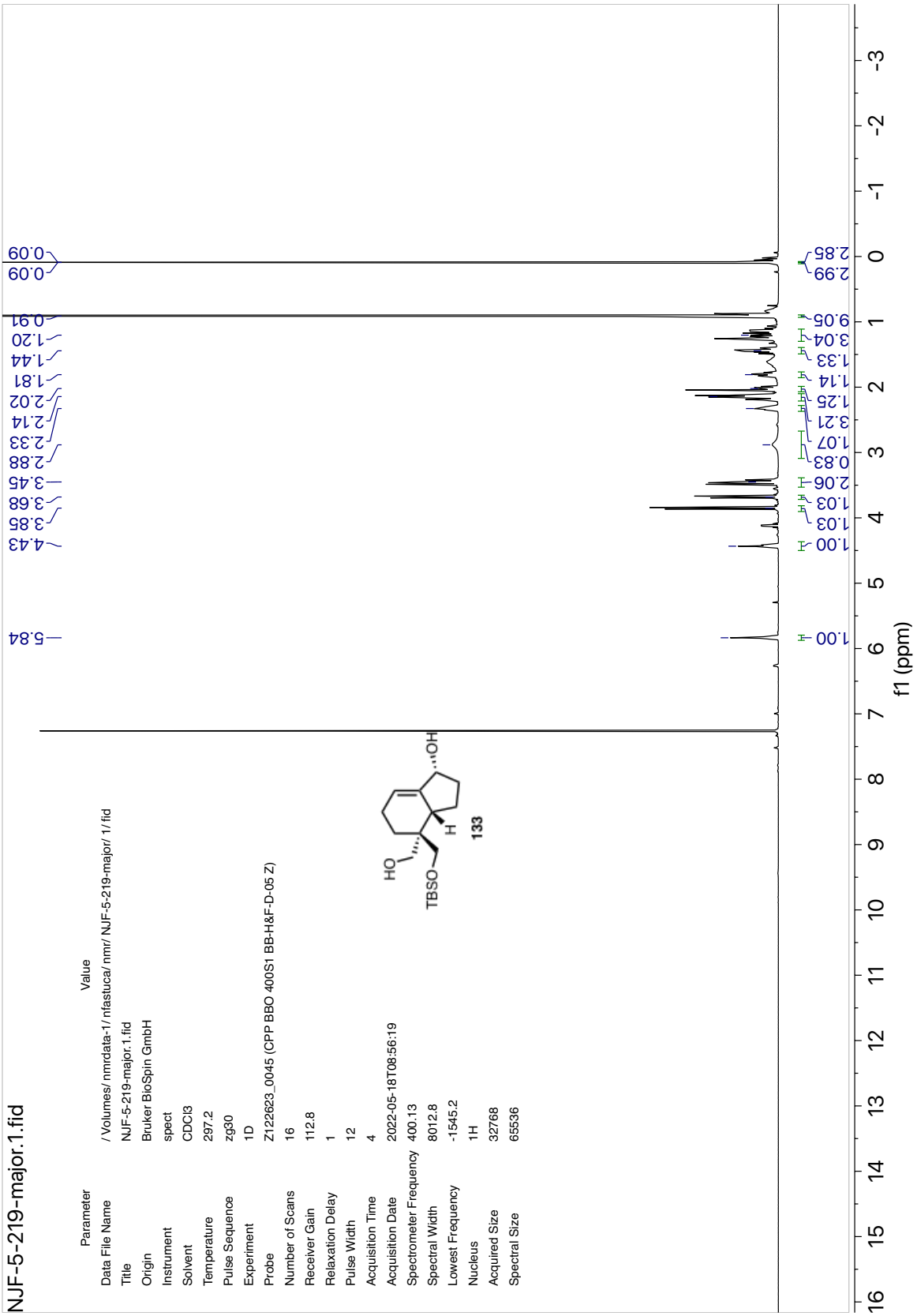
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-214/ 4/ fid
Title	NJF-5-214.4.fid
Origin	Bruker BioSpin GmbH
Instrument	spect
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Experiment	1D
Probe	Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	1
Pulse Width	10
Acquisition Time	1
Acquisition Date	2022-05-10T23:12:56
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1442.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

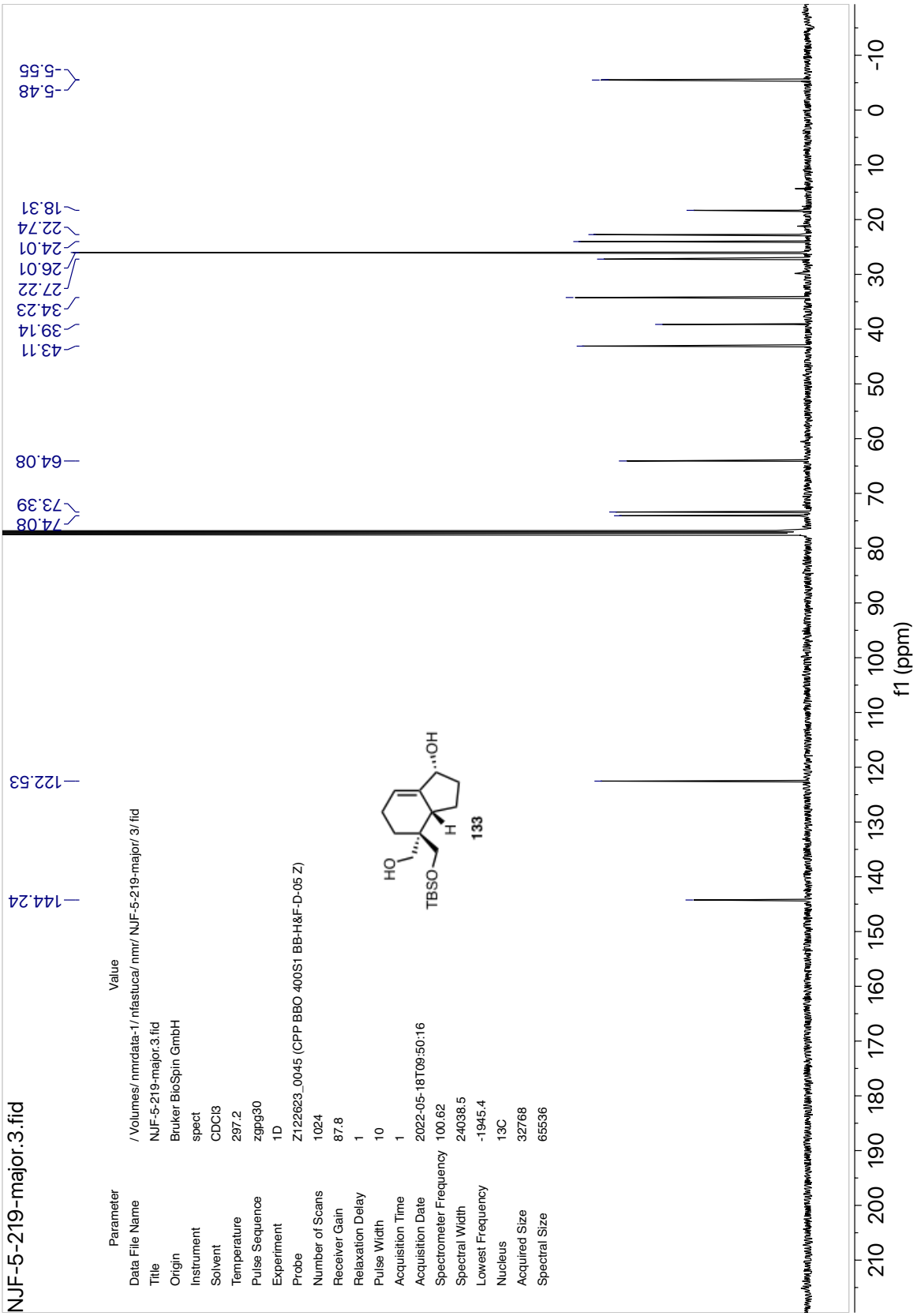
129

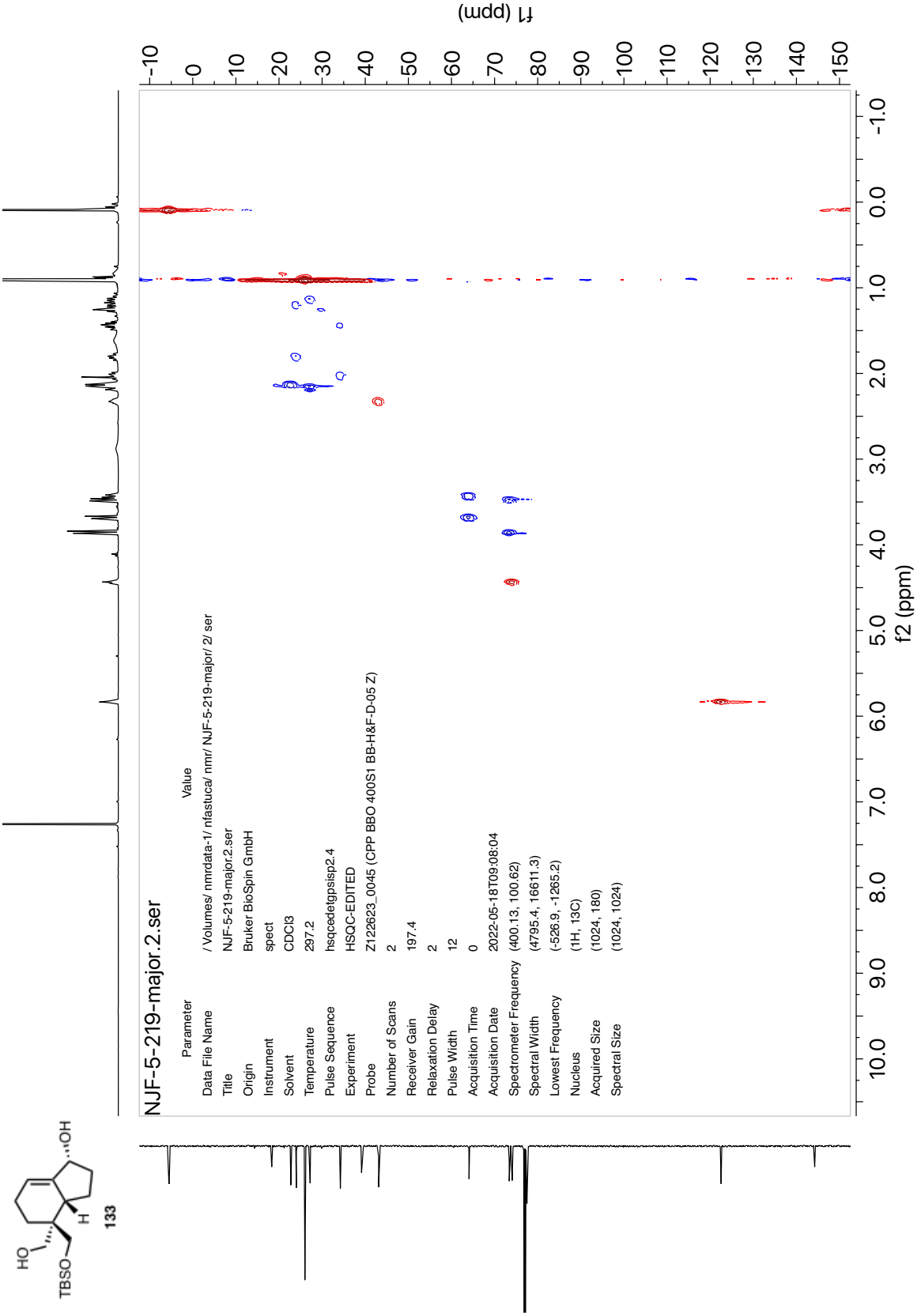

MeO
H
O
O
129
NJF-2-296.3.ser
Parameter Value
Data File Name / Volumes/ nmrdata-1/ nfastuca/ nmr/ NJF-2-296/ 3/ ser
Title NJF-2-296.3.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.2
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 11.7000
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-526.9, -1265.2)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
f1 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f2 (ppm)

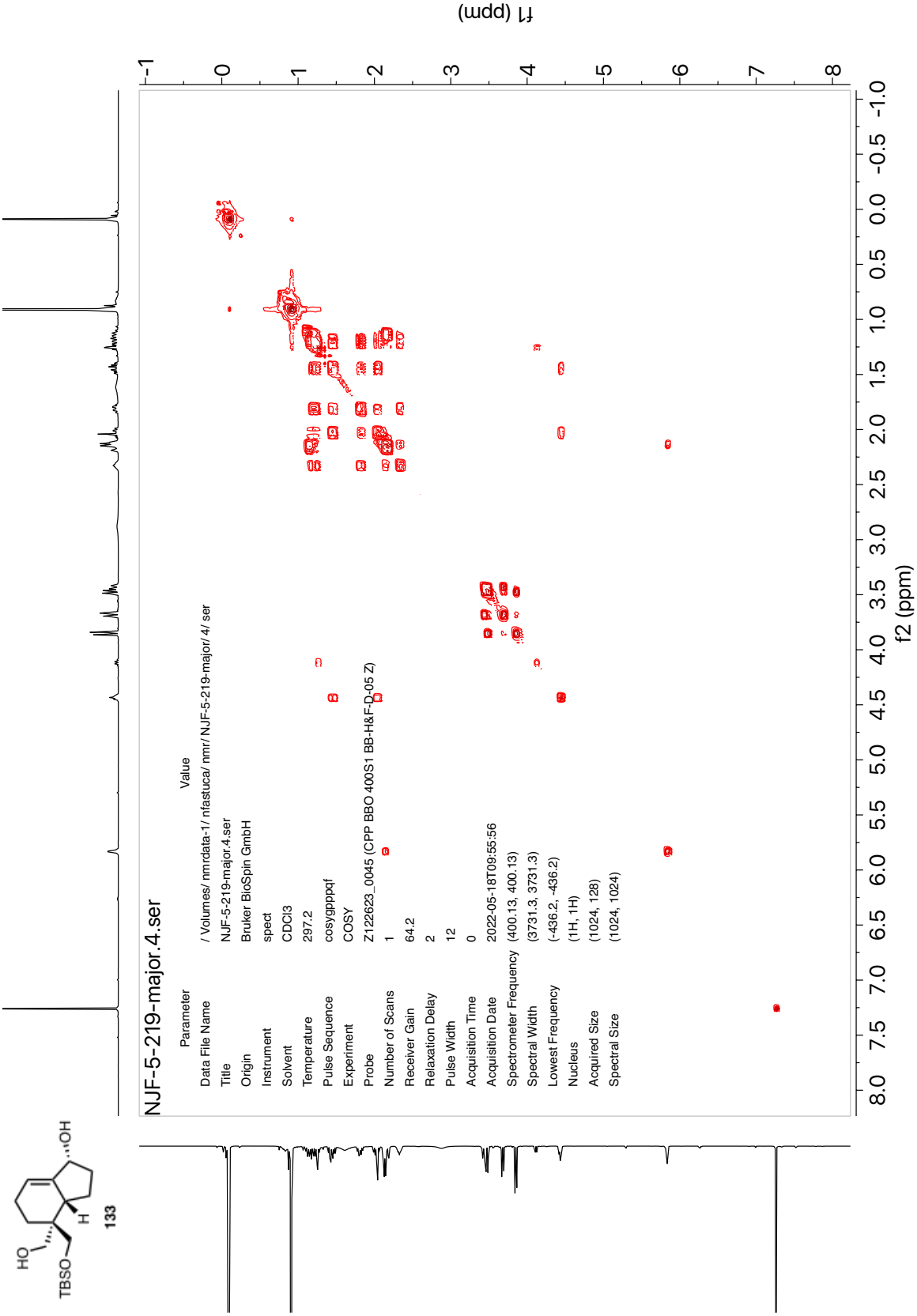

NJF-3-075
new experiment
Parameter Value
Title NJF-3-075
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 24
Receiver Gain 40
Relaxation Delay 2.0000
Pulse Width 2.6500
Spectrometer Frequency 599.60
Spectral Width 9611.9
Lowest Frequency -1194.7
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
HO
TBSO
H
O
131
7.26 C6D6
6.80
3.89
3.74
3.57
3.42
2.65
2.48
2.31
2.17
2.06
1.47
1.20
0.93
0.11
0.92
1.00
1.03
1.02
1.00
0.98
0.96
2.97
2.46
1.05
1.16
1.02
9.01
5.80
f1 (ppm)

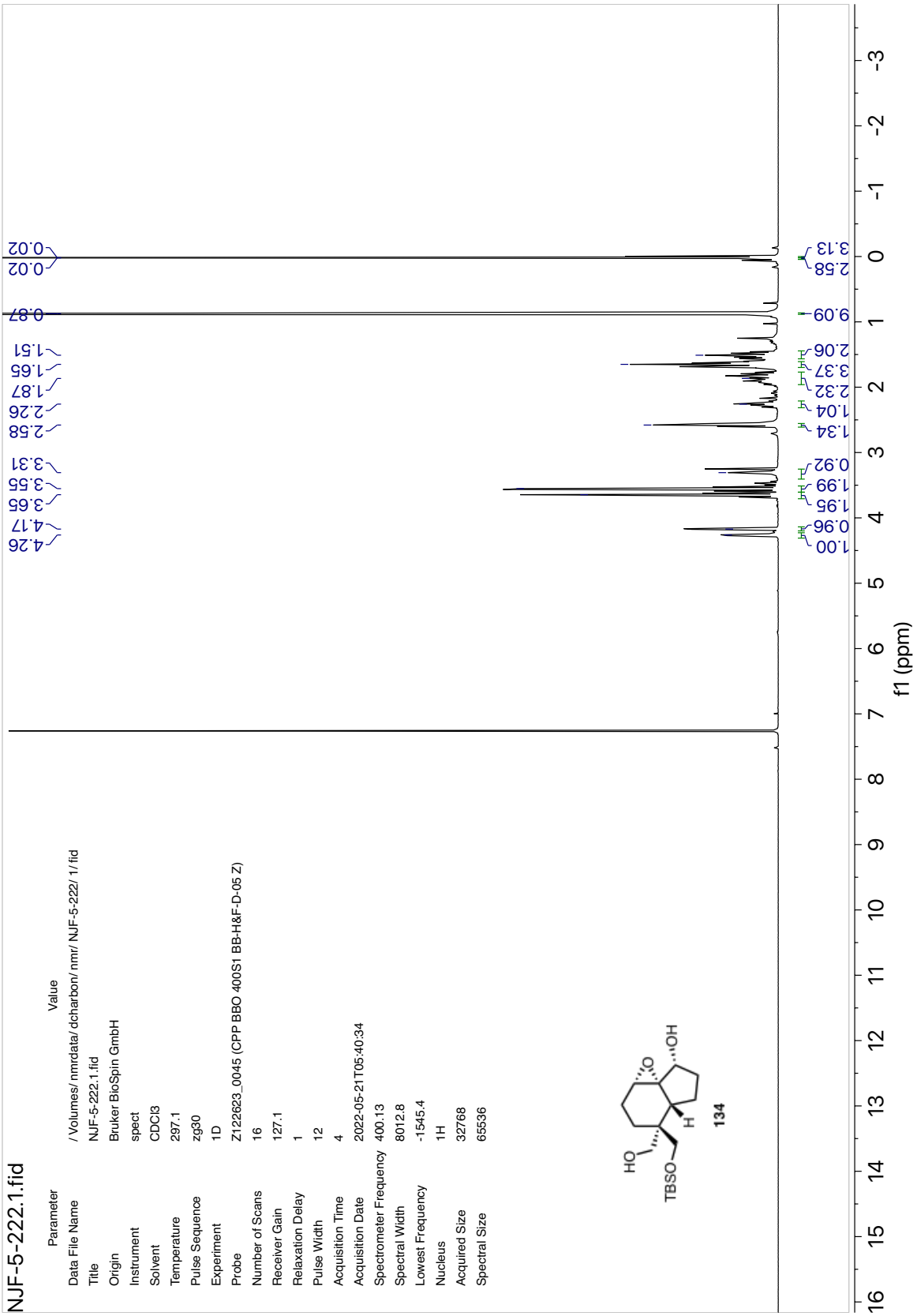

NJF-5-213-major.2.fid
205.21
138.04
133.18
72.30
63.43
43.33
39.30
38.30
27.09
26.00
23.27
22.10
18.32
-5.45
-5.53
HO
TBSO
H
O
131
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-213-major/ 2/ fid
Title
NJF-5-213-major.2.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
zgpg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
512
Receiver Gain
72.0
Relaxation Delay
1
Pulse Width
10
Acquisition Time
1
Acquisition Date
2022-05-12T03:08:27
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1945.3
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

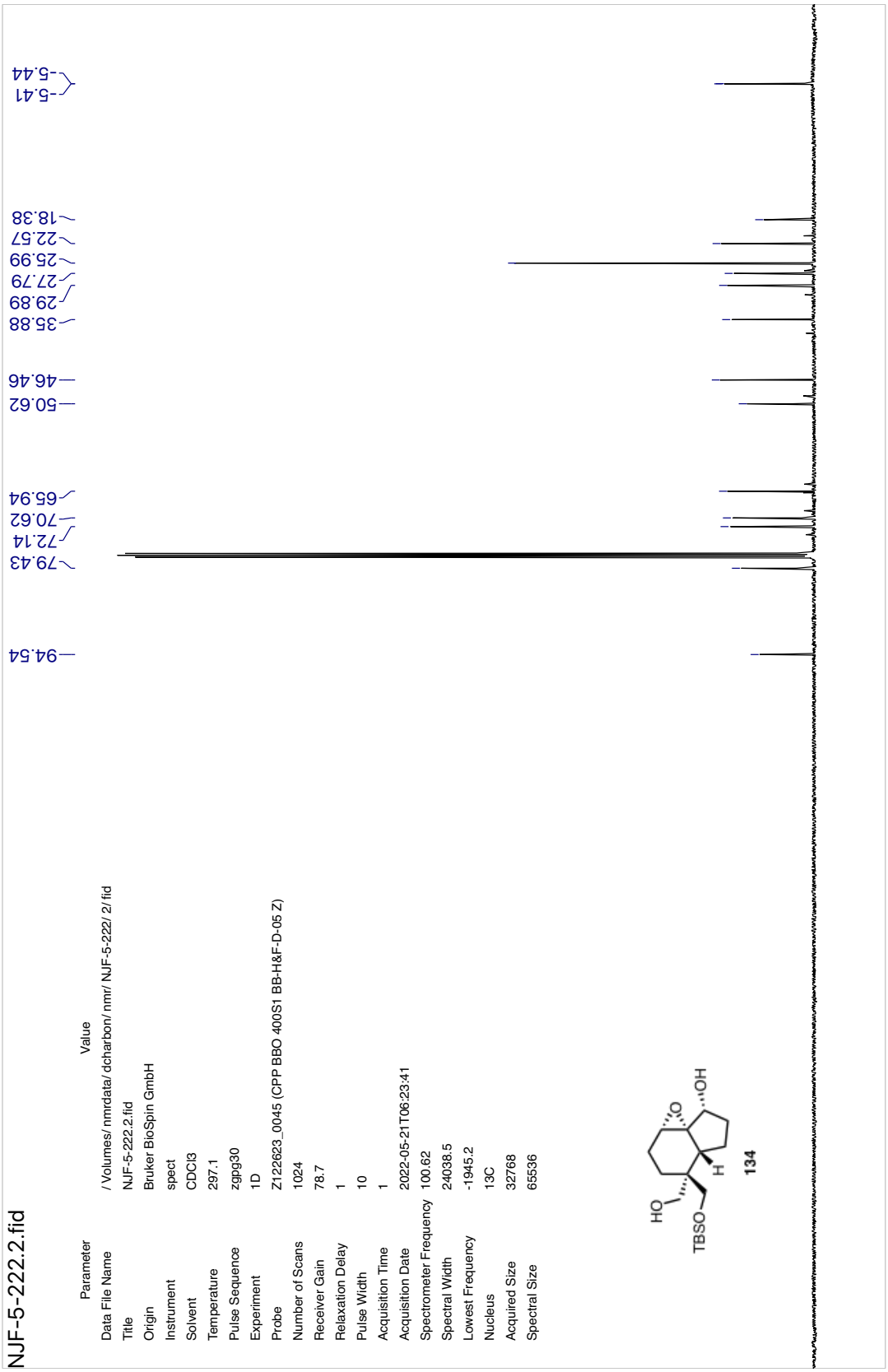

NJF-5-219-major.1.fid
Parameter
Value
Data File Name
/ Volumes/ nmrdata-1/ nfastuca/ nmr/ NJF-5-219-major/ 1/ fid
Title
NJF-5-219-major.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
zg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
16
Receiver Gain
112.8
Relaxation Delay
1
Pulse Width
12
Acquisition Time
4
Acquisition Date
2022-05-18T08:56:19
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.2
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
HO
TBSO
H
OH
133
5.84
4.43
3.85
3.68
3.45
2.88
2.33
2.14
2.02
1.81
1.44
1.20
0.91
0.09
0.09
1.00
2.99
2.85
9.05
3.04
1.33
1.14
1.25
3.21
1.07
0.83
2.06
1.03
1.03
1.00
f1 (ppm)

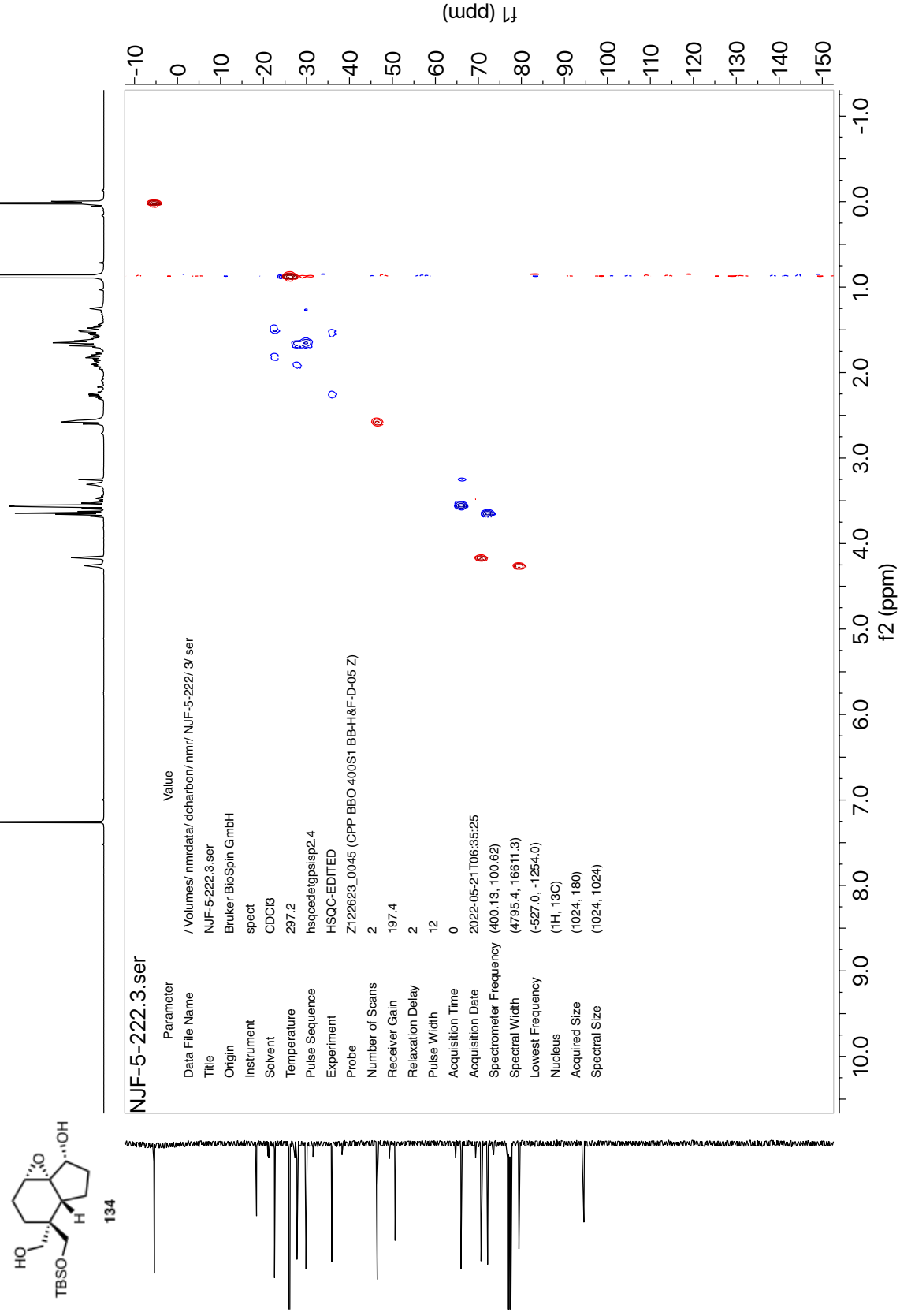

NJF-5-219-major.3.fid
Parameter
Value
Data File Name
/ Volumes/ nmrdata-1/ nfastuca/ nmr/ NJF-5-219-major/ 3/ fid
Title
NJF-5-219-major.3.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
zgpg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
1024
Receiver Gain
87.8
Relaxation Delay
1
Pulse Width
10
Acquisition Time
1
Acquisition Date
2022-05-18T09:50:16
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1945.4
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
144.24
122.53
74.08
73.39
64.08
43.11
39.14
34.23
27.22
26.01
24.01
22.74
18.31
-5.48
-5.55
HO
TBSO
H
OH
133
f1 (ppm)

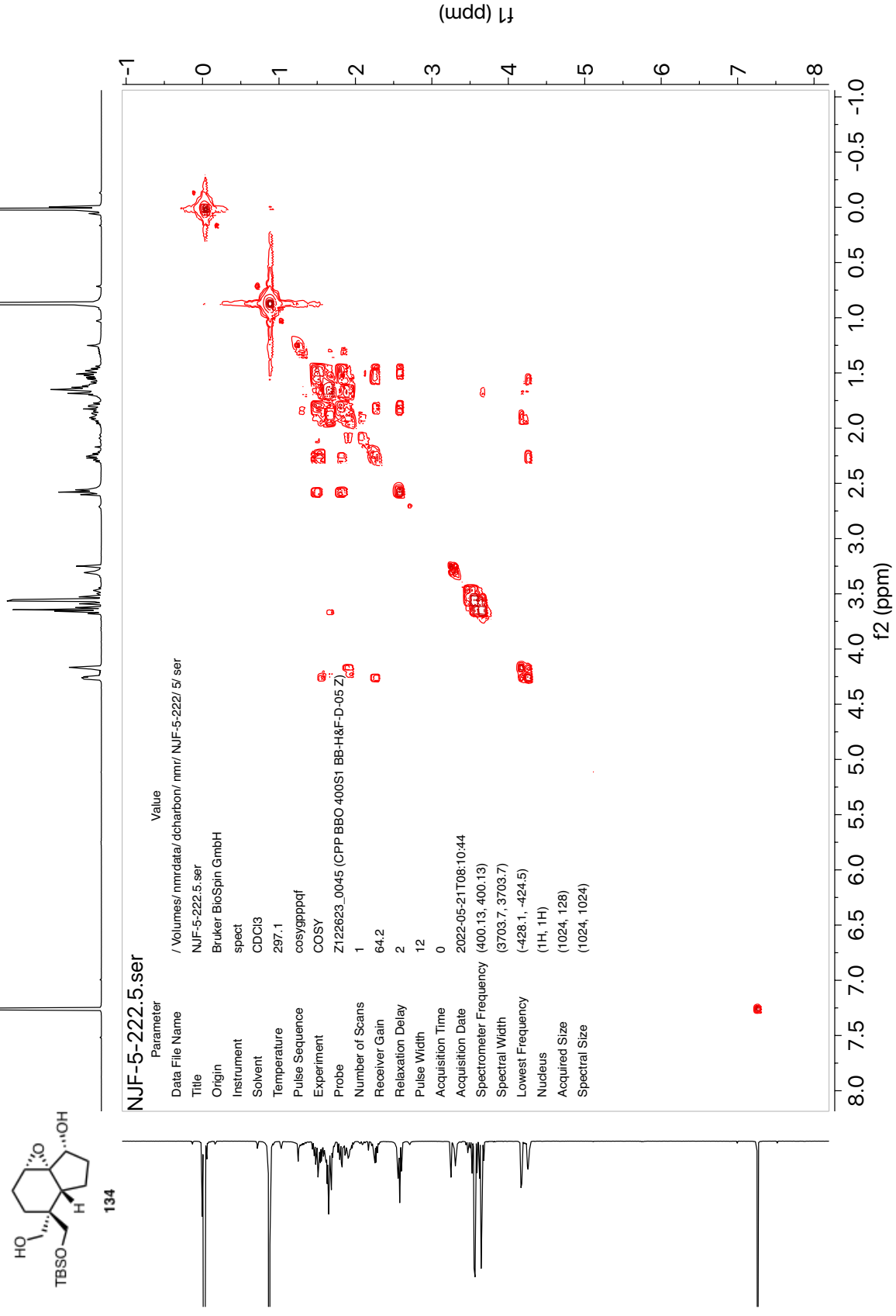

NJF-5-219-major.2.ser
Parameter Value
Data File Name / Volumes/ nmrdata-1/ nfastuca/ nmr/ NJF-5-219-major/ 2/ ser
Title NJF-5-219-major.2.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 2
Pulse Width 12
Acquisition Time 0
Acquisition Date 2022-05-18T09:08:04
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-526.9, -1265.2)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
f1 (ppm)
f2 (ppm)
HO
TBSO
H
OH
133

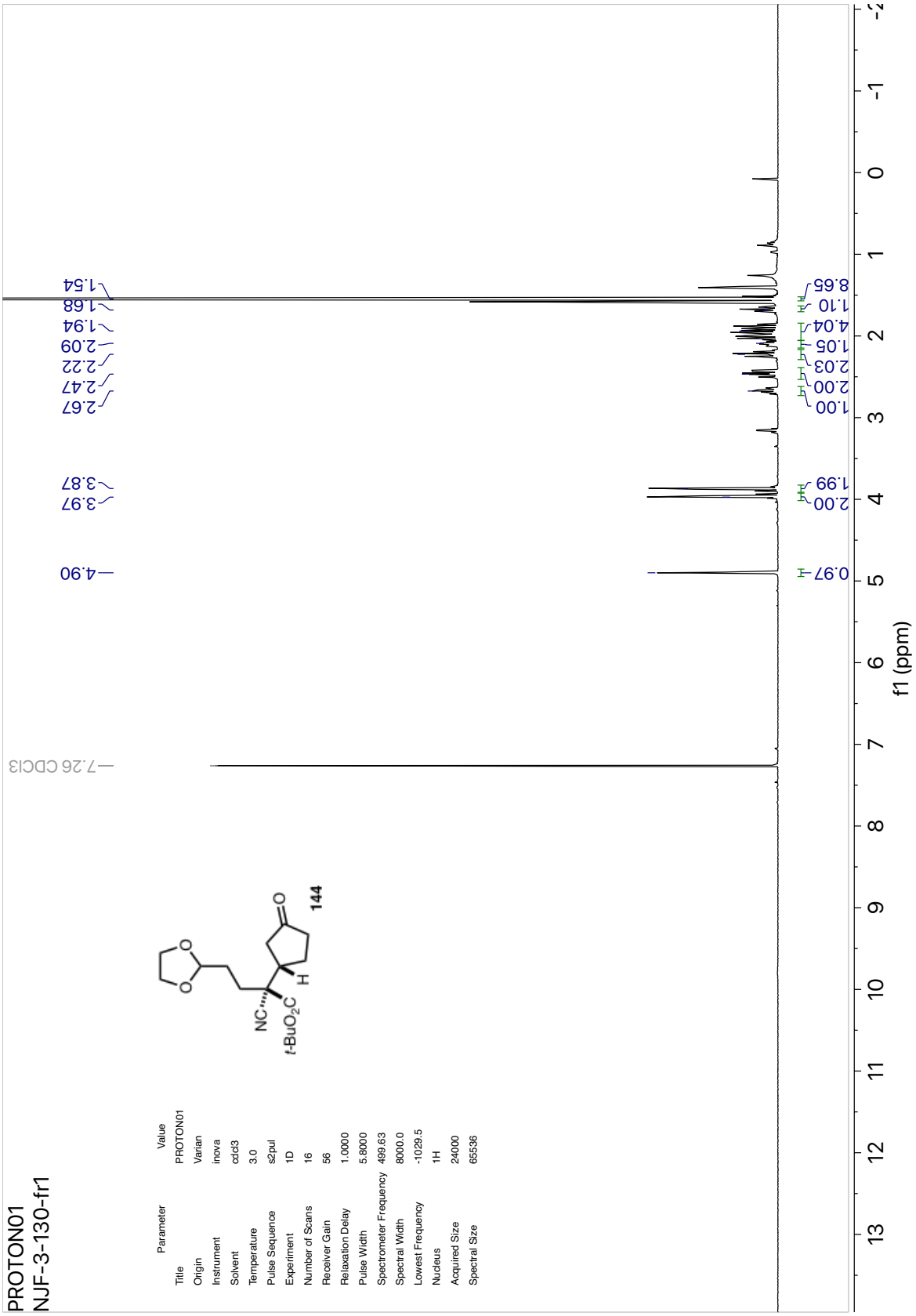

NJF-5-219-major.4.ser
Parameter Value
Data File Name / Volumes/ nmrdata-1/ nfastuca/ nmr/ NJF-5-219-major/ 4/ ser
Title NJF-5-219-major.4.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence cosygpppqf
Experiment COSY
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 1
Receiver Gain 64.2
Relaxation Delay 2
Pulse Width 12
Acquisition Time 0
Acquisition Date 2022-05-18T09:55:56
Spectrometer Frequency (400.13, 400.13)
Spectral Width (3731.3, 3731.3)
Lowest Frequency (-436.2, -436.2)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
f2 (ppm)
f1 (ppm)
HO
TBSO
H
OH
133

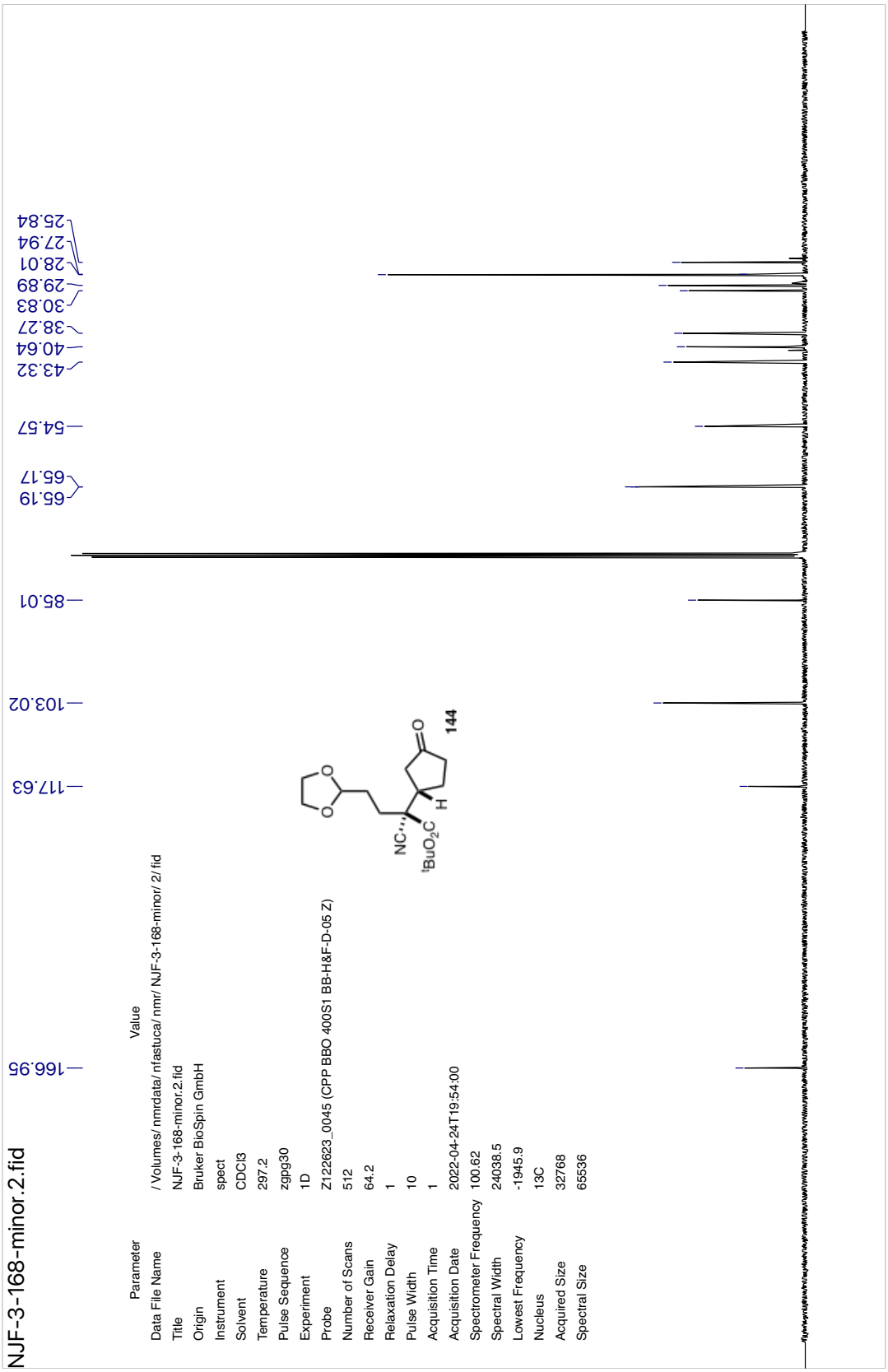

NJF-5-222.1.fid
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ dcharbon/ nmr/ NJF-5-222/ 1/ fid
Title
NJF-5-222.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.1
Pulse Sequence
zg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
16
Receiver Gain
127.1
Relaxation Delay
1
Pulse Width
12
Acquisition Time
4
Acquisition Date
2022-05-21T05:40:34
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.4
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
HO
TBSO
O
OH
H
134
0.02
0.02
0.87
1.51
1.65
1.87
2.26
2.58
3.31
3.55
3.65
4.17
4.26
3.13
2.58
9.09
2.06
3.37
2.32
1.04
1.34
0.92
1.99
1.95
0.96
1.00
f1 (ppm)


NJF-5-222.2.fid
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ dcharbon/ nmr/ NJF-5-222/ 2/ fid
Title
NJF-5-222.2.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.1
Pulse Sequence
zgpg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
1024
Receiver Gain
78.7
Relaxation Delay
1
Pulse Width
10
Acquisition Time
1
Acquisition Date
2022-05-21T06:23:41
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1945.2
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
HO
TBSO
O
OH
H
134
-5.41
-5.44
18.38
22.57
25.99
27.79
29.89
35.88
46.46
50.62
65.94
70.62
72.14
79.43
94.54
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NJF-5-222.3.ser
Parameter Value
Data File Name /Volumes/ nmrdata/ dcharbon/ nmr/ NJF-5-222/ 3/ ser
Title NJF-5-222.3.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 2
Pulse Width 12
Acquisition Time 0
Acquisition Date 2022-05-21T06:35:25
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-527.0, -1254.0)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
f1 (ppm)
f2 (ppm)
HO
TBSO
OH
O
H
134


NJF-5-222.5.ser
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ dcharbon/ nmr/ NJF-5-222/ 5/ ser
Title
NJF-5-222.5.ser
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.1
Pulse Sequence
cosygpppqf
Experiment
COSY
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
1
Receiver Gain
64.2
Relaxation Delay
2
Pulse Width
12
Acquisition Time
0
Acquisition Date
2022-05-21T08:10:44
Spectrometer Frequency
(400.13, 400.13)
Spectral Width
(3703.7, 3703.7)
Lowest Frequency
(-428.1, -424.5)
Nucleus
(1H, 1H)
Acquired Size
(1024, 128)
Spectral Size
(1024, 1024)
f2 (ppm)
f1 (ppm)
HO
TBSO
O
OH
H
134


PROTON01
NJF-3-130-fr1
Parameter Value
Title PROTON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 3.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 16
Receiver Gain 56
Relaxation Delay 1.0000
Pulse Width 5.8000
Spectrometer Frequency 499.63
Spectral Width 8000.0
Lowest Frequency -1029.5
Nucleus 1H
Acquired Size 24000
Spectral Size 65536
NC
t-BuO2C
H
144
7.26 CDCl3
4.90
3.97
3.87
2.67
2.47
2.22
2.09
1.94
1.68
1.54
0.97
1.99
2.00
1.00
2.00
2.03
1.05
4.04
1.10
8.65
f1 (ppm)


NJF-3-168-minor.2.fid
Parameter
Value
Data File Name
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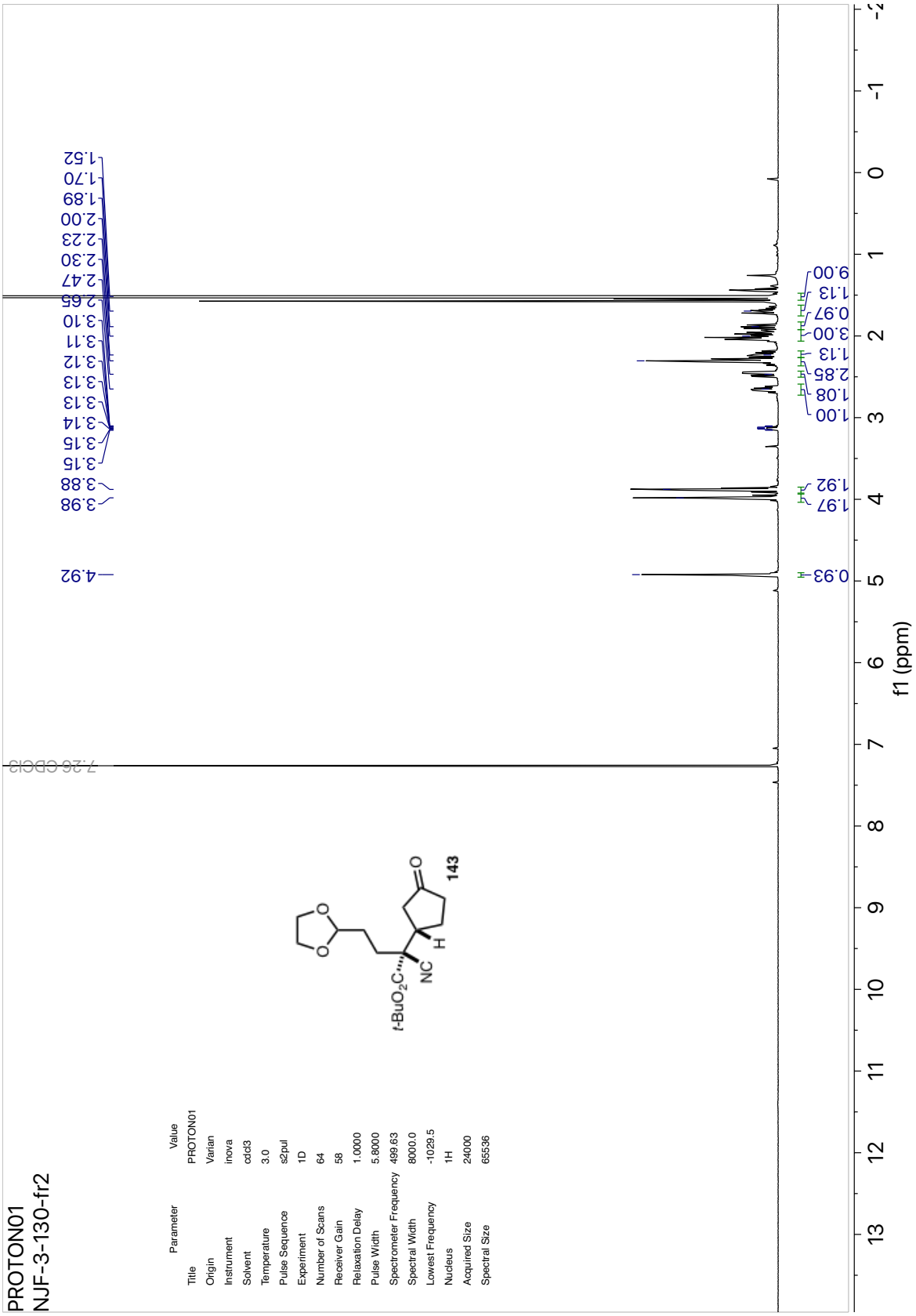
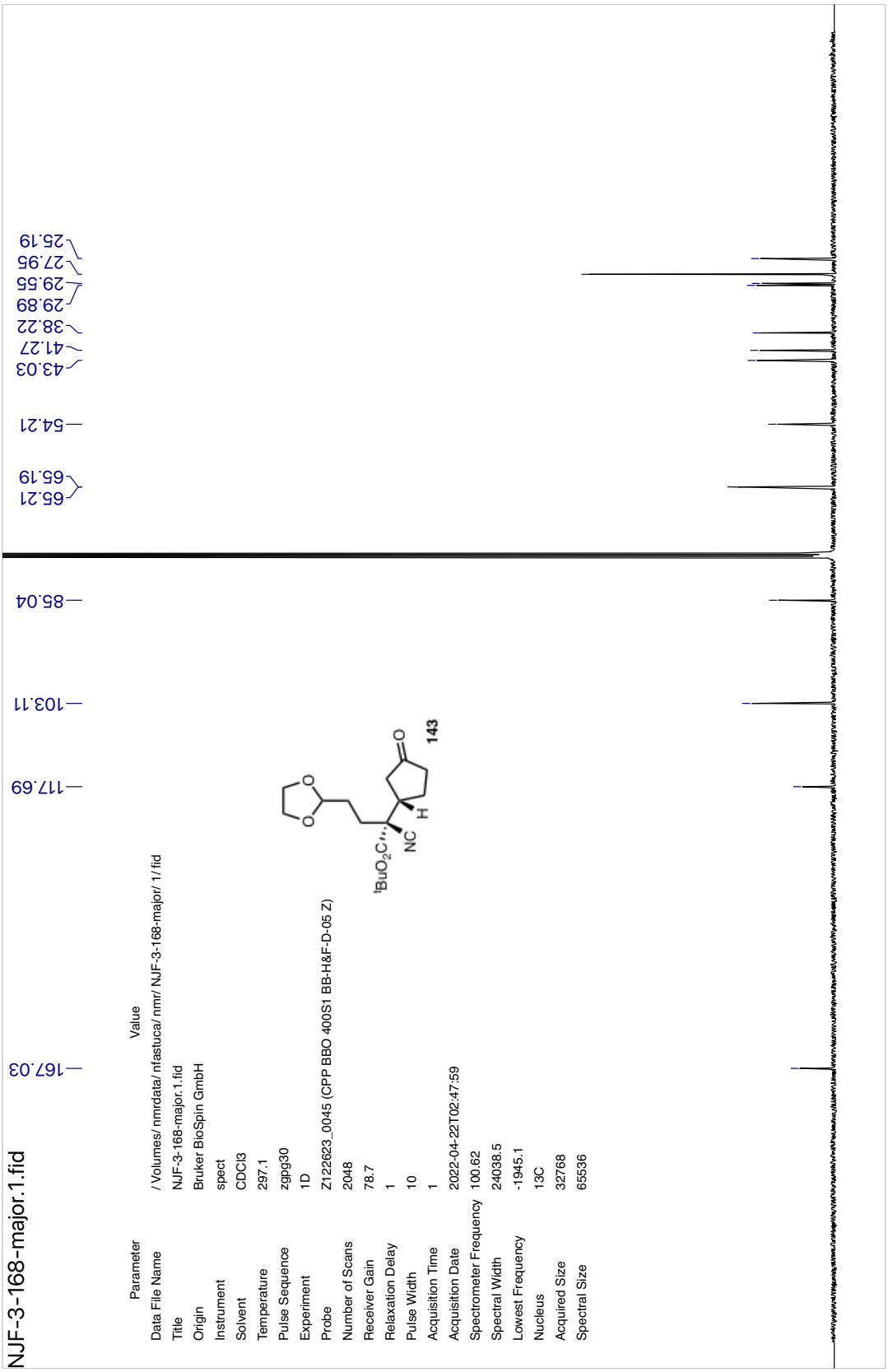
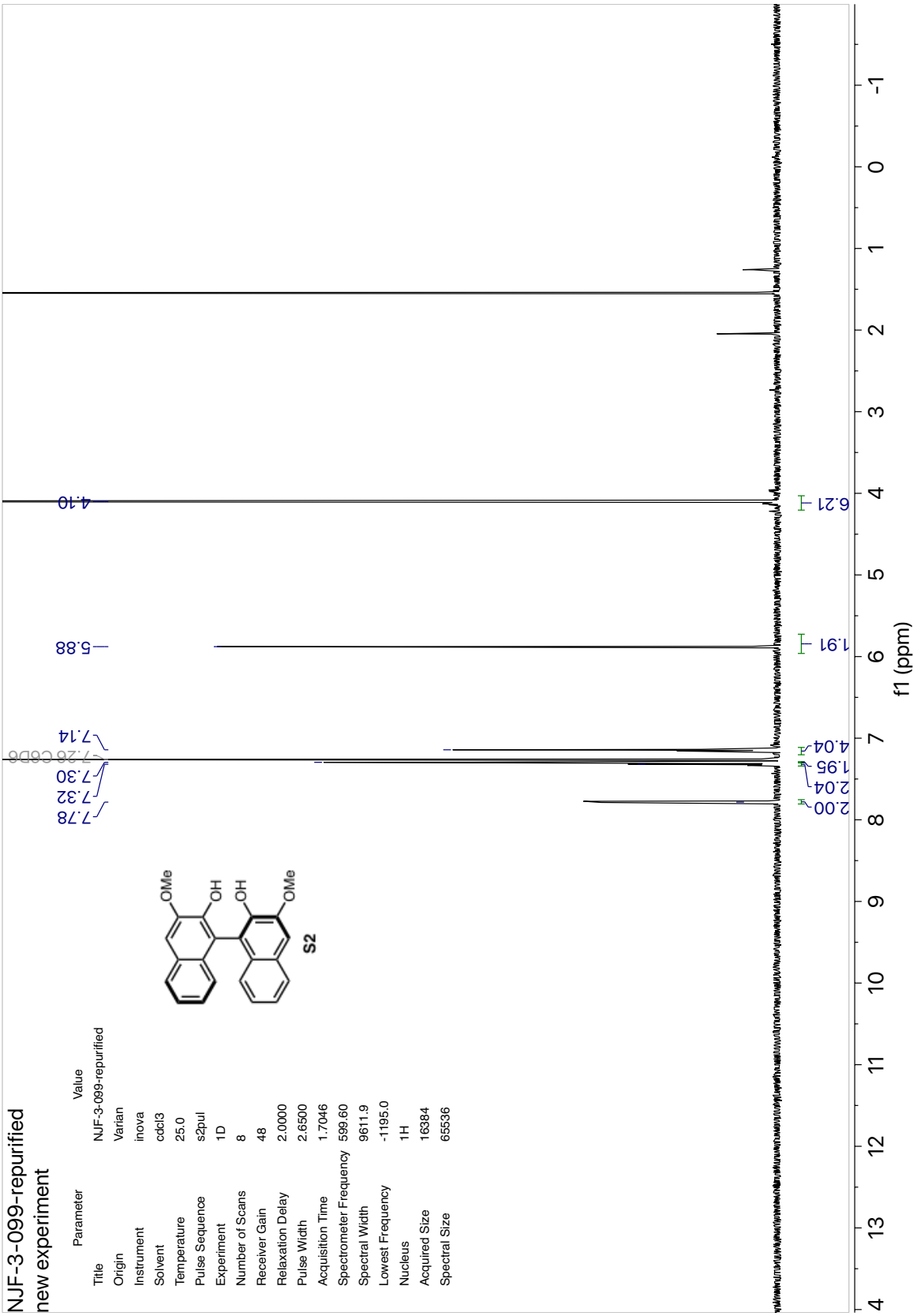
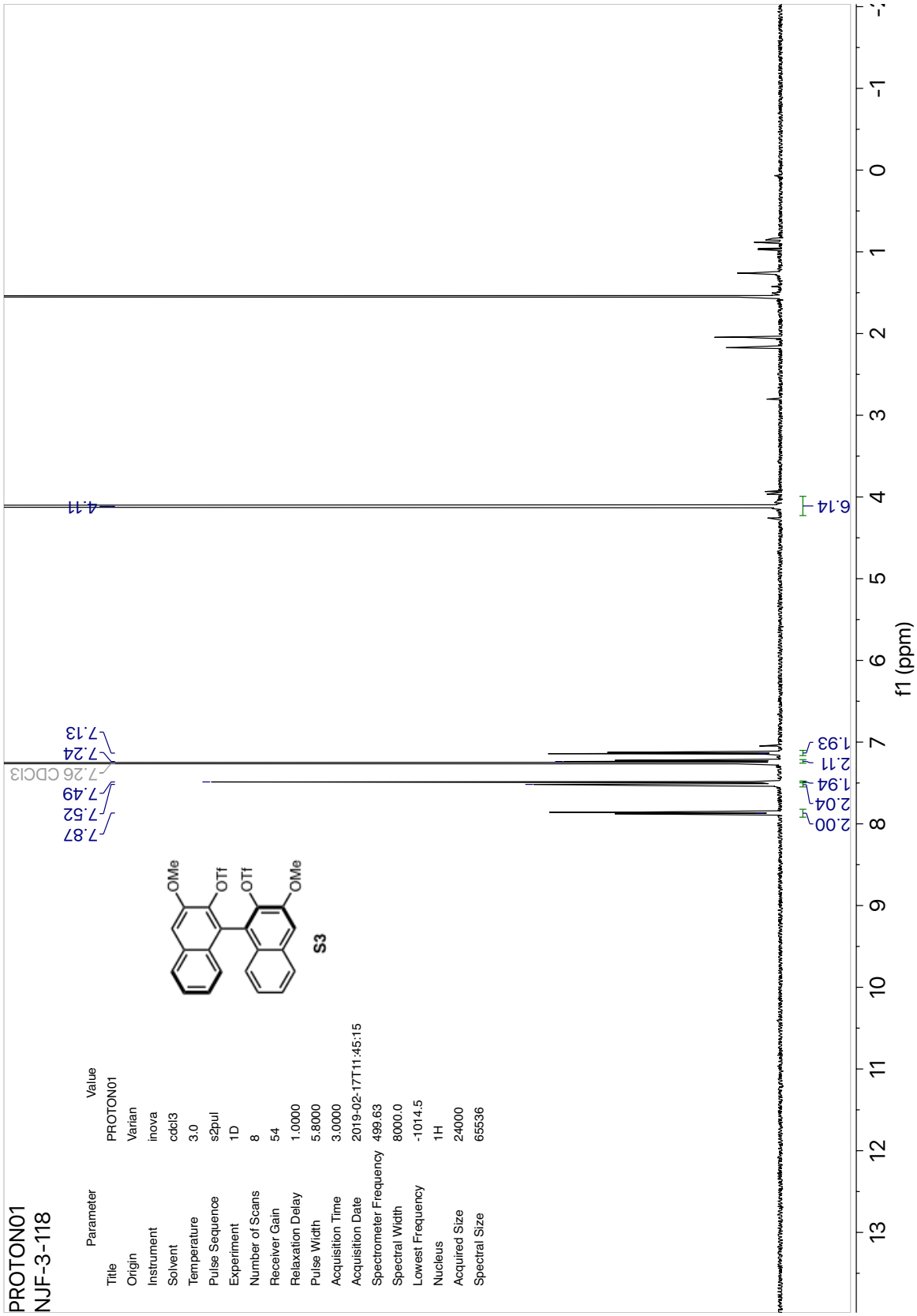
Title
NJF-3-168-minor.2.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
zgpg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
512
Receiver Gain
64.2
Relaxation Delay
1
Pulse Width
10
Acquisition Time
1
Acquisition Date
2022-04-24T19:54:00
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1945.9
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
166.95
117.63
103.02
85.01
65.19
65.17
54.57
43.32
40.64
38.27
30.83
29.89
28.01
27.94
25.84
144
f1 (ppm)

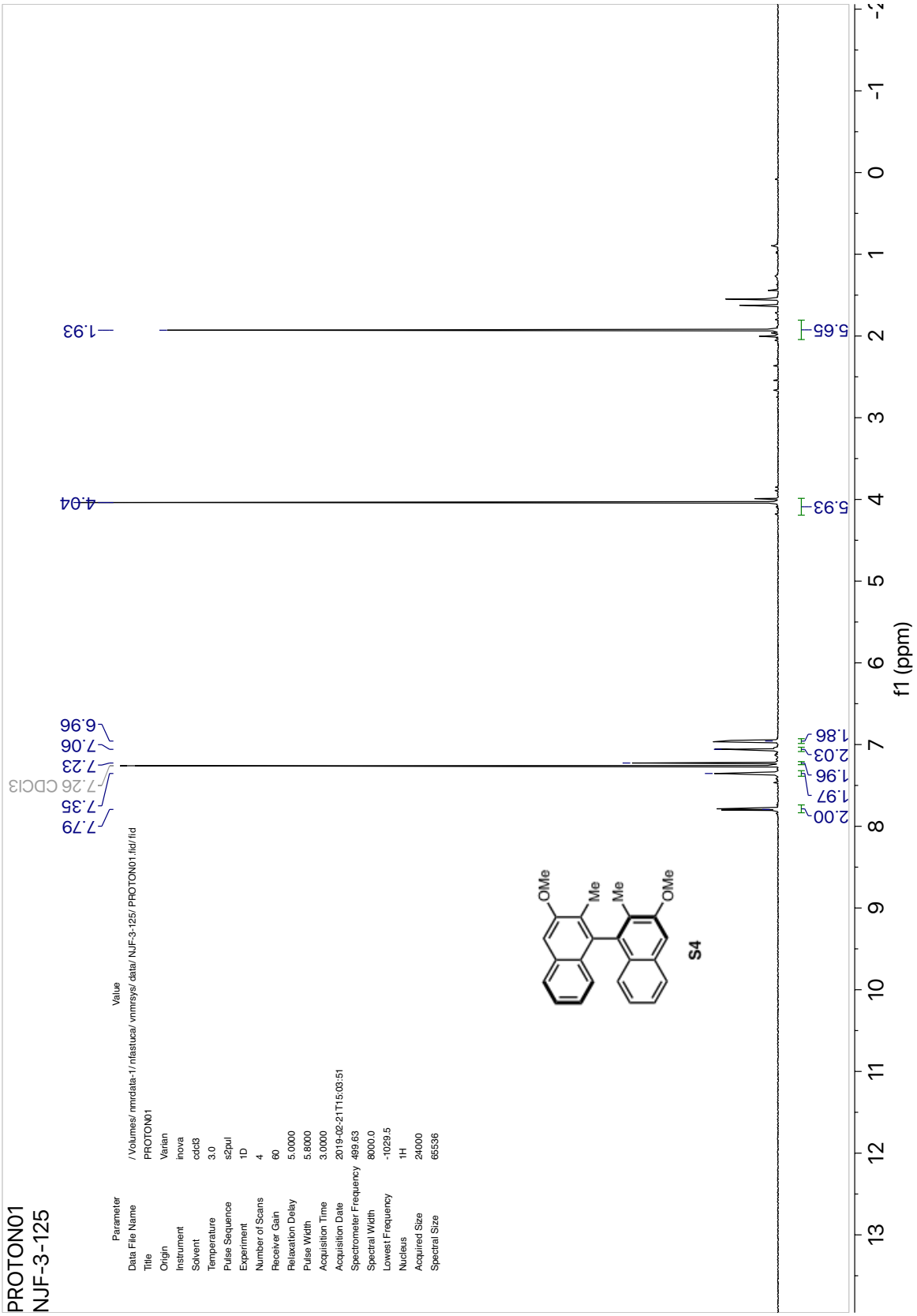

PROTON01
NJF-3-130-fr2
Parameter Value
Title PROTON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 3.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 64
Receiver Gain 58
Relaxation Delay 1.0000
Pulse Width 5.8000
Spectrometer Frequency 499.63
Spectral Width 8000.0
Lowest Frequency -1029.5
Nucleus 1H
Acquired Size 24000
Spectral Size 65536
7.26 CDCl3
4.92
3.98
3.88
3.15
3.15
3.14
3.13
3.13
3.12
3.11
3.10
2.65
2.47
2.30
2.23
2.00
1.89
1.70
1.52
0.93
1.97
1.92
1.00
1.08
2.85
1.13
3.00
0.97
1.13
9.00
t-BuO2C
NC
H
O
O
O
O
143
f1 (ppm)

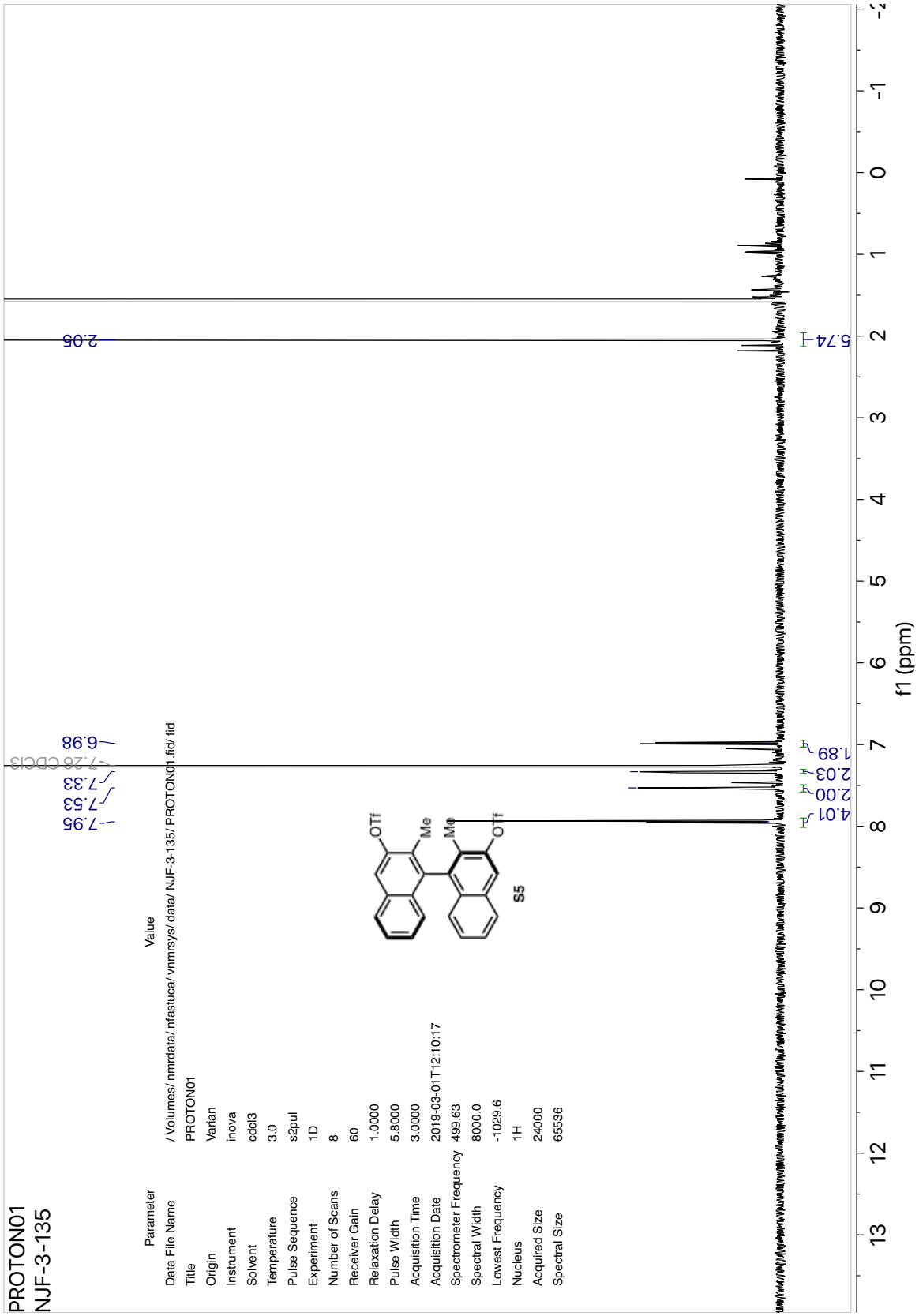


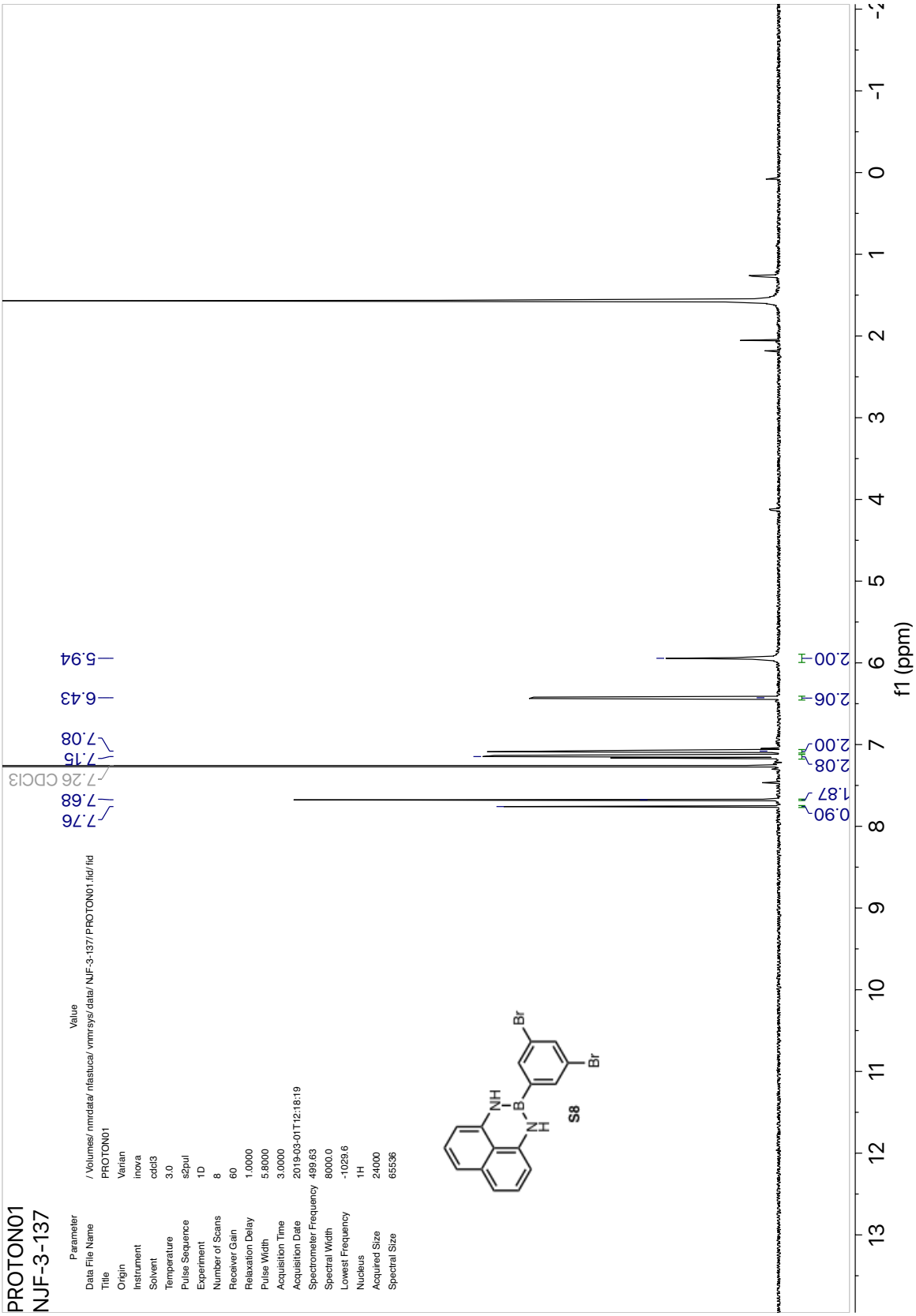
Parameter	Value
Data File Name	/Volumes/nmrdata/nfastuca/nmr/NJF-3-168-major/1/fid
Title	NJF-3-168-major.1.fid
Origin	Bruker BioSpin GmbH
Instrument	spect
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Experiment	1D
Probe	Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans	2048
Receiver Gain	78.7
Relaxation Delay	1
Pulse Width	10
Acquisition Time	1
Acquisition Date	2022-04-22T02:47:59
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536


NJF-3-099-repurified
new experiment
Parameter Value
Title NJF-3-099-repurified
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 8
Receiver Gain 48
Relaxation Delay 2.0000
Pulse Width 2.6500
Acquisition Time 1.7046
Spectrometer Frequency 599.60
Spectral Width 9611.9
Lowest Frequency -1195.0
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
OMe
OH
OH
OMe
S2
7.78
7.32
7.30
7.26 C6D6
7.14
5.88
4.10
2.00
2.04
1.95
4.04
1.91
6.21
f1 (ppm)


PROTON01
NJF-3-118
Parameter Value
Title PROTON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 3.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 8
Receiver Gain 54
Relaxation Delay 1.0000
Pulse Width 5.8000
Acquisition Time 3.0000
Acquisition Date 2019-02-17T11:45:15
Spectrometer Frequency 499.63
Spectral Width 8000.0
Lowest Frequency -1014.5
Nucleus 1H
Acquired Size 24000
Spectral Size 65536
OMe
OTf
OTf
OMe
S3
7.87
7.52
7.49
7.26 CDCl3
7.24
7.13
4.11
6.14
2.00
2.04
1.94
2.11
1.93
f1 (ppm)


PROTON01
NJF-3-125
Parameter Value
Data File Name / Volumes/ nmrdata-1/ nfastuca/ vnmrsys/ data/ NJF-3-125/ PROTON01.fid/ fid
Title PROTON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 3.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 4
Receiver Gain 60
Relaxation Delay 5.0000
Pulse Width 5.8000
Acquisition Time 3.0000
Acquisition Date 2019-02-21T15:03:51
Spectrometer Frequency 499.63
Spectral Width 8000.0
Lowest Frequency -1029.5
Nucleus 1H
Acquired Size 24000
Spectral Size 65536
7.79
7.35
7.26 CDCl3
7.23
7.06
6.96
4.04
1.93
2.00
1.97
1.96
2.03
1.86
5.93
5.65
OMe
Me
Me
OMe
S4
f1 (ppm)


PROTON01
NJF-3-135
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ vnmrsys/ data/ NJF-3-135/ PROTON01.fid/ fid
Title
PROTON01
Origin
Varian
Instrument
inova
Solvent
cdcl3
Temperature
3.0
Pulse Sequence
s2pul
Experiment
1D
Number of Scans
8
Receiver Gain
60
Relaxation Delay
1.0000
Pulse Width
5.8000
Acquisition Time
3.0000
Acquisition Date
2019-03-01T12:10:17
Spectrometer Frequency
499.63
Spectral Width
8000.0
Lowest Frequency
-1029.6
Nucleus
1H
Acquired Size
24000
Spectral Size
65536
OTf
Me
Me
OTf
S5
7.95
7.53
7.33
7.26 CDCl3
6.98
2.05
5.74
4.01
2.00
2.03
1.89
f1 (ppm)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NJF-3-137
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Data File Name
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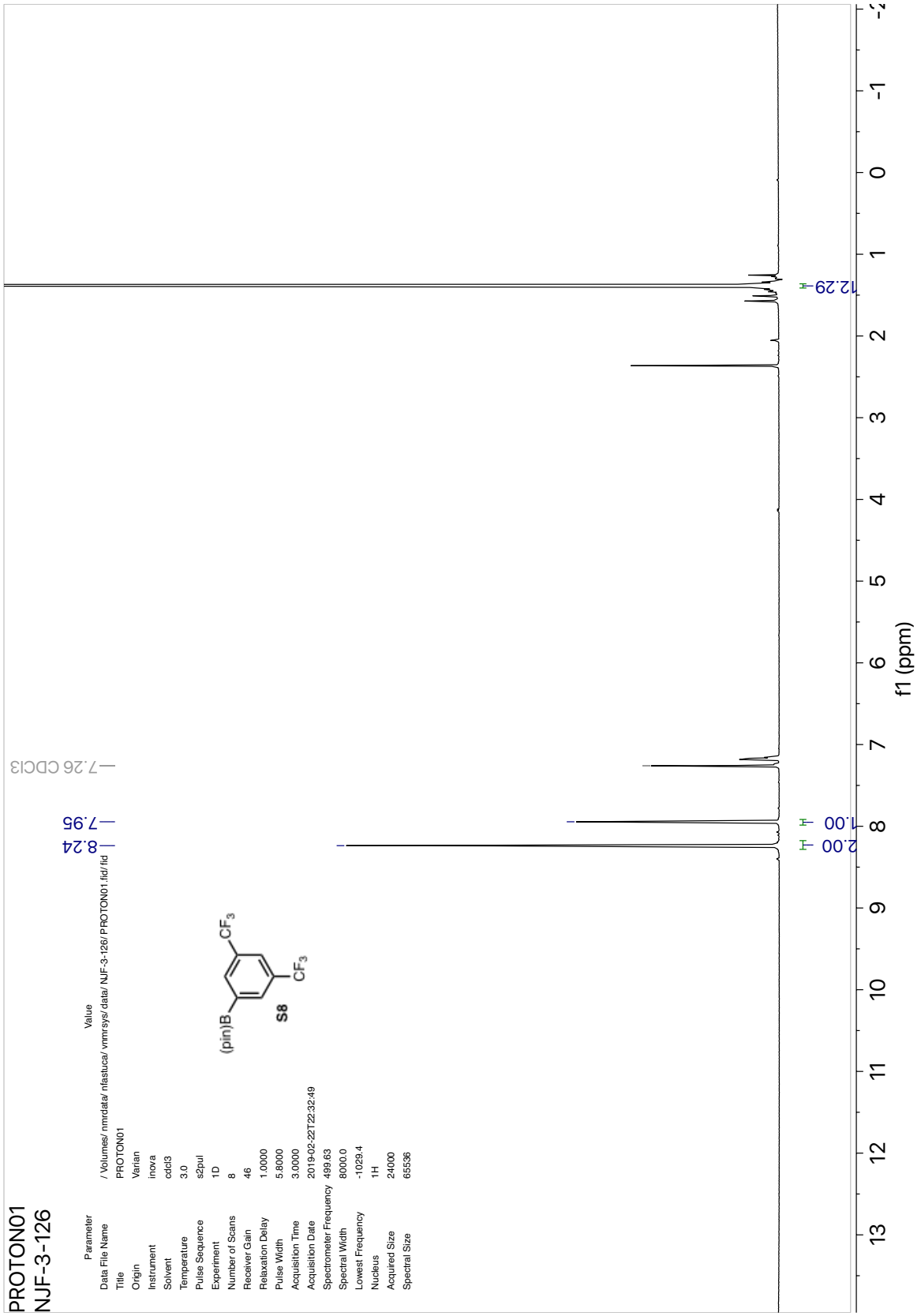
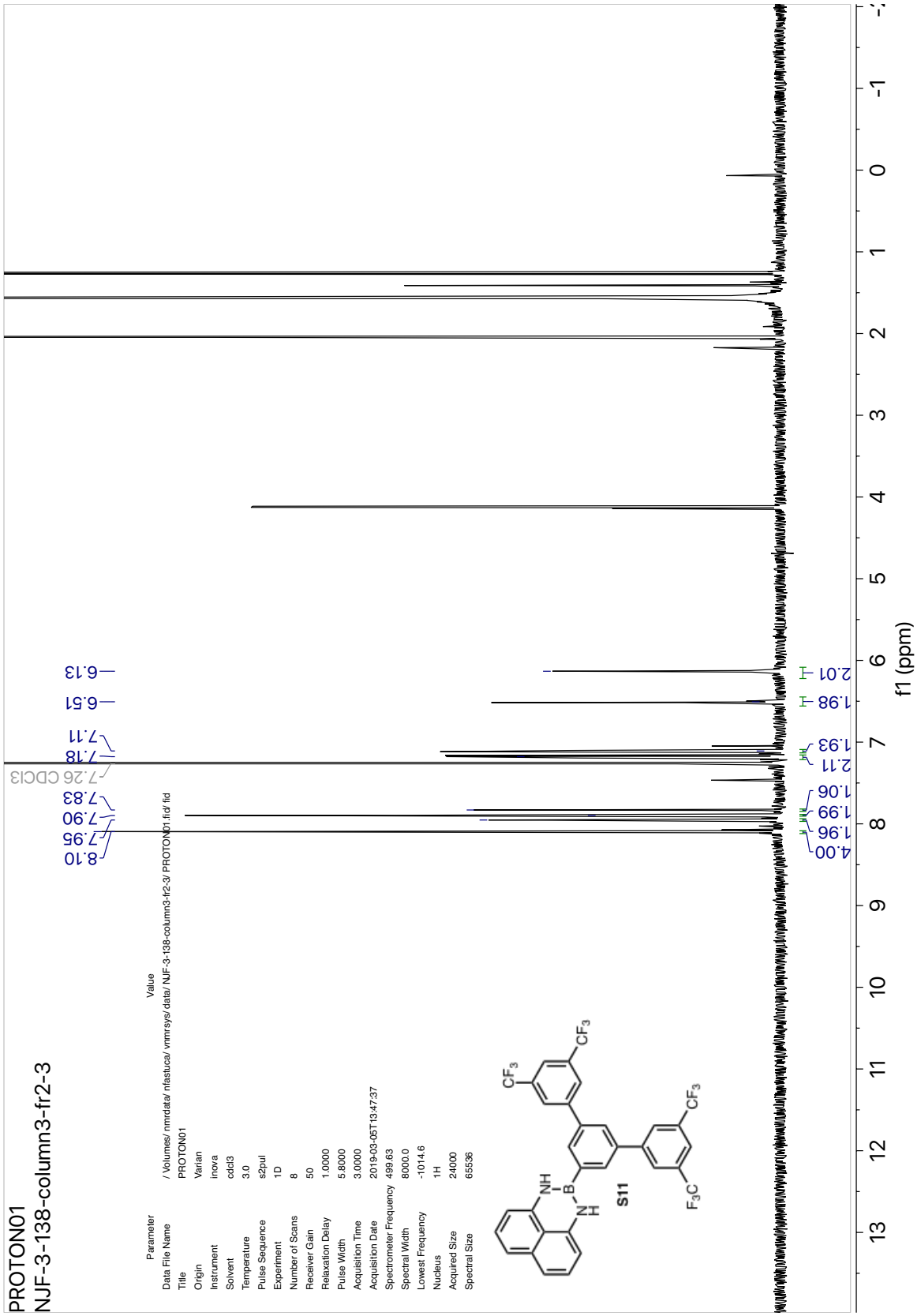
Title
PROTON01
Origin
Varian
Instrument
inova
Solvent
cdcl3
Temperature
3.0
Pulse Sequence
s2pul
Experiment
1D
Number of Scans
8
Receiver Gain
60
Relaxation Delay
1.0000
Pulse Width
5.8000
Acquisition Time
3.0000
Acquisition Date
2019-03-01T12:18:19
Spectrometer Frequency
499.63
Spectral Width
8000.0
Lowest Frequency
-1029.6
Nucleus
1H
Acquired Size
24000
Spectral Size
65536
7.76
7.68
7.26 CDCl3
7.15
7.08
6.43
5.94
0.90
1.87
2.08
2.00
2.06
2.00
NH
B
N
H
Br
Br
S8
f1 (ppm)


PROTON01
NJF-3-126
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ vnmrsys/ data/ NJF-3-126/ PROTON01.fid/ fid
Title
PROTON01
Origin
Varian
Instrument
inova
Solvent
cdcl3
Temperature
3.0
Pulse Sequence
s2pul
Experiment
1D
Number of Scans
8
Receiver Gain
46
Relaxation Delay
1.0000
Pulse Width
5.8000
Acquisition Time
3.0000
Acquisition Date
2019-02-22T22:32:49
Spectrometer Frequency
499.63
Spectral Width
8000.0
Lowest Frequency
-1029.4
Nucleus
1H
Acquired Size
24000
Spectral Size
65536
(pin)B
CF3
CF3
S8
7.26 CDCl3
7.95
8.24
12.29
1.00
2.00
f1 (ppm)


PROTON01
NJF-3-138-column3-fr2-3
Parameter
Value
Data File Name
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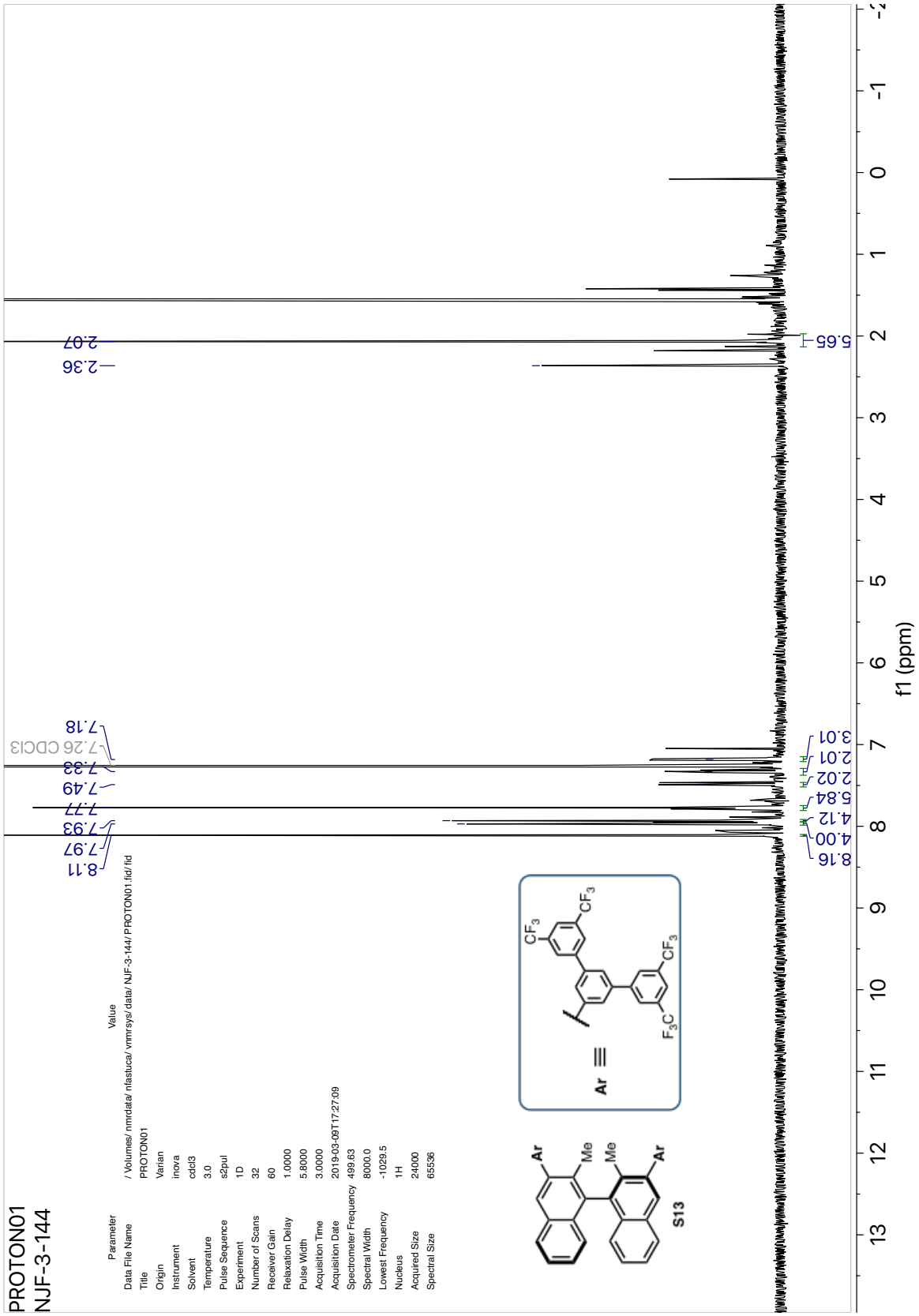
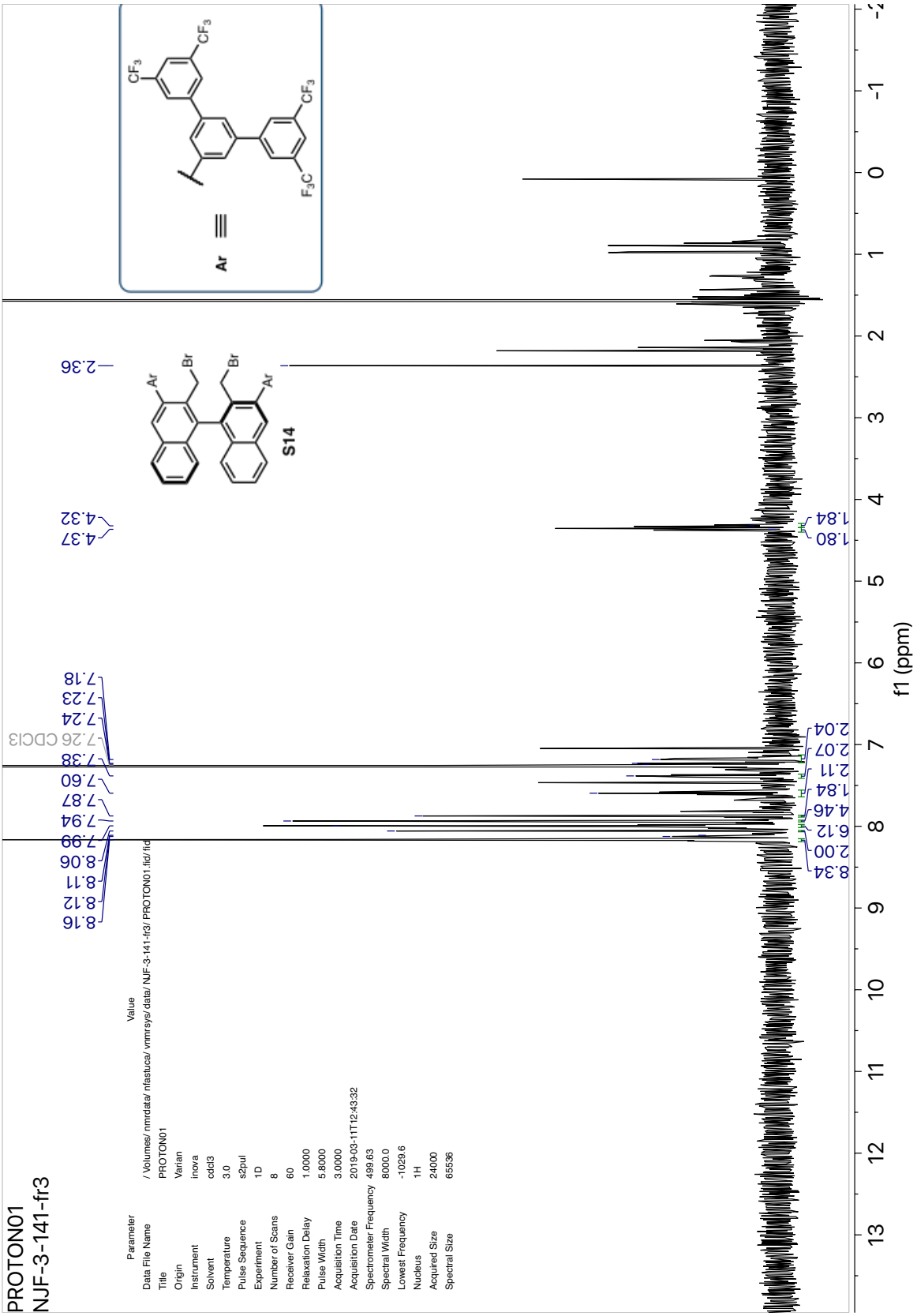
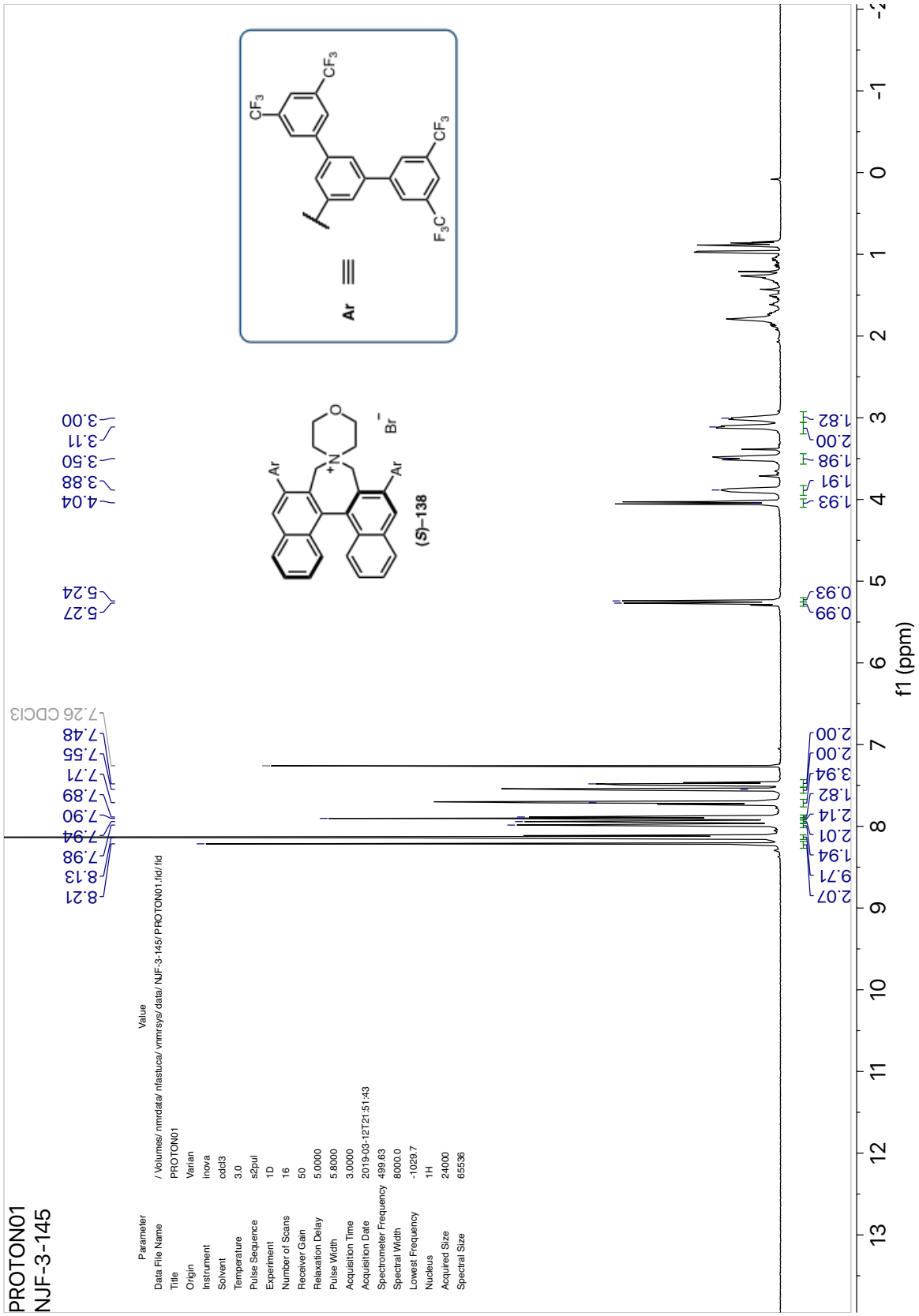
Title
PROTON01
Origin
Varian
Instrument
inova
Solvent
cdcl3
Temperature
3.0
Pulse Sequence
s2pul
Experiment
1D
Number of Scans
8
Receiver Gain
50
Relaxation Delay
1.0000
Pulse Width
5.8000
Acquisition Time
3.0000
Acquisition Date
2019-03-05T13:47:37
Spectrometer Frequency
499.63
Spectral Width
8000.0
Lowest Frequency
-1014.6
Nucleus
1H
Acquired Size
24000
Spectral Size
65536
8.10
7.95
7.90
7.83
7.26 CDCl3
7.18
7.11
6.51
6.13
4.00
1.96
1.99
1.06
2.11
1.93
1.98
2.01
S11
f1 (ppm)


PROTON01
NJF-3-144
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ vnmrsys/ data/ NJF-3-144/ PROTON01.fid/ fid
Title PROTON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 3.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 32
Receiver Gain 60
Relaxation Delay 1.0000
Pulse Width 5.8000
Acquisition Time 3.0000
Acquisition Date 2019-03-09T17:27:09
Spectrometer Frequency 499.63
Spectral Width 8000.0
Lowest Frequency -1029.5
Nucleus 1H
Acquired Size 24000
Spectral Size 65536
8.11
7.97
7.93
7.77
7.49
7.33
7.26 CDCl3
7.18
2.36
2.07
5.65
8.16
4.00
4.12
5.84
2.02
2.01
3.01
Ar
Me
Me
Ar
S13
CF3
CF3
CF3
F3C
Ar ≡
f1 (ppm)


PROTON01
NJF-3-141-fr3
Parameter
Value
Data File Name / Volumes/ nmrdata/ nfastuca/ vnmrsys/ data/ NJF-3-141-fr3/ PROTON01.fid/ fid
Title PROTON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 3.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 8
Receiver Gain 60
Relaxation Delay 1.0000
Pulse Width 5.8000
Acquisition Time 3.0000
Acquisition Date 2019-03-11T12:43:32
Spectrometer Frequency 499.63
Spectral Width 8000.0
Lowest Frequency -1029.6
Nucleus 1H
Acquired Size 24000
Spectral Size 65536
S14
Ar
CF3
F3C
CDCl3
f1 (ppm)

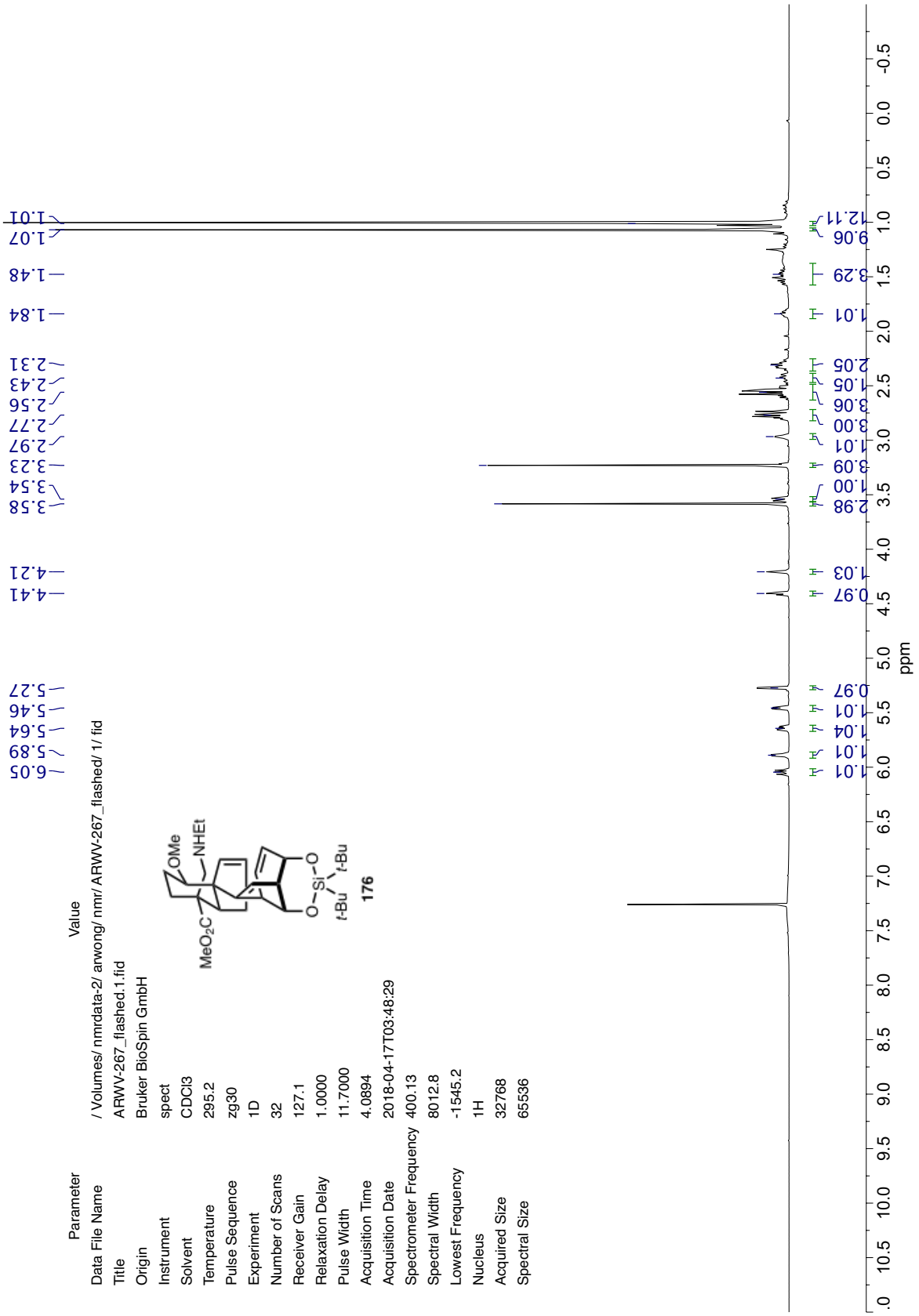

PROTON01
NJF-3-145
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ vnmrsys/ data/ NJF-3-145/ PROTON01.fid/ fid
Title PROTON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 3.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 16
Receiver Gain 50
Relaxation Delay 5.0000
Pulse Width 5.8000
Acquisition Time 3.0000
Acquisition Date 2019-03-12T21:51:43
Spectrometer Frequency 499.63
Spectral Width 8000.0
Lowest Frequency -1029.7
Nucleus 1H
Acquired Size 24000
Spectral Size 65536
8.21
8.13
7.98
7.94
7.90
7.89
7.71
7.55
7.48
7.26 CDCl3
5.27
5.24
4.04
3.88
3.50
3.11
3.00
2.07
9.71
1.94
2.01
2.14
1.82
3.94
2.00
2.00
0.99
0.93
1.93
1.91
1.98
2.00
1.82
Ar
Ar
Br
(S)–138
CF3
CF3
CF3
F3C
Ar
f1 (ppm)

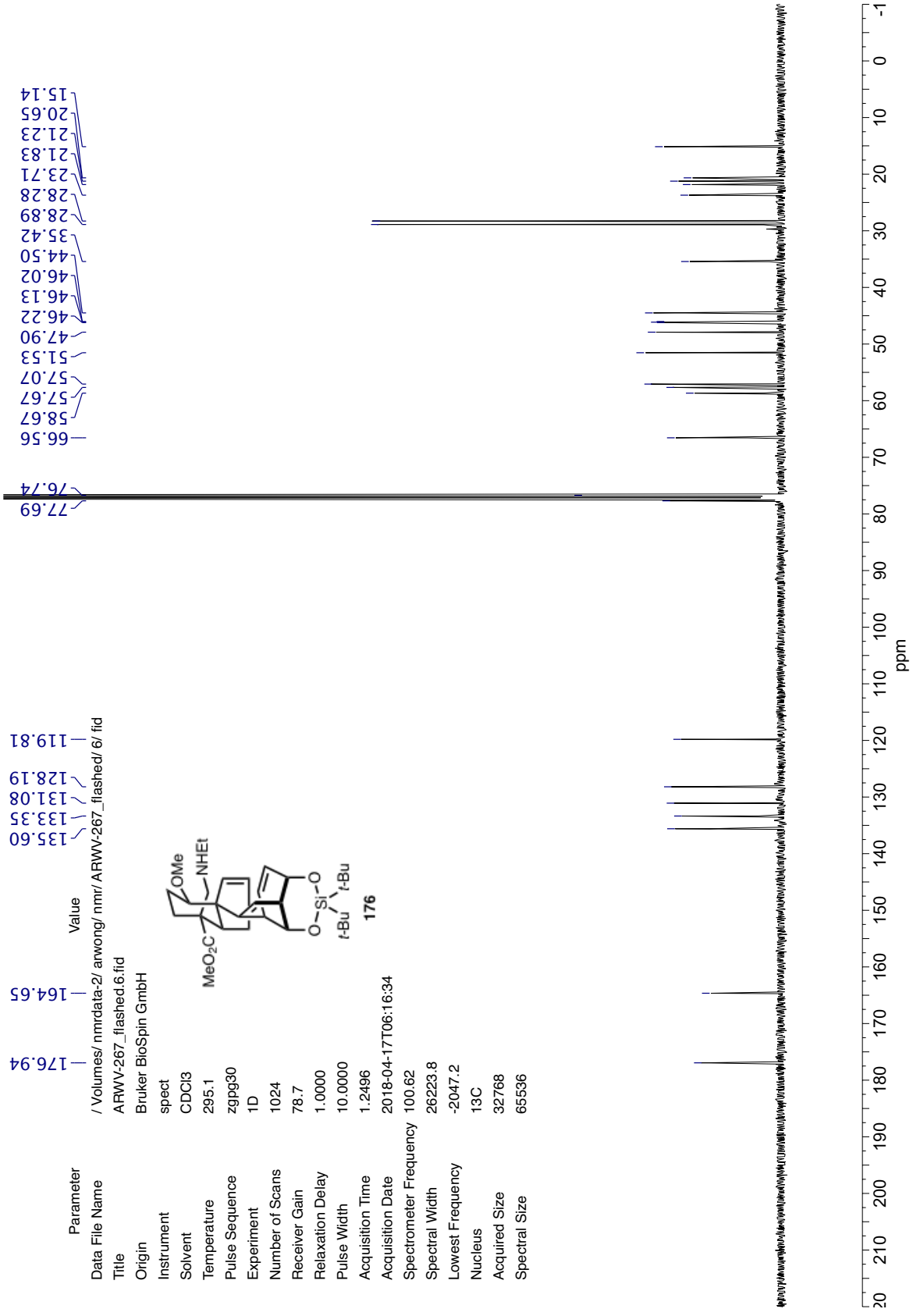
Appendix 3

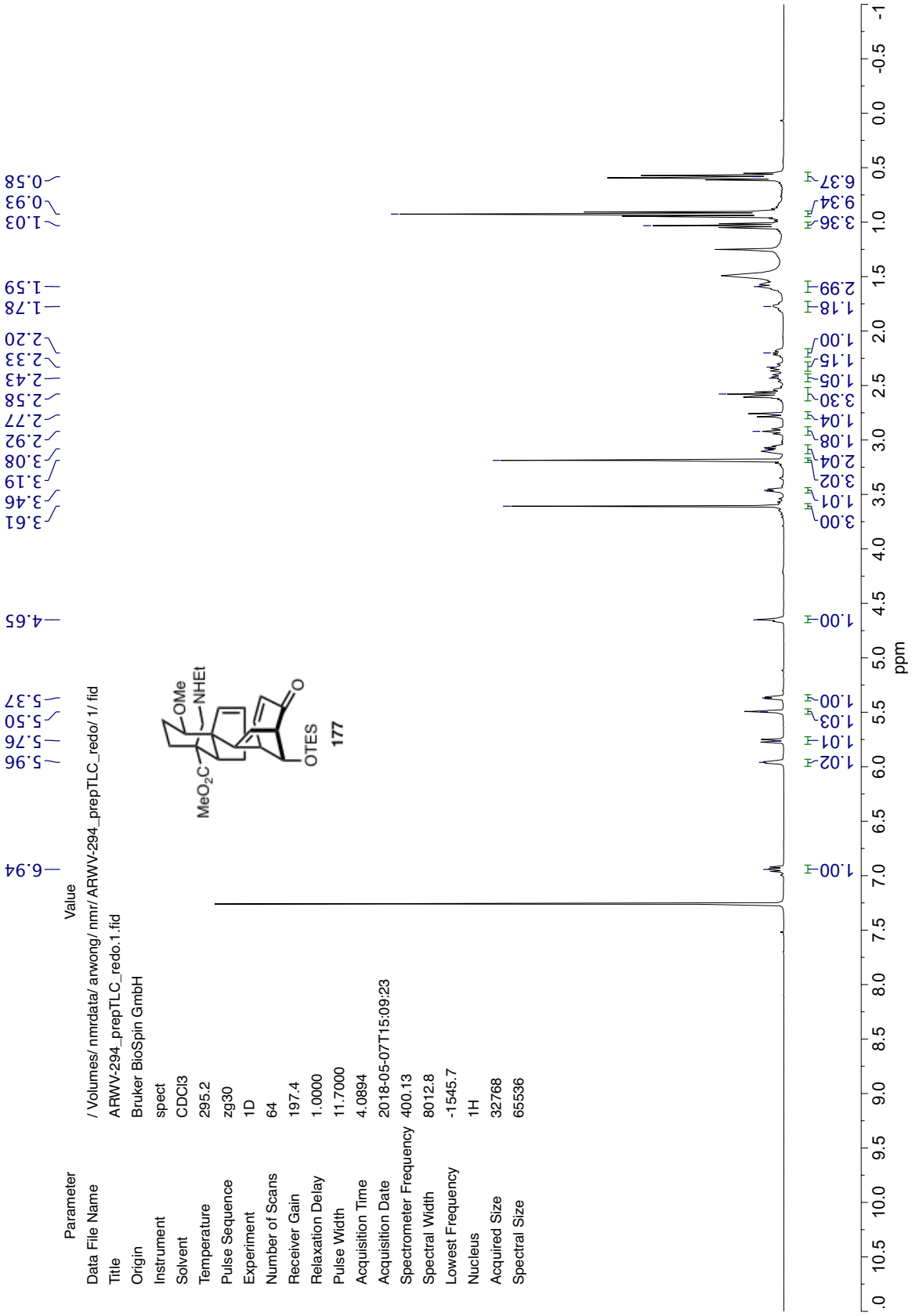
Spectra Relevant to Chapter 4:

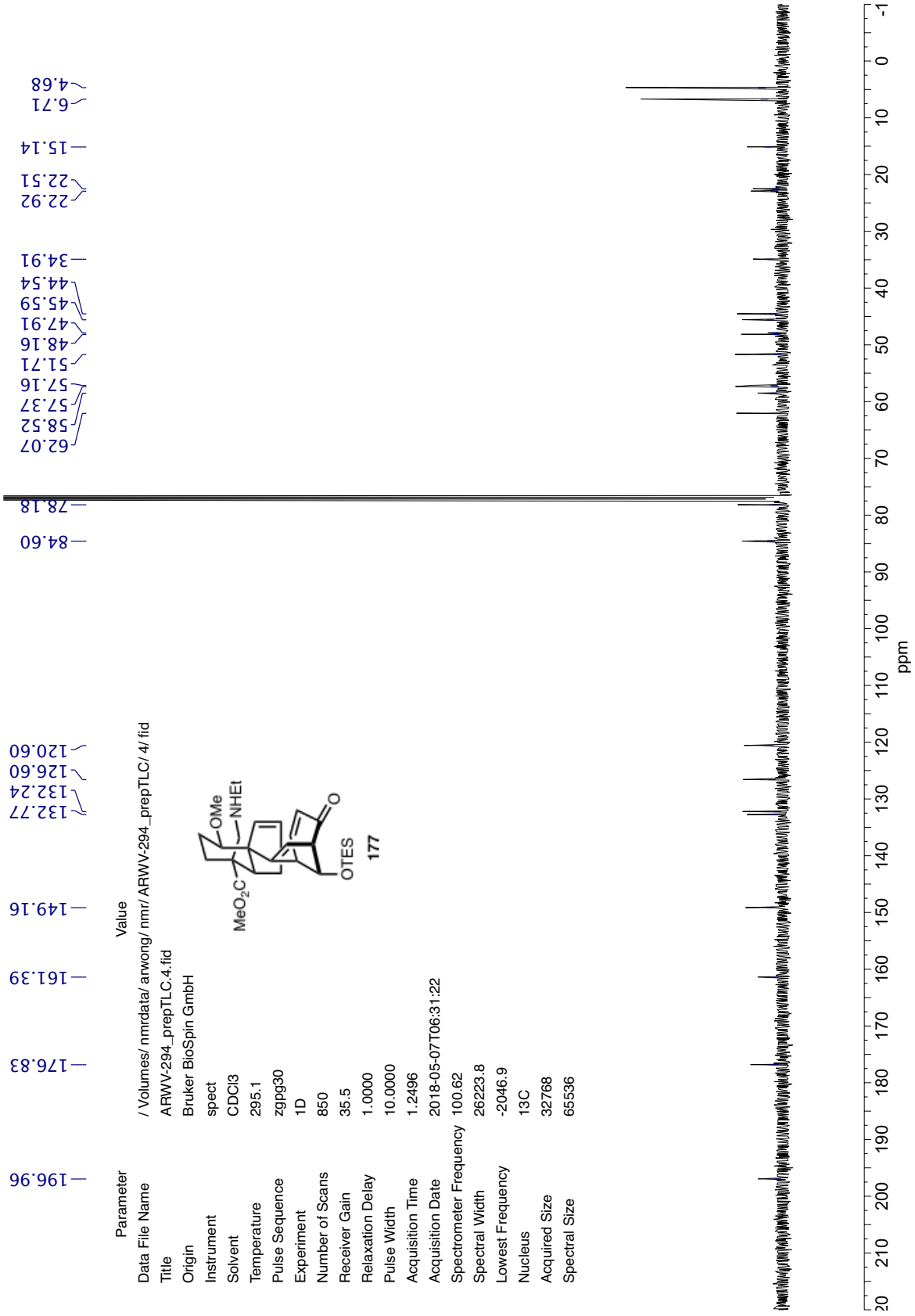
Completion of Aconitine Core and Synthesis of (–)-Talatisamine,

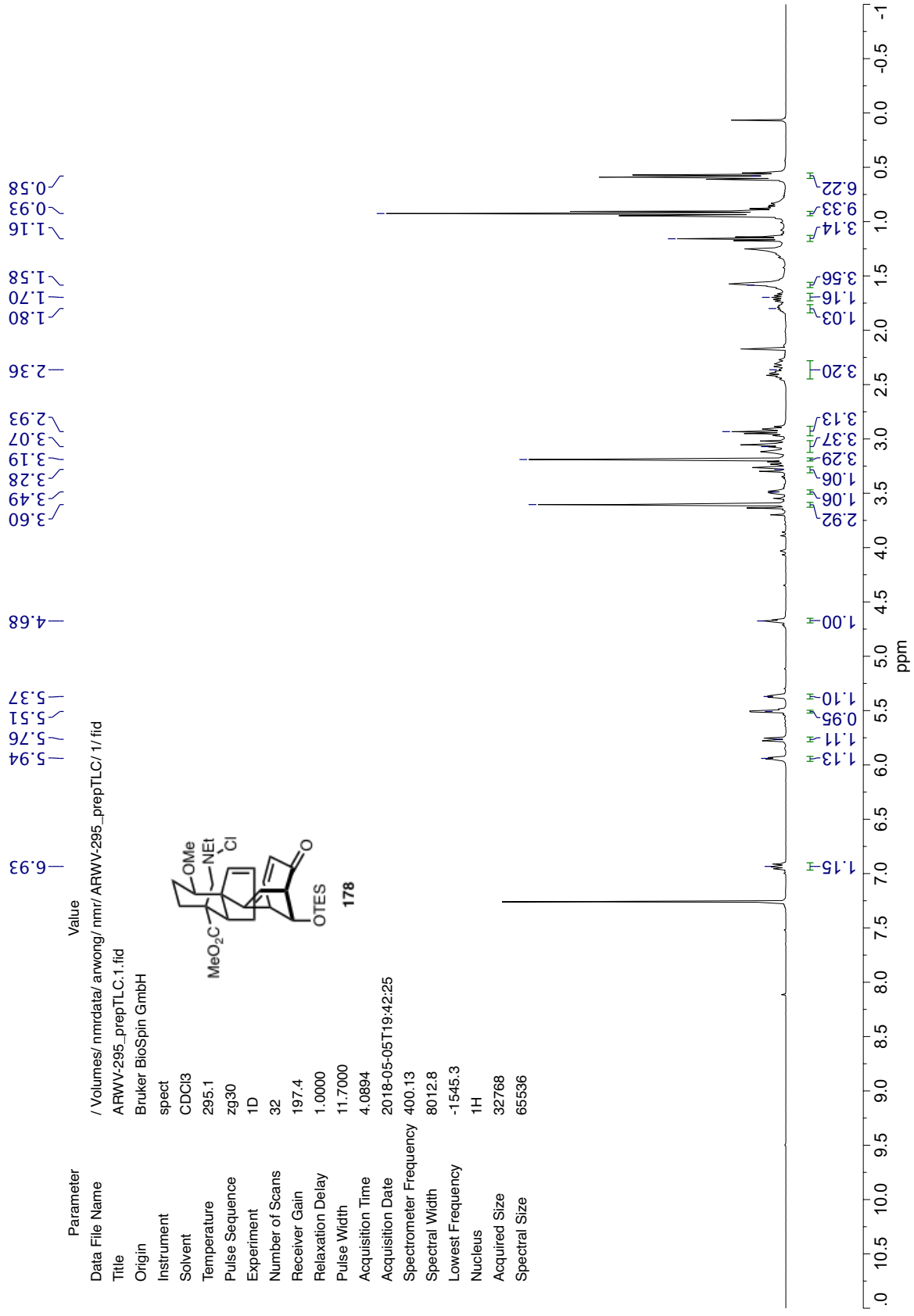
(–)-Liljestrandisine, and (–)-Liljestrandinine

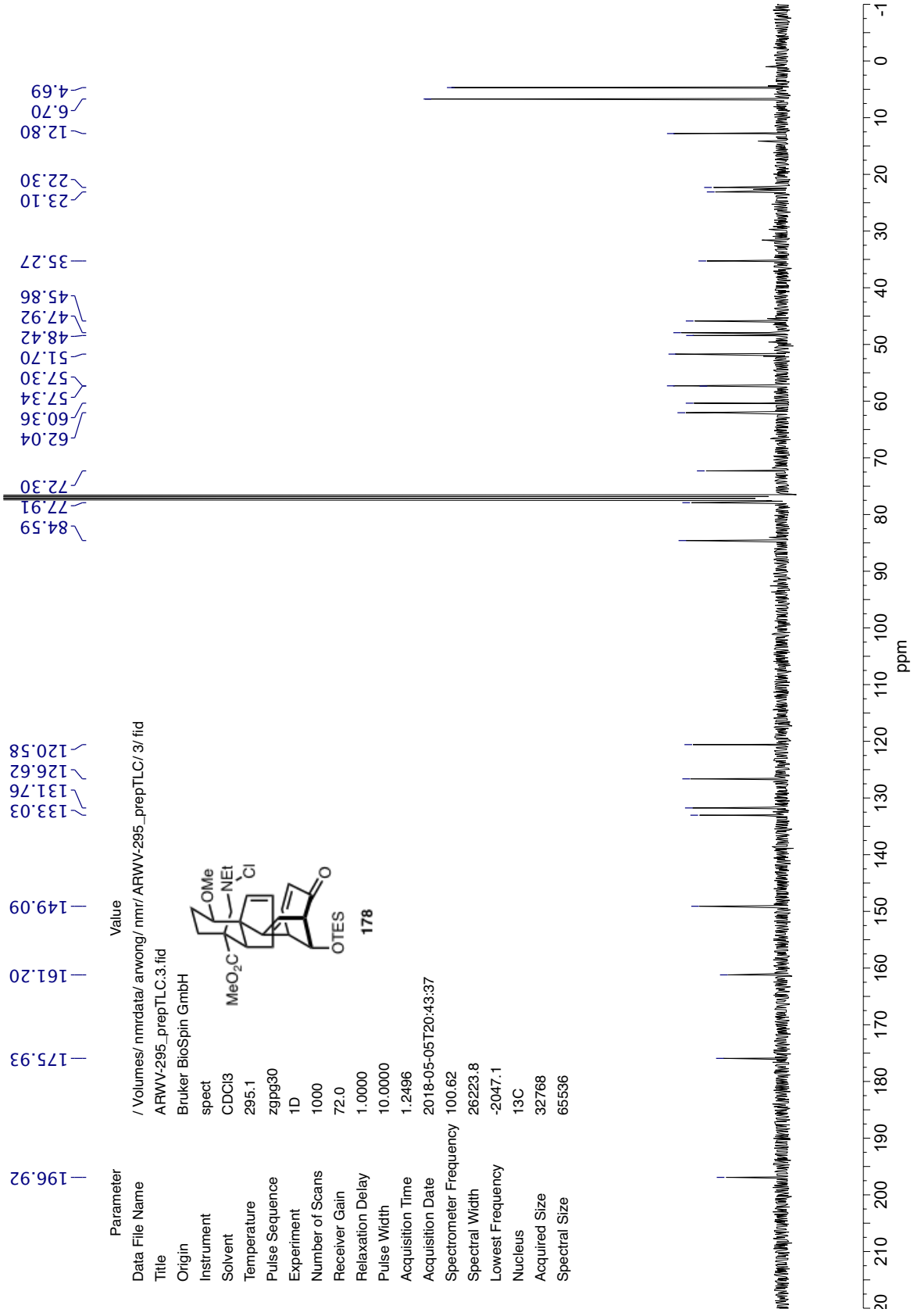

Parameter
Value
Data File Name
/ Volumes/ nmrdata-2/ arwong/ nmr/ ARWV-267_flashed/ 1/ fid
Title
ARWV-267_flashed.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.2
Pulse Sequence
zg30
Experiment
1D
Number of Scans
32
Receiver Gain
127.1
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2018-04-17T03:48:29
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.2
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
OMe
NHEt
MeO2C
O
Si
O
t-Bu
t-Bu
176
6.05
5.89
5.64
5.46
5.27
4.41
4.21
3.58
3.54
3.23
2.97
2.77
2.56
2.43
2.31
1.84
1.48
1.07
1.01
1.01
1.04
1.01
0.97
2.98
1.00
3.09
1.01
3.00
3.06
1.05
2.05
3.29
9.06
12.11
0.97
1.03
ppm

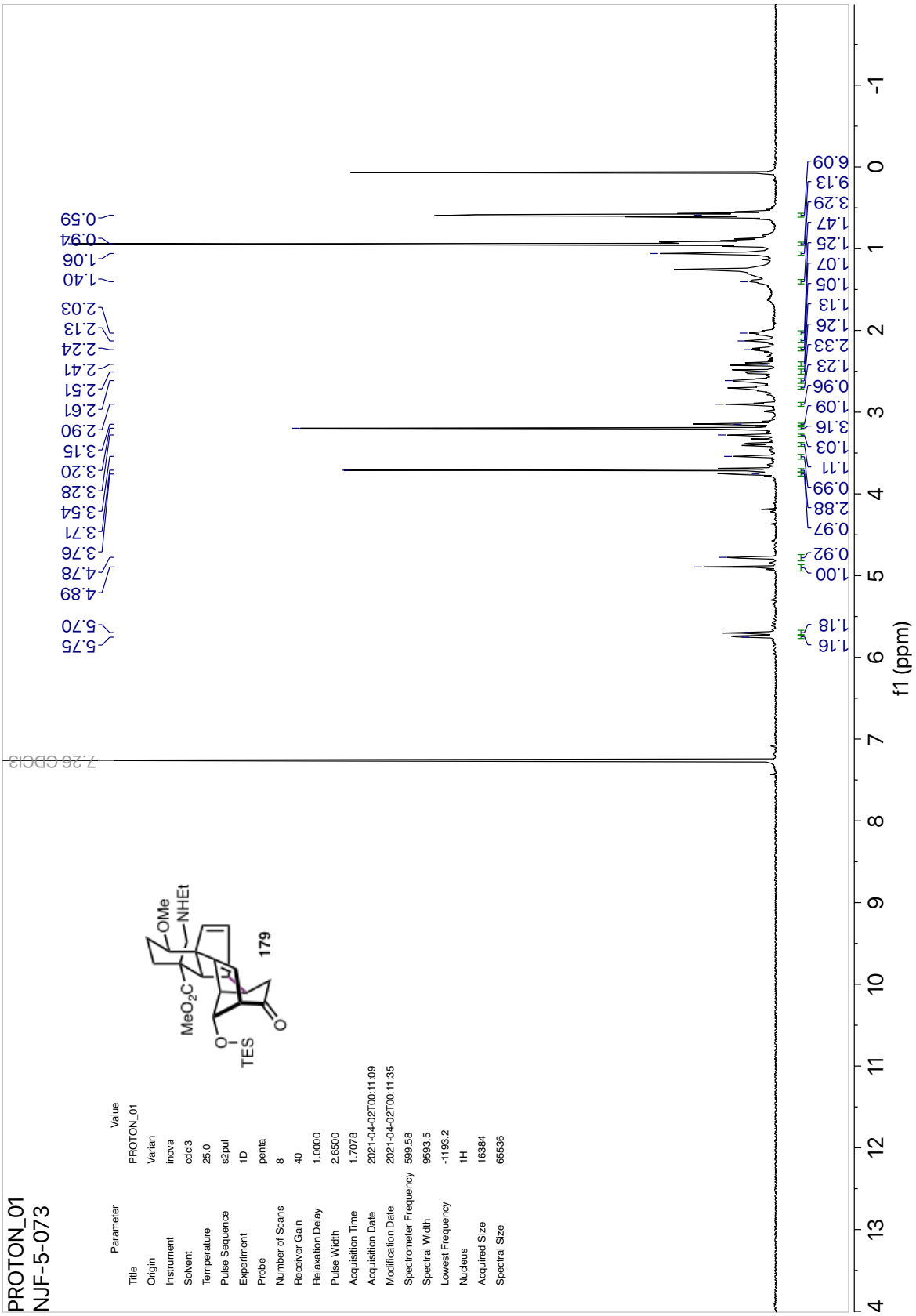

Parameter Value
Data File Name / Volumes/ nmrdata-2/ arwong/ nmr/ ARWV-267_flashed/ 6/ fid
Title ARWV-267_flashed.6.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 1024
Receiver Gain 78.7
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.2496
Acquisition Date 2018-04-17T06:16:34
Spectrometer Frequency 100.62
Spectral Width 26223.8
Lowest Frequency -2047.2
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
MeO2C
OMe
NHEt
O
Si
t-Bu
t-Bu
176
176.94
164.65
135.60
133.35
131.08
128.19
119.81
77.69
76.74
66.56
58.67
57.67
57.07
51.53
47.90
46.22
46.13
46.02
44.50
35.42
28.89
28.28
23.71
21.83
21.23
20.65
15.14
ppm

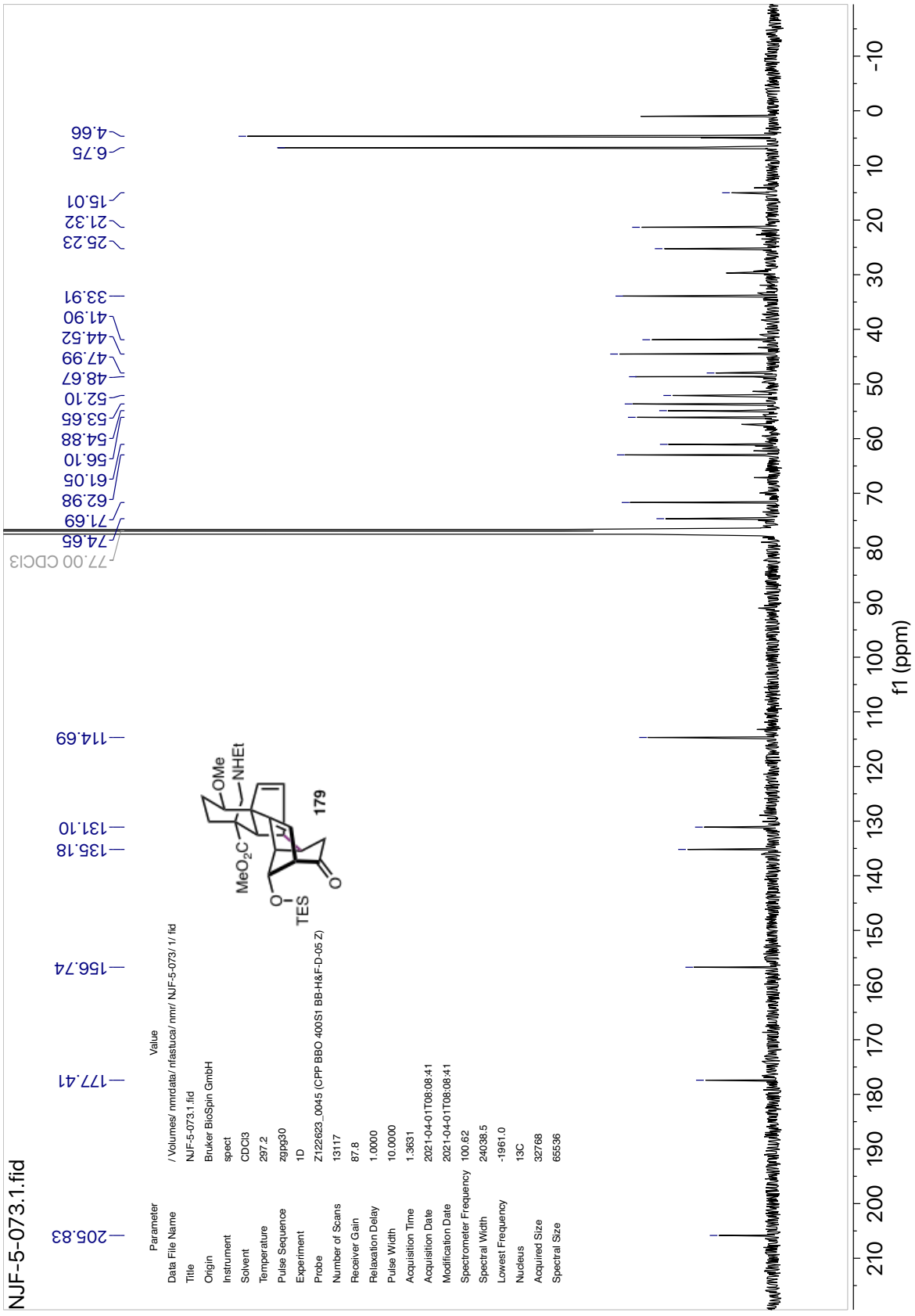

Parameter
Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWV-294_prepTLC_redo/ 1/ fid
Title ARWV-294_prepTLC_redo.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.2
Pulse Sequence zg30
Experiment 1D
Number of Scans 64
Receiver Gain 197.4
Relaxation Delay 1.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Acquisition Date 2018-05-07T15:09:23
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.7
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
OMe
NHEt
MeO2C
OTES
177
ppm

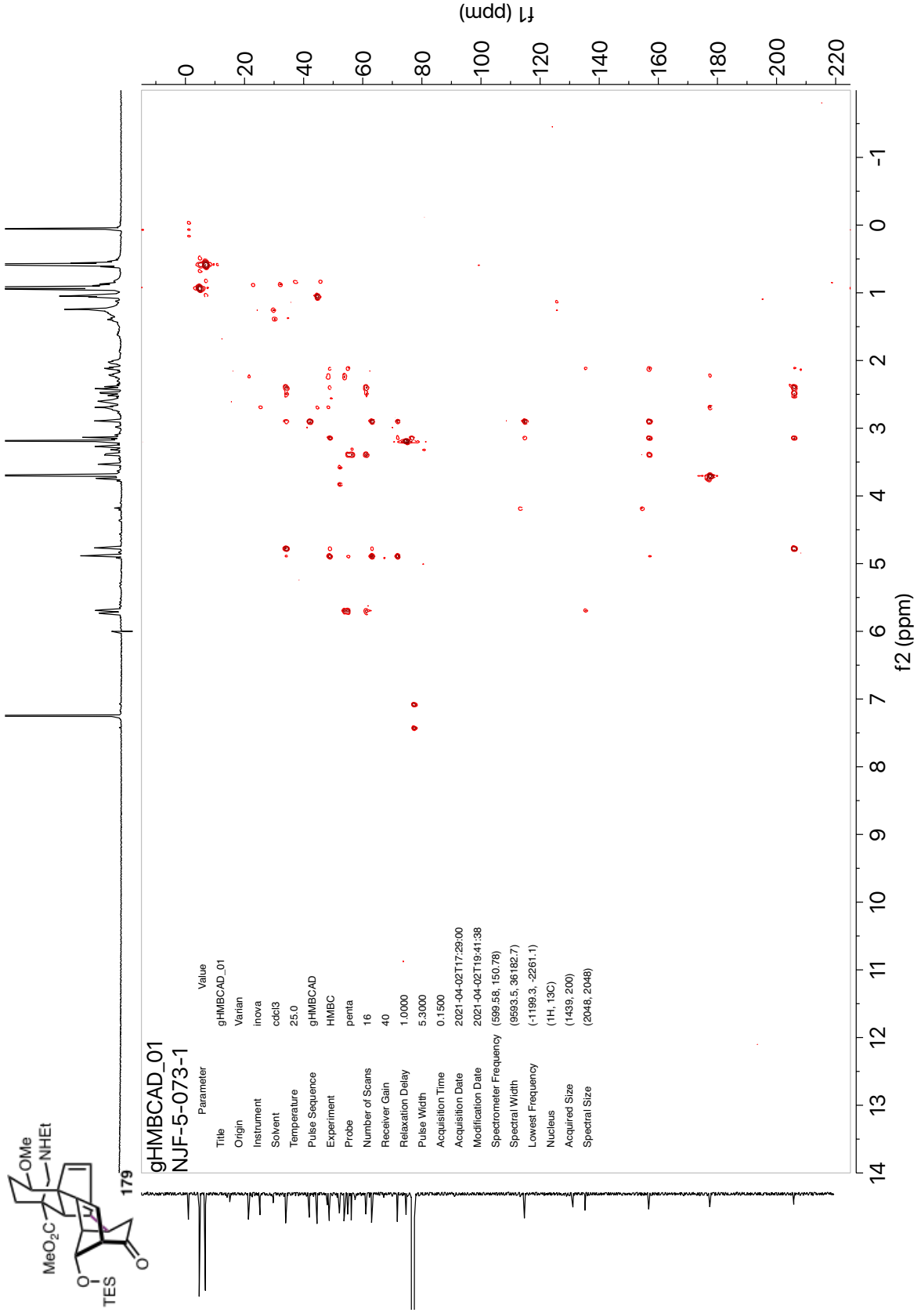

4.68
6.71
15.14
22.51
22.92
34.91
44.54
45.59
47.91
48.16
51.71
57.16
57.37
58.52
62.07
78.18
84.60
120.60
126.60
132.24
132.77
149.16
161.39
176.83
196.96
OMe
NHEt
MeO2C
OTES
O
177
Parameter
Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWV-294_prepTLC/ 4/ fid
Title ARWV-294_prepTLC.4.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 850
Receiver Gain 35.5
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.2496
Acquisition Date 2018-05-07T06:31:22
Spectrometer Frequency 100.62
Spectral Width 26223.8
Lowest Frequency -2046.9
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
ppm

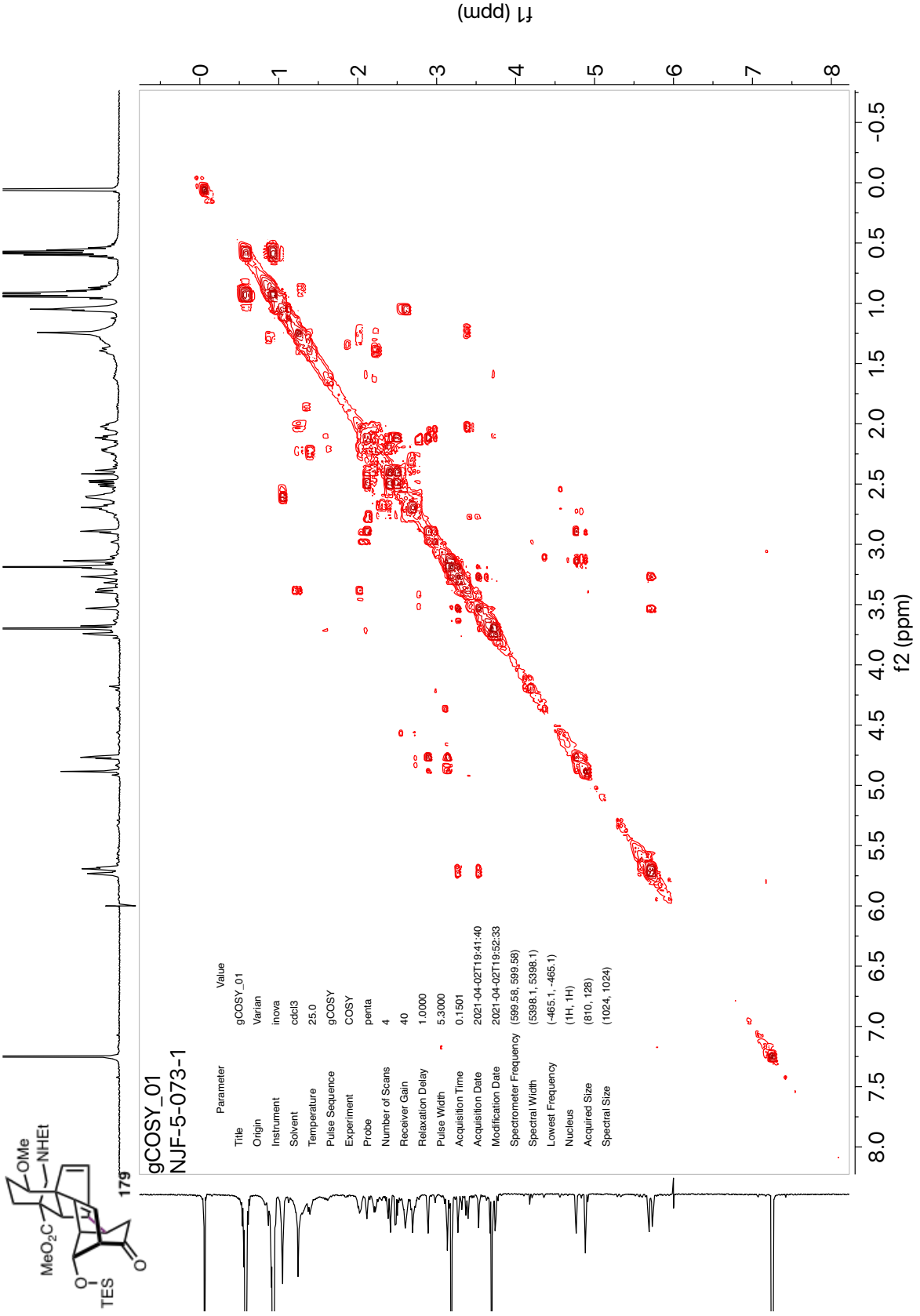

Parameter
Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWV-295_prepTLC/ 1/ fid
Title
ARWV-295_prepTLC.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zg30
Experiment
1D
Number of Scans
32
Receiver Gain
197.4
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2018-05-05T19:42:25
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.3
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
OMe
NEt
Cl
MeO2C
OTES
O
178
6.93
5.94
5.76
5.51
5.37
4.68
3.60
3.49
3.28
3.19
3.07
2.93
2.36
1.80
1.70
1.58
1.16
0.93
0.58
1.15
1.13
1.11
0.95
1.10
1.00
2.92
1.06
1.06
3.29
3.37
3.13
3.20
1.03
1.16
3.56
3.14
9.33
6.22
ppm

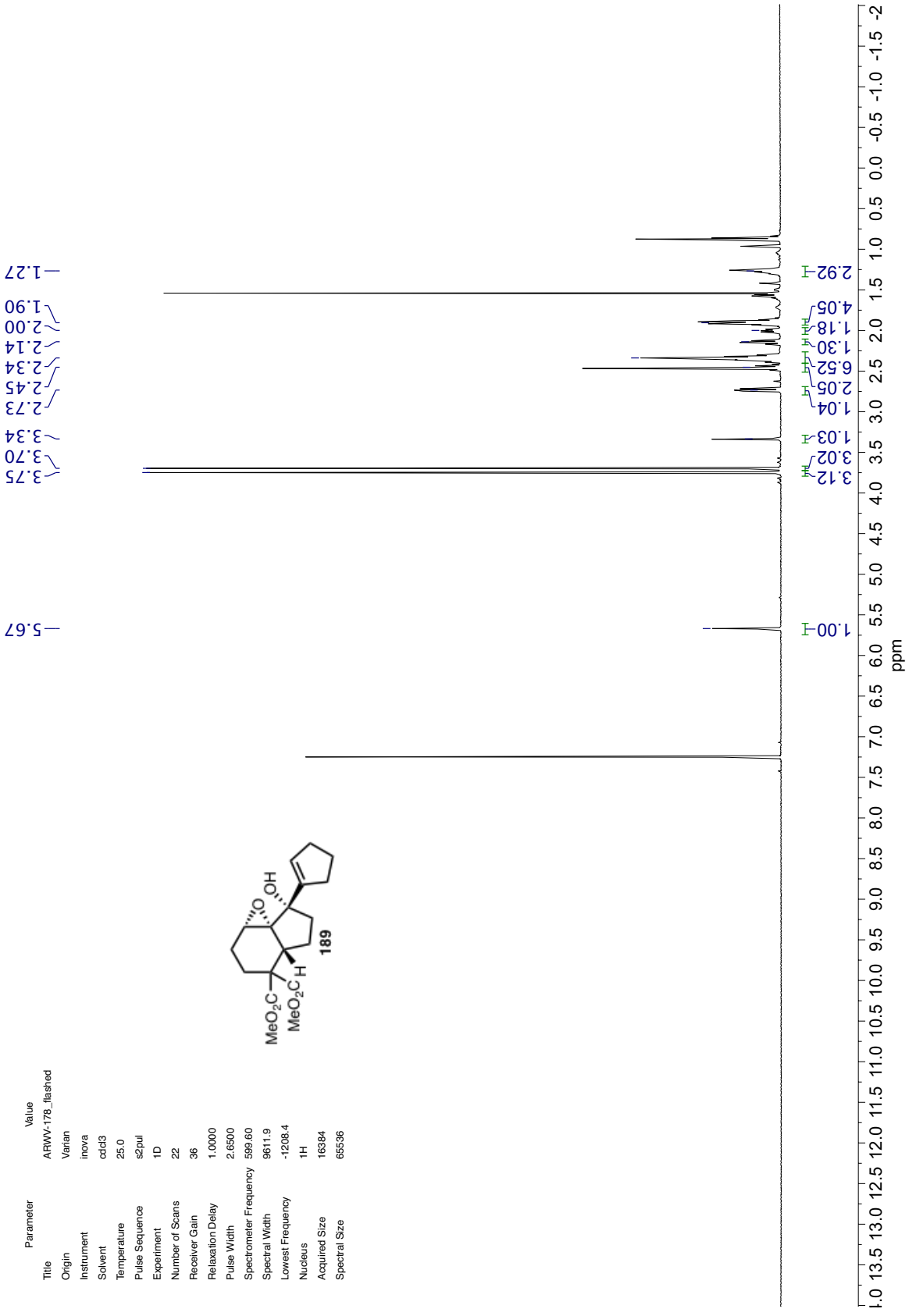

4.69
6.70
12.80
22.30
23.10
35.27
45.86
47.92
48.42
51.70
57.30
57.34
60.36
62.04
72.30
77.91
84.59
120.58
126.62
131.76
133.03
149.09
161.20
175.93
196.92
OMe
NEt
Cl
MeO2C
OTES
O
178
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWV-295_prepTLC/ 3/ fid
Title
ARWV-295_prepTLC.3.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zgpg30
Experiment
1D
Number of Scans
1000
Receiver Gain
72.0
Relaxation Delay
1.0000
Pulse Width
10.0000
Acquisition Time
1.2496
Acquisition Date
2018-05-05T20:43:37
Spectrometer Frequency
100.62
Spectral Width
26223.8
Lowest Frequency
-2047.1
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
ppm

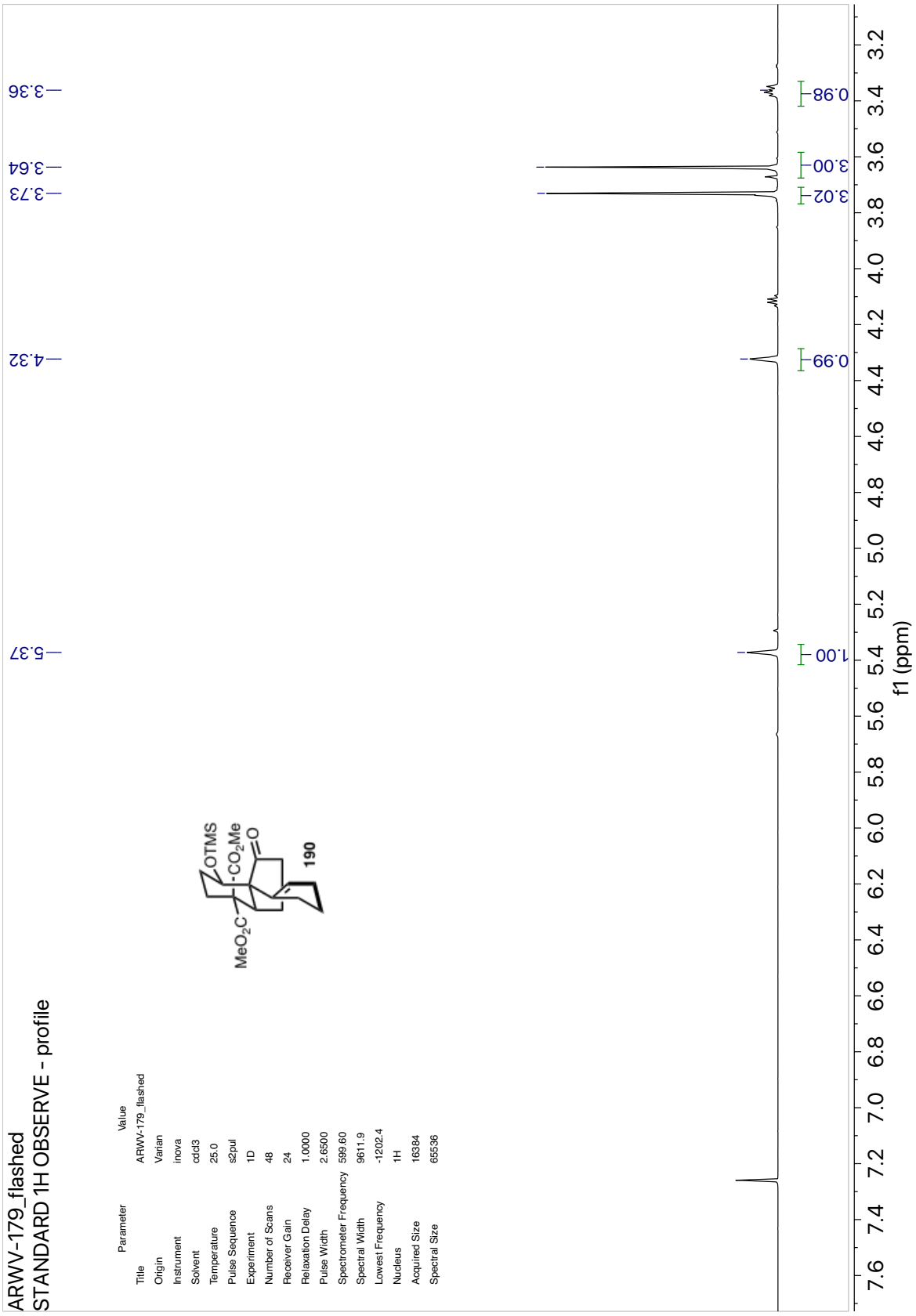

PROTON_01
NJF-5-073
Parameter Value
Title PROTON_01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe penta
Number of Scans 8
Receiver Gain 40
Relaxation Delay 1.0000
Pulse Width 2.6500
Acquisition Time 1.7078
Acquisition Date 2021-04-02T00:11:09
Modification Date 2021-04-02T00:11:35
Spectrometer Frequency 599.58
Spectral Width 9593.5
Lowest Frequency -1193.2
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
OMe
NHEt
MeO2C
O
TES
O
179
7.26 CDCl3
5.75
5.70
4.89
4.78
3.76
3.71
3.54
3.28
3.20
3.15
2.90
2.61
2.51
2.41
2.24
2.13
2.03
1.40
1.06
0.94
0.59
6.09
9.13
3.29
1.47
1.25
1.07
1.05
1.13
1.26
2.33
1.23
0.96
1.09
3.16
1.03
1.11
0.99
2.88
0.97
0.92
1.00
1.18
1.16
f1 (ppm)

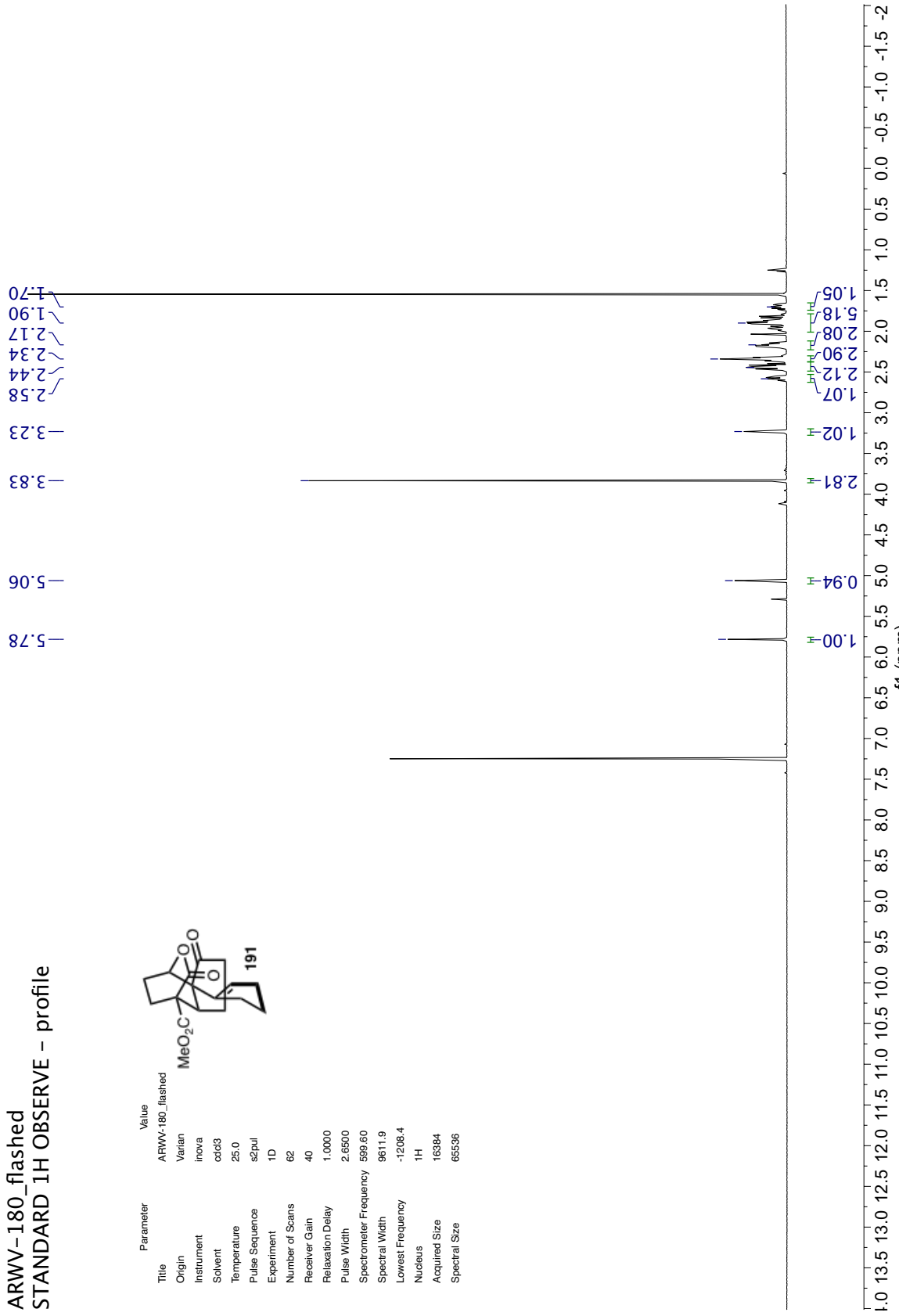

NJF-5-073.1.fid
205.83
177.41
156.74
135.18
131.10
114.69
77.00 CDCl3
74.65
71.69
62.98
61.05
56.10
54.88
53.65
52.10
48.67
47.99
44.52
41.90
33.91
25.23
21.32
15.01
6.75
4.66
OMe
NHEt
MeO2C
O
TES
O
179
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-073/ 1/ fid
Title NJF-5-073.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence zgpg30
Experiment 1D
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 13117
Receiver Gain 87.8
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2021-04-01T08:08:41
Modification Date 2021-04-01T08:08:41
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1961.0
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

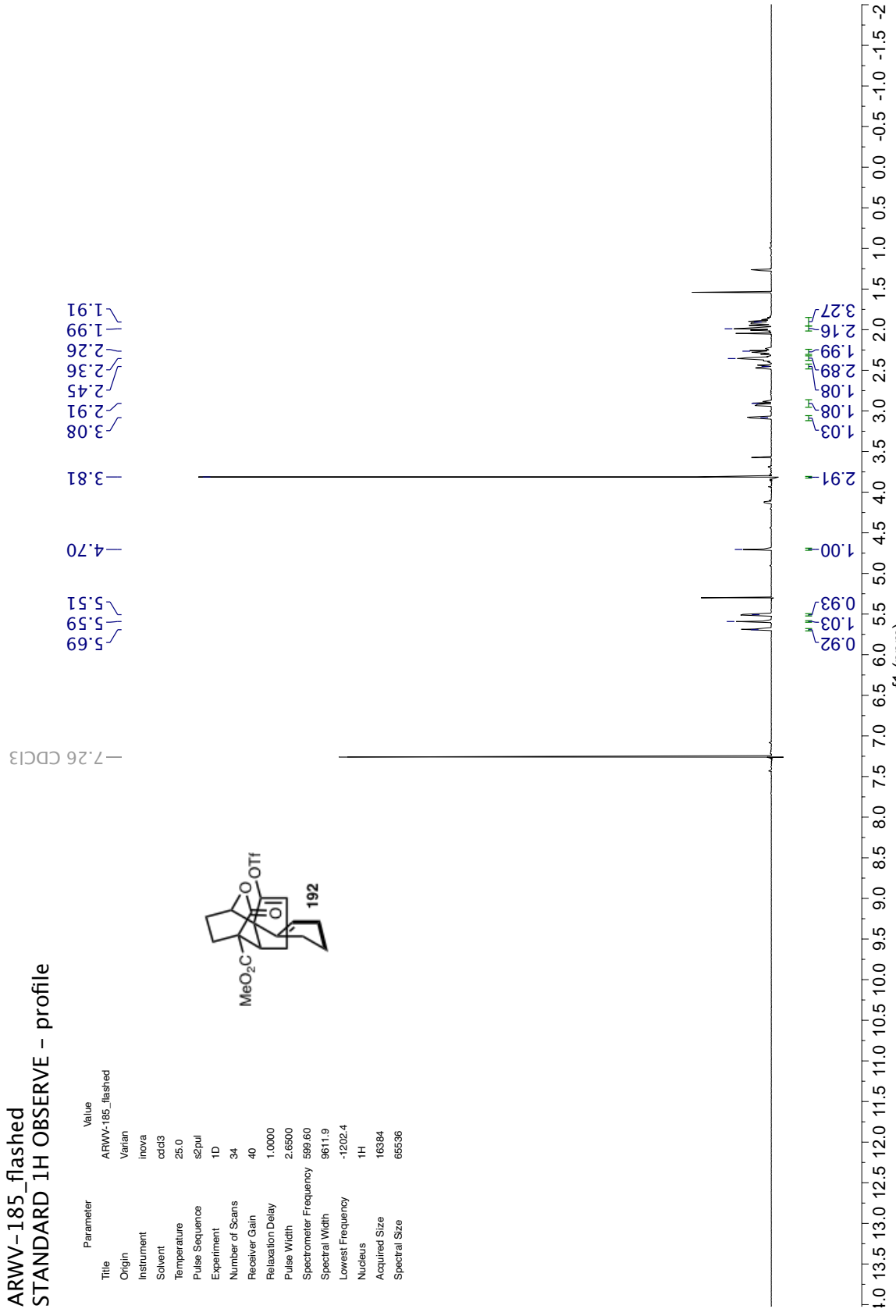

gHMBCAD_01
NJF-5-073-1
Parameter Value
Title gHMBCAD_01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence gHMBCAD
Experiment HMBC
Probe penta
Number of Scans 16
Receiver Gain 40
Relaxation Delay 1.0000
Pulse Width 5.3000
Acquisition Time 0.1500
Acquisition Date 2021-04-02T17:29:00
Modification Date 2021-04-02T19:41:38
Spectrometer Frequency (599.58, 150.78)
Spectral Width (9593.5, 36182.7)
Lowest Frequency (-1199.3, -2261.1)
Nucleus (1H, 13C)
Acquired Size (1439, 200)
Spectral Size (2048, 2048)
179
OMe
NHEt
MeO2C
TES
f1 (ppm)
f2 (ppm)

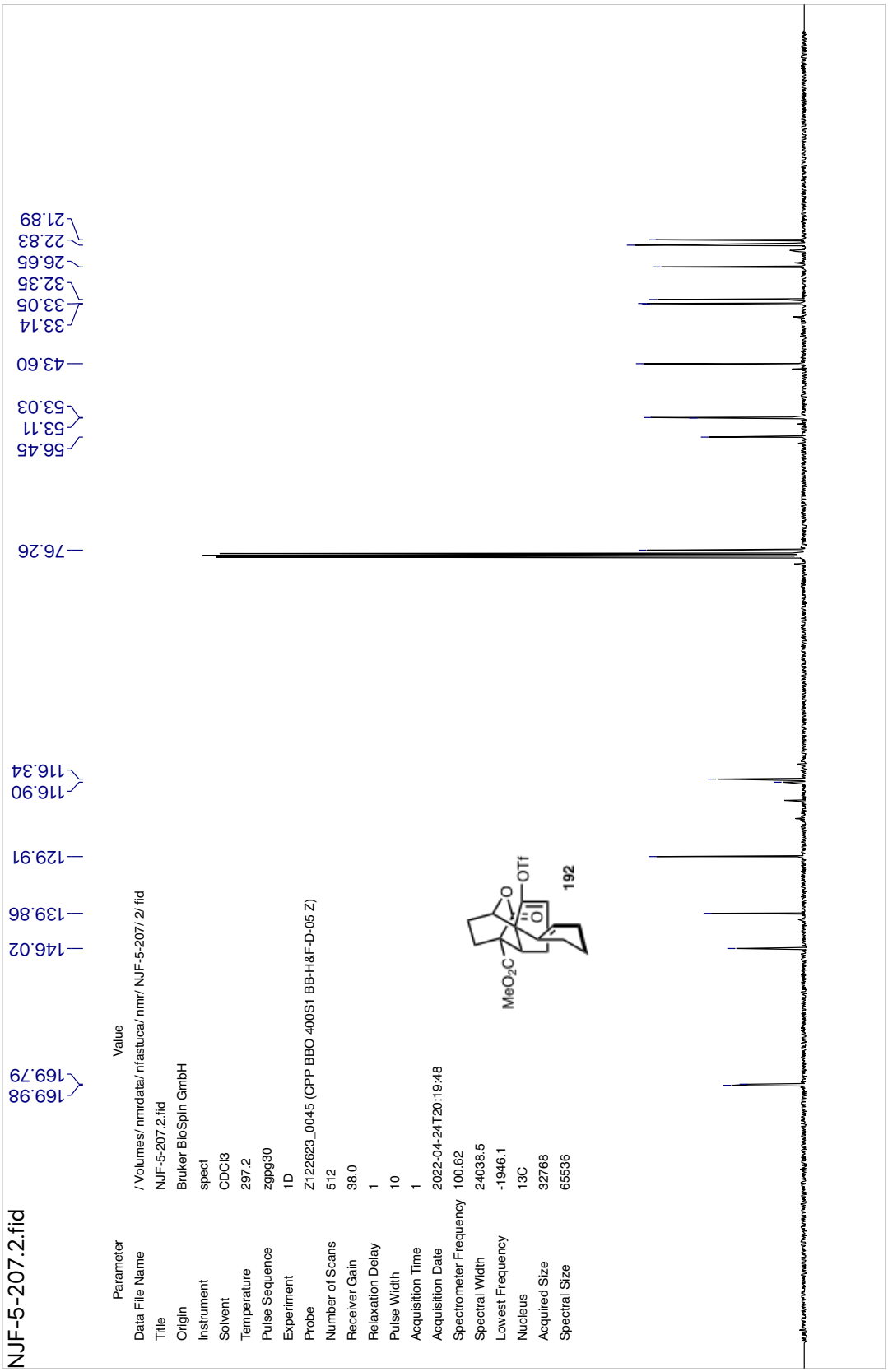

gCOSY_01
NJF-5-073-1
Parameter Value
Title gCOSY_01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence gCOSY
Experiment COSY
Probe penta
Number of Scans 4
Receiver Gain 40
Relaxation Delay 1.0000
Pulse Width 5.3000
Acquisition Time 0.1501
Acquisition Date 2021-04-02T19:41:40
Modification Date 2021-04-02T19:52:33
Spectrometer Frequency (599.58, 599.58)
Spectral Width (5398.1, 5398.1)
Lowest Frequency (-465.1, -465.1)
Nucleus (1H, 1H)
Acquired Size (810, 128)
Spectral Size (1024, 1024)
179
OMe
NHEt
MeO2C
TES
O
f1 (ppm)
f2 (ppm)

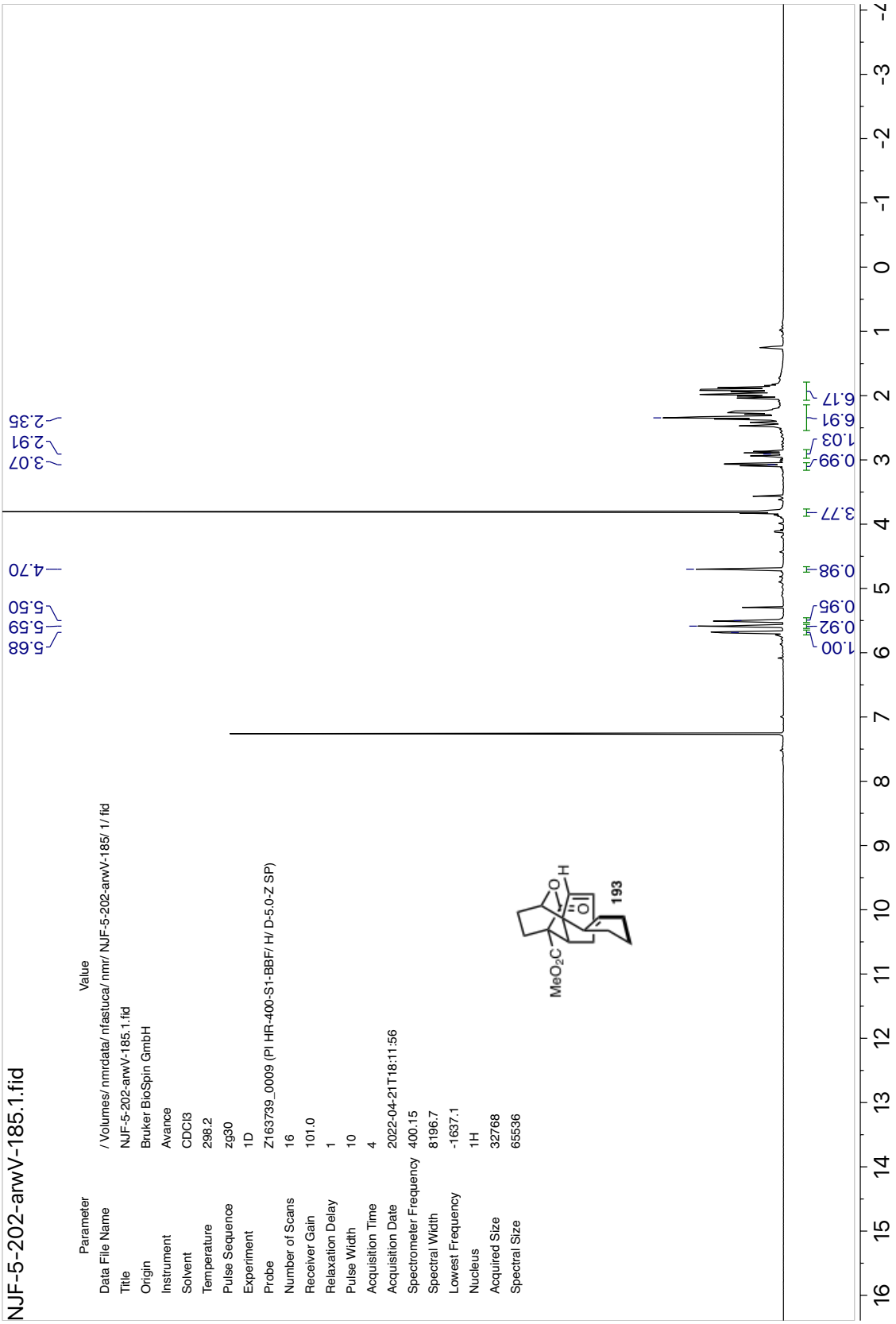

Parameter Value
Title ARWV-178_flashed
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 22
Receiver Gain 36
Relaxation Delay 1.0000
Pulse Width 2.6500
Spectrometer Frequency 599.60
Spectral Width 9611.9
Lowest Frequency -1208.4
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
MeO2C
MeO2C
HO
189
5.67
3.75
3.70
3.34
2.73
2.45
2.34
2.14
2.00
1.90
1.27
1.00
3.12
3.02
1.03
1.04
2.05
6.52
1.30
1.18
4.05
2.92
ppm

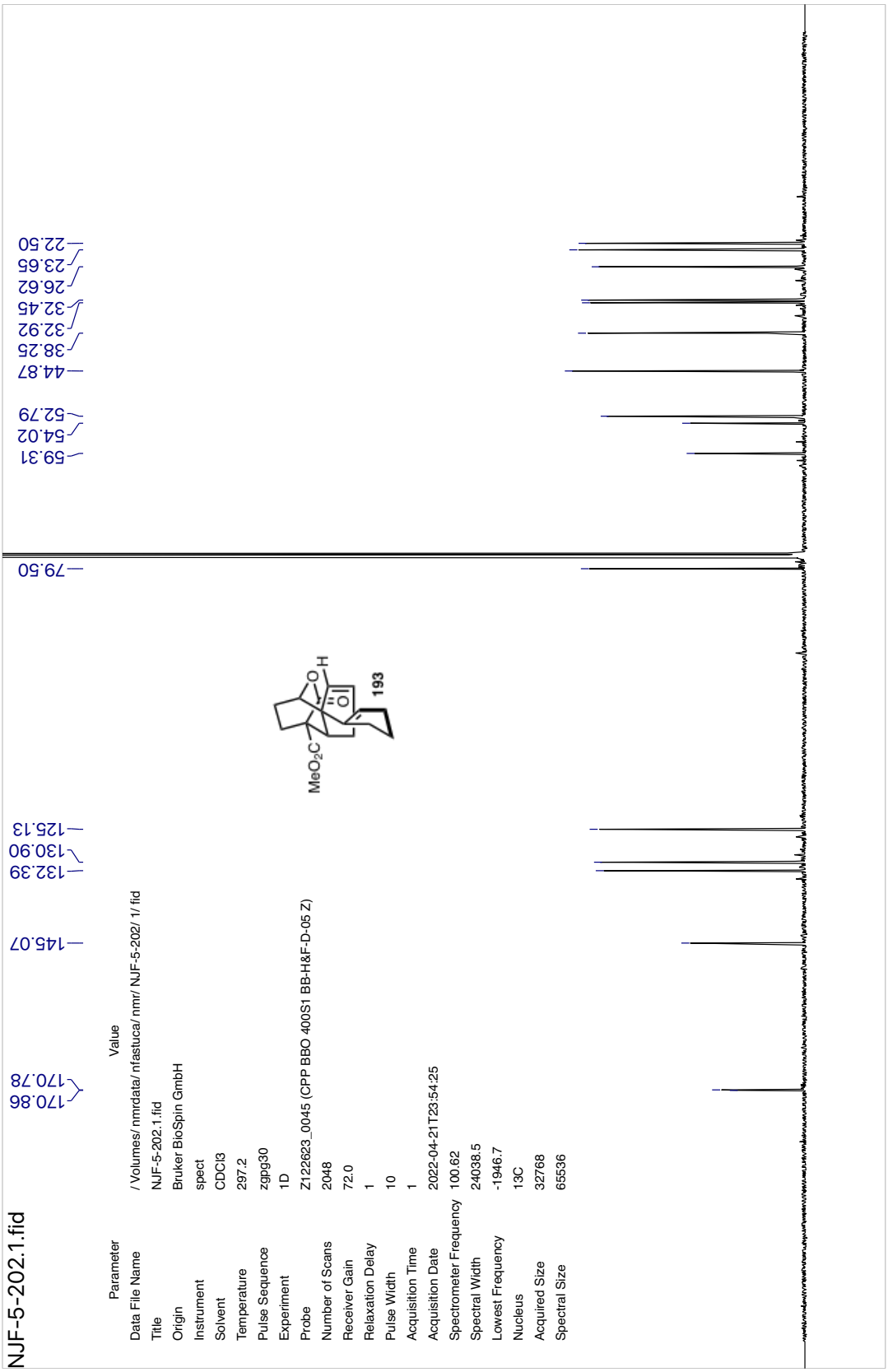

ARWV-179_flashed
STANDARD 1H OBSERVE - profile
Parameter Value
Title ARWV-179_flashed
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 48
Receiver Gain 24
Relaxation Delay 1.0000
Pulse Width 2.6500
Spectrometer Frequency 599.60
Spectral Width 9611.9
Lowest Frequency -1202.4
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
OTMS
-CO2Me
O
MeO2C
190
5.37
4.32
3.73
3.64
3.36
1.00
0.99
3.02
3.00
0.98
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2
f1 (ppm)

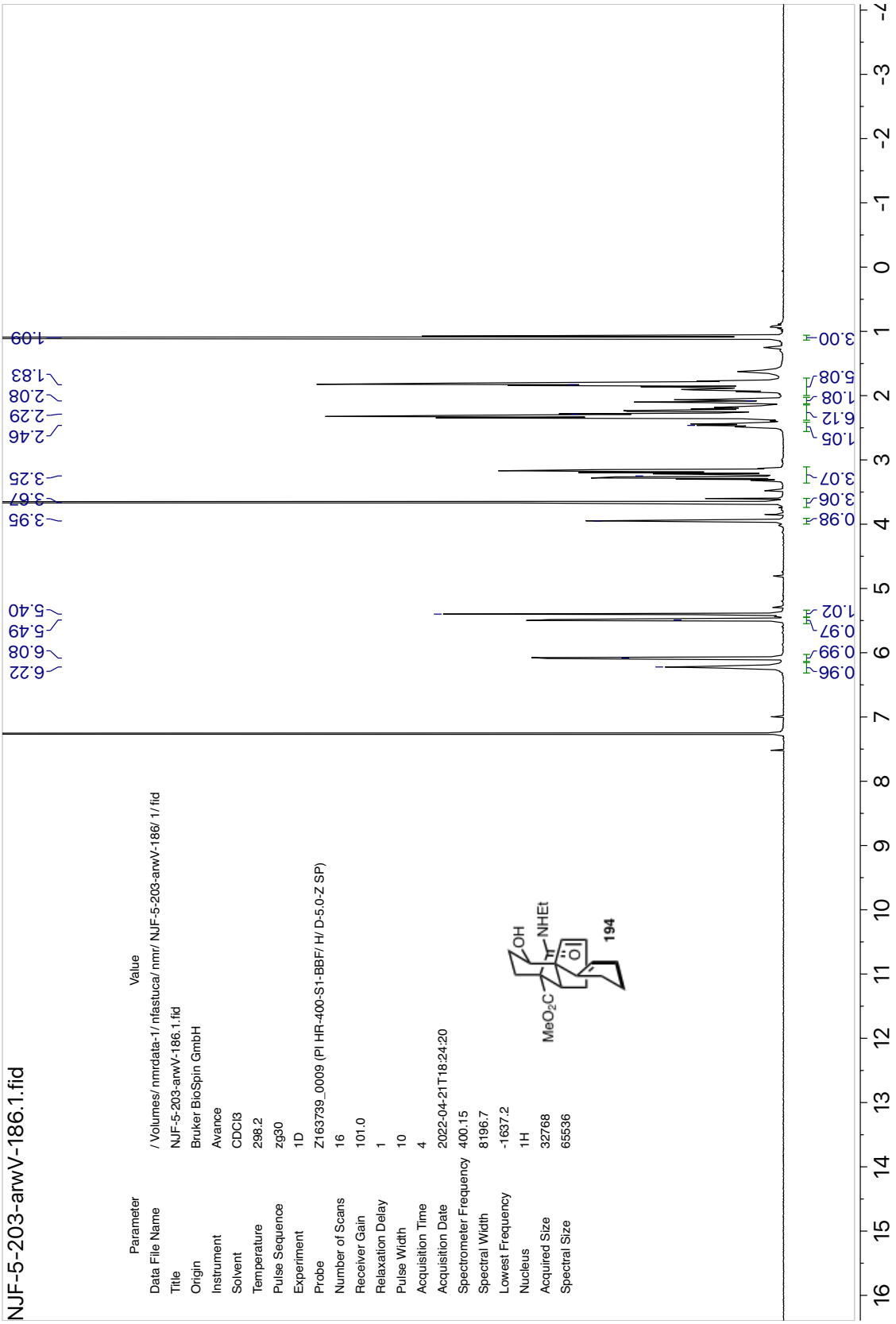

ARWV-180_flashed
STANDARD 1H OBSERVE - profile
Parameter Value
Title ARWV-180_flashed
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 62
Receiver Gain 40
Relaxation Delay 1.0000
Pulse Width 2.6500
Spectrometer Frequency 599.60
Spectral Width 9611.9
Lowest Frequency -1208.4
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
MeO2C
191
7.70
7.58
7.44
7.34
7.17
7.00
6.83
6.23
5.78
5.06
1.07
2.12
2.90
2.08
5.18
1.05
1.02
2.81
0.94
1.00
f1 (ppm)

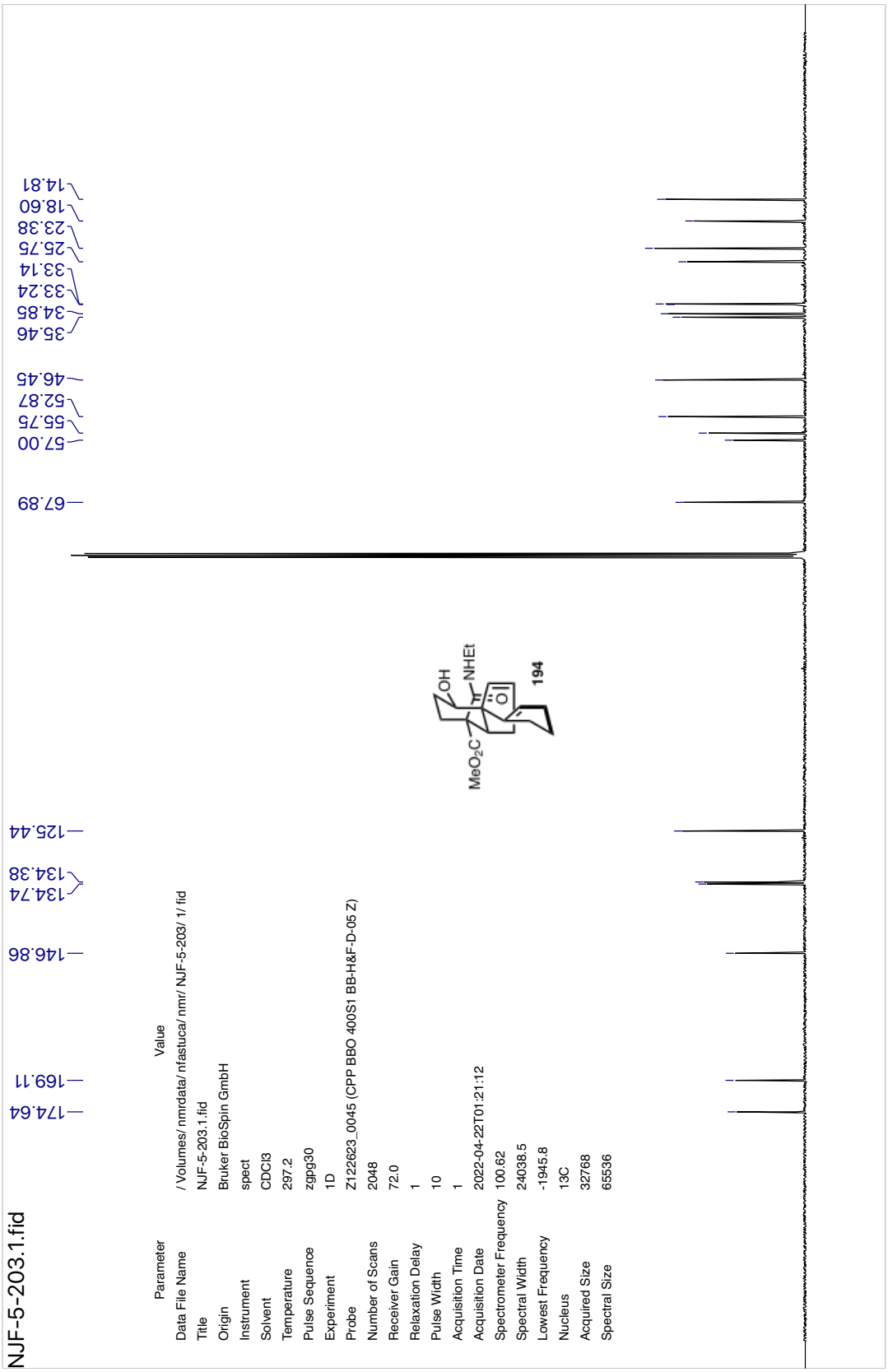

ARWV-185_flashed
STANDARD 1H OBSERVE - profile
Parameter Value
Title ARWV-185_flashed
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 34
Receiver Gain 40
Relaxation Delay 1.0000
Pulse Width 2.6500
Spectrometer Frequency 599.60
Spectral Width 9611.9
Lowest Frequency -1202.4
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
MeO2C
OTf
192
7.26 CDCl3
5.69
5.59
5.51
4.70
3.81
3.08
2.91
2.45
2.36
2.26
1.99
1.91
0.92
1.03
0.93
1.00
2.91
1.03
1.08
1.08
2.89
1.99
2.16
3.27
f1 (ppm)

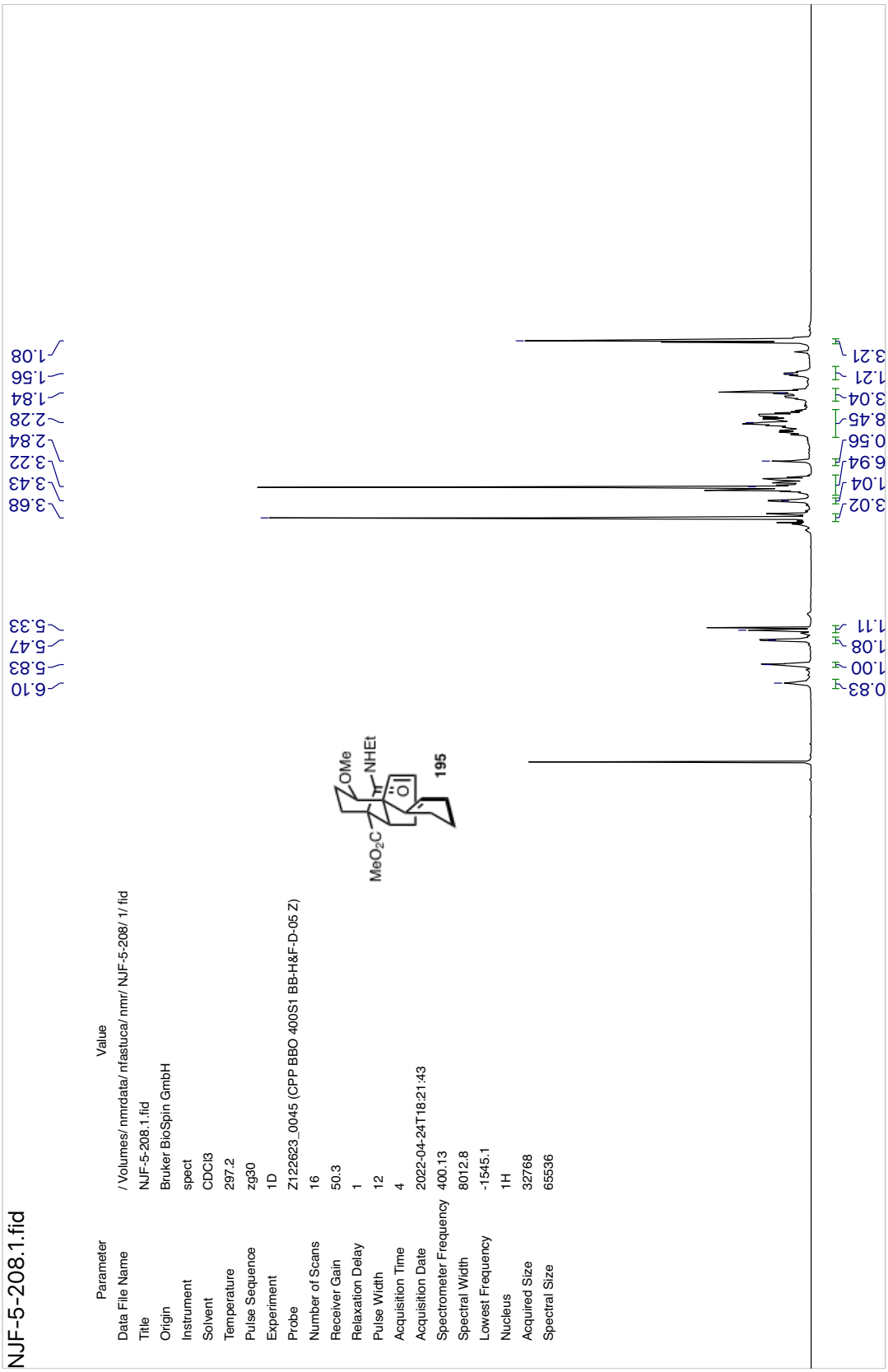

NJF-5-207.2.fid
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-207 / 2/ fid
Title
NJF-5-207.2.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
zgpg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
512
Receiver Gain
38.0
Relaxation Delay
1
Pulse Width
10
Acquisition Time
1
Acquisition Date
2022-04-24T20:19:48
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1946.1
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
169.98
169.79
146.02
139.86
129.91
116.90
116.34
76.26
56.45
53.11
53.03
43.60
33.14
33.05
32.35
26.65
22.83
21.89
MeO2C
OTf
192
f1 (ppm)

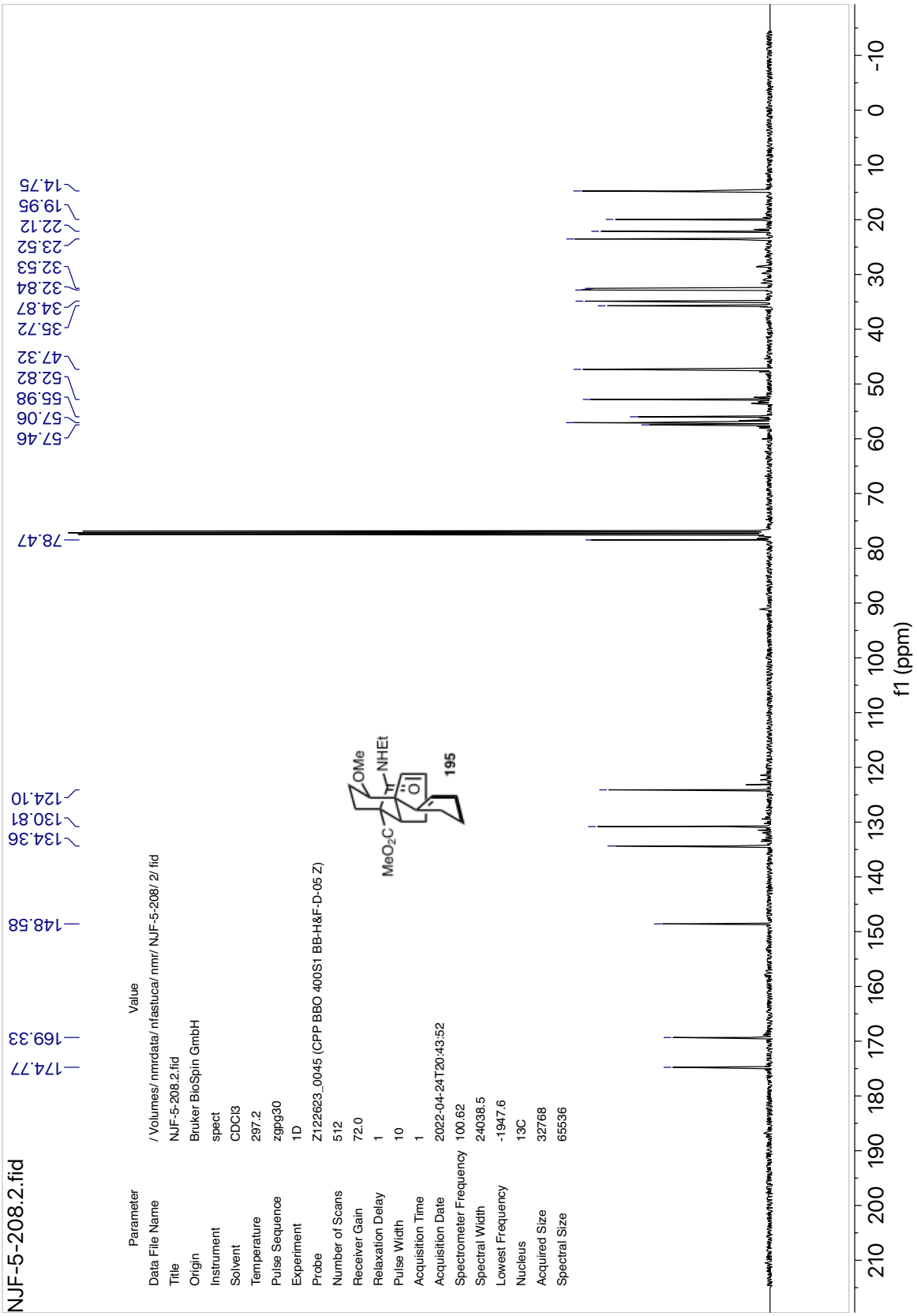

NJF-5-202-arwV-185.1.fid
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-202-arwV-185/ 1/ fid
Title
NJF-5-202-arwV-185.1.fid
Origin
Bruker BioSpin GmbH
Instrument
Avance
Solvent
CDCl3
Temperature
298.2
Pulse Sequence
zg30
Experiment
1D
Probe
Z163739_0009 (PI HR-400-S1-BBF/ H/ D-5.0-Z SP)
Number of Scans
16
Receiver Gain
101.0
Relaxation Delay
1
Pulse Width
10
Acquisition Time
4
Acquisition Date
2022-04-21T18:11:56
Spectrometer Frequency
400.15
Spectral Width
8196.7
Lowest Frequency
-1637.1
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
MeO2C
193
5.68
5.59
5.50
4.70
3.07
2.91
2.35
1.00
0.92
0.95
0.98
3.77
0.99
1.03
6.91
6.17
f1 (ppm)

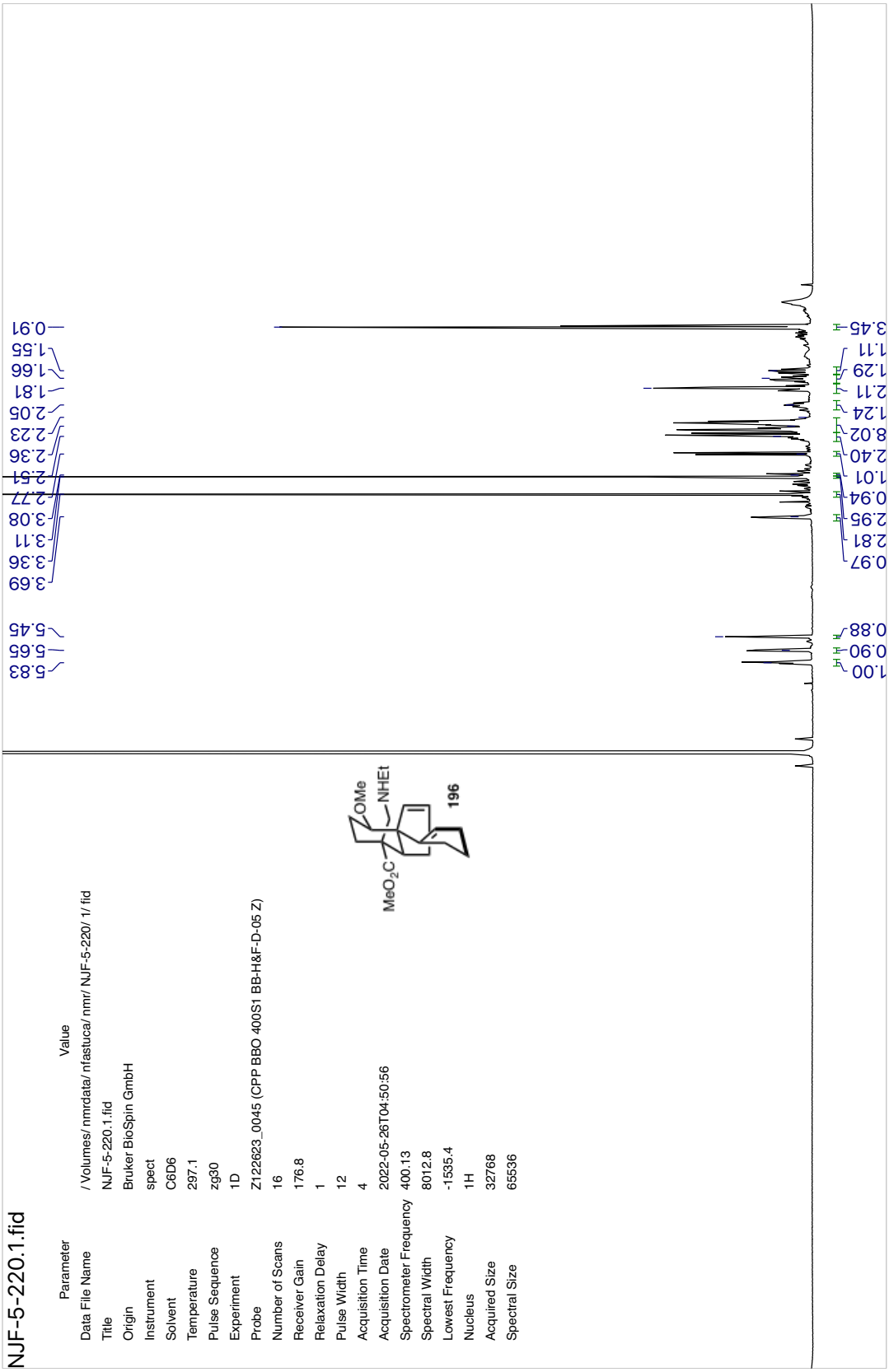

NJF-5-202.1.fid
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-202/ 1/ fid
Title
NJF-5-202.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
zgpg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
2048
Receiver Gain
72.0
Relaxation Delay
1
Pulse Width
10
Acquisition Time
1
Acquisition Date
2022-04-21T23:54:25
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1946.7
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
170.86
170.78
145.07
132.39
130.90
125.13
79.50
59.31
54.02
52.79
44.87
38.25
32.92
32.45
26.62
23.65
22.50
MeO2C
193
f1 (ppm)

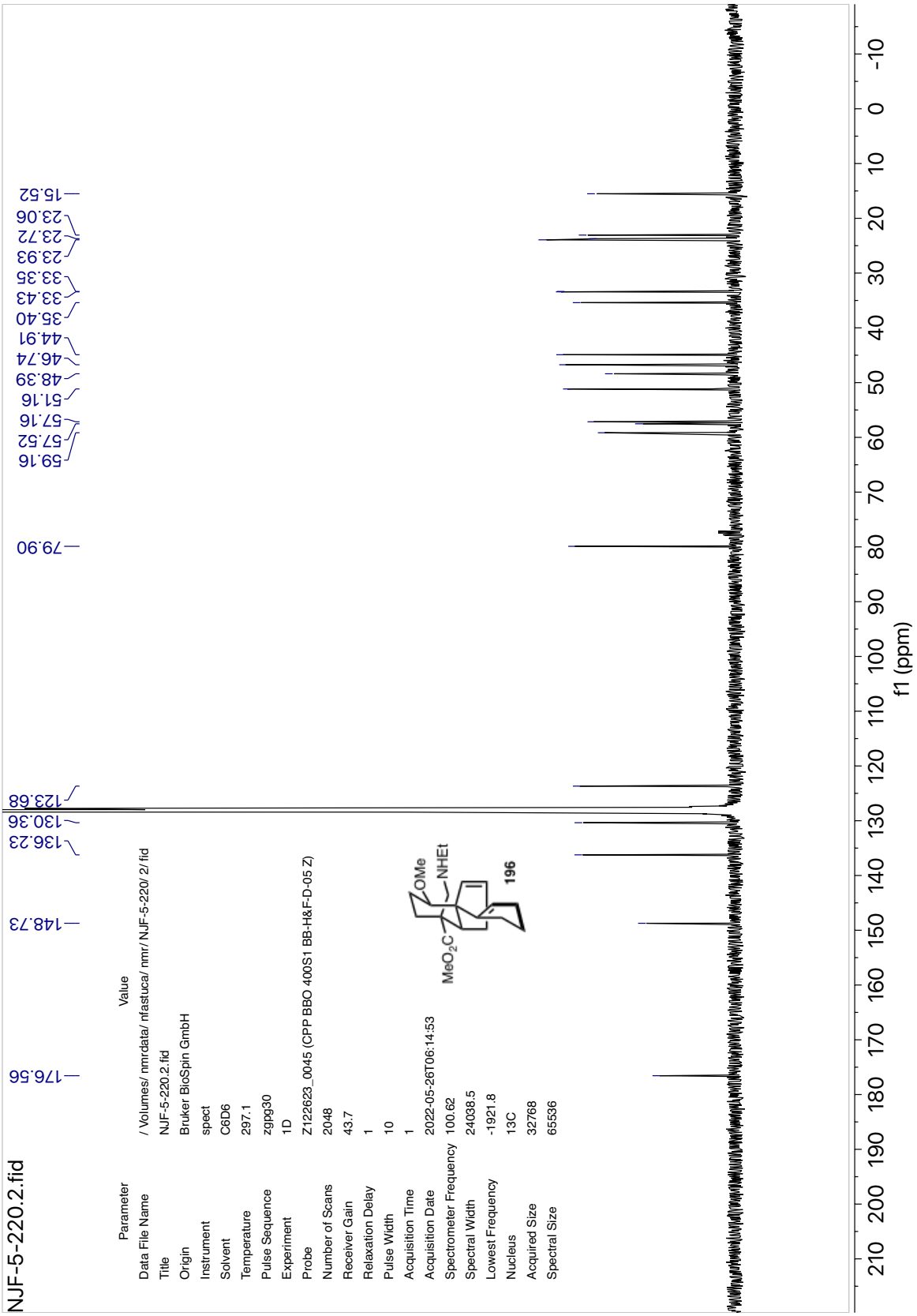

NJF-5-203-arwV-186.1.fid
Parameter
Value
Data File Name
/ Volumes/ nmrdata-1/ nfastuca/ nmr/ NJF-5-203-arwV-186/ 1/ fid
Title
NJF-5-203-arwV-186.1.fid
Origin
Bruker BioSpin GmbH
Instrument
Avance
Solvent
CDCl3
Temperature
298.2
Pulse Sequence
zg30
Experiment
1D
Probe
Z163739_0009 (PI HR-400-S1-BBF/ H/ D-5.0-Z SP)
Number of Scans
16
Receiver Gain
101.0
Relaxation Delay
1
Pulse Width
10
Acquisition Time
4
Acquisition Date
2022-04-21T18:24:20
Spectrometer Frequency
400.15
Spectral Width
8196.7
Lowest Frequency
-1637.2
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
MeO2C
OH
NHEt
194
6.22
6.08
5.49
5.40
3.95
3.67
3.25
2.46
2.29
2.08
1.83
1.09
0.96
0.99
0.97
1.02
0.98
3.06
3.07
1.05
6.12
1.08
5.08
3.00
f1 (ppm)

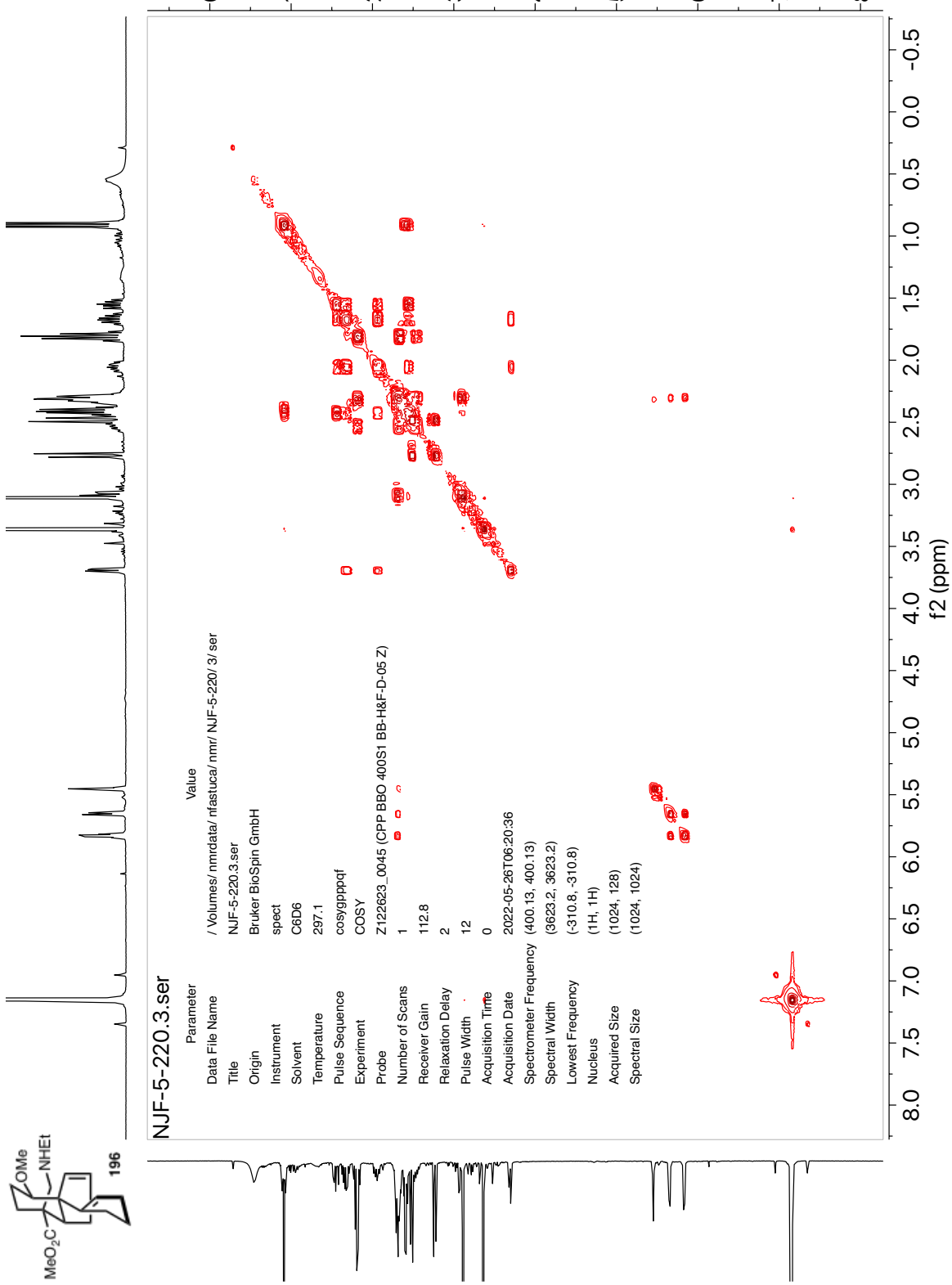

NJF-5-203.1.fid
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-203/ 1/ fid
Title NJF-5-203.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence zgpg30
Experiment 1D
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 2048
Receiver Gain 72.0
Relaxation Delay 1
Pulse Width 10
Acquisition Time 1
Acquisition Date 2022-04-22T01:21:12
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1945.8
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
174.64
169.11
146.86
134.74
134.38
125.44
67.89
57.00
55.75
52.87
46.45
35.46
34.85
33.24
33.14
25.75
23.38
18.60
14.81
MeO2C
OH
NHEt
194
f1 (ppm)

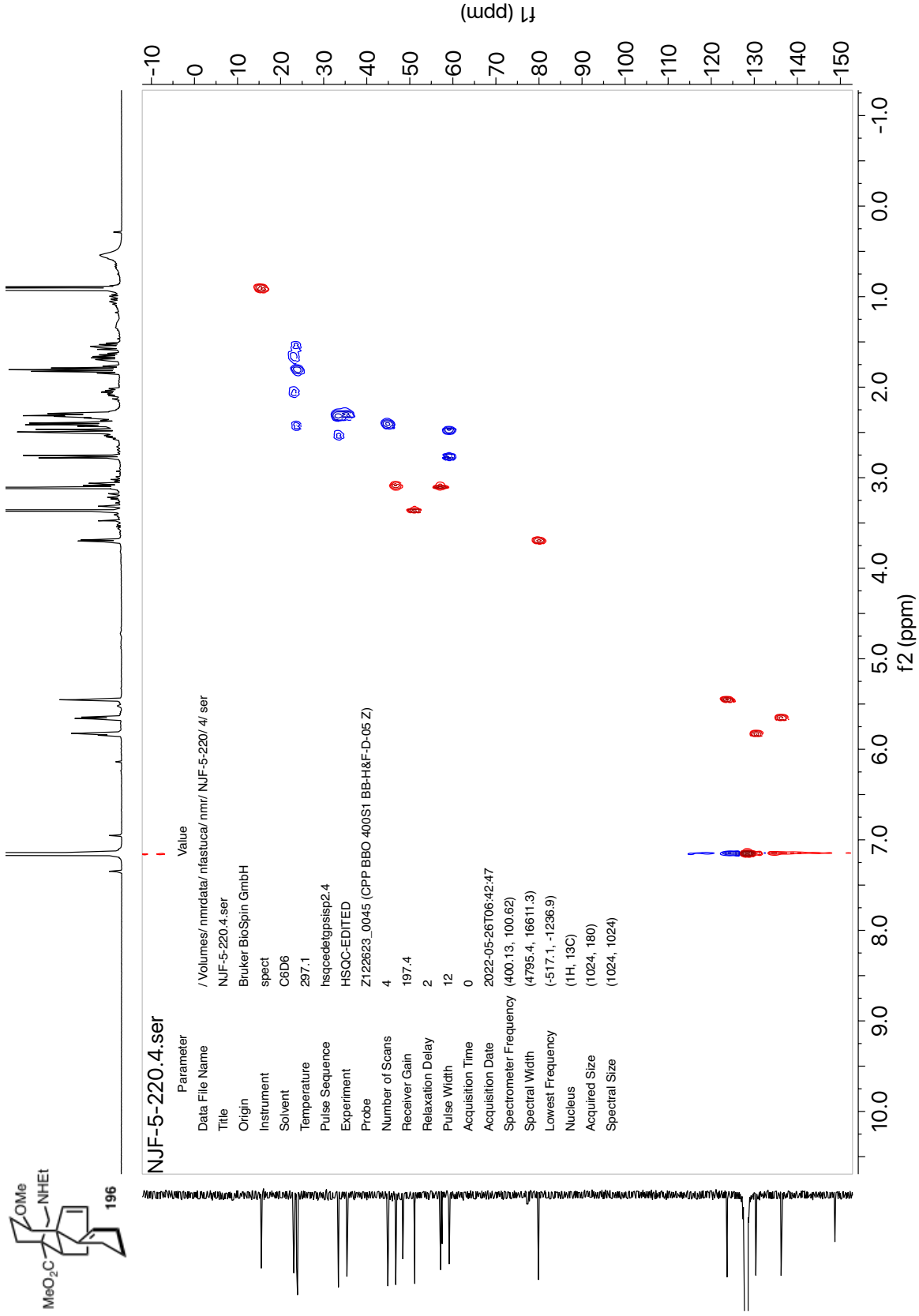

NJF-5-208.1.fid
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-208/ 1/ fid
Title
NJF-5-208.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
zg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
16
Receiver Gain
50.3
Relaxation Delay
1
Pulse Width
12
Acquisition Time
4
Acquisition Date
2022-04-24T18:21:43
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.1
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
MeO2C
OMe
NHEt
O
195
6.10
5.83
5.47
5.33
3.68
3.43
3.22
2.84
2.28
1.84
1.56
1.08
0.83
1.00
1.08
1.11
3.02
1.04
6.94
0.56
8.45
3.04
1.21
3.21
f1 (ppm)

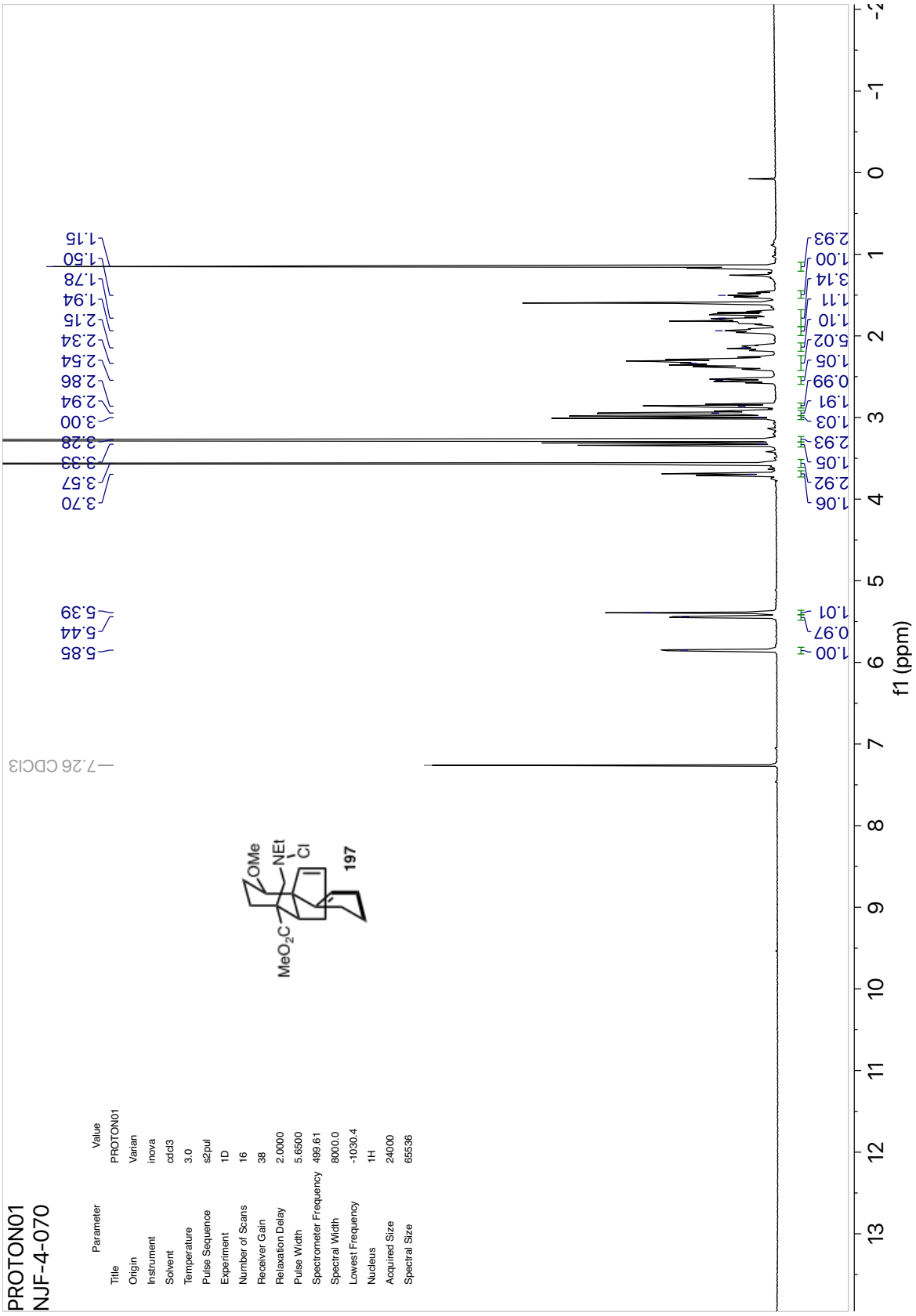

NJF-5-208.2.fid
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-208/ 2/ fid
Title NJF-5-208.2.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence zgpg30
Experiment 1D
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 512
Receiver Gain 72.0
Relaxation Delay 1
Pulse Width 10
Acquisition Time 1
Acquisition Date 2022-04-24T20:43:52
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1947.6
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
174.77
169.33
148.58
134.36
130.81
124.10
78.47
57.46
57.06
55.98
52.82
47.32
35.72
34.87
32.84
32.53
23.52
22.12
19.95
14.75
OMe
NHEt
MeO2C
195
f1 (ppm)

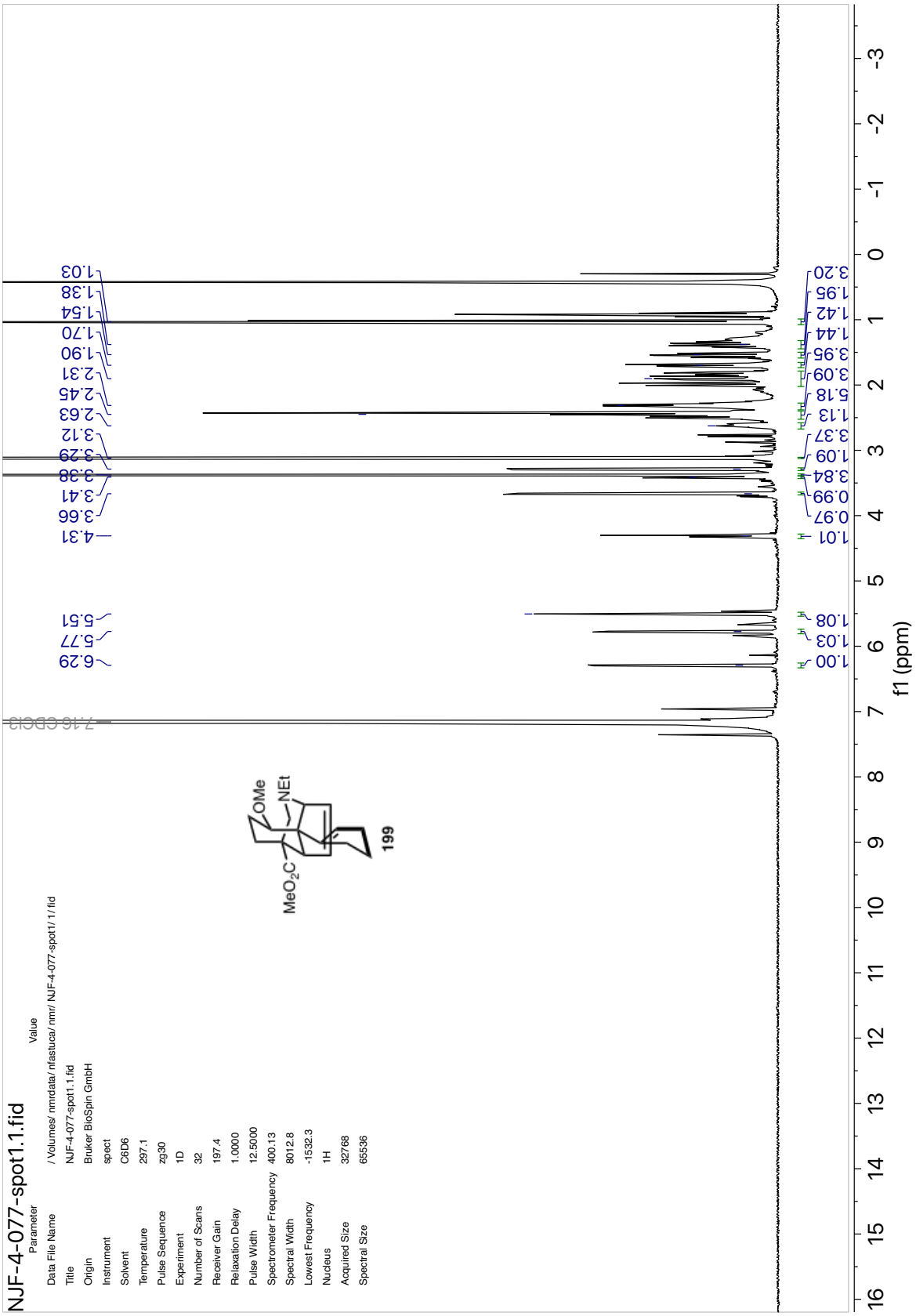

NJF-5-220.1.fid
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-220/ 1/ fid
Title
NJF-5-220.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
C6D6
Temperature
297.1
Pulse Sequence
zg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
16
Receiver Gain
176.8
Relaxation Delay
1
Pulse Width
12
Acquisition Time
4
Acquisition Date
2022-05-26T04:50:56
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1535.4
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
OMe
NHEt
MeO2C
196
5.83
5.65
5.45
3.69
3.36
3.11
3.08
2.77
2.51
2.36
2.23
2.05
1.81
1.66
1.55
0.91
3.45
1.11
1.29
2.11
1.24
8.02
2.40
1.01
0.94
2.95
2.81
0.97
1.00
0.90
0.88
f1 (ppm)

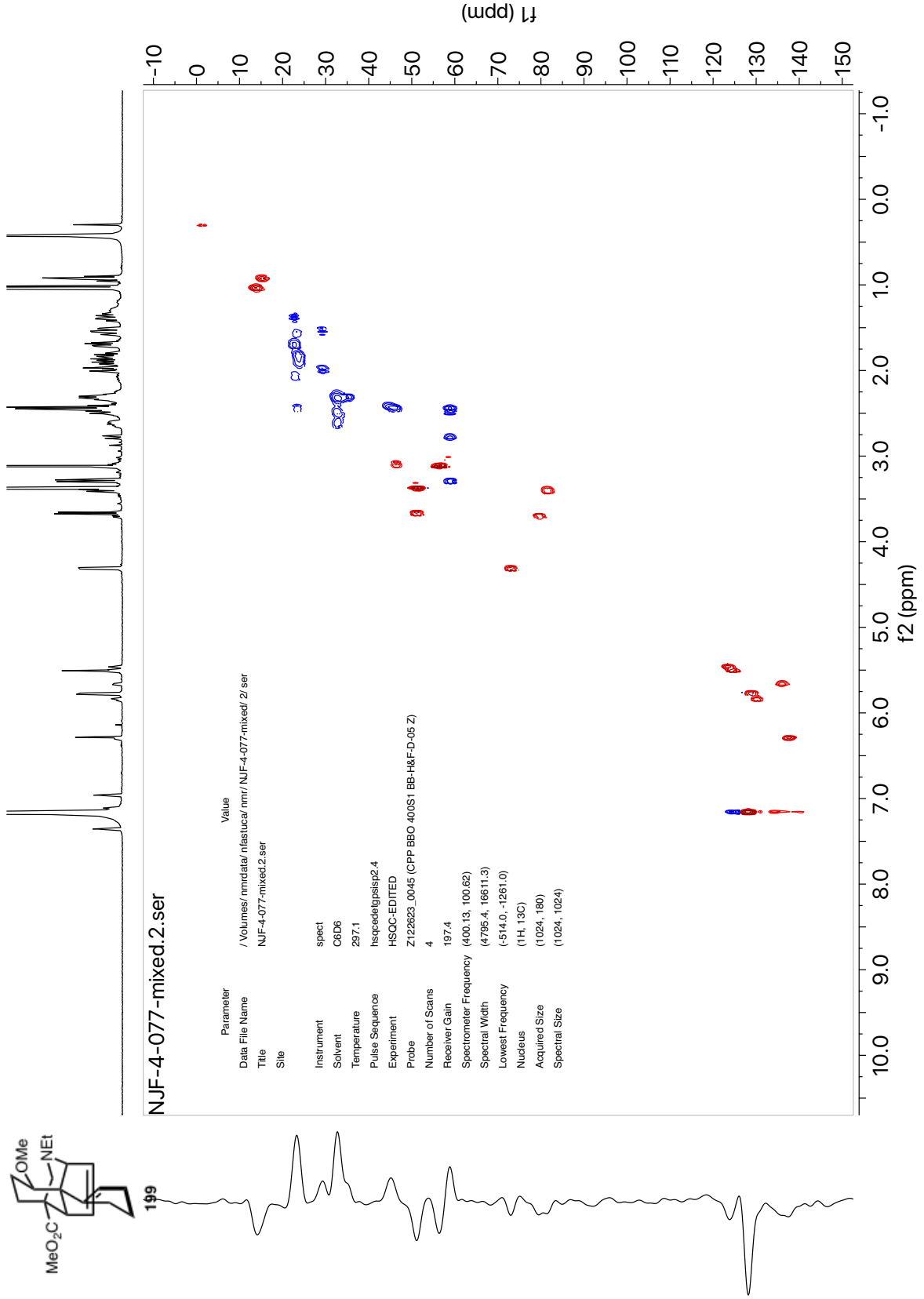

NJF-5-220.2.fid
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-220/ 2/ fid
Title NJF-5-220.2.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent C6D6
Temperature 297.1
Pulse Sequence zgpg30
Experiment 1D
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 2048
Receiver Gain 43.7
Relaxation Delay 1
Pulse Width 10
Acquisition Time 1
Acquisition Date 2022-05-26T06:14:53
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1921.8
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
OMe
NHEt
MeO2C
196
176.56
148.73
136.23
130.36
123.68
79.90
59.16
57.52
57.16
51.16
48.39
46.74
44.91
35.40
33.43
33.35
23.93
23.72
23.06
15.52
f1 (ppm)

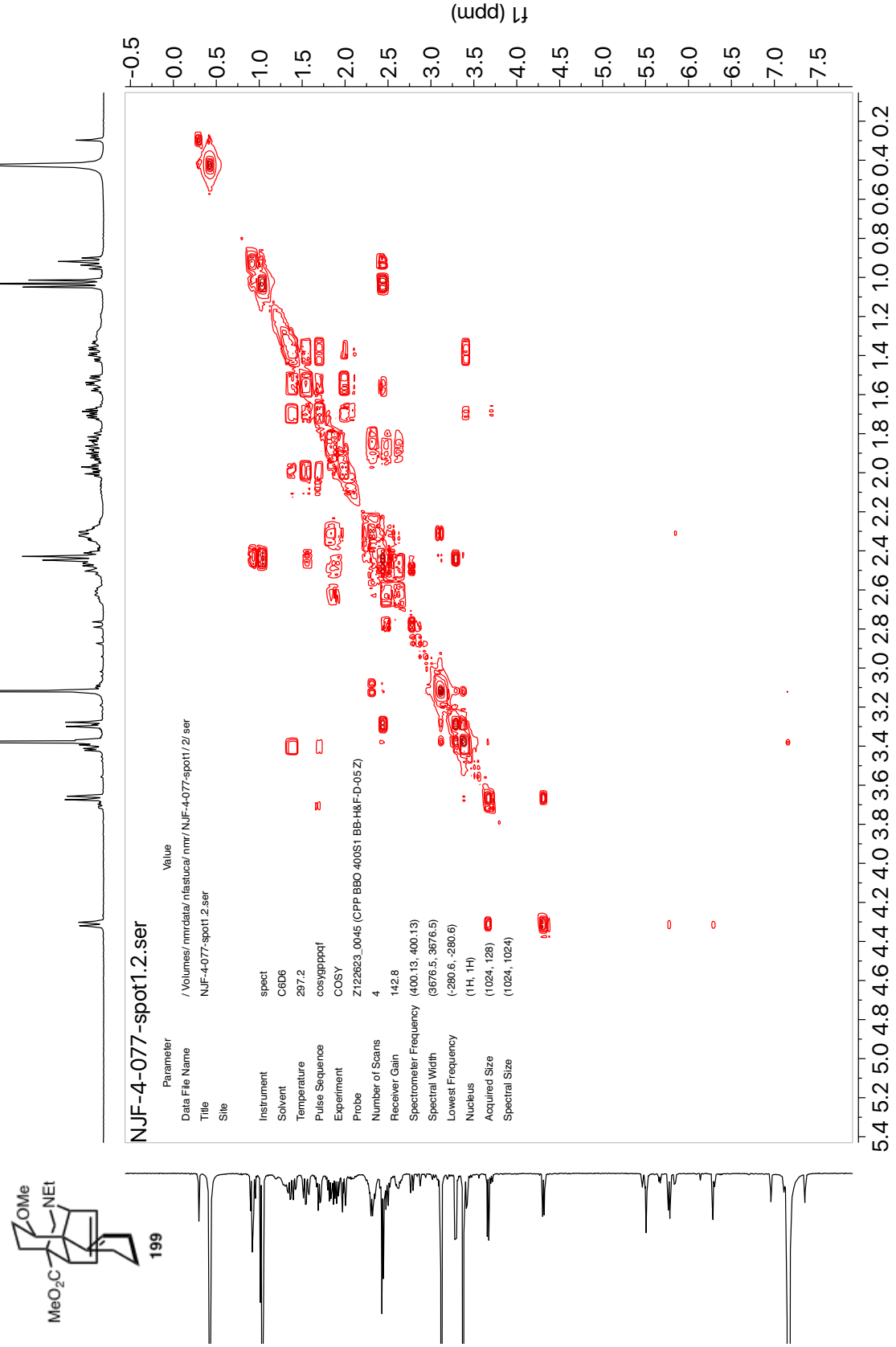

196
OMe
NHEt
MeO2C
NJF-5-220.3.ser
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-220/ 3/ ser
Title NJF-5-220.3.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent C6D6
Temperature 297.1
Pulse Sequence cosygpppqf
Experiment COSY
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 1
Receiver Gain 112.8
Relaxation Delay 2
Pulse Width 12
Acquisition Time 0
Acquisition Date 2022-05-26T06:20:36
Spectrometer Frequency (400.13, 400.13)
Spectral Width (3623.2, 3623.2)
Lowest Frequency (-310.8, -310.8)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
f1 (ppm)
f2 (ppm)

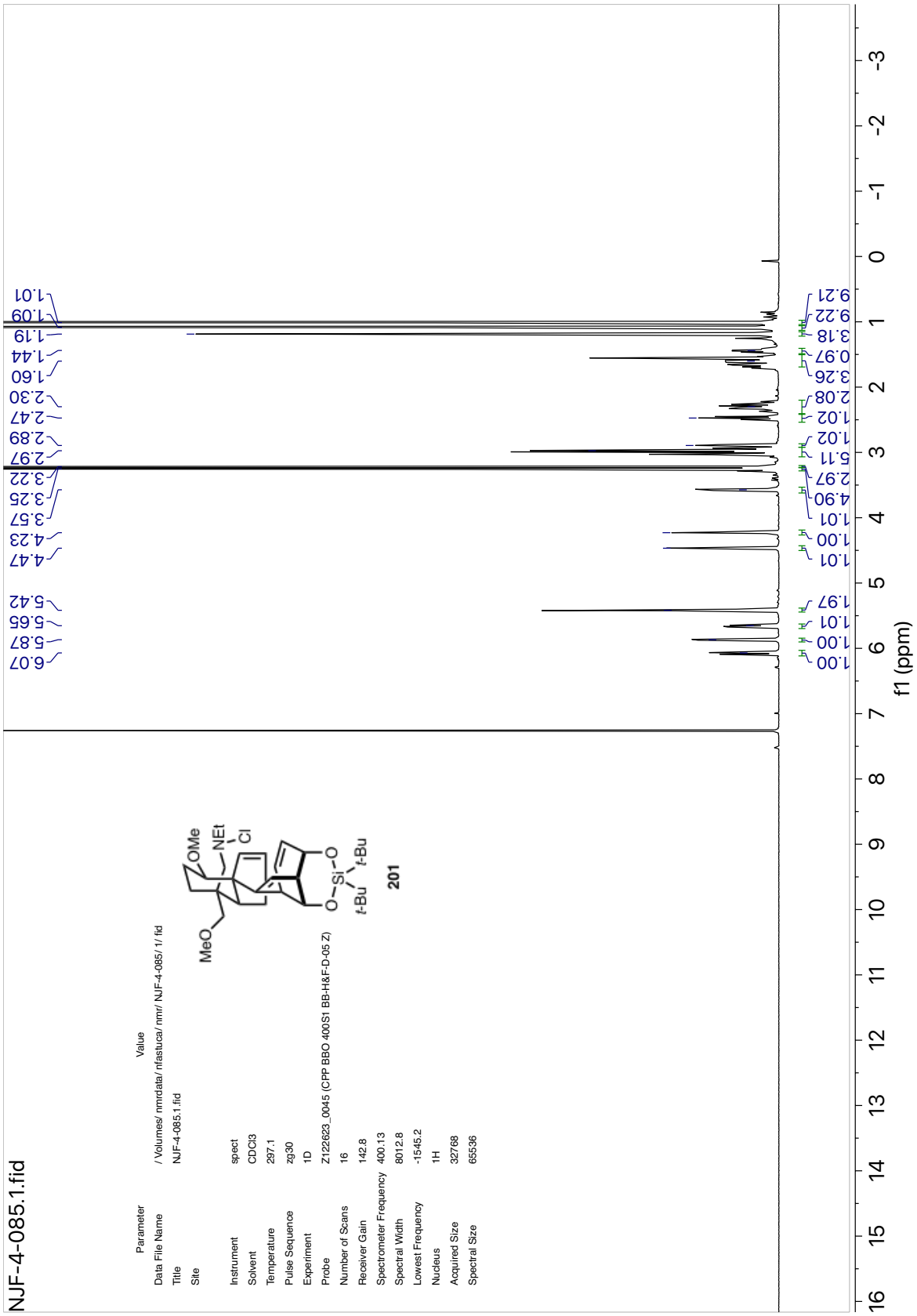

196
NJF-5-220.4.ser
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-220/ 4/ ser
Title NJF-5-220.4.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent C6D6
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2
Pulse Width 12
Acquisition Time 0
Acquisition Date 2022-05-26T06:42:47
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-517.1, -1236.9)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
f2 (ppm)
f1 (ppm)

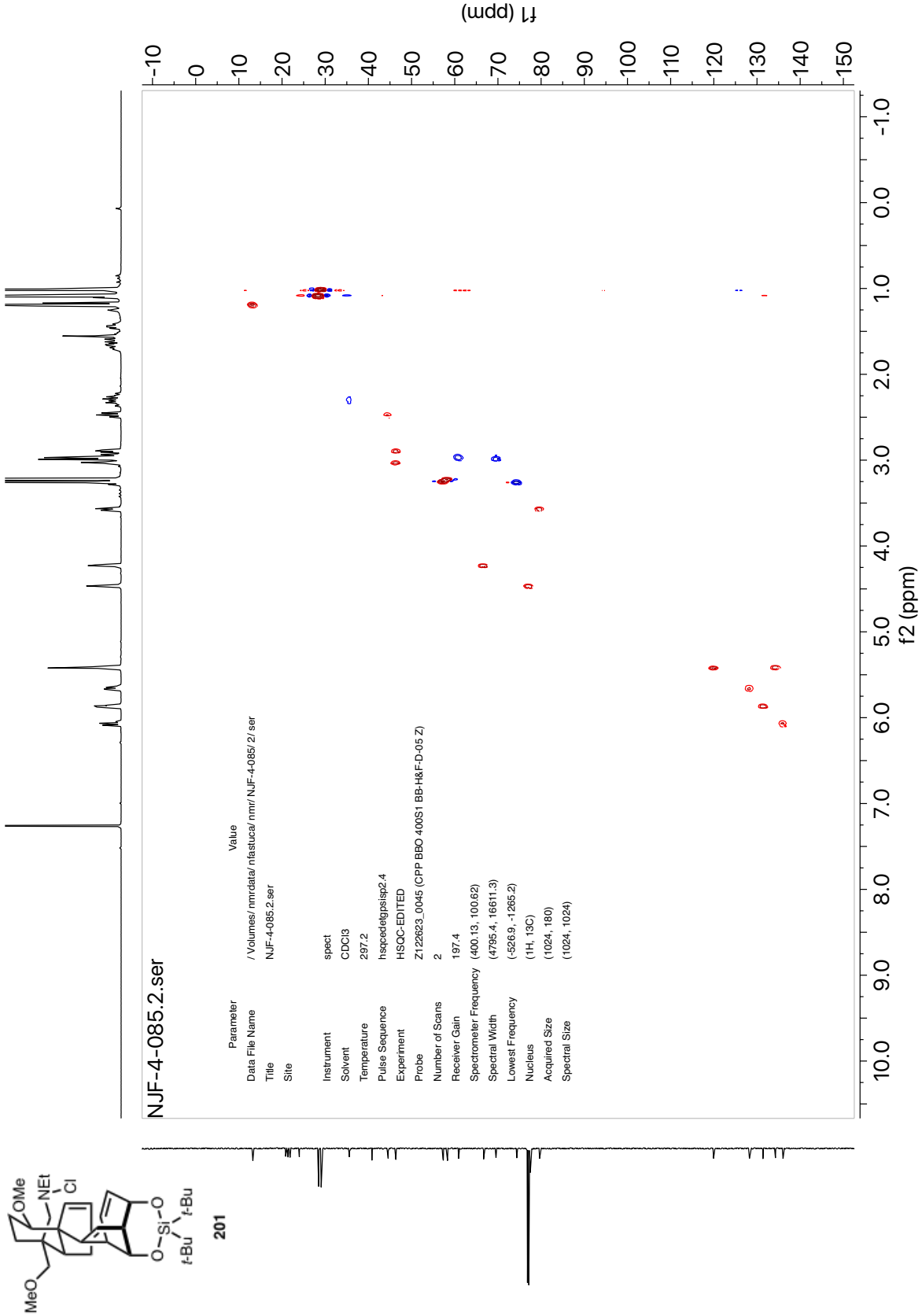

PROTON01
NJF-4-070
Parameter Value
Title PROTON01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 3.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 16
Receiver Gain 38
Relaxation Delay 2.0000
Pulse Width 5.6500
Spectrometer Frequency 499.61
Spectral Width 8000.0
Lowest Frequency -1030.4
Nucleus 1H
Acquired Size 24000
Spectral Size 65536
7.26 CDCl3
5.85
5.44
5.39
3.70
3.57
3.33
3.28
3.00
2.94
2.86
2.54
2.34
2.15
1.94
1.78
1.50
1.15
1.00
0.97
1.01
1.06
2.92
1.05
2.93
1.03
1.91
0.99
1.05
5.02
1.10
1.11
3.14
1.00
2.93
OMe
NEt
Cl
MeO2C
197
f1 (ppm)

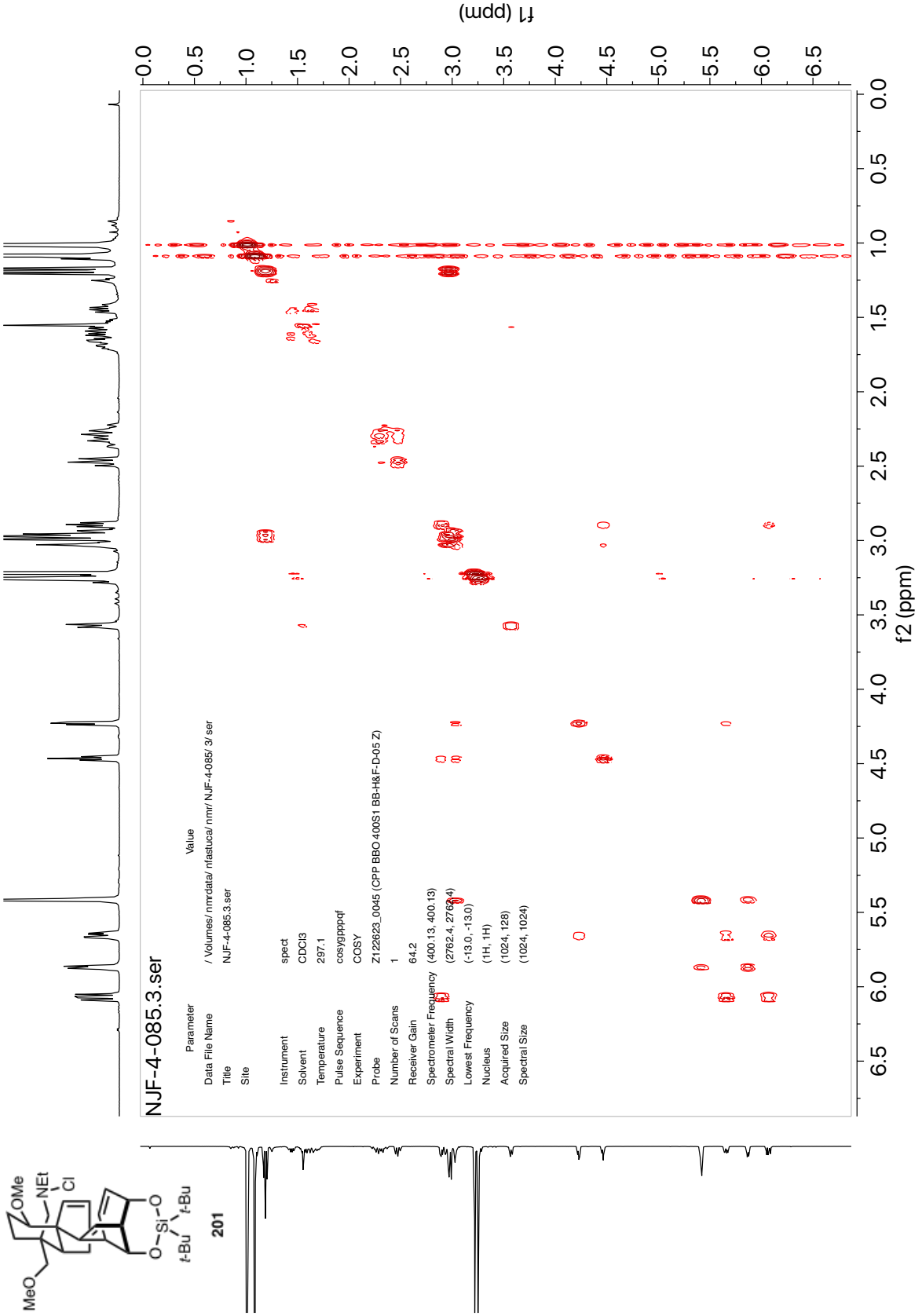

NJF-4-077-spot1.1.fid
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-077-spot1/ 1/ fid
Title NJF-4-077-spot1.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent C6D6
Temperature 297.1
Pulse Sequence zg30
Experiment 1D
Number of Scans 32
Receiver Gain 197.4
Relaxation Delay 1.0000
Pulse Width 12.5000
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1532.3
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
OMe
NEt
MeO2C
199
7.16 CDCl3
6.29
5.77
5.51
4.31
3.66
3.41
3.38
3.29
3.12
2.63
2.45
2.31
1.90
1.70
1.54
1.38
1.03
1.00
1.03
1.08
1.01
0.97
0.99
3.84
1.09
3.37
1.13
5.18
3.09
3.95
1.44
1.42
1.95
3.20
f1 (ppm)

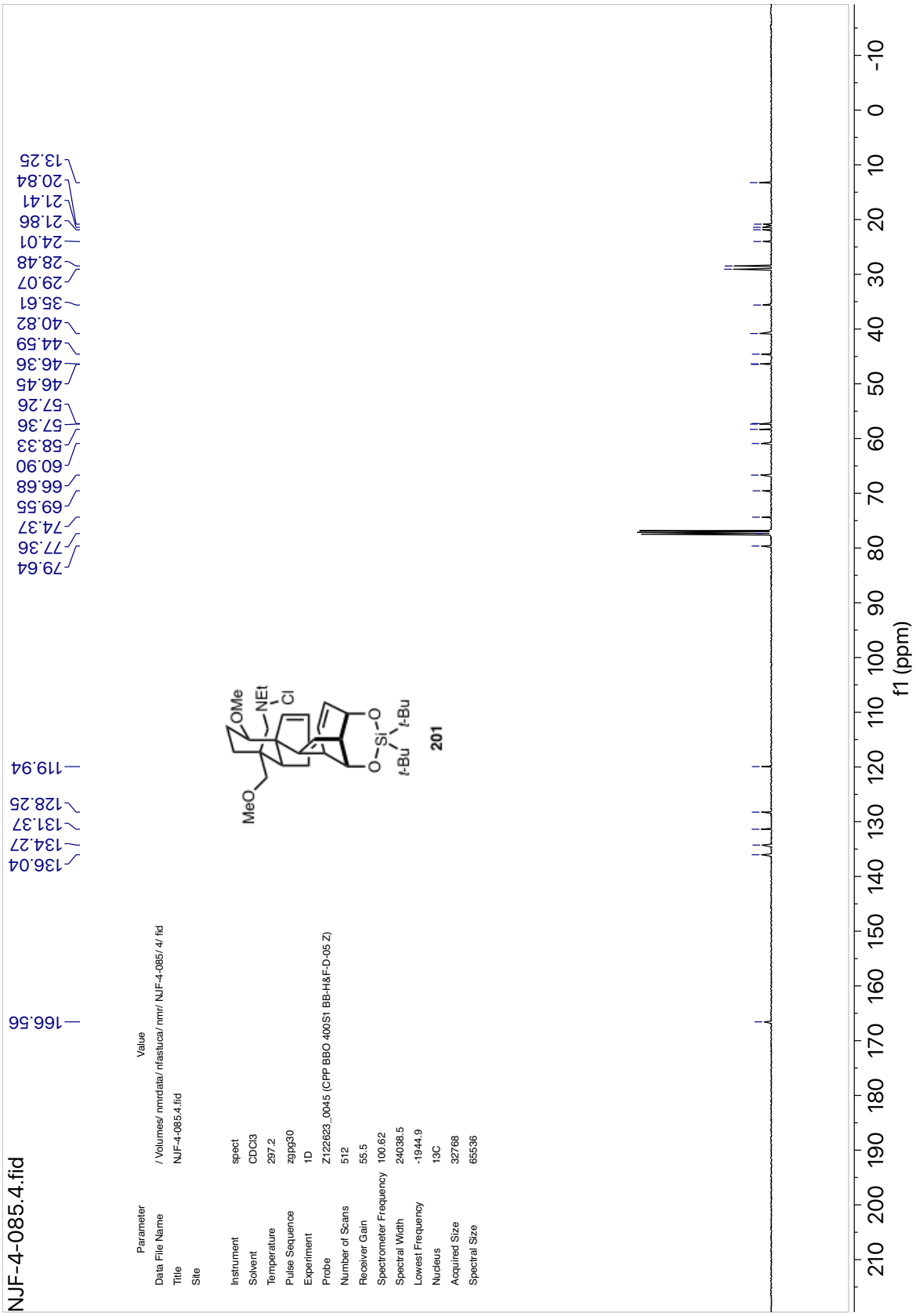

NJF-4-077-mixed.2.ser
Parameter Value
Data File Name / Volumes/ nmrdata/ ntastuca/ nmr/ NJF-4-077-mixed/ 2/ ser
Title NJF-4-077-mixed.2.ser
Site
Instrument spect
Solvent C6D6
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 4
Receiver Gain 197.4
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-514.0, -1261.0)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
f1 (ppm)
f2 (ppm)
OMe
NEt
MeO2C

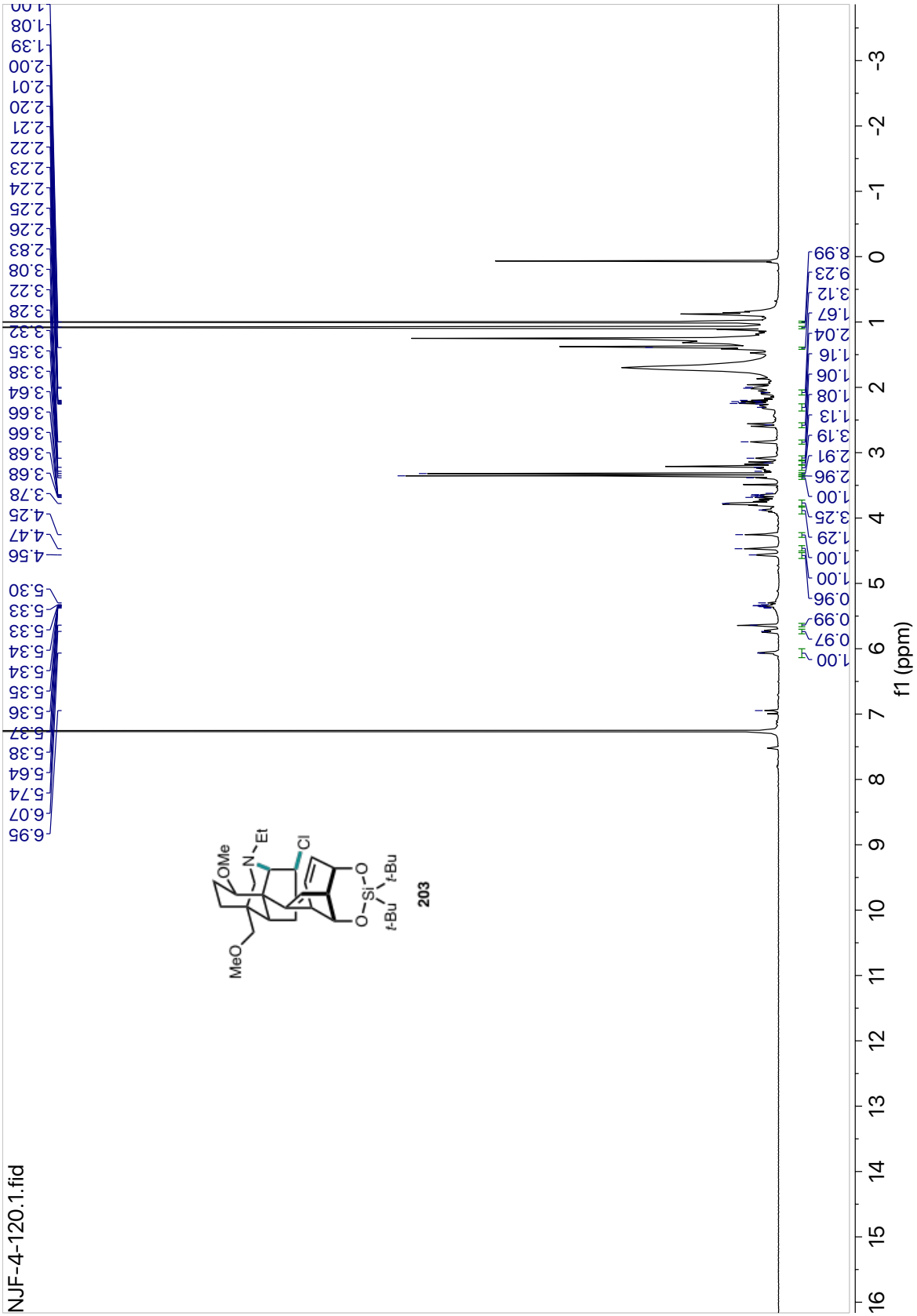

NJF-4-077-spot1.2.ser
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-077-spot1 / 2/ ser
Title NJF-4-077-spot1 2.ser
Site
Instrument spect
Solvent C6D6
Temperature 297.2
Pulse Sequence cosygpppqf
Experiment COSY
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 4
Receiver Gain 142.8
Spectrometer Frequency (400.13, 400.13)
Spectral Width (3676.5, 3676.5)
Lowest Frequency (-280.6, -280.6)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
f1 (ppm)
f2 (ppm)
OMe
NEt
MeO2C
199

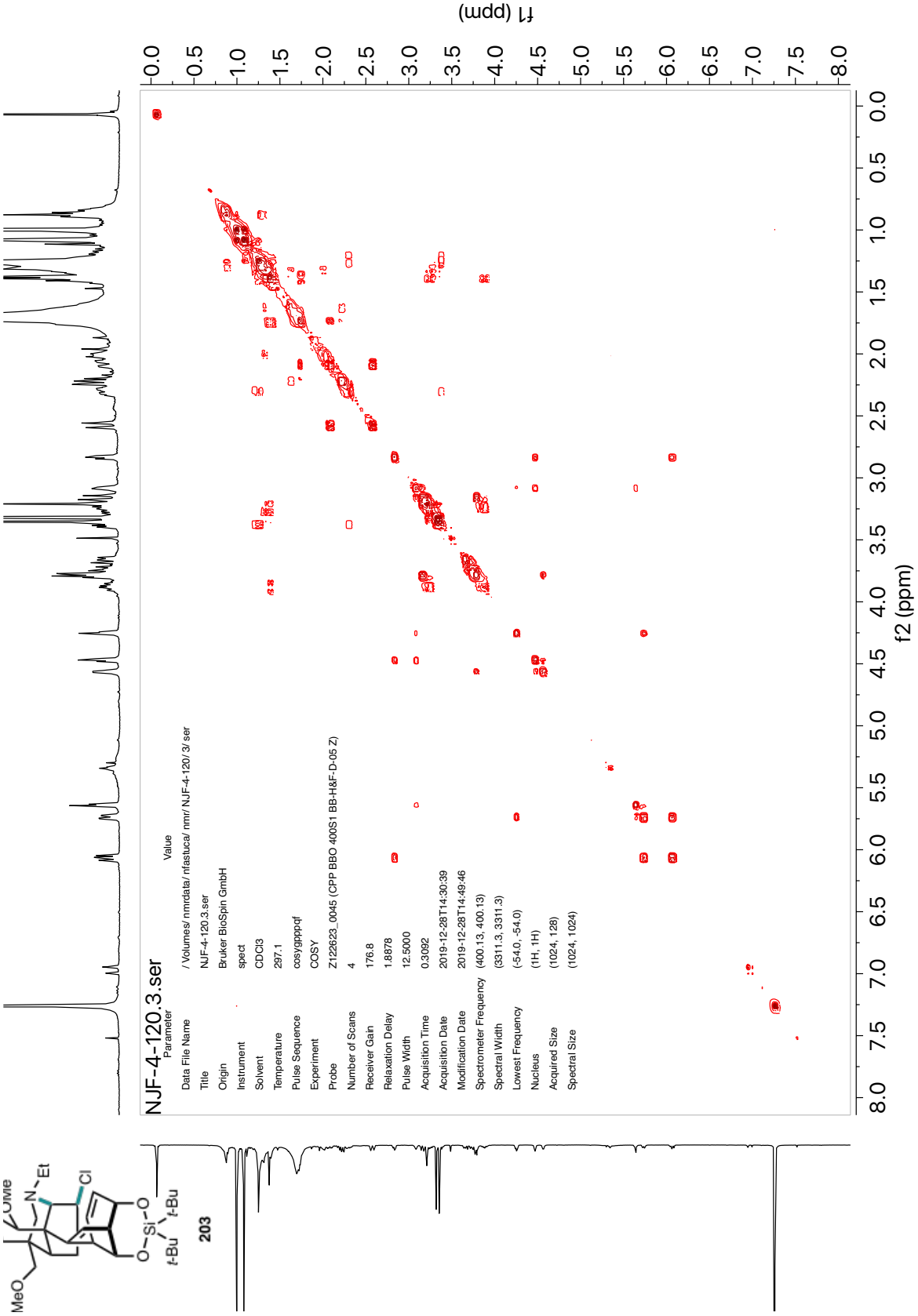

NJF-4-085.1.fid
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-085/ 1/ fid
Title NJF-4-085.1.fid
Site
Instrument spect
Solvent CDCl3
Temperature 297.1
Pulse Sequence zg30
Experiment 1D
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 16
Receiver Gain 142.8
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.2
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
MeO
OMe
NEt
Cl
O
Si
O
t-Bu
t-Bu
201
6.07
5.87
5.65
5.42
4.47
4.23
3.57
3.25
3.22
2.97
2.89
2.47
2.30
1.60
1.44
1.19
1.09
1.01
1.00
1.01
1.97
1.00
1.01
4.90
2.97
5.11
1.02
1.02
2.08
3.26
0.97
3.18
9.22
9.21
f1 (ppm)

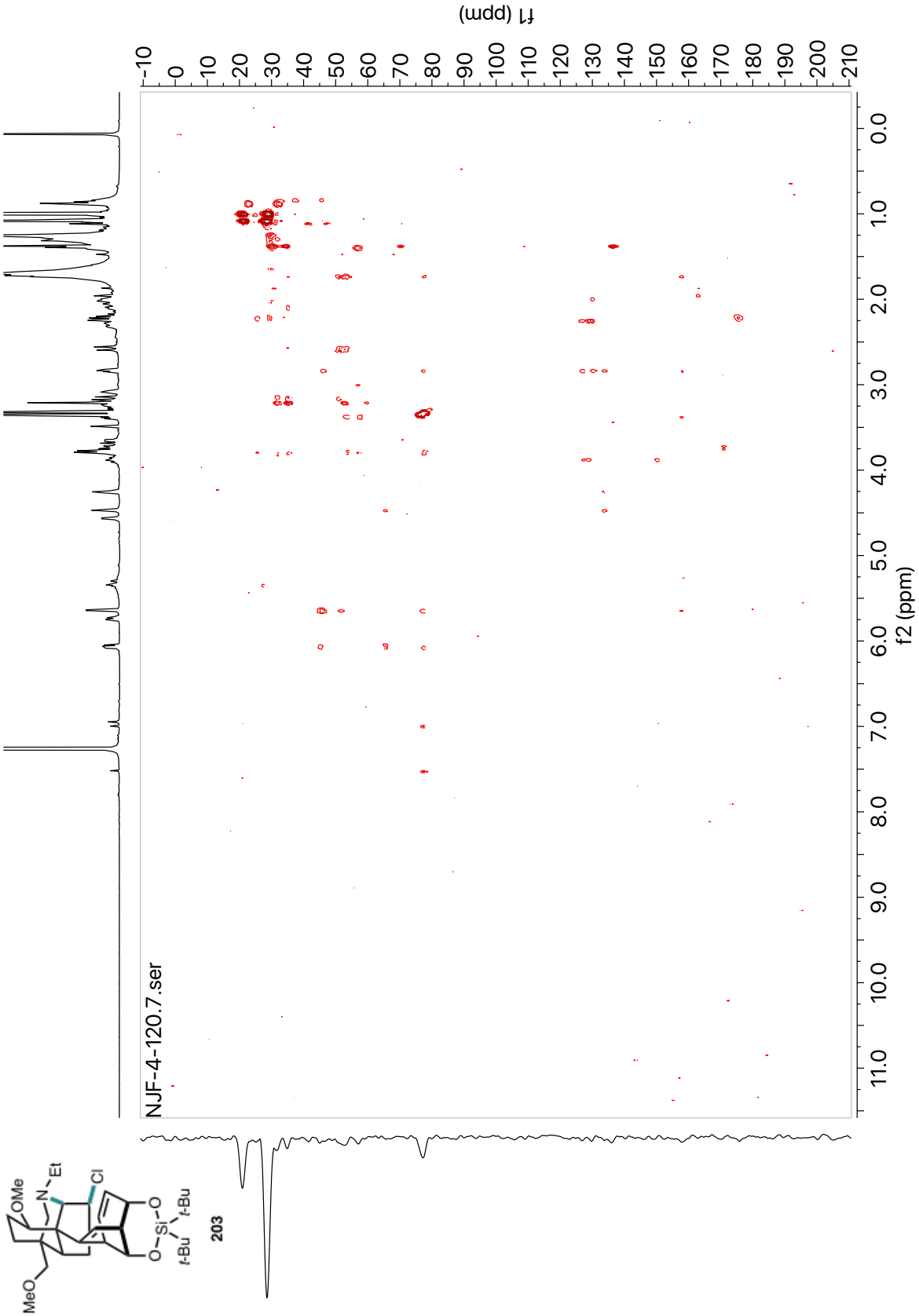

NJF-4-085.2.ser
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-085/ 2/ ser
Title NJF-4-085.2.ser
Site
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 2
Receiver Gain 197.4
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-526.9, -1265.2)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
f2 (ppm)
f1 (ppm)
MeO
OMe
NEt
Cl
O
Si
O
t-Bu
t-Bu
201

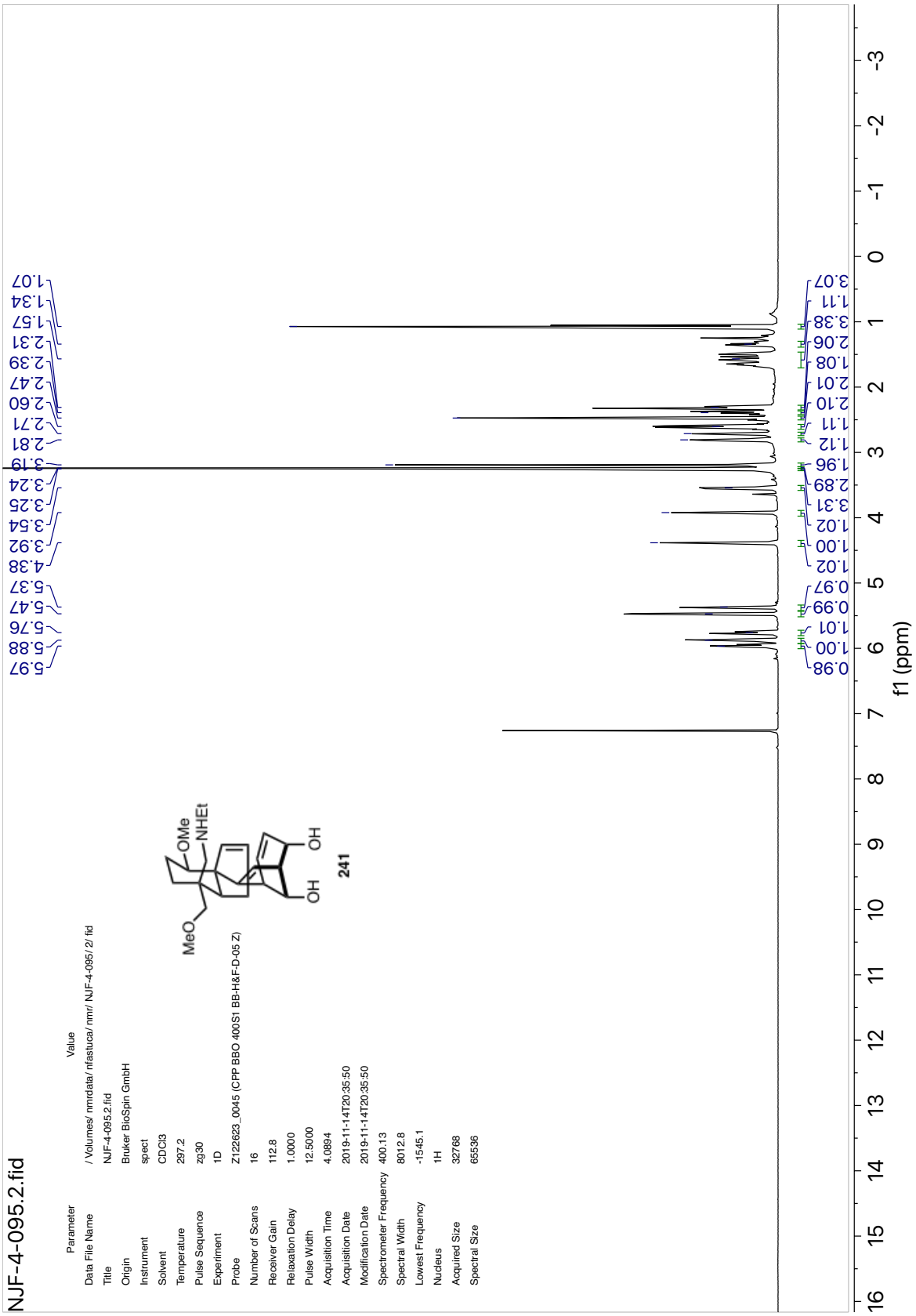

NJF-4-085.3.ser
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-085/ 3/ ser
Title NJF-4-085.3.ser
Site
Instrument spect
Solvent CDCl3
Temperature 297.1
Pulse Sequence cosygpppqf
Experiment COSY
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 1
Receiver Gain 64.2
Spectrometer Frequency (400.13, 400.13)
Spectral Width (2762.4, 2762.4)
Lowest Frequency (-13.0, -13.0)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
f1 (ppm)
f2 (ppm)
OMe
NEt
Cl
MeO
O
Si
t-Bu
t-Bu
O
201

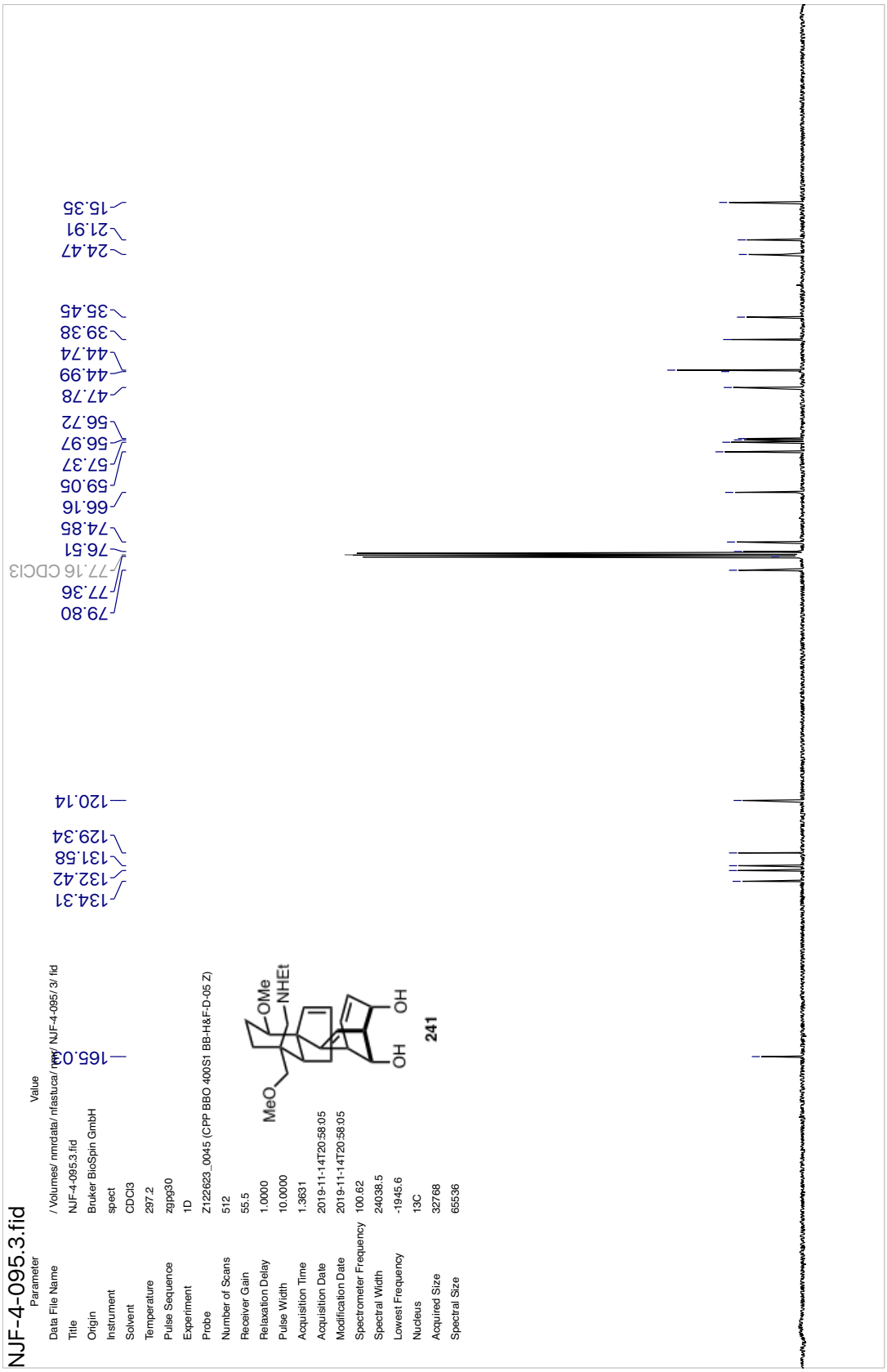

NJF-4-085.4.fid
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-085/ 4/ fid
Title NJF-4-085.4.fid
Site
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence zgpg30
Experiment 1D
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 512
Receiver Gain 55.5
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1944.9
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
166.56
136.04
134.27
131.37
128.25
119.94
79.64
77.36
74.37
69.55
66.68
60.90
58.33
57.36
57.26
46.45
46.36
44.59
40.82
35.61
29.07
28.48
24.01
21.86
21.41
20.84
13.25
OMe
NEt
Cl
MeO
O
Si
O
t-Bu
t-Bu
201
f1 (ppm)

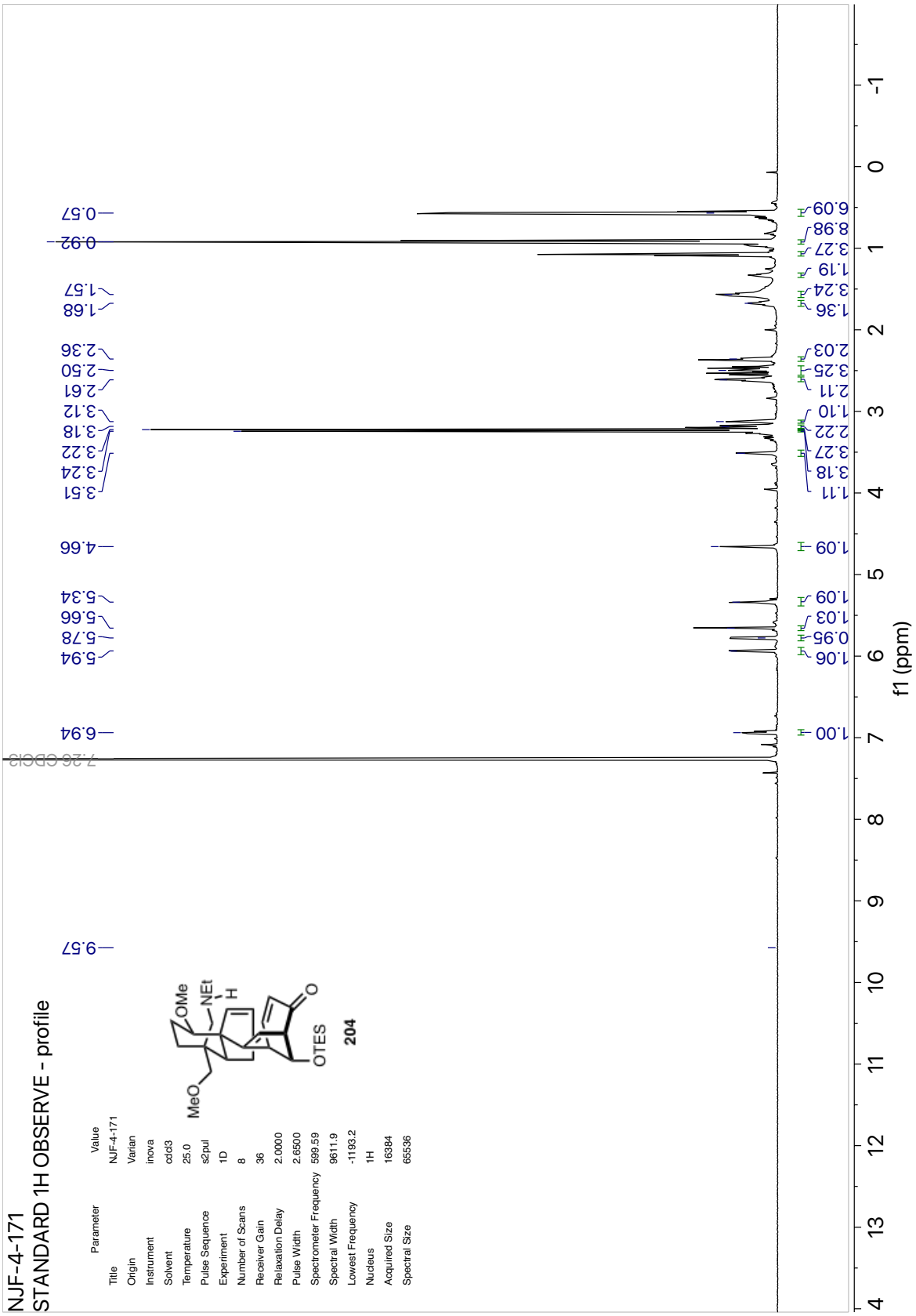

NJF-4-120.1.fid
f1 (ppm)
OMe
N
Et
Cl
MeO
O
Si
O
t-Bu
t-Bu
203

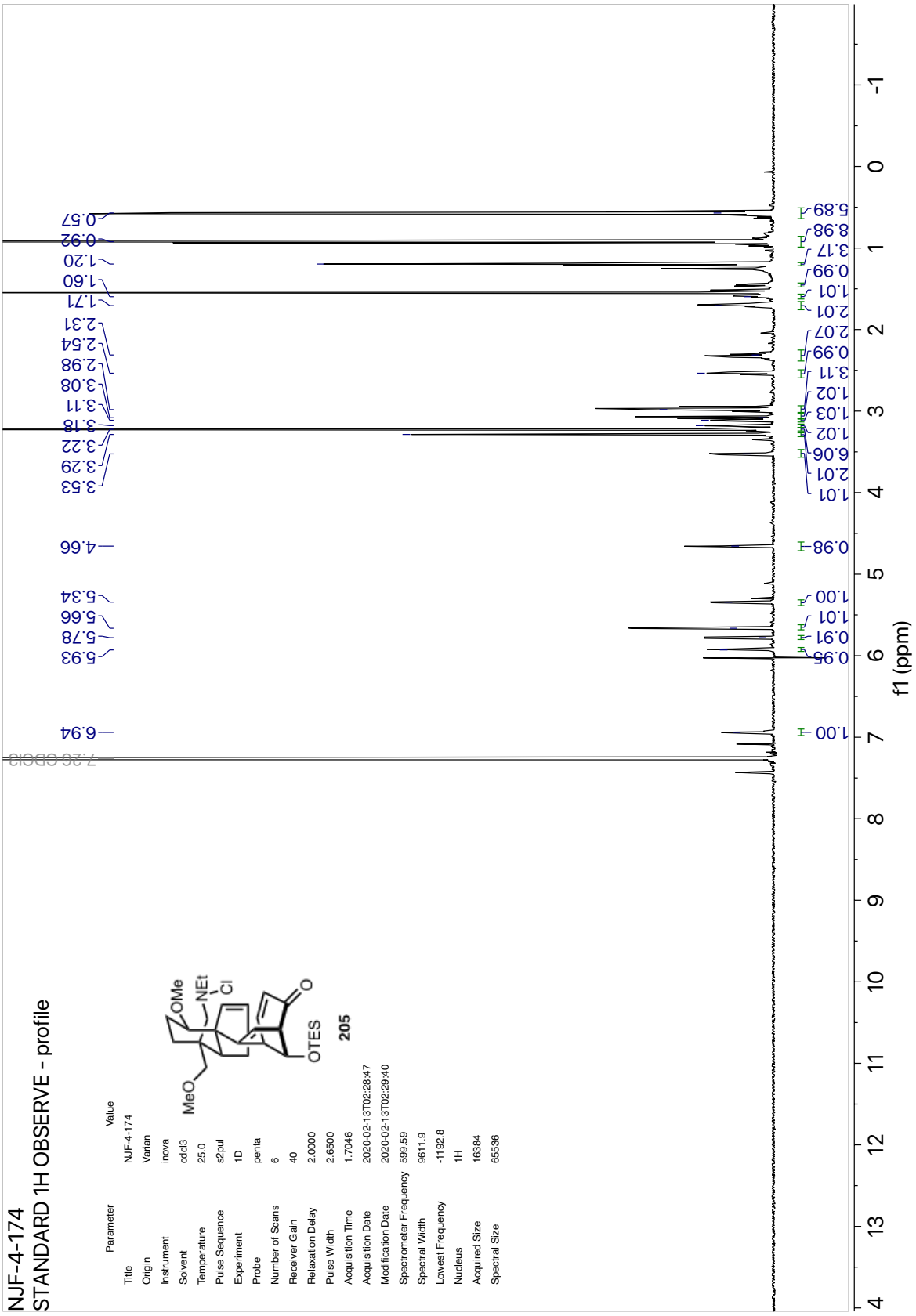

NJF-4-120.3.ser
Parameter
Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-120/ 3/ ser
Title NJF-4-120.3.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.1
Pulse Sequence cosygpppqf
Experiment COSY
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 4
Receiver Gain 176.8
Relaxation Delay 1.8878
Pulse Width 12.5000
Acquisition Time 0.3092
Acquisition Date 2019-12-28T14:30:39
Modification Date 2019-12-28T14:49:46
Spectrometer Frequency (400.13, 400.13)
Spectral Width (3311.3, 3311.3)
Lowest Frequency (-54.0, -54.0)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
f1 (ppm)
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
MeO
OMe
N
Et
Cl
O
Si
O
t-Bu
t-Bu
203

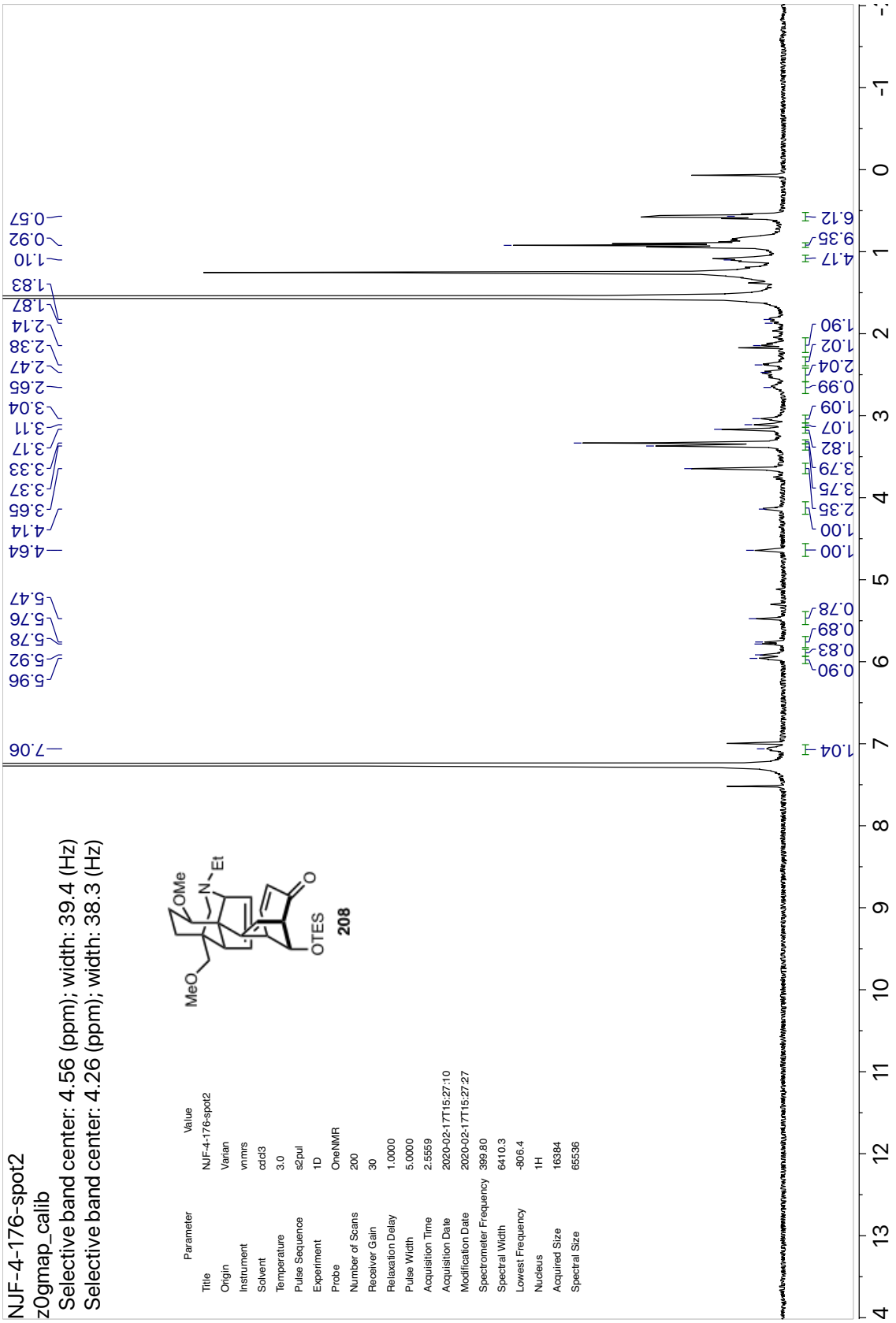

f1 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f2 (ppm)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
NJF-4-120.7.ser
OMe
N
Et
Cl
O
Si
O
t-Bu
t-Bu
MeO
203

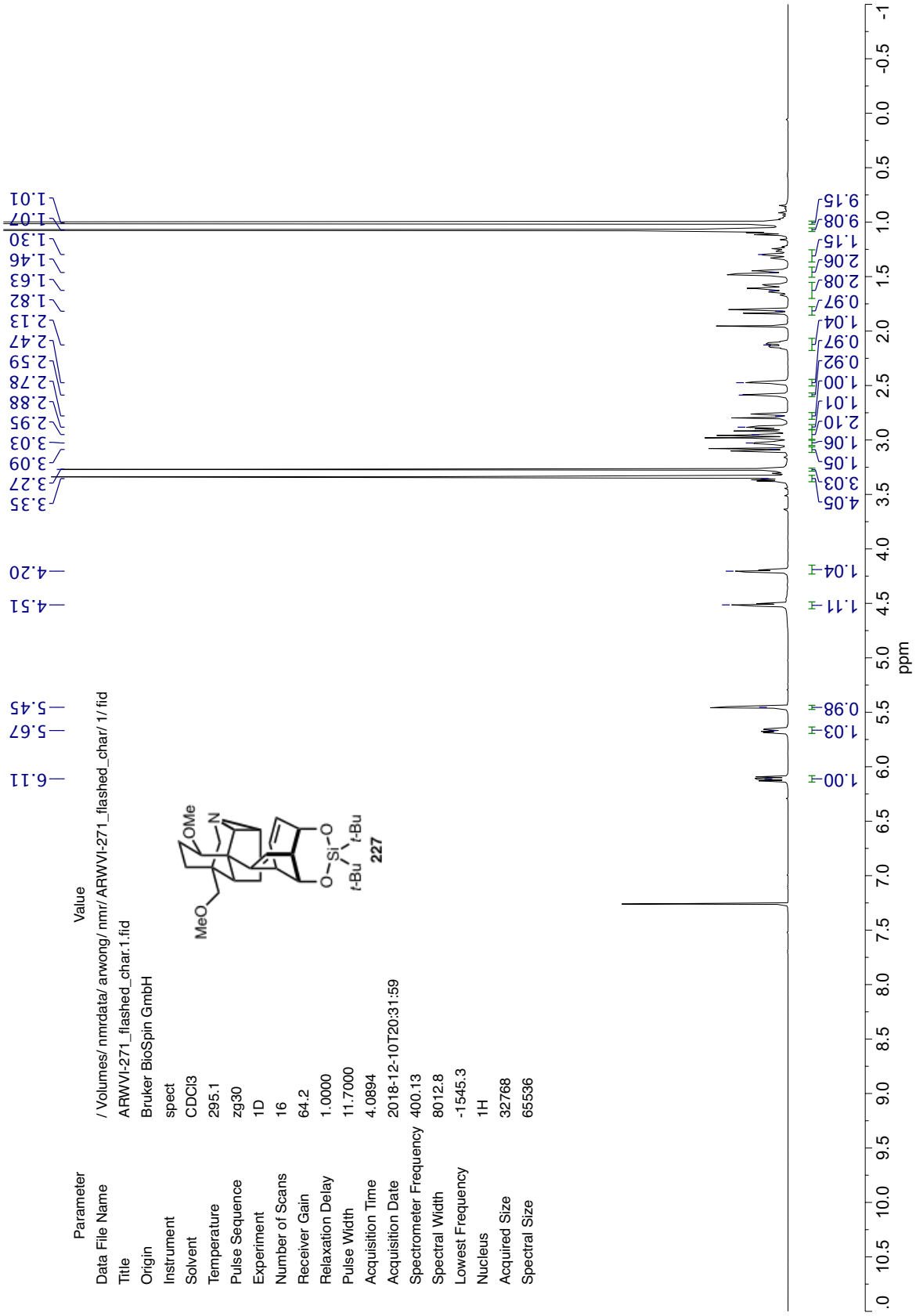

NJF-4-095.2.fid
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-095/ 2/ fid
Title NJF-4-095.2.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence zg30
Experiment 1D
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 16
Receiver Gain 112.8
Relaxation Delay 1.0000
Pulse Width 12.5000
Acquisition Time 4.0894
Acquisition Date 2019-11-14T20:35:50
Modification Date 2019-11-14T20:35:50
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.1
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
MeO
OMe
NHEt
OH
OH
241
5.97
5.88
5.76
5.47
5.37
4.38
3.92
3.54
3.25
3.24
3.19
2.81
2.71
2.60
2.47
2.39
2.31
1.57
1.34
1.07
0.98
1.00
1.01
0.99
0.97
1.02
1.00
1.02
3.31
2.89
1.96
1.12
1.11
2.10
2.01
1.08
2.06
3.38
1.11
3.07
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

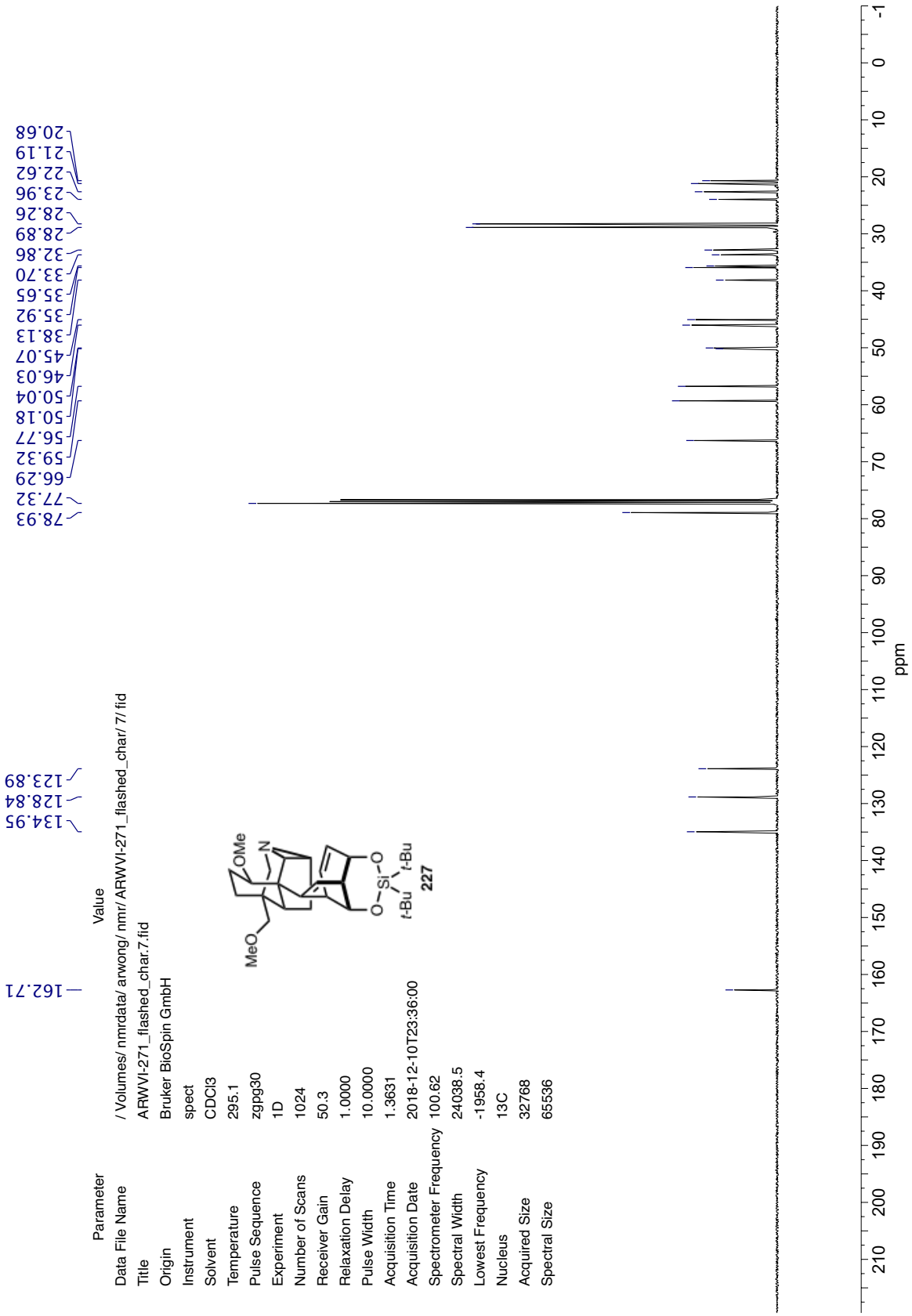

NJF-4-095.3.fid
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-4-095/ 3/ fid
Title NJF-4-095.3.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence zgpg30
Experiment 1D
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 512
Receiver Gain 55.5
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2019-11-14T20:58:05
Modification Date 2019-11-14T20:58:05
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1945.6
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
MeO
OMe
NHEt
OH
OH
241
165.02
134.31
132.42
131.58
129.34
120.14
79.80
77.36
77.16 CDCl3
76.51
74.85
66.16
59.05
57.37
56.97
56.72
47.78
44.99
44.74
39.38
35.45
24.47
21.91
15.35
f1 (ppm)


NJF-4-171
STANDARD 1H OBSERVE - profile
Parameter Value
Title NJF-4-171
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 8
Receiver Gain 36
Relaxation Delay 2.0000
Pulse Width 2.6500
Spectrometer Frequency 599.59
Spectral Width 9611.9
Lowest Frequency -1193.2
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
MeO
OMe
NEt
H
OTES
O
204
9.57
6.94
7.26 CDCl3
5.94
5.78
5.66
5.34
4.66
3.51
3.24
3.22
3.18
3.12
2.61
2.50
2.36
1.68
1.57
0.92
0.57
1.00
1.09
1.09
1.03
0.95
1.06
1.11
3.18
3.27
2.22
1.10
2.11
3.25
2.03
1.36
3.24
1.19
3.27
8.98
6.09
f1 (ppm)

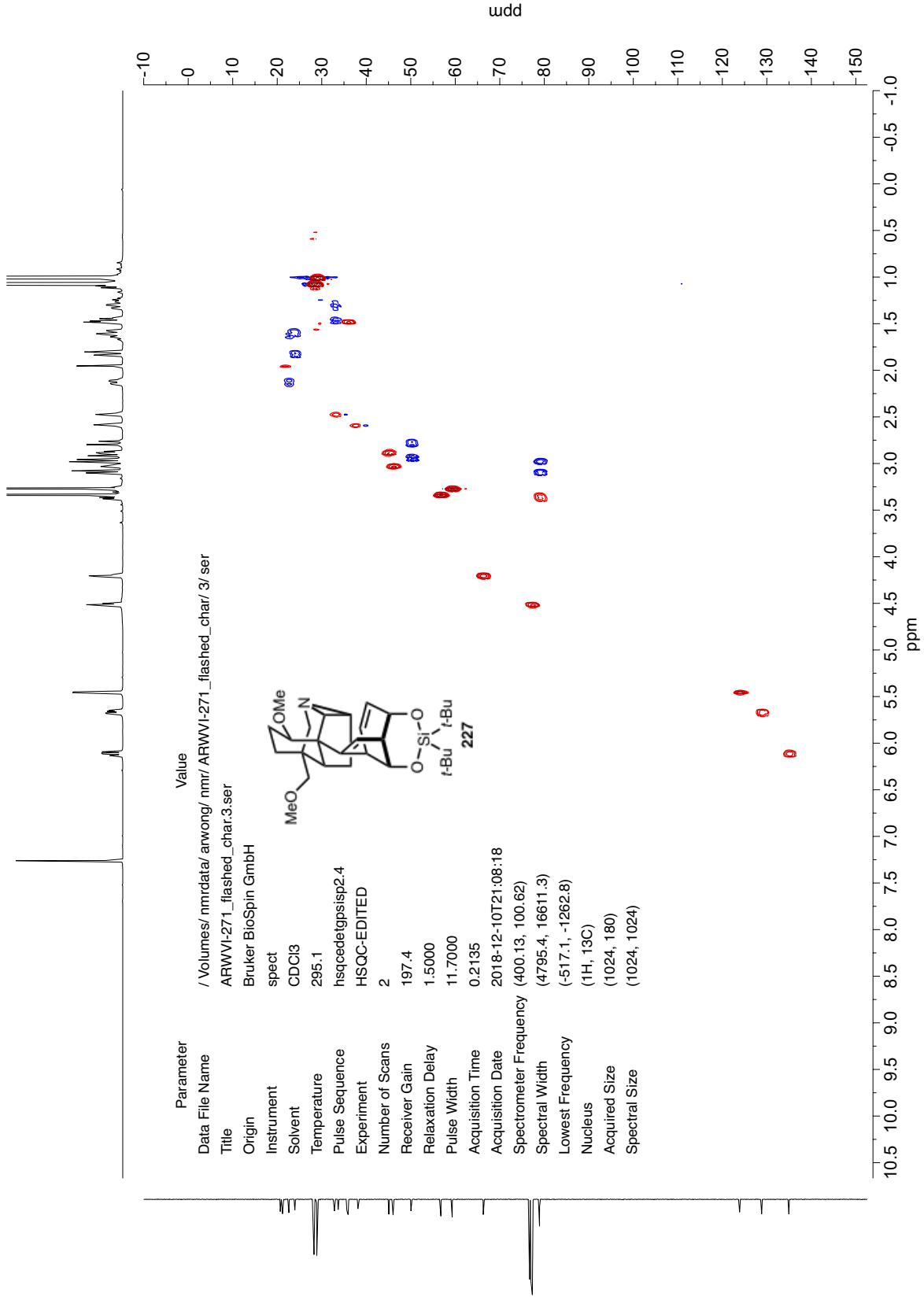

NJF-4-174
STANDARD 1H OBSERVE - profile
Parameter Value
Title NJF-4-174
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe penta
Number of Scans 6
Receiver Gain 40
Relaxation Delay 2.0000
Pulse Width 2.6500
Acquisition Time 1.7046
Acquisition Date 2020-02-13T02:28:47
Modification Date 2020-02-13T02:29:40
Spectrometer Frequency 599.59
Spectral Width 9611.9
Lowest Frequency -1192.8
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
MeO
OMe
NEt
Cl
OTES
O
205
7.26 CDCl3
6.94
5.93
5.78
5.66
5.34
4.66
3.53
3.29
3.22
3.18
3.11
3.08
2.98
2.54
2.31
1.71
1.60
1.20
0.92
0.57
1.00
0.95
0.91
1.01
1.00
0.98
1.01
2.01
6.06
1.02
1.03
1.02
3.11
0.99
2.07
2.01
1.01
0.99
3.17
8.98
5.89
f1 (ppm)

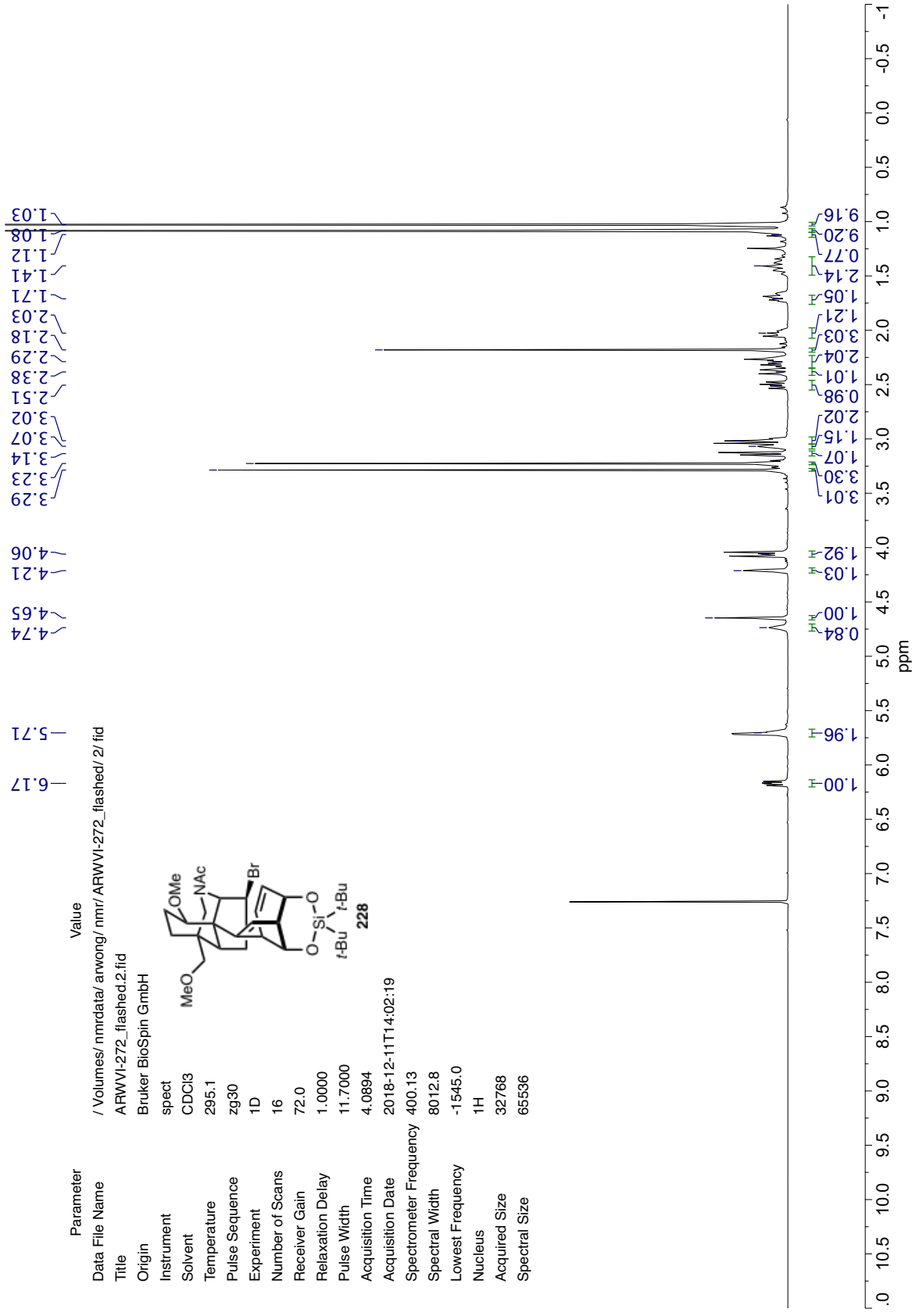

NJF-4-176-spot2
z0gmap_calib
Selective band center: 4.56 (ppm); width: 39.4 (Hz)
Selective band center: 4.26 (ppm); width: 38.3 (Hz)
Parameter Value
Title NJF-4-176-spot2
Origin Varian
Instrument vnmrs
Solvent cdcl3
Temperature 3.0
Pulse Sequence s2pul
Experiment 1D
Probe OneNMR
Number of Scans 200
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 5.0000
Acquisition Time 2.5559
Acquisition Date 2020-02-17T15:27:10
Modification Date 2020-02-17T15:27:27
Spectrometer Frequency 399.80
Spectral Width 6410.3
Lowest Frequency -806.4
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
MeO
OMe
N
Et
OTES
O
208
7.06
5.96
5.92
5.78
5.76
5.47
4.64
4.14
3.65
3.37
3.33
3.17
3.11
3.04
2.65
2.47
2.38
2.14
1.87
1.83
1.10
0.92
0.57
1.04
0.90
0.83
0.89
0.78
1.00
2.35
3.75
3.79
1.82
1.07
1.09
0.99
2.04
1.02
1.90
4.17
9.35
6.12
f1 (ppm)

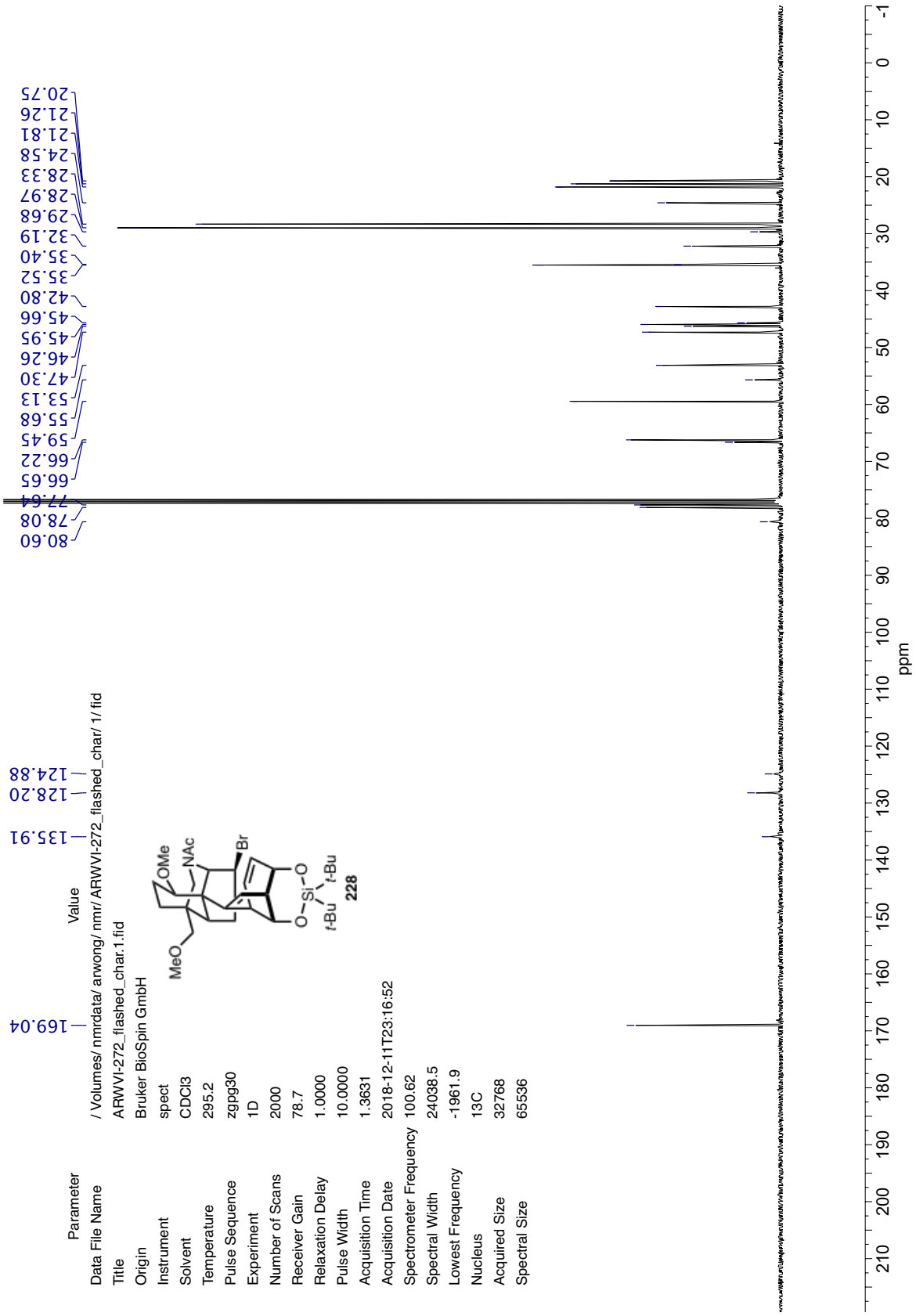

Parameter
Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWVI-271_flashed_char/ 1/ fid
Title
ARWVI-271_flashed_char.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zg30
Experiment
1D
Number of Scans
16
Receiver Gain
64.2
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2018-12-10T20:31:59
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.3
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
OMe
N
MeO
O
Si
O
t-Bu
t-Bu
227
6.11
5.67
5.45
4.51
4.20
3.35
3.27
3.09
3.03
2.95
2.88
2.78
2.59
2.47
2.13
1.82
1.63
1.46
1.30
1.07
1.01
1.00
0.98
1.03
1.04
1.11
4.05
3.03
1.05
1.06
2.10
1.01
1.00
0.92
0.97
1.04
0.97
2.08
2.06
1.15
9.08
9.15
ppm

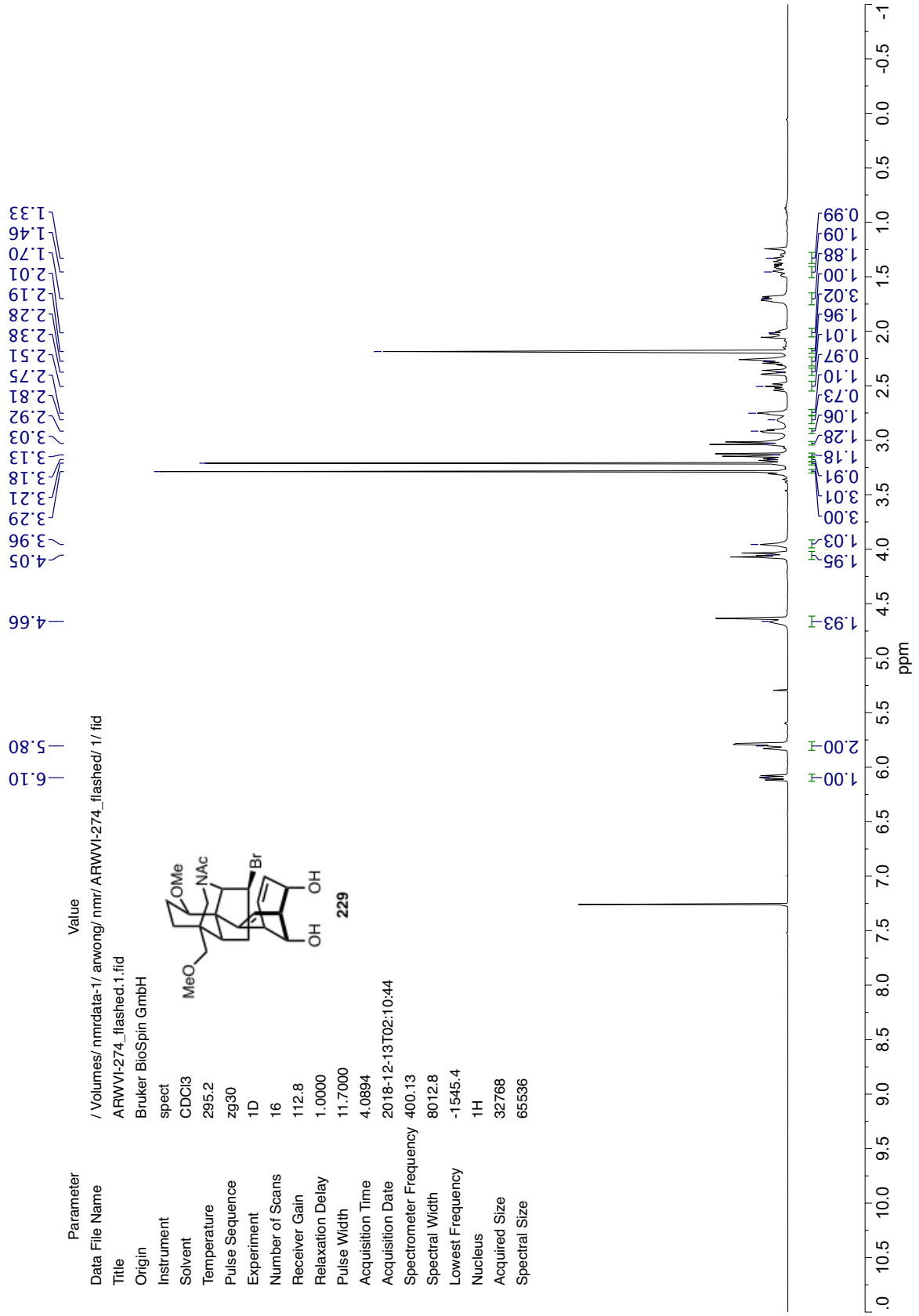


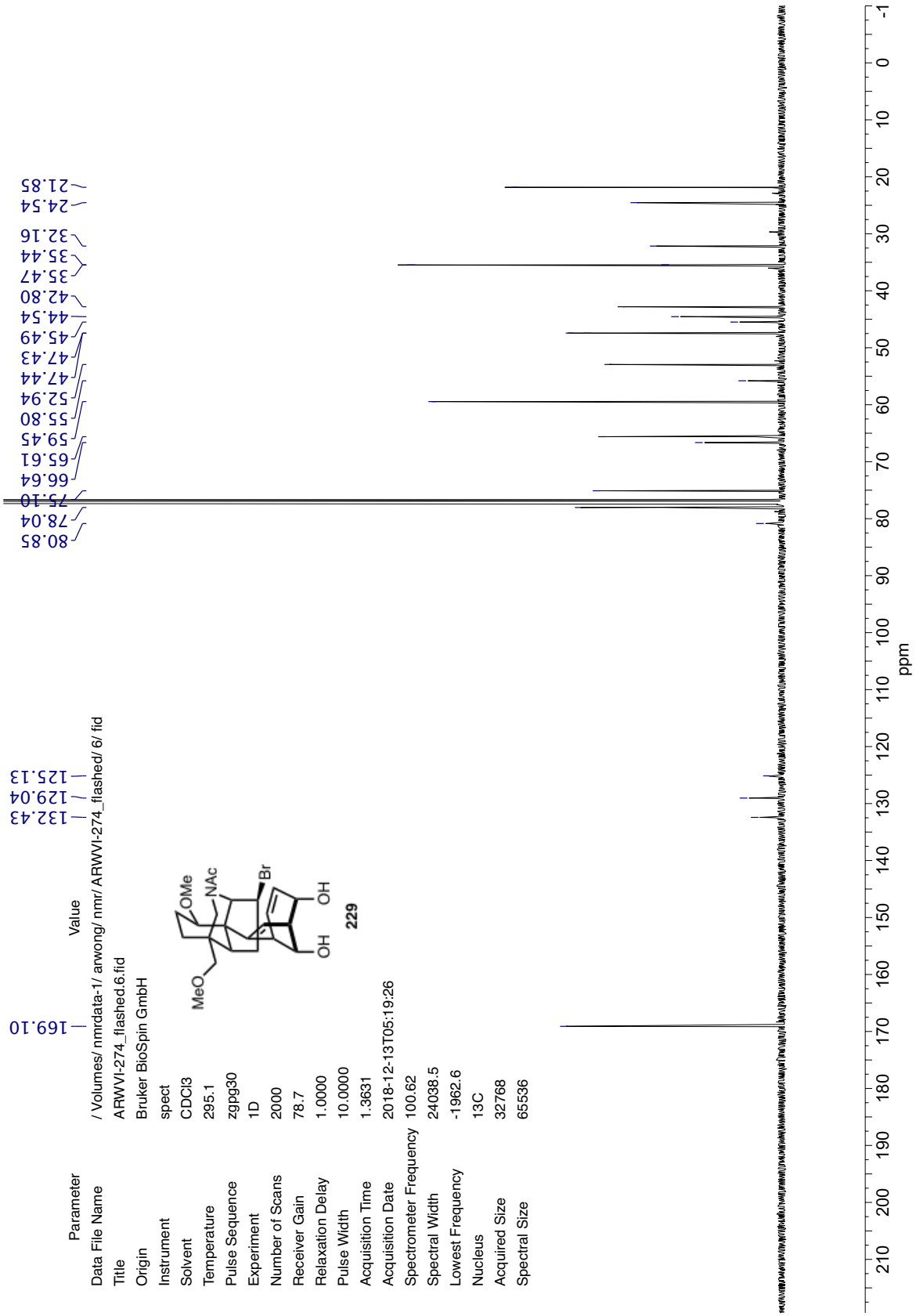
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ arwong/ nmr/ ARWVI-271_flashed_char/ 7/ fid
Title	ARWVI-271_flashed_char.7.fid
Origin	Bruker BioSpin GmbH
Instrument	spect
Solvent	CDCl3
Temperature	295.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	1024
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2018-12-10T23:36:00
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

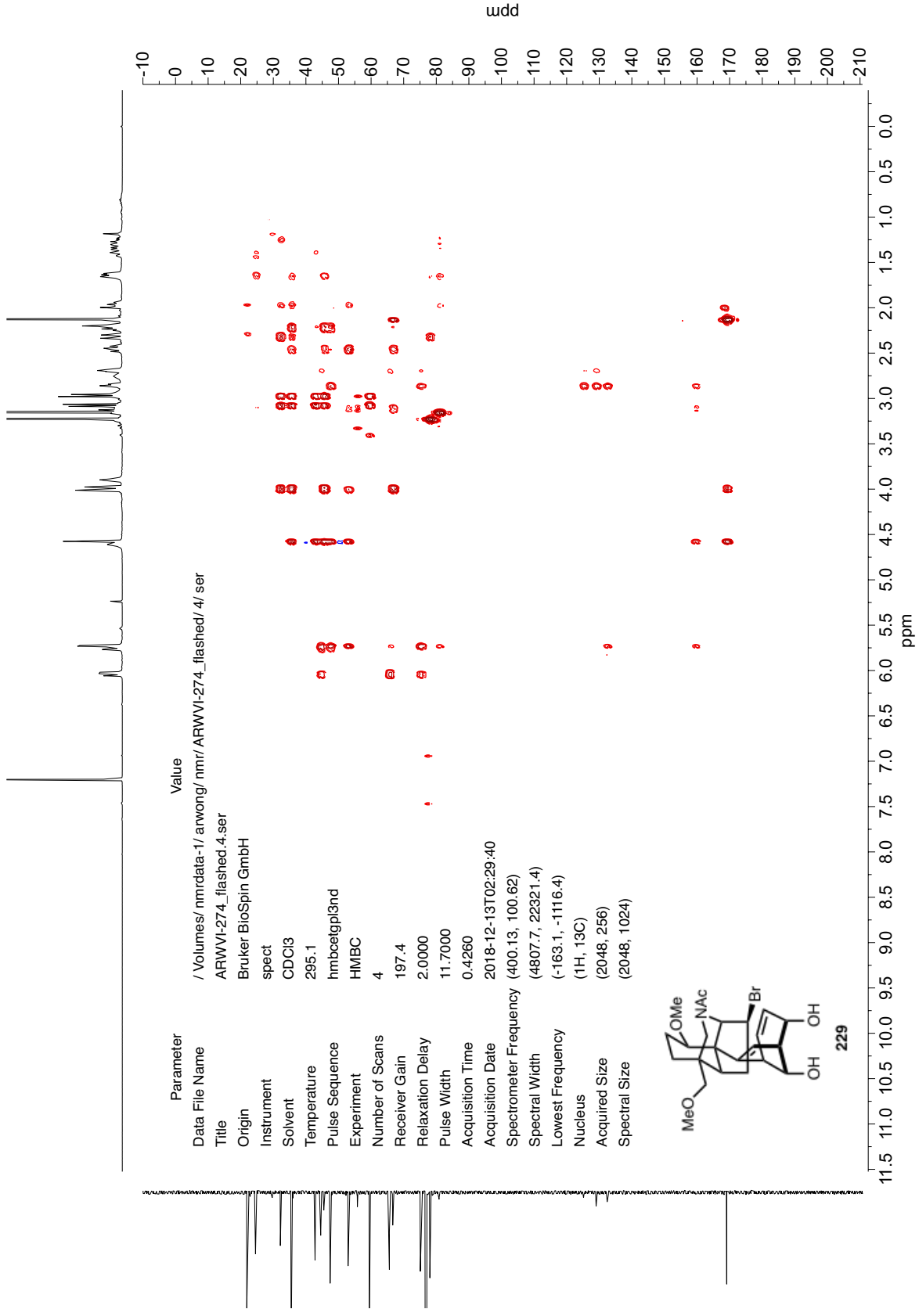

ppm
ppm
Parameter Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-271_flashed_char/ 3/ ser
Title ARWVI-271_flashed_char.3.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 11.7000
Acquisition Time 0.2135
Acquisition Date 2018-12-10T21:08:18
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-517.1, -1262.8)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
MeO
OMe
N
O
Si
O
t-Bu
t-Bu
227

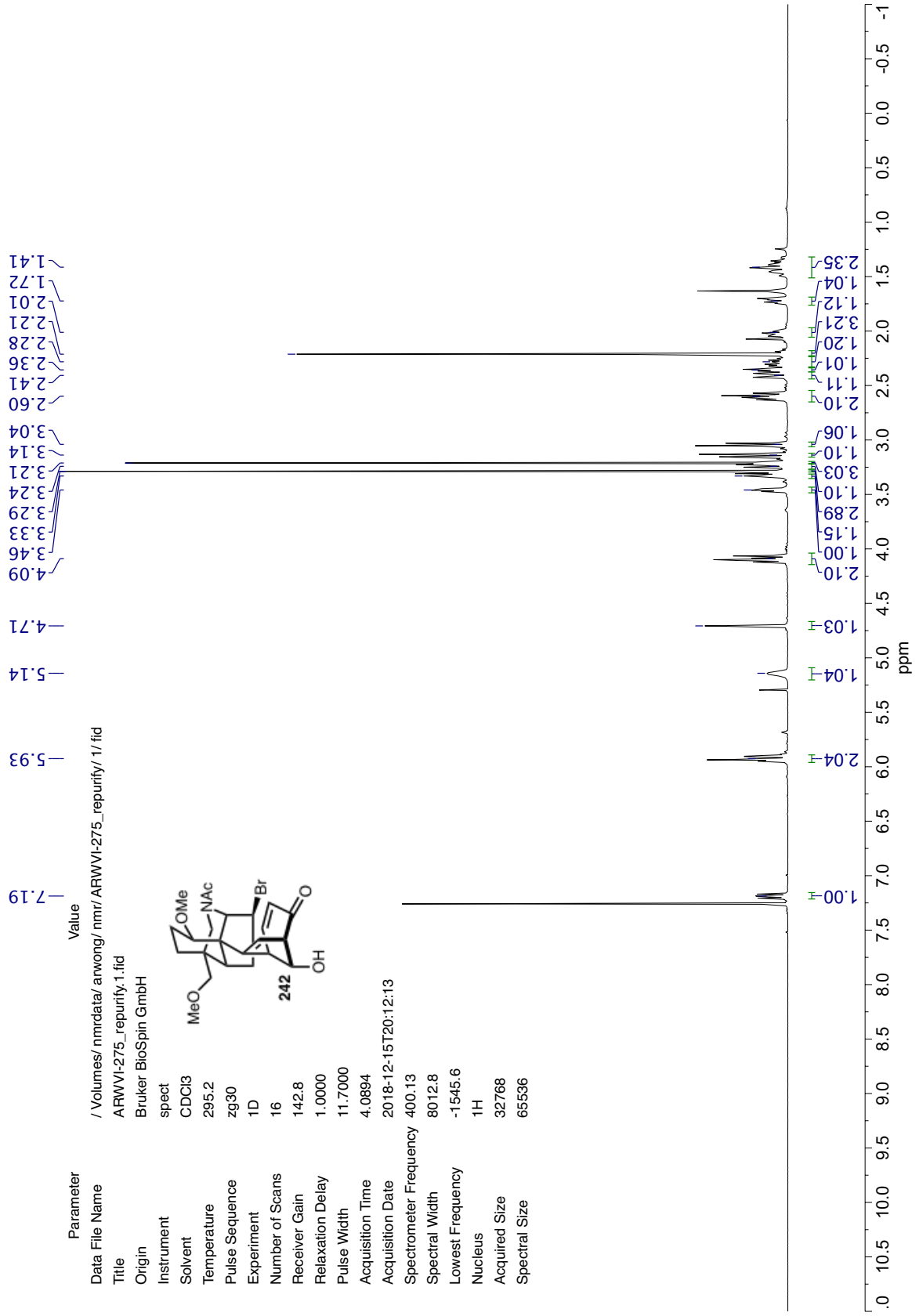

Parameter
Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWVI-272_flashed/ 2/ fid
Title
ARWVI-272_flashed.2.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zg30
Experiment
1D
Number of Scans
16
Receiver Gain
72.0
Relaxation Delay
1.0000
Pulse Width
11.7000
Acquisition Time
4.0894
Acquisition Date
2018-12-11T14:02:19
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.0
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
OMe
NAc
MeO
Br
O
Si
O
t-Bu
t-Bu
228
ppm

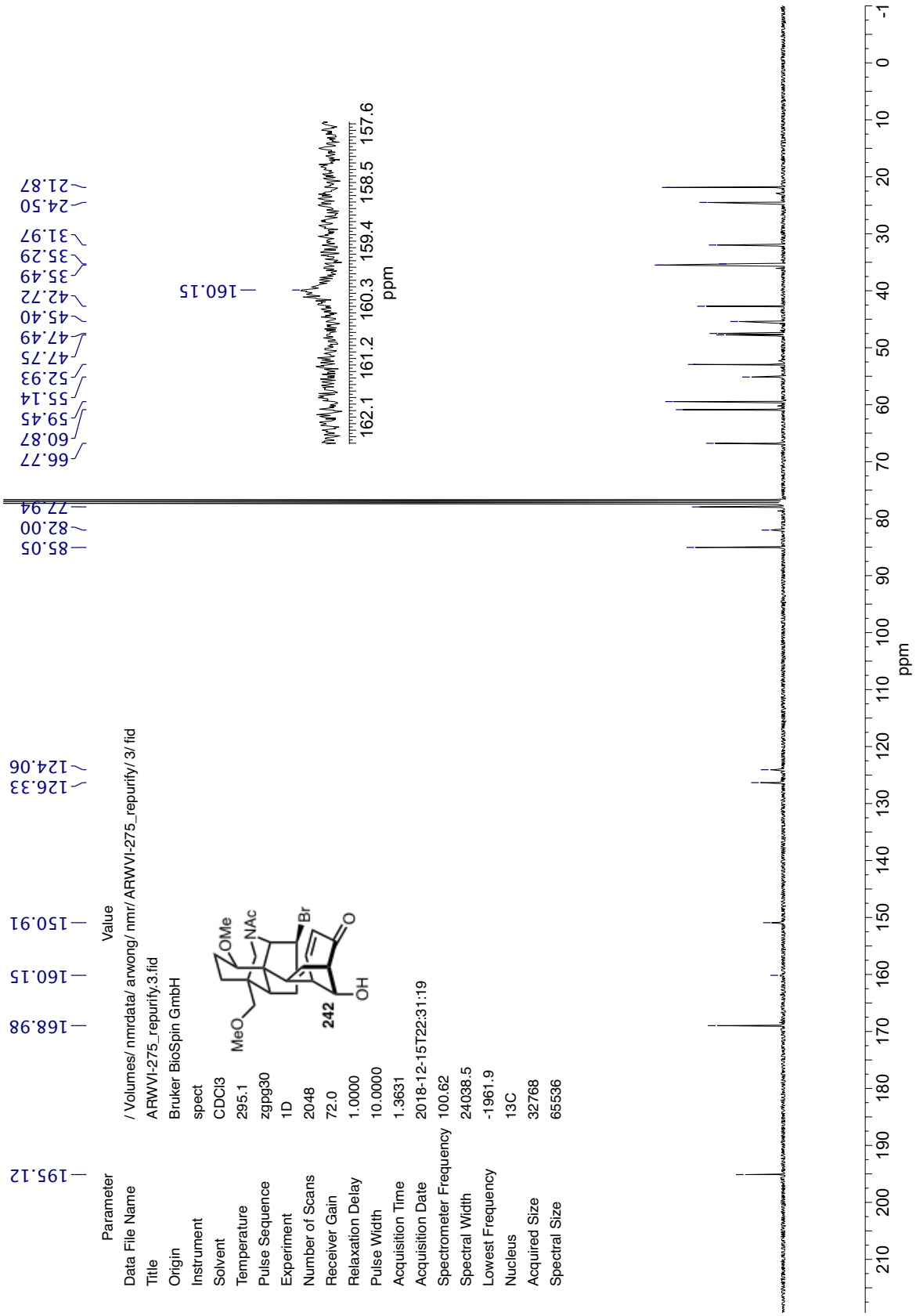

Parameter Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-272_flashed_char/ 1/ fid
Title ARWVI-272_flashed_char.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.2
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 2000
Receiver Gain 78.7
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2018-12-11T23:16:52
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1961.9
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
MeO
OMe
NAc
Br
O
Si
O
t-Bu
t-Bu
228
169.04
135.91
128.20
124.88
80.60
78.08
77.64
66.65
66.22
59.45
55.68
53.13
47.30
46.26
45.95
45.66
42.80
35.52
35.40
32.19
29.68
28.97
28.33
24.58
21.81
21.26
20.75
ppm

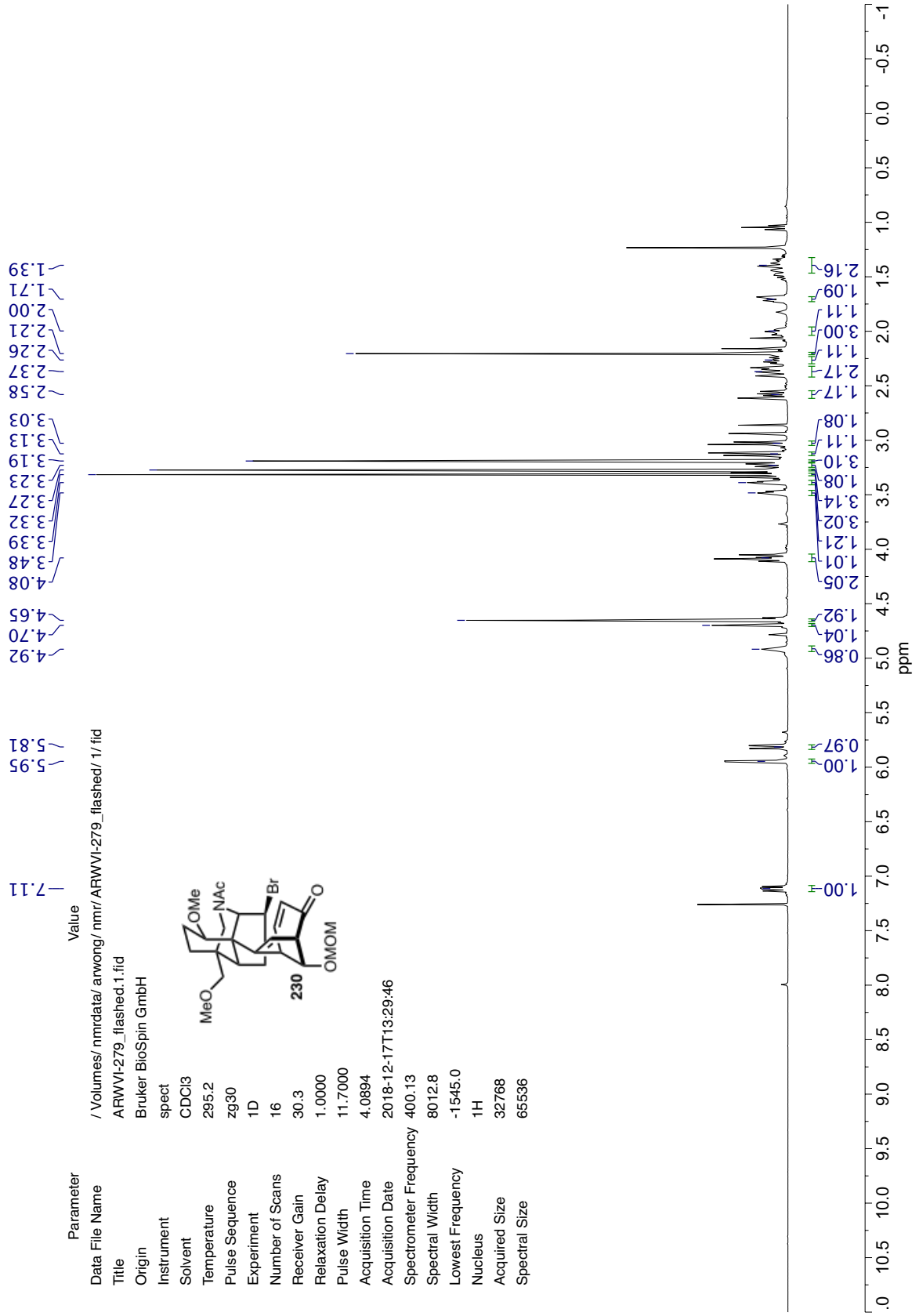

Parameter
Value
Data File Name / Volumes/ nmrdata-1/ arwong/ nmr/ ARWVI-274_flashed/ 1/ fid
Title ARWVI-274_flashed.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.2
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 112.8
Relaxation Delay 1.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Acquisition Date 2018-12-13T02:10:44
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.4
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
OMe
NAc
Br
MeO
OH
OH
229
6.10
5.80
4.66
4.05
3.96
3.29
3.21
3.18
3.13
3.03
2.92
2.81
2.75
2.51
2.38
2.28
2.19
2.01
1.70
1.46
1.33
1.00
2.00
1.93
1.95
1.03
3.00
3.01
0.91
1.18
1.28
1.06
0.73
1.10
0.97
1.01
1.96
3.02
1.00
1.88
1.09
0.99
ppm

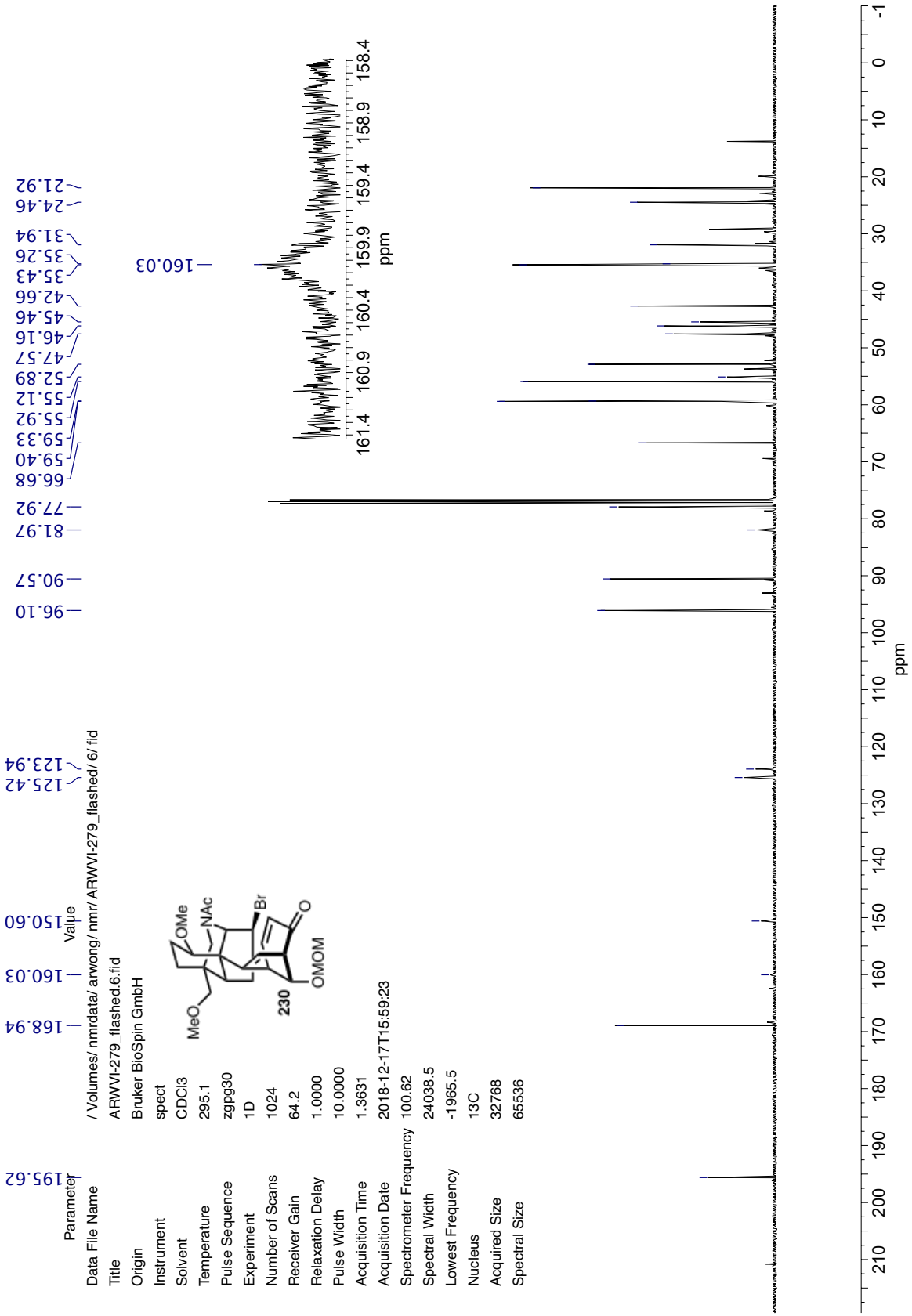

169.10
132.43
129.04
125.13
80.85
78.04
75.10
66.64
65.61
59.45
55.80
52.94
47.44
47.43
45.49
44.54
42.80
35.47
35.44
32.16
24.54
21.85
OMe
NAc
Br
MeO
OH
OH
229
Parameter
Value
Data File Name / Volumes/ nmrdata-1/ arwong/ nmr/ ARWVI-274_flashed/ 6/ fid
Title ARWVI-274_flashed.6.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 2000
Receiver Gain 78.7
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2018-12-13T05:19:26
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1962.6
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
ppm


ppm
ppm
Parameter
Value
Data File Name
/ Volumes/ nmrdata-1/ arwong/ nmr/ ARWVI-274_flashed/ 4/ ser
Title
ARWVI-274_flashed 4.ser
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
hmbcetgpl3nd
Experiment
HMBC
Number of Scans
4
Receiver Gain
197.4
Relaxation Delay
2.0000
Pulse Width
11.7000
Acquisition Time
0.4260
Acquisition Date
2018-12-13T02:29:40
Spectrometer Frequency
(400.13, 100.62)
Spectral Width
(4807.7, 22321.4)
Lowest Frequency
(-163.1, -1116.4)
Nucleus
(1H, 13C)
Acquired Size
(2048, 256)
Spectral Size
(2048, 1024)
MeO
OMe
NAc
Br
OH
OH
229


Parameter
Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-275_repurify/ 1/ fid
Title ARWVI-275_repurify.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.2
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 142.8
Relaxation Delay 1.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Acquisition Date 2018-12-15T20:12:13
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.6
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
OMe
NAc
Br
O
MeO
OH
242
7.19
5.93
5.14
4.71
4.09
3.46
3.33
3.29
3.24
3.21
3.14
3.04
2.60
2.41
2.36
2.28
2.21
2.01
1.72
1.41
1.00
2.04
1.04
1.03
2.10
1.00
1.15
2.89
1.10
3.03
1.10
1.06
2.10
1.11
1.01
1.20
3.21
1.12
1.04
2.35
ppm


195.12
168.98
160.15
150.91
126.33
124.06
85.05
82.00
77.94
66.77
60.87
59.45
55.14
52.93
47.75
47.49
45.40
42.72
35.49
35.29
31.97
24.50
21.87
160.15
162.1 161.2 160.3 159.4 158.5 157.6
ppm
OMe
NAc
Br
O
MeO
242
OH
Parameter
Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-275_repurify/ 3/ fid
Title ARWVI-275_repurify.3.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 2048
Receiver Gain 72.0
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2018-12-15T22:31:19
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1961.9
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
ppm


Parameter
Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-279_flashed/ 1/ fid
Title ARWVI-279_flashed.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.2
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 30.3
Relaxation Delay 1.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Acquisition Date 2018-12-17T13:29:46
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.0
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
OMe
NAc
MeO
Br
O
OMOM
230
7.11
5.95
5.81
4.92
4.70
4.65
4.08
3.48
3.39
3.32
3.27
3.23
3.19
3.13
3.03
2.58
2.37
2.26
2.21
2.00
1.71
1.39
1.00
0.97
1.00
1.92
1.04
0.86
2.05
1.01
1.21
3.02
3.14
1.08
3.10
1.11
1.08
1.17
2.17
1.11
3.00
1.11
1.09
2.16
ppm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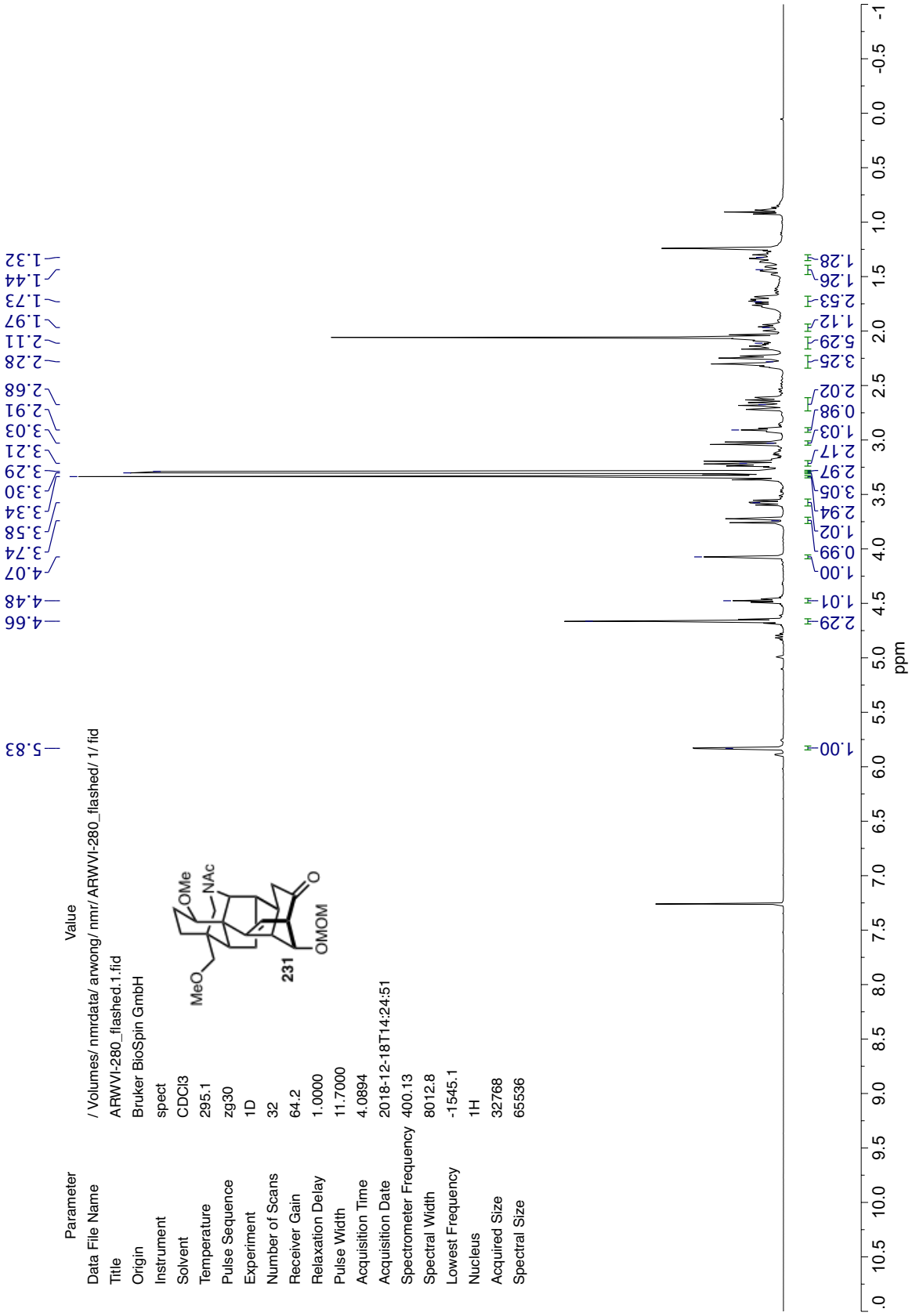
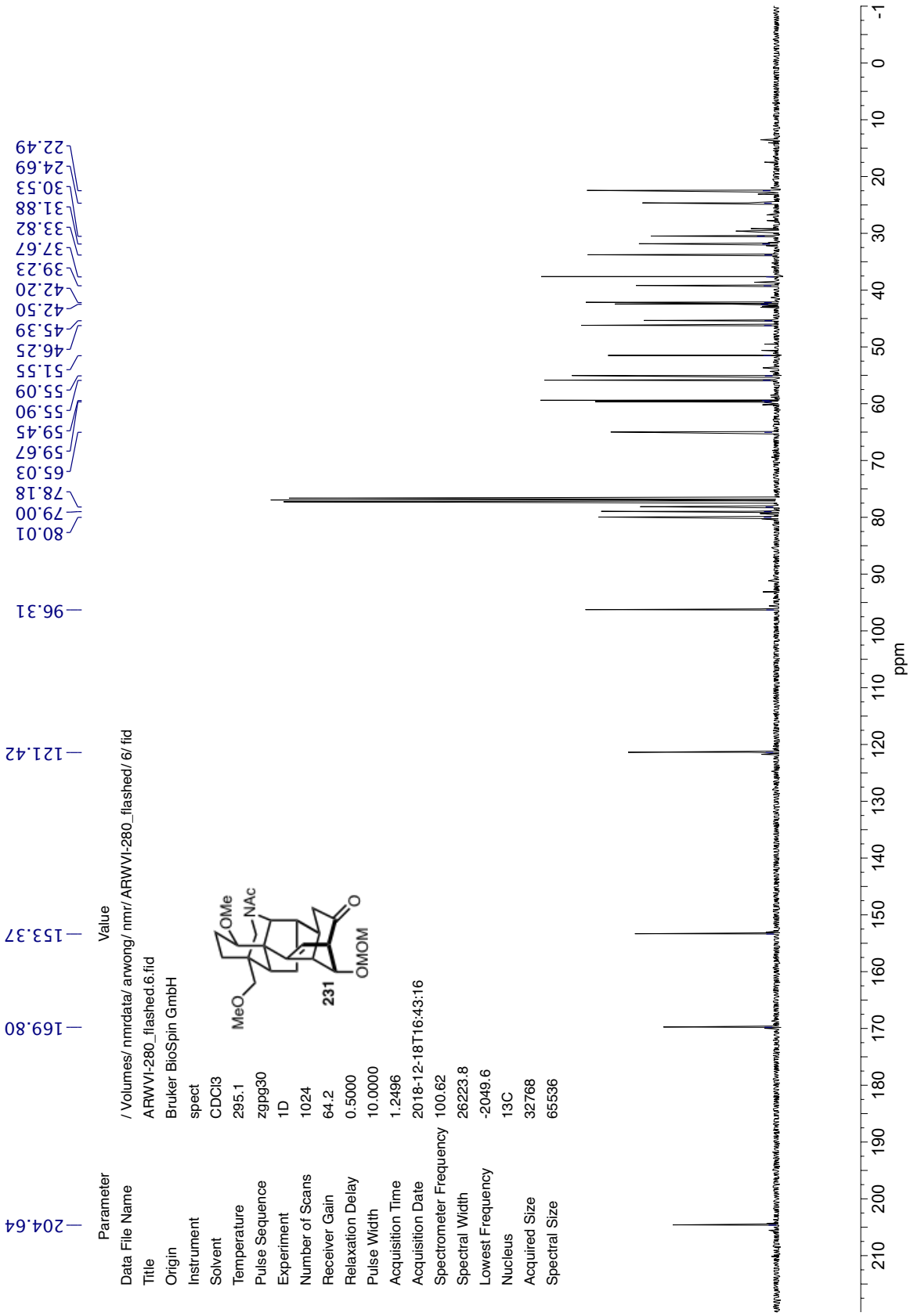
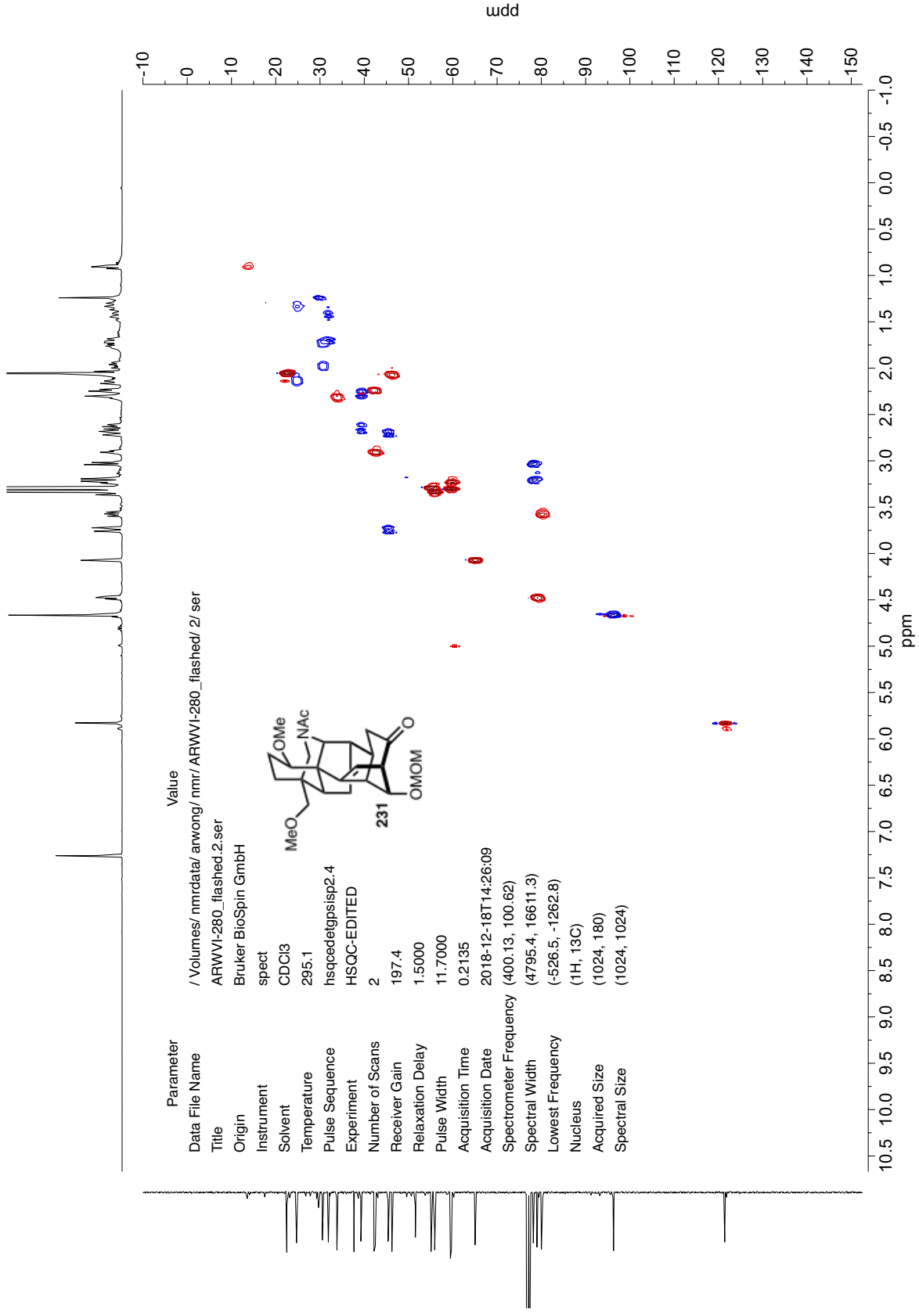
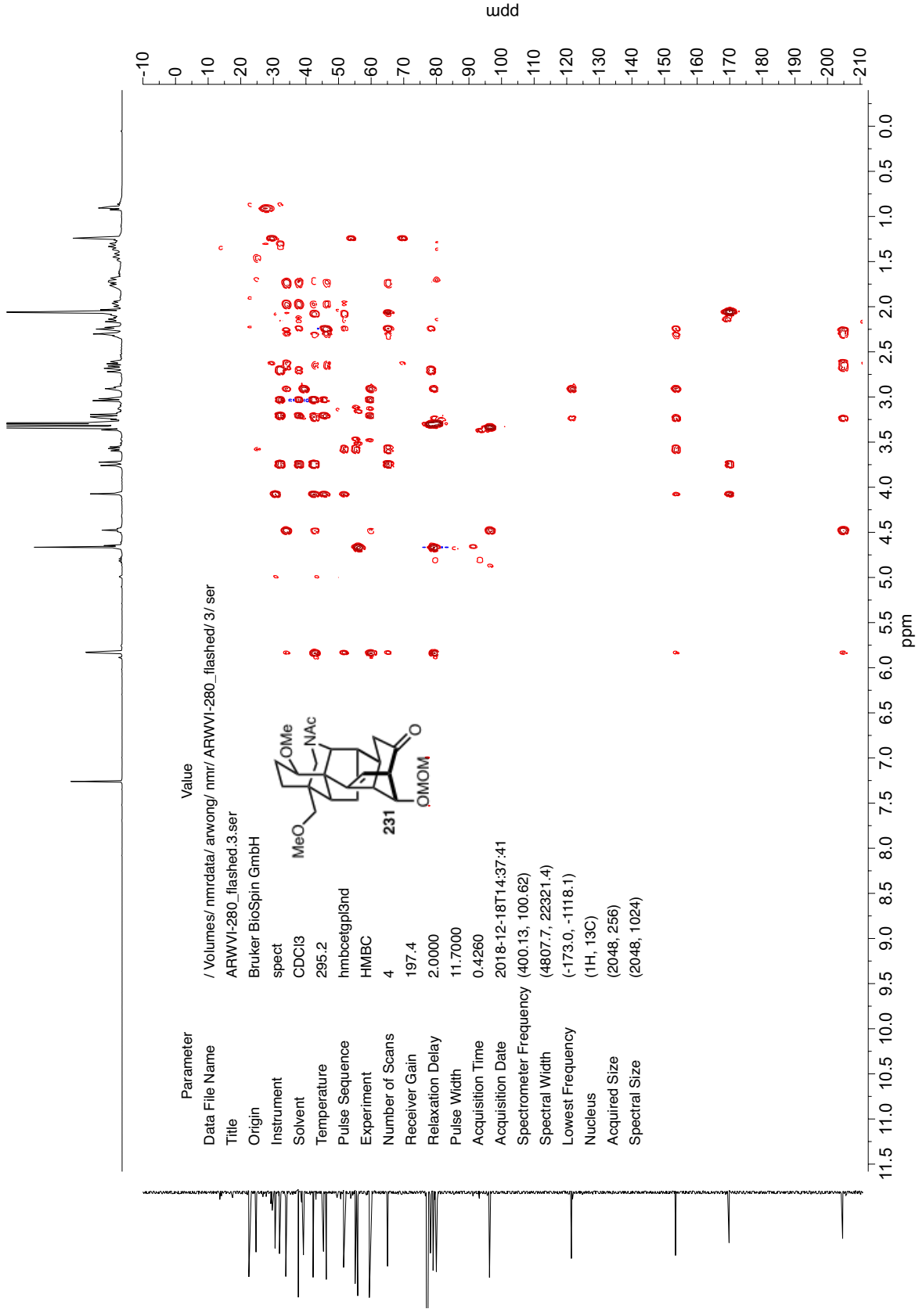
Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-279_flashed/ 6/ fid
Title ARWVI-279_flashed.6.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 1024
Receiver Gain 64.2
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2018-12-17T15:59:23
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1965.5
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
195.62
168.94
160.03
150.60
125.42
123.94
96.10
90.57
81.97
77.92
66.68
59.40
59.33
55.92
55.12
52.89
47.57
46.16
45.46
42.66
35.43
35.26
31.94
24.46
21.92
MeO
OMe
NAc
Br
O
OMOM
230
160.03
161.4
160.9
160.4
159.9
159.4
158.9
158.4
ppm
ppm

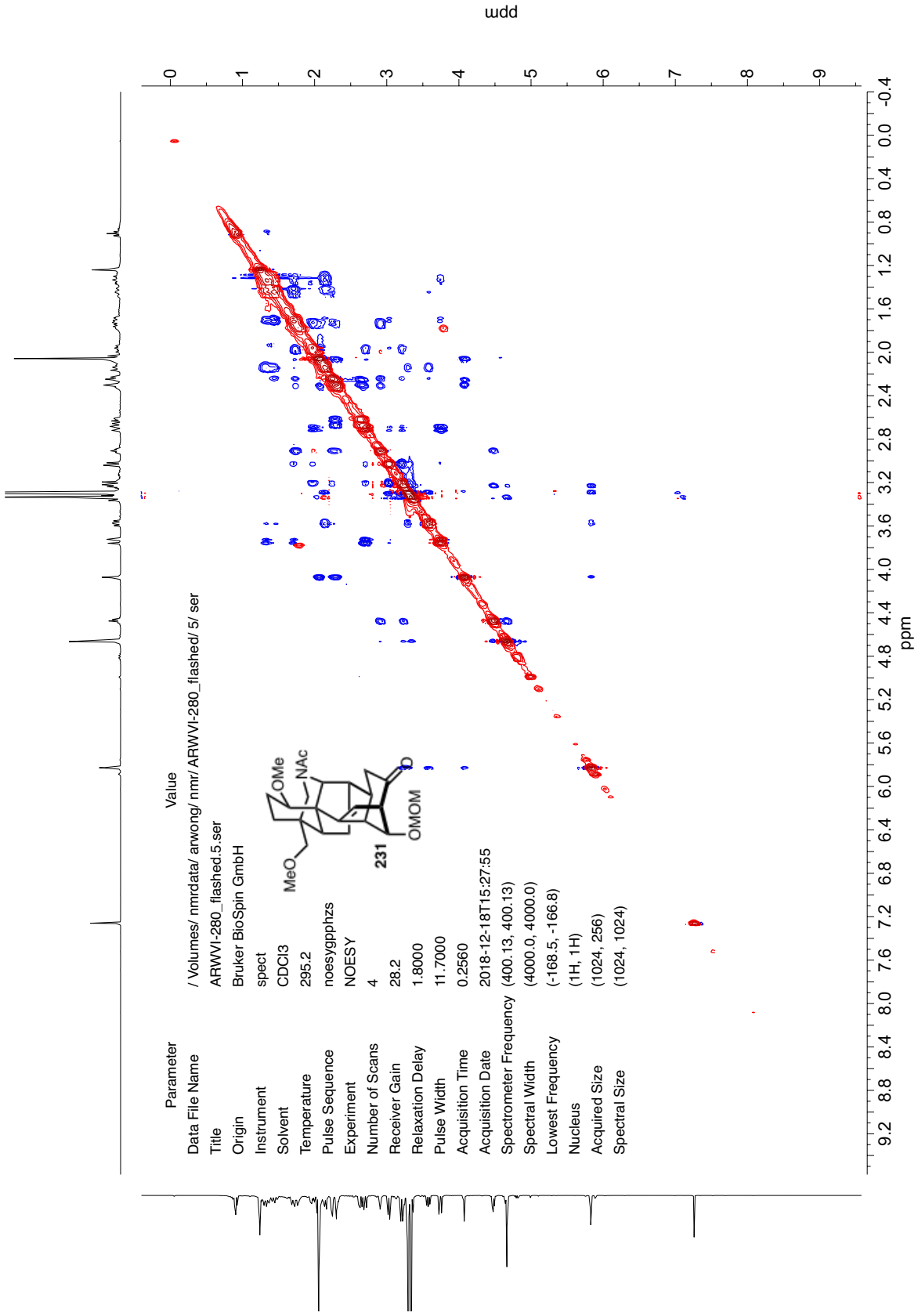

Parameter
Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-280_flashed/ 1/ fid
Title ARWVI-280_flashed.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence zg30
Experiment 1D
Number of Scans 32
Receiver Gain 64.2
Relaxation Delay 1.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Acquisition Date 2018-12-18T14:24:51
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.1
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
MeO
OMe
NAc
OMOM
O
231
5.83
4.66
4.48
4.07
3.74
3.58
3.34
3.30
3.29
3.21
3.03
2.91
2.68
2.28
2.11
1.97
1.73
1.44
1.32
1.00
2.29
1.01
1.00
0.99
1.02
2.94
3.05
2.97
2.17
1.03
0.98
2.02
3.25
5.29
1.12
2.53
1.26
1.28
ppm

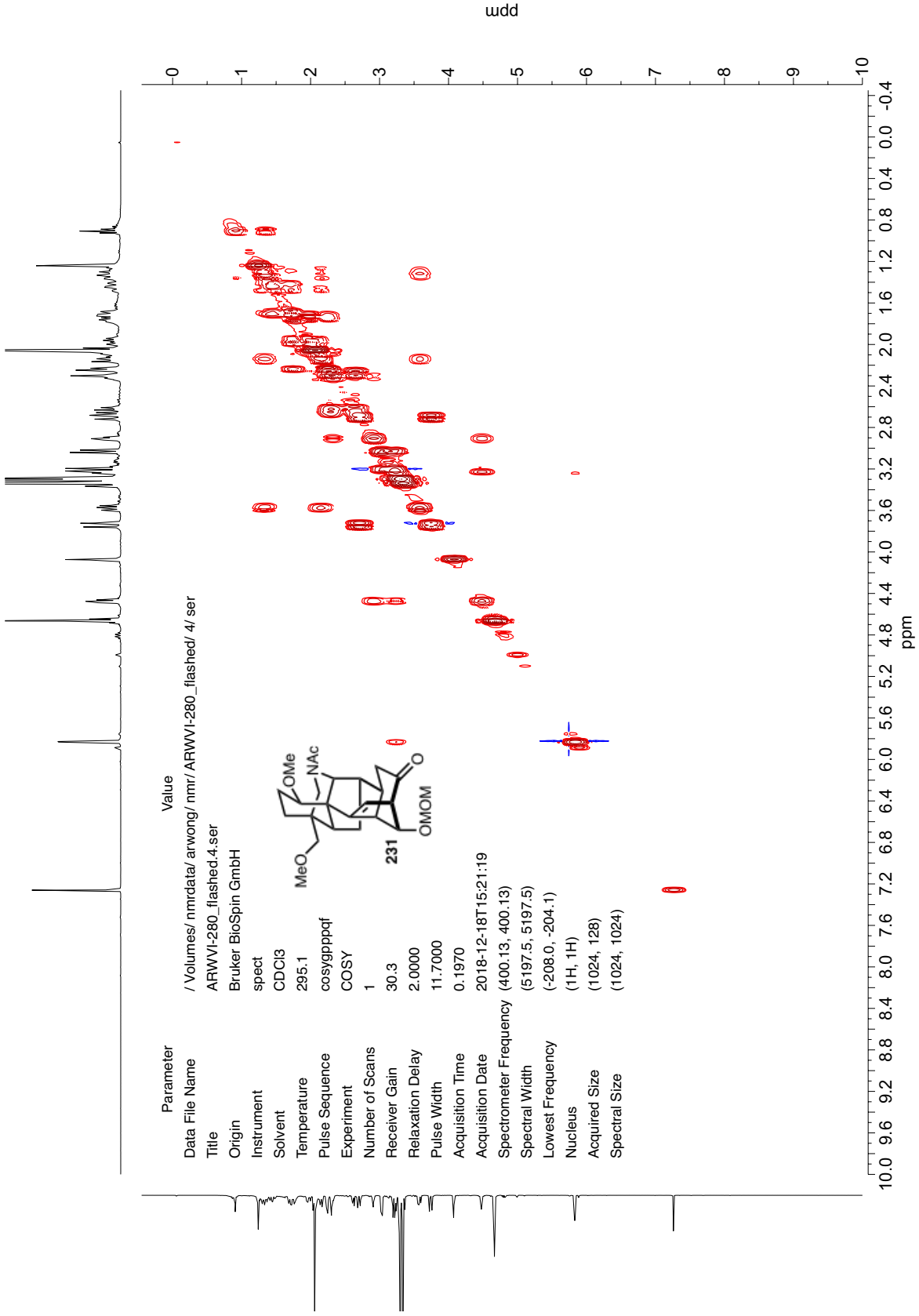


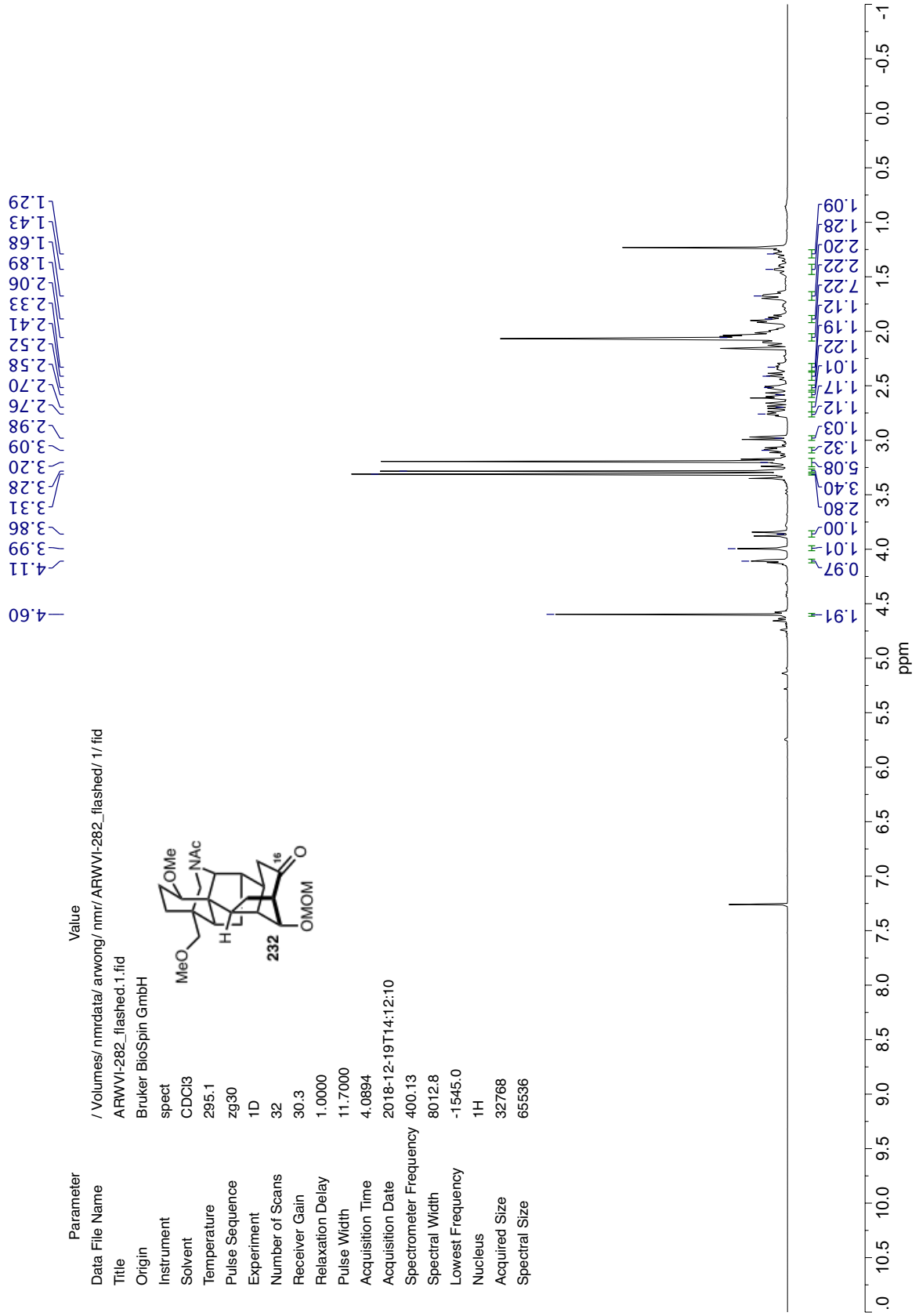
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ arwong/ nmr/ ARWVI-280_flashed/ 6/ fid
Title	ARWVI-280_flashed.6.fid
Origin	Bruker BioSpin GmbH
Instrument	spect
Solvent	CDCl3
Temperature	295.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	1024
Receiver Gain	64.2
Relaxation Delay	0.5000
Pulse Width	10.0000
Acquisition Time	1.2496
Acquisition Date	2018-12-18T16:43:16
Spectrometer Frequency	100.62
Spectral Width	26223.8
Lowest Frequency	-2049.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

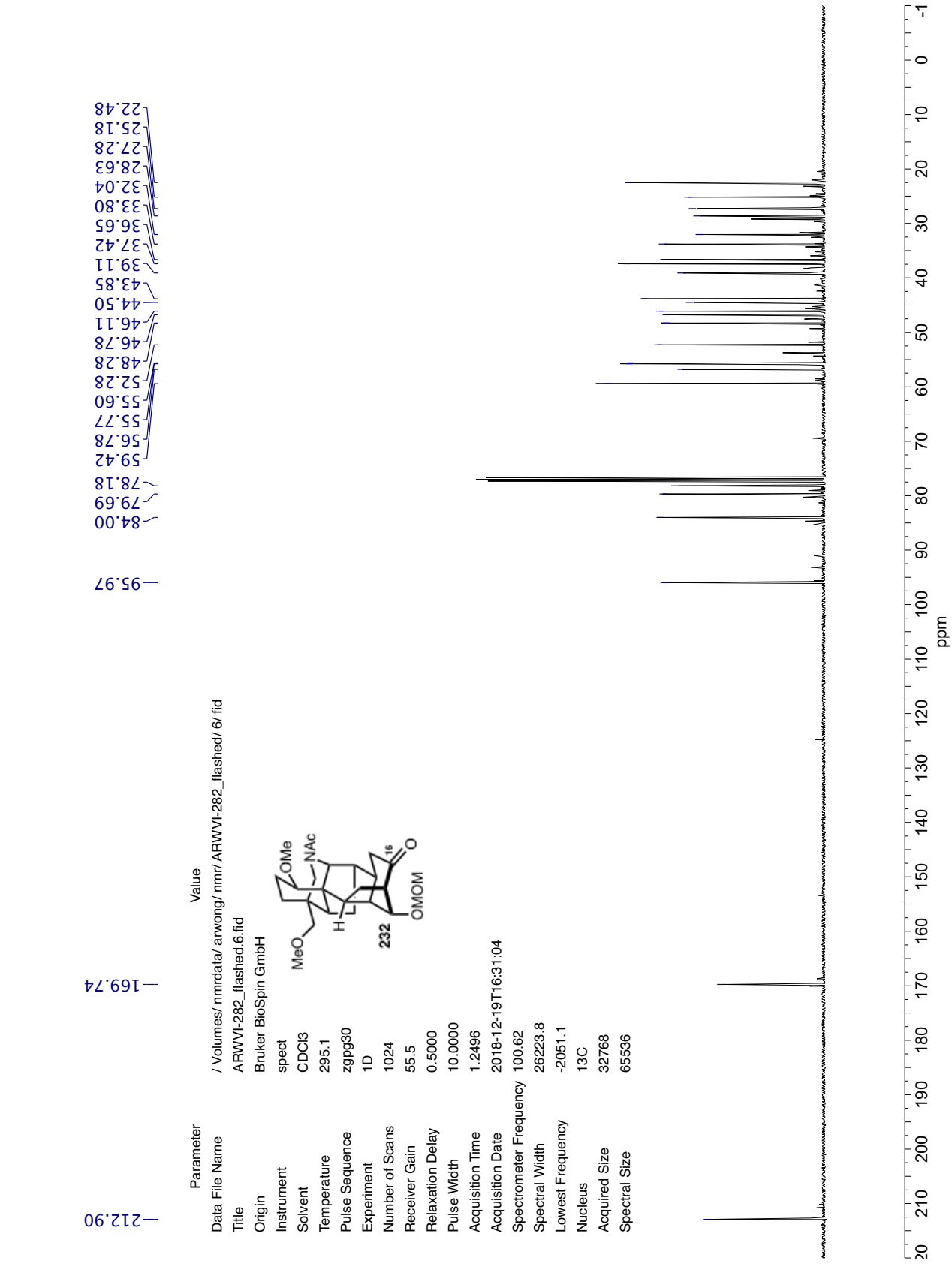

ppm
ppm
OMe
NAc
MeO
231
OMOM
O
Parameter Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-280_flashed/ 2/ ser
Title ARWVI-280_flashed.2.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 11.7000
Acquisition Time 0.2135
Acquisition Date 2018-12-18T14:26:09
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-526.5, -1262.8)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)

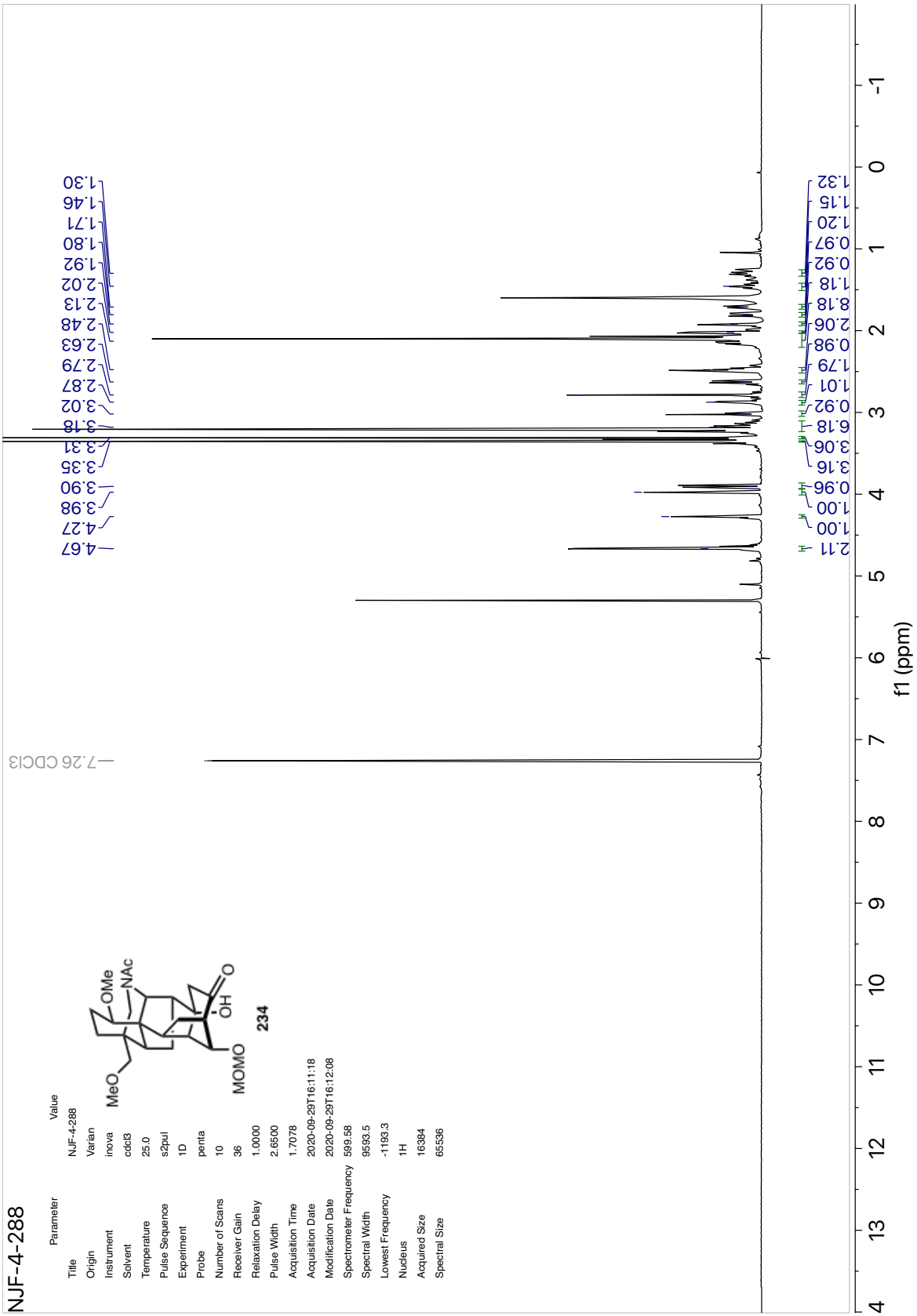

ppm
ppm
MeO
OMe
NAc
OMOM
O
231
Parameter
Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWVI-280_flashed/ 3/ ser
Title
ARWVI-280_flashed.3.ser
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.2
Pulse Sequence
hmbcetgpl3nd
Experiment
HMBC
Number of Scans
4
Receiver Gain
197.4
Relaxation Delay
2.0000
Pulse Width
11.7000
Acquisition Time
0.4260
Acquisition Date
2018-12-18T14:37:41
Spectrometer Frequency
(400.13, 100.62)
Spectral Width
(4807.7, 22321.4)
Lowest Frequency
(-173.0, -1118.1)
Nucleus
(1H, 13C)
Acquired Size
(2048, 256)
Spectral Size
(2048, 1024)

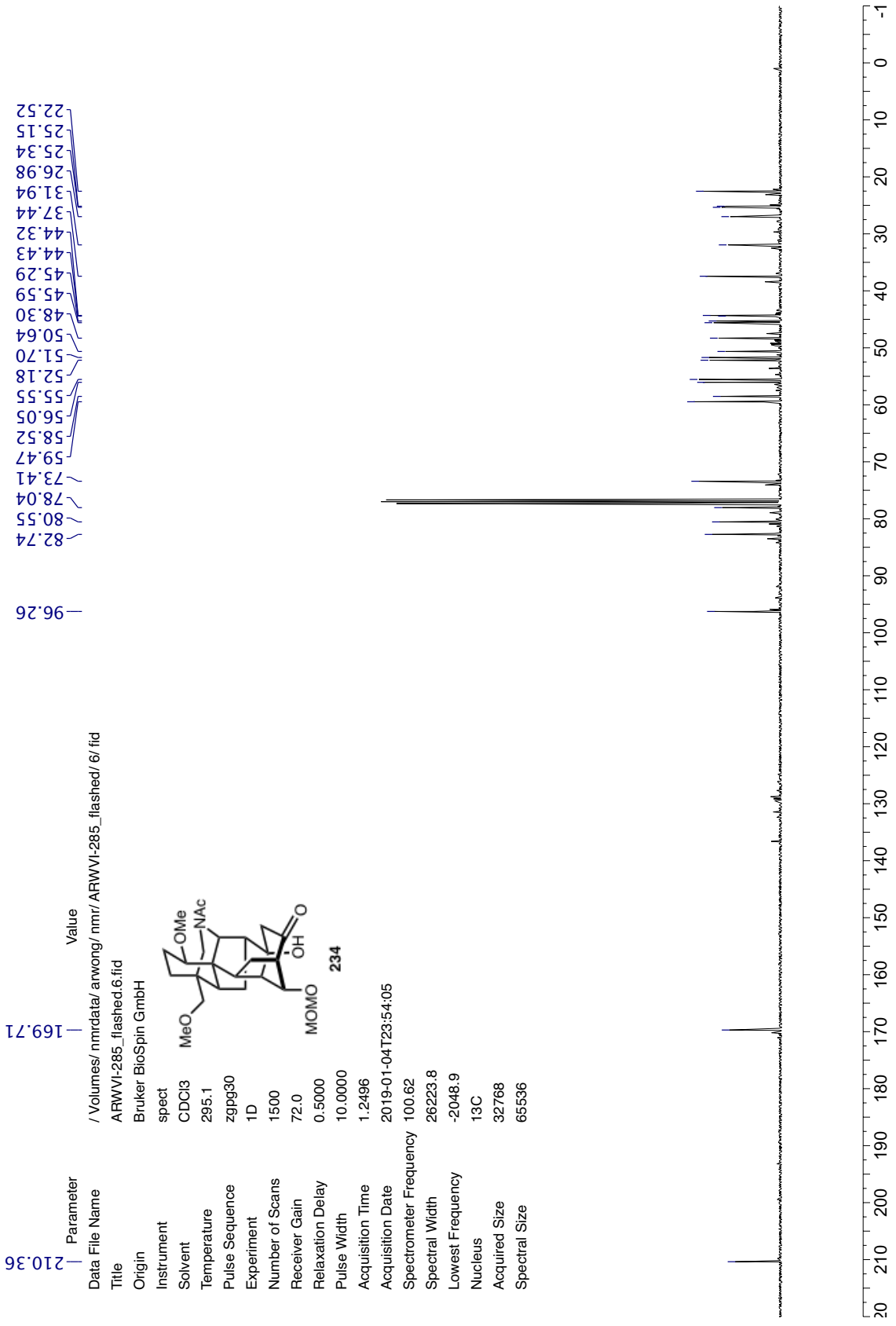

ppm
ppm
Parameter Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-280_flashed/ 5/ ser
Title ARWVI-280_flashed.5.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.2
Pulse Sequence noesygpphzs
Experiment NOESY
Number of Scans 4
Receiver Gain 28.2
Relaxation Delay 1.8000
Pulse Width 11.7000
Acquisition Time 0.2560
Acquisition Date 2018-12-18T15:27:55
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-168.5, -166.8)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
MeO
OMe
NAc
231
OMOM
D

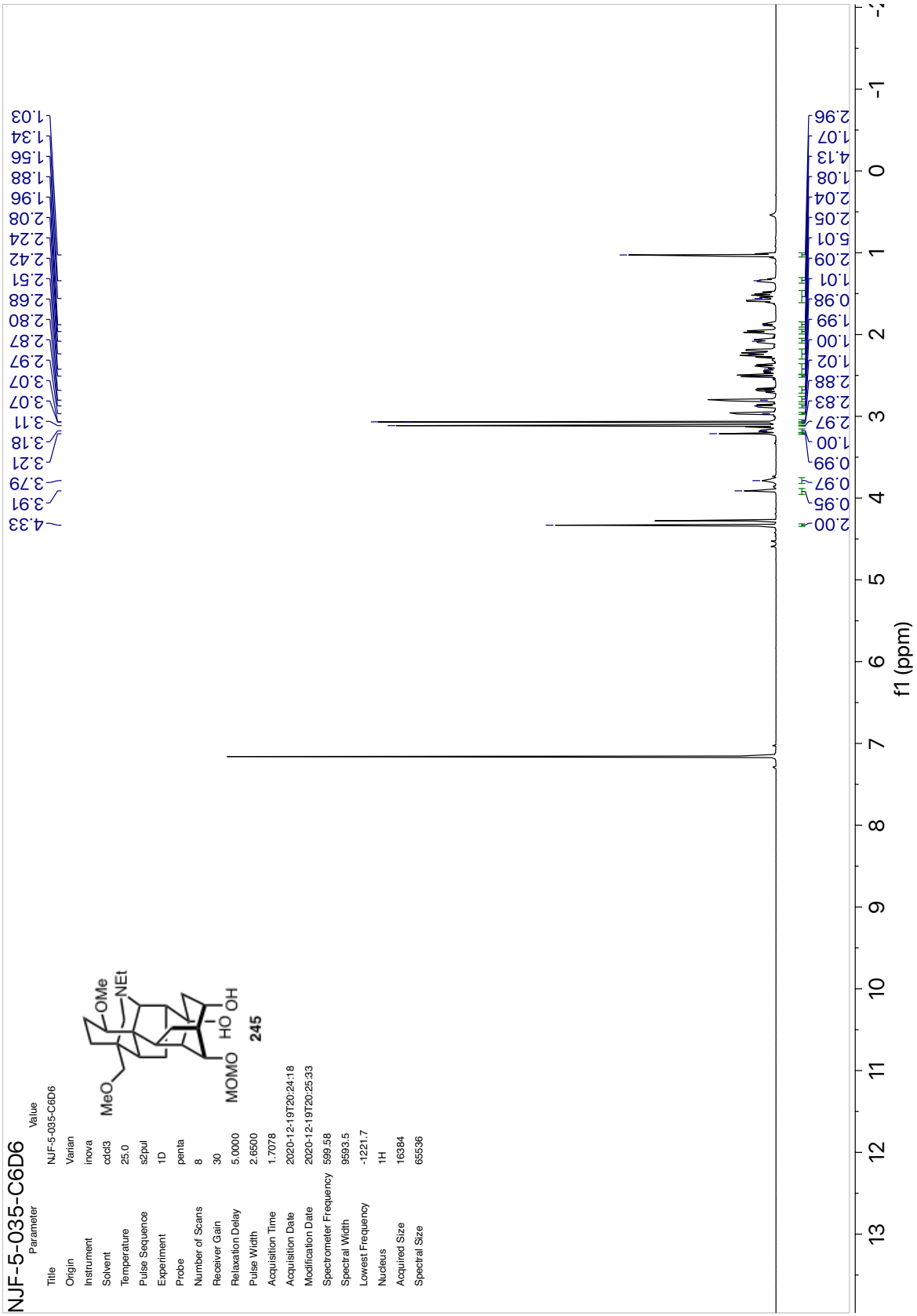

ppm
ppm
MeO
OMe
NAc
OMOM
O
231
Parameter Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-280_flashed/ 4/ ser
Title ARWVI-280_flashed.4.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence cosygpppqf
Experiment COSY
Number of Scans 1
Receiver Gain 30.3
Relaxation Delay 2.0000
Pulse Width 11.7000
Acquisition Time 0.1970
Acquisition Date 2018-12-18T15:21:19
Spectrometer Frequency (400.13, 400.13)
Spectral Width (5197.5, 5197.5)
Lowest Frequency (-208.0, -204.1)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)

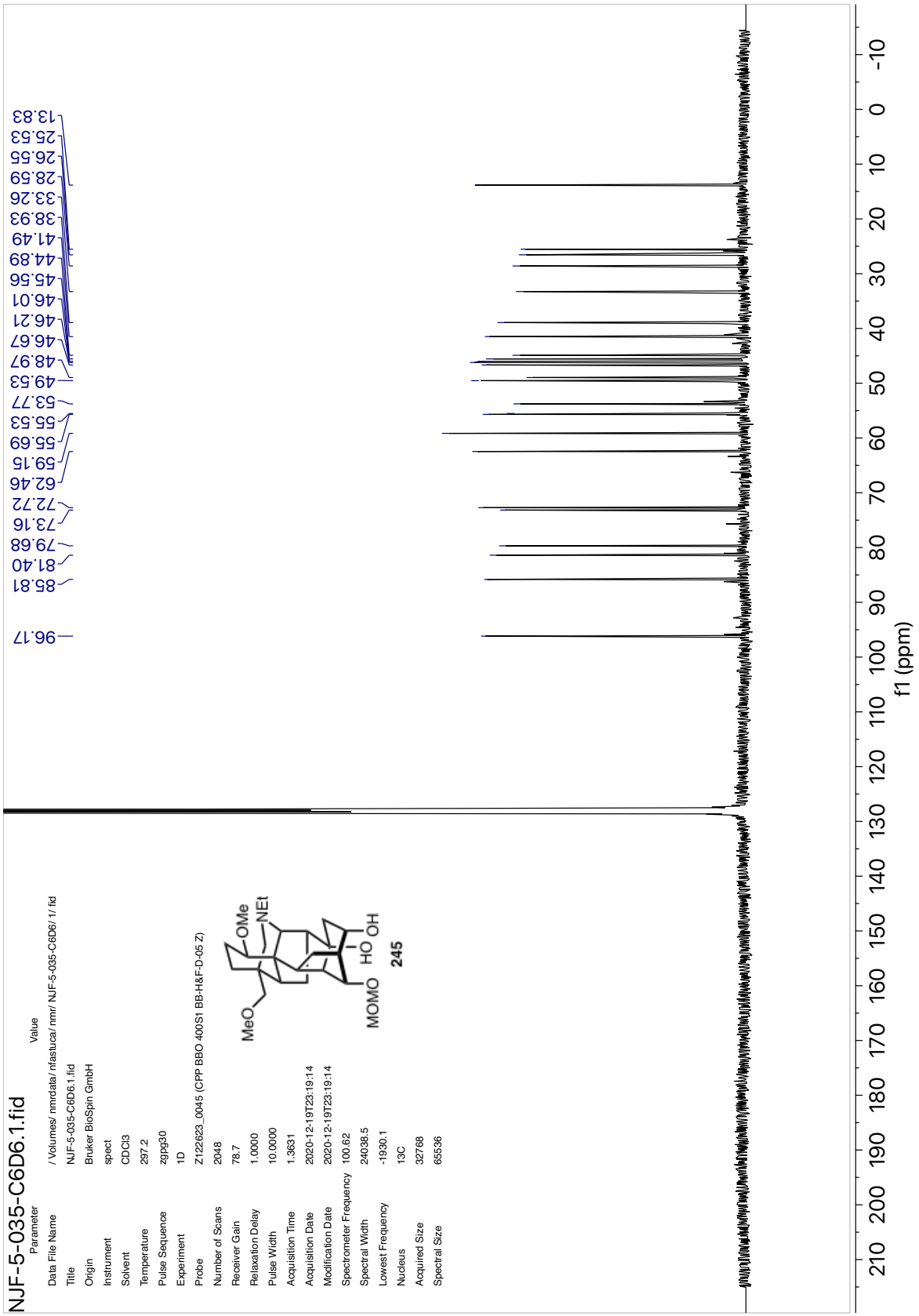

Parameter
Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-282_flashed/ 1/ fid
Title ARWVI-282_flashed.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence zg30
Experiment 1D
Number of Scans 32
Receiver Gain 30.3
Relaxation Delay 1.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Acquisition Date 2018-12-19T14:12:10
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.0
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
MeO
OMe
NAc
H
232
15
O
OMOM
4.60
4.11
3.99
3.86
3.31
3.28
3.20
3.09
2.98
2.76
2.70
2.58
2.52
2.41
2.33
2.06
1.89
1.68
1.43
1.29
1.91
0.97
1.00
1.01
2.80
3.40
5.08
1.32
1.03
1.12
1.17
1.01
1.22
1.19
1.12
7.22
2.22
2.20
1.28
1.09
ppm

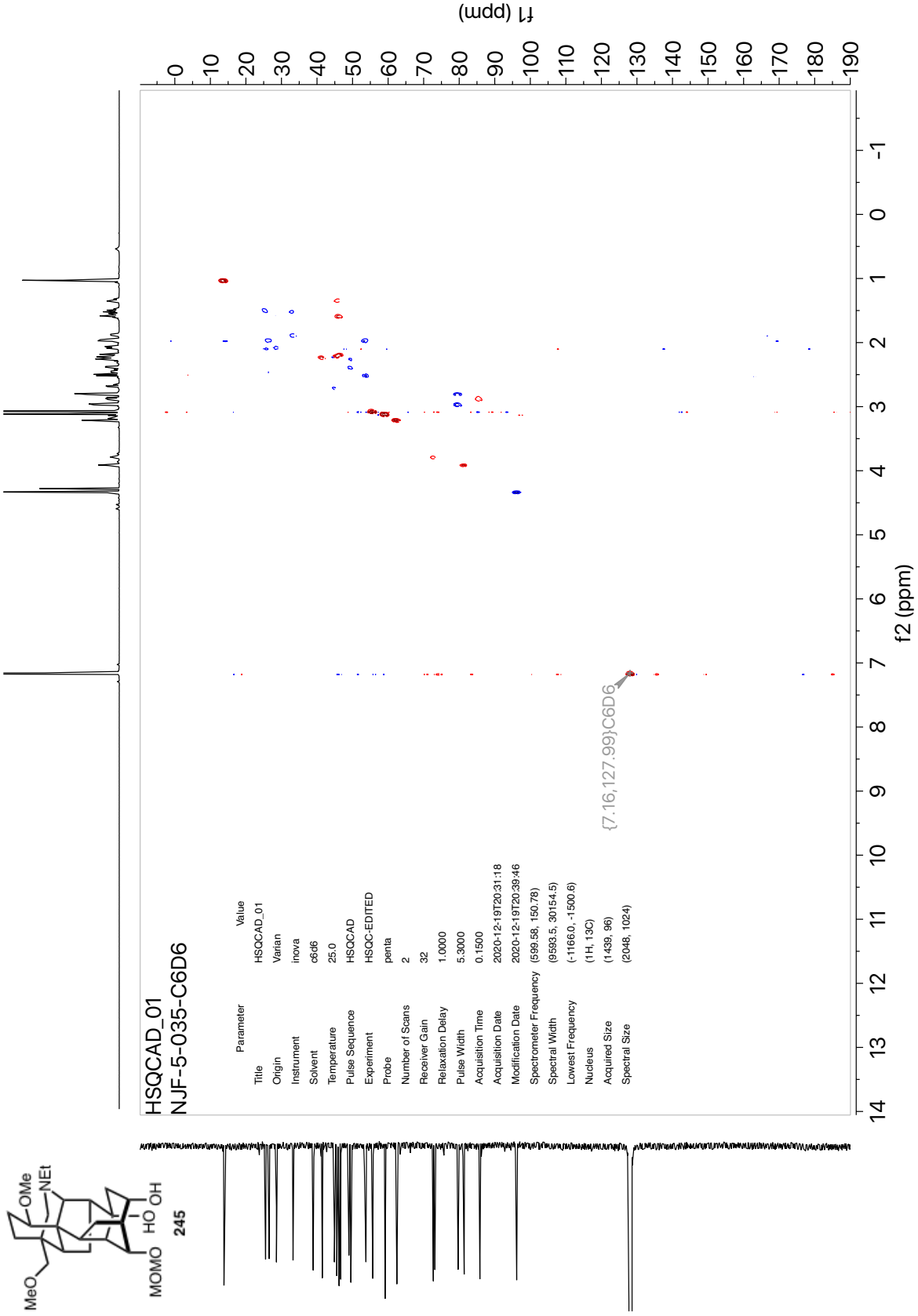

212.90
169.74
95.97
84.00
79.69
78.18
59.42
56.78
55.77
55.60
52.28
48.28
46.78
46.11
44.50
43.85
39.11
37.42
36.65
33.80
32.04
28.63
27.28
25.18
22.48
Parameter
Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-282_flashed/ 6/ fid
Title ARWVI-282_flashed.6.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 1024
Receiver Gain 55.5
Relaxation Delay 0.5000
Pulse Width 10.0000
Acquisition Time 1.2496
Acquisition Date 2018-12-19T16:31:04
Spectrometer Frequency 100.62
Spectral Width 26223.8
Lowest Frequency -2051.1
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
MeO
OMe
NAc
H
OMOM
16
O
232
ppm

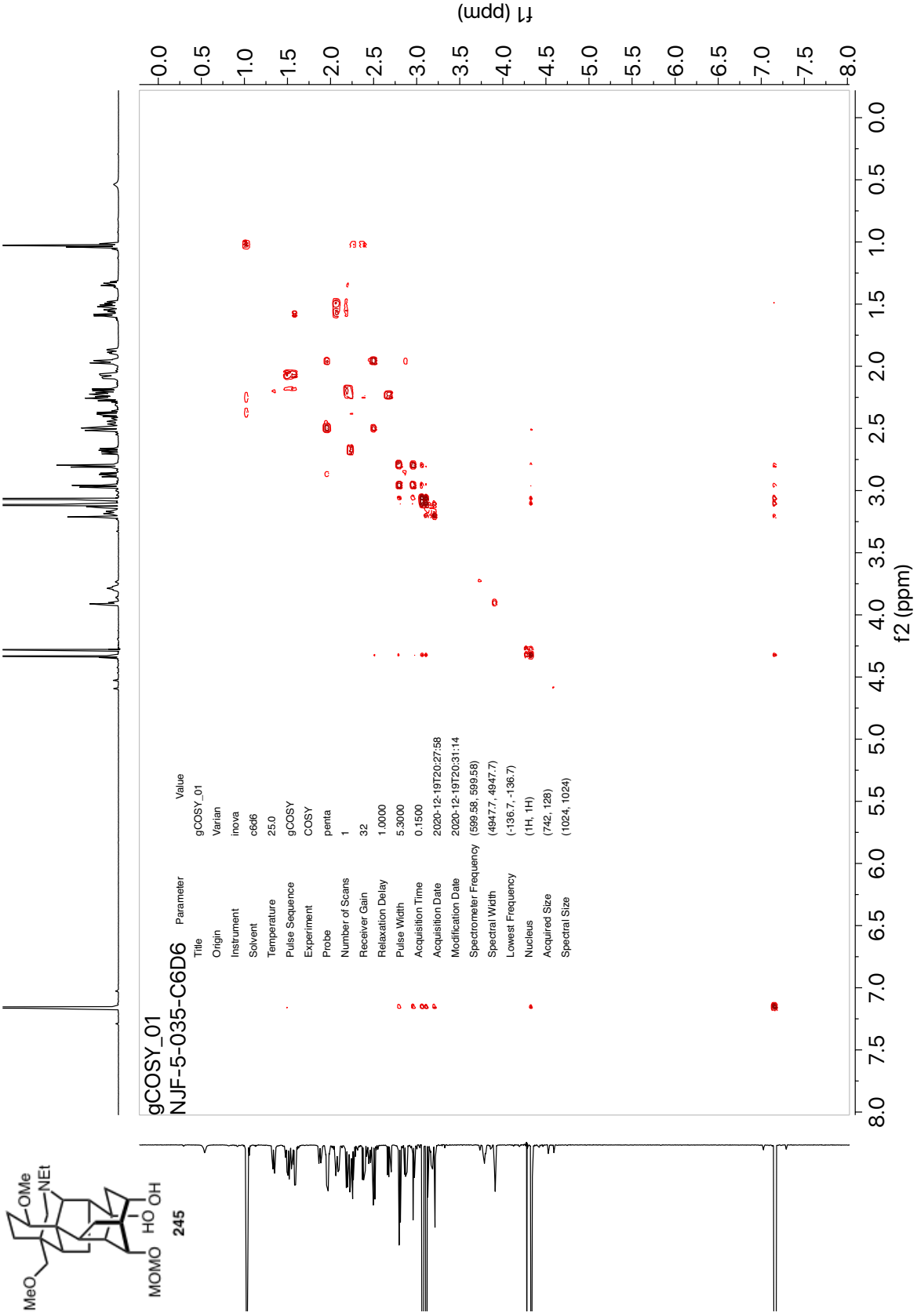

NJF-4-288
Parameter Value
Title NJF-4-288
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe penta
Number of Scans 10
Receiver Gain 36
Relaxation Delay 1.0000
Pulse Width 2.6500
Acquisition Time 1.7078
Acquisition Date 2020-09-29T16:11:18
Modification Date 2020-09-29T16:12:08
Spectrometer Frequency 599.58
Spectral Width 9593.5
Lowest Frequency -1193.3
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
MeO
OMe
NAc
OH
O
MOMO
234
7.26 CDCl3
4.67
4.27
3.98
3.90
3.35
3.31
3.18
3.02
2.87
2.79
2.63
2.48
2.13
2.02
1.92
1.80
1.71
1.46
1.30
2.11
1.00
1.00
0.96
3.16
3.06
6.18
0.92
1.01
1.79
0.98
2.06
8.18
1.18
0.92
0.97
1.20
1.15
1.32
f1 (ppm)

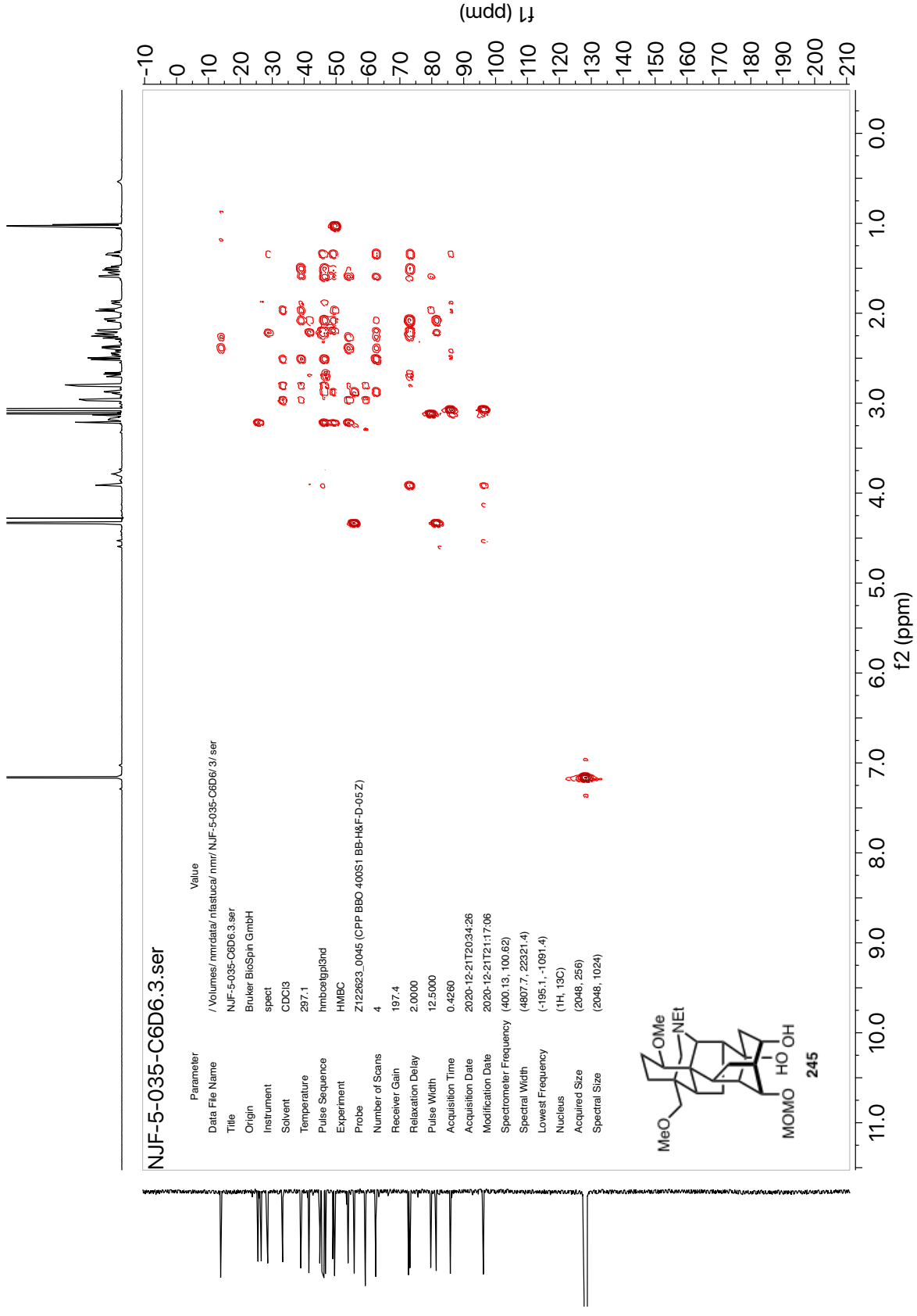

210.36
169.71
96.26
82.74
80.55
78.04
73.41
59.47
58.52
56.05
55.55
52.18
51.70
50.64
48.30
45.59
45.29
44.43
44.32
37.44
31.94
26.98
25.34
25.15
22.52
Parameter
Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-285_flashed/ 6/ fid
Title ARWVI-285_flashed.6.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 1500
Receiver Gain 72.0
Relaxation Delay 0.5000
Pulse Width 10.0000
Acquisition Time 1.2496
Acquisition Date 2019-01-04T23:54:05
Spectrometer Frequency 100.62
Spectral Width 26223.8
Lowest Frequency -2048.9
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
MeO
OMe
NAc
OH
O
MOMO
234
ppm

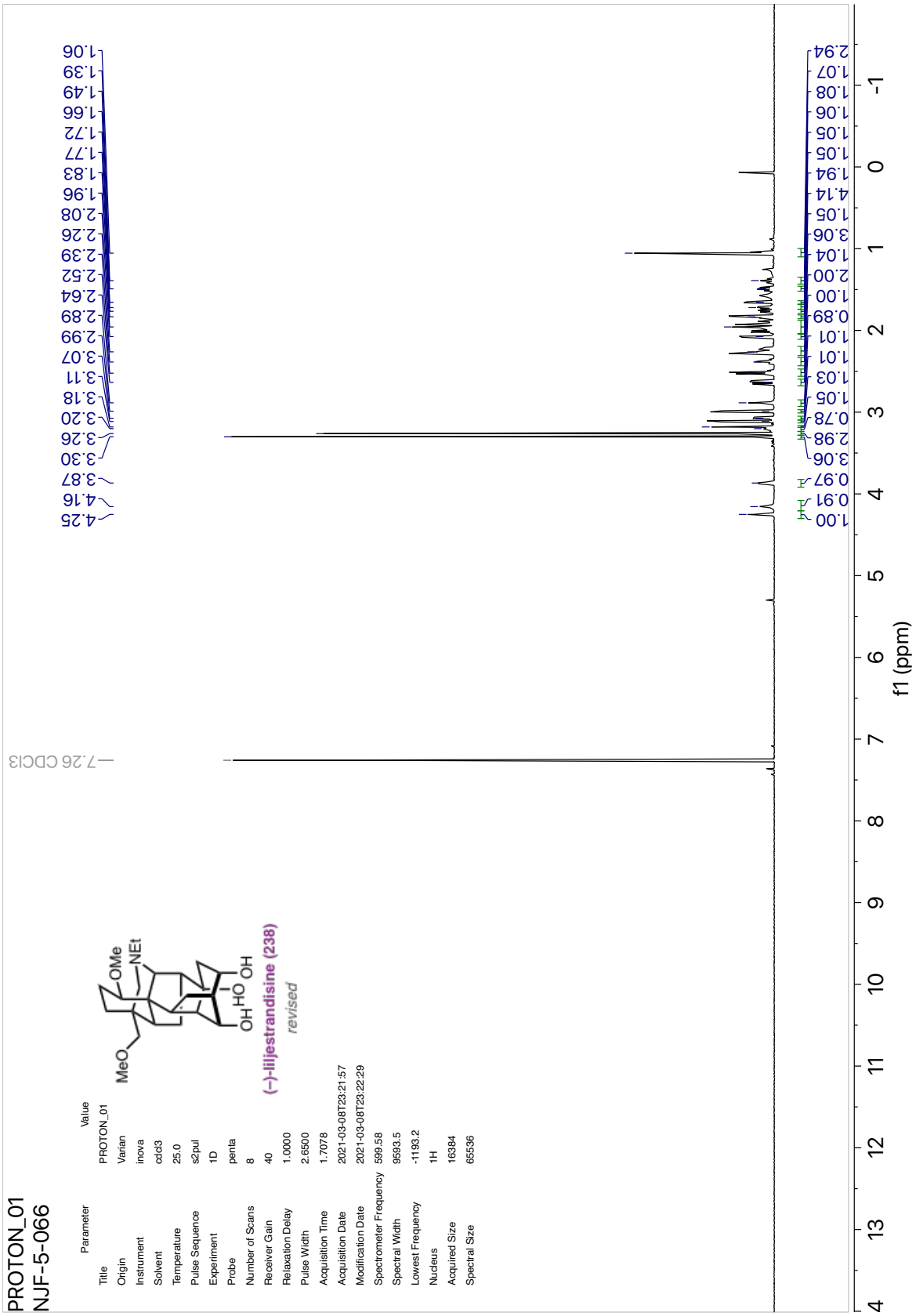

NJF-5-035-C6D6
Parameter Value
Title NJF-5-035-C6D6
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe penta
Number of Scans 8
Receiver Gain 30
Relaxation Delay 5.0000
Pulse Width 2.6500
Acquisition Time 1.7078
Acquisition Date 2020-12-19T20:24:18
Modification Date 2020-12-19T20:25:33
Spectrometer Frequency 599.58
Spectral Width 9593.5
Lowest Frequency -1221.7
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
MeO
OMe
NEt
MOMO
HO
OH
245
4.33
3.91
3.79
3.21
3.18
3.11
3.07
3.07
2.97
2.87
2.80
2.68
2.51
2.42
2.24
2.08
1.96
1.88
1.56
1.34
1.03
2.00
0.95
0.97
0.99
1.00
2.97
2.83
2.88
1.02
1.00
1.99
0.98
1.01
2.09
5.01
2.05
2.04
1.08
4.13
1.07
2.96
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

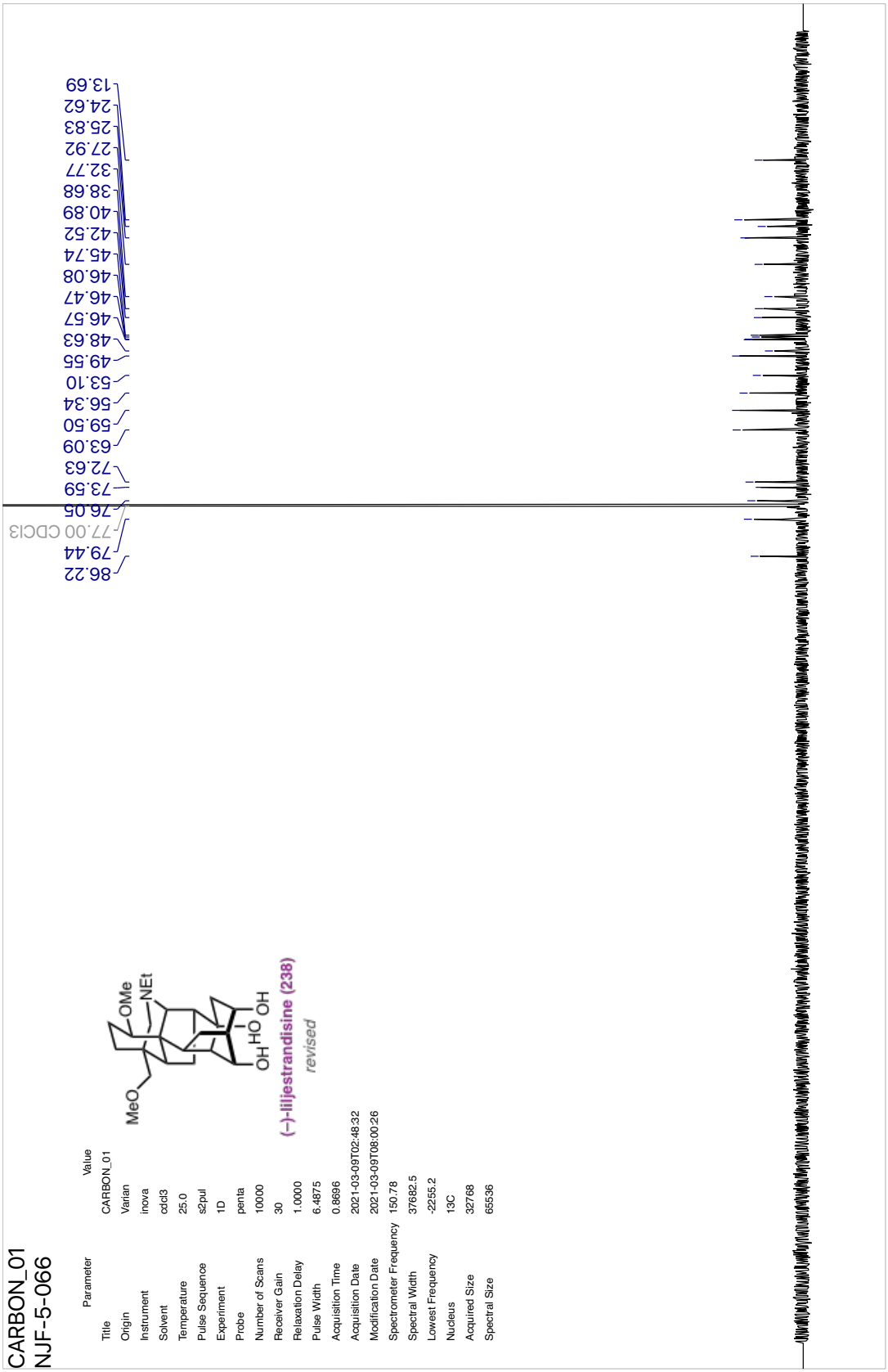

NJF-5-035-C6D6.1.fid
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-035-C6D6/ 1/ fid
Title NJF-5-035-C6D6.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.2
Pulse Sequence zgpg30
Experiment 1D
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 2048
Receiver Gain 78.7
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2020-12-19T23:19:14
Modification Date 2020-12-19T23:19:14
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1930.1
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
MeO
OMe
NEt
MOMO
HO
OH
245
96.17
85.81
81.40
79.68
73.16
72.72
62.46
59.15
55.69
55.53
53.77
49.53
48.97
46.67
46.21
46.01
45.56
44.89
41.49
38.93
33.26
28.59
26.55
25.53
13.83
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

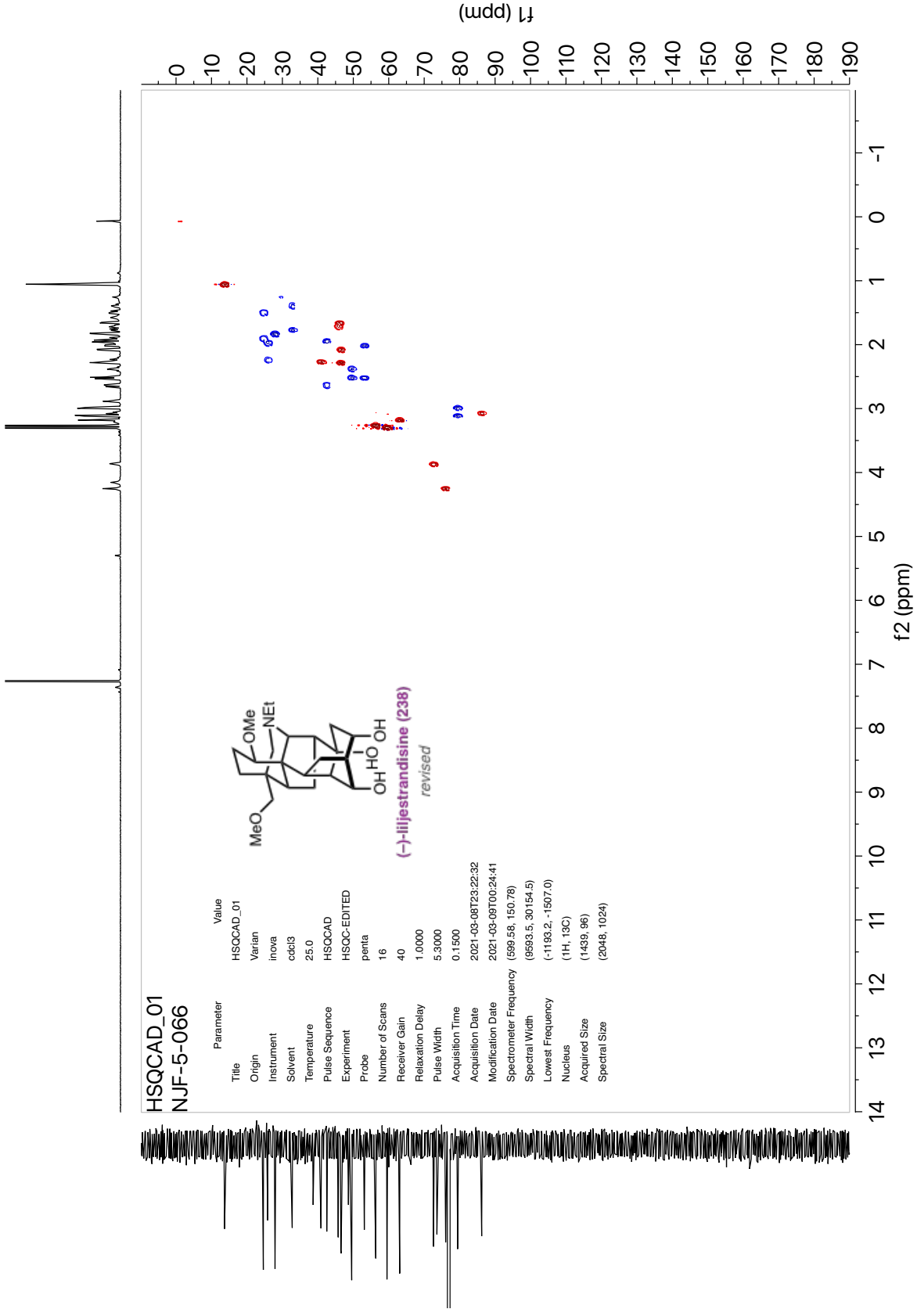

HSQCAD_01
NJF-5-035-C6D6
Parameter Value
Title HSQCAD_01
Origin Varian
Instrument inova
Solvent c6d6
Temperature 25.0
Pulse Sequence HSQCAD
Experiment HSQC-EDITED
Probe penta
Number of Scans 2
Receiver Gain 32
Relaxation Delay 1.0000
Pulse Width 5.3000
Acquisition Time 0.1500
Acquisition Date 2020-12-19T20:31:18
Modification Date 2020-12-19T20:39:46
Spectrometer Frequency (599.58, 150.78)
Spectral Width (9593.5, 30154.5)
Lowest Frequency (-1166.0, -1500.6)
Nucleus (1H, 13C)
Acquired Size (1439, 96)
Spectral Size (2048, 1024)
{7.16,127.99}C6D6
f1 (ppm)
f2 (ppm)
MeO
OMe
NEt
MOMO
HO
OH
245

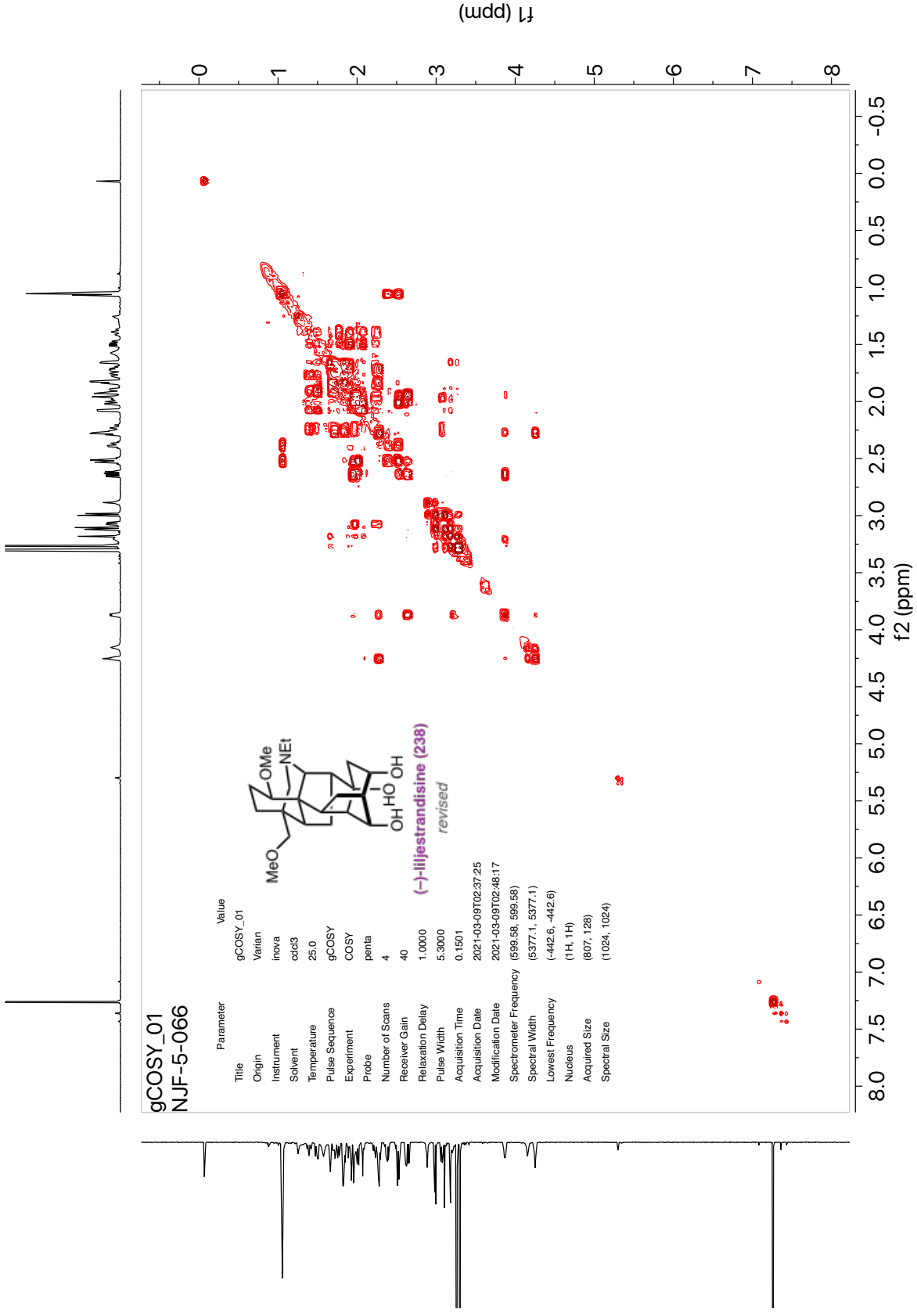

gCOSY_01
NJF-5-035-C6D6
Parameter Value
Title gCOSY_01
Origin Varian
Instrument inova
Solvent c6d6
Temperature 25.0
Pulse Sequence gCOSY
Experiment COSY
Probe penta
Number of Scans 1
Receiver Gain 32
Relaxation Delay 1.0000
Pulse Width 5.3000
Acquisition Time 0.1500
Acquisition Date 2020-12-19T20:27:58
Modification Date 2020-12-19T20:31:14
Spectrometer Frequency (599.58, 599.58)
Spectral Width (4947.7, 4947.7)
Lowest Frequency (-136.7, -136.7)
Nucleus (1H, 1H)
Acquired Size (742, 128)
Spectral Size (1024, 1024)
f1 (ppm)
f2 (ppm)
MeO
OMe
NEt
MOMO
HO
OH
245

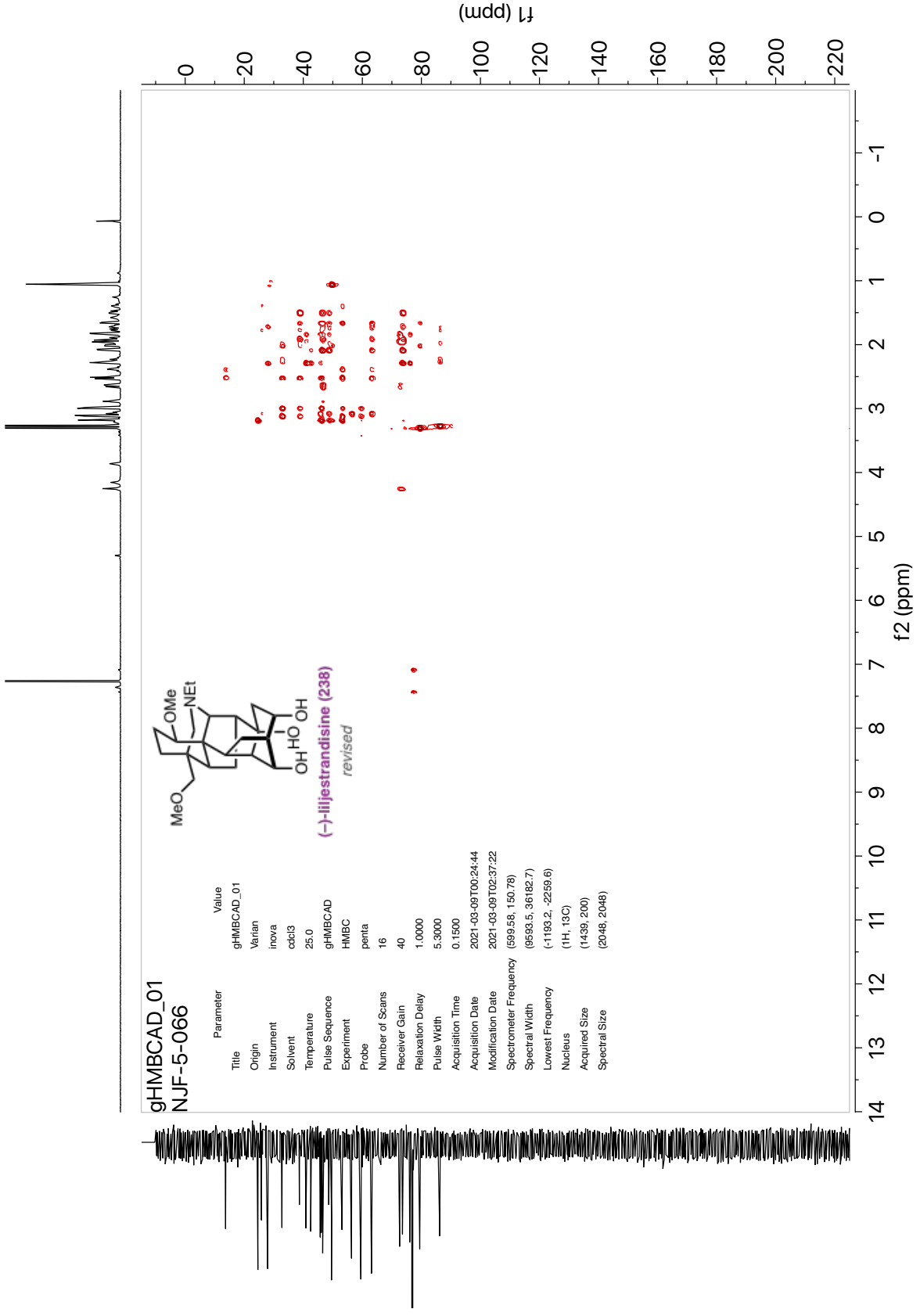

NJF-5-035-C6D6.3.ser
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-035-C6D6/ 3/ ser
Title NJF-5-035-C6D6.3.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 297.1
Pulse Sequence hmbcetgpl3nd
Experiment HMBC
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-12-21T20:34:26
Modification Date 2020-12-21T21:17:06
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-195.1, -1091.4)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
MeO
OMe
NEt
MOMO
HO
OH
245
f2 (ppm)
f1 (ppm)


PROTON_01
NJF-5-066
Parameter Value
Title PROTON_01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe penta
Number of Scans 8
Receiver Gain 40
Relaxation Delay 1.0000
Pulse Width 2.6500
Acquisition Time 1.7078
Acquisition Date 2021-03-08T23:21:57
Modification Date 2021-03-08T23:22:29
Spectrometer Frequency 599.58
Spectral Width 9593.5
Lowest Frequency -1193.2
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
MeO
OMe
NEt
OH
HO
OH
(–)-liljestrandisine (238)
revised
7.26 CDCl3
f1 (ppm)

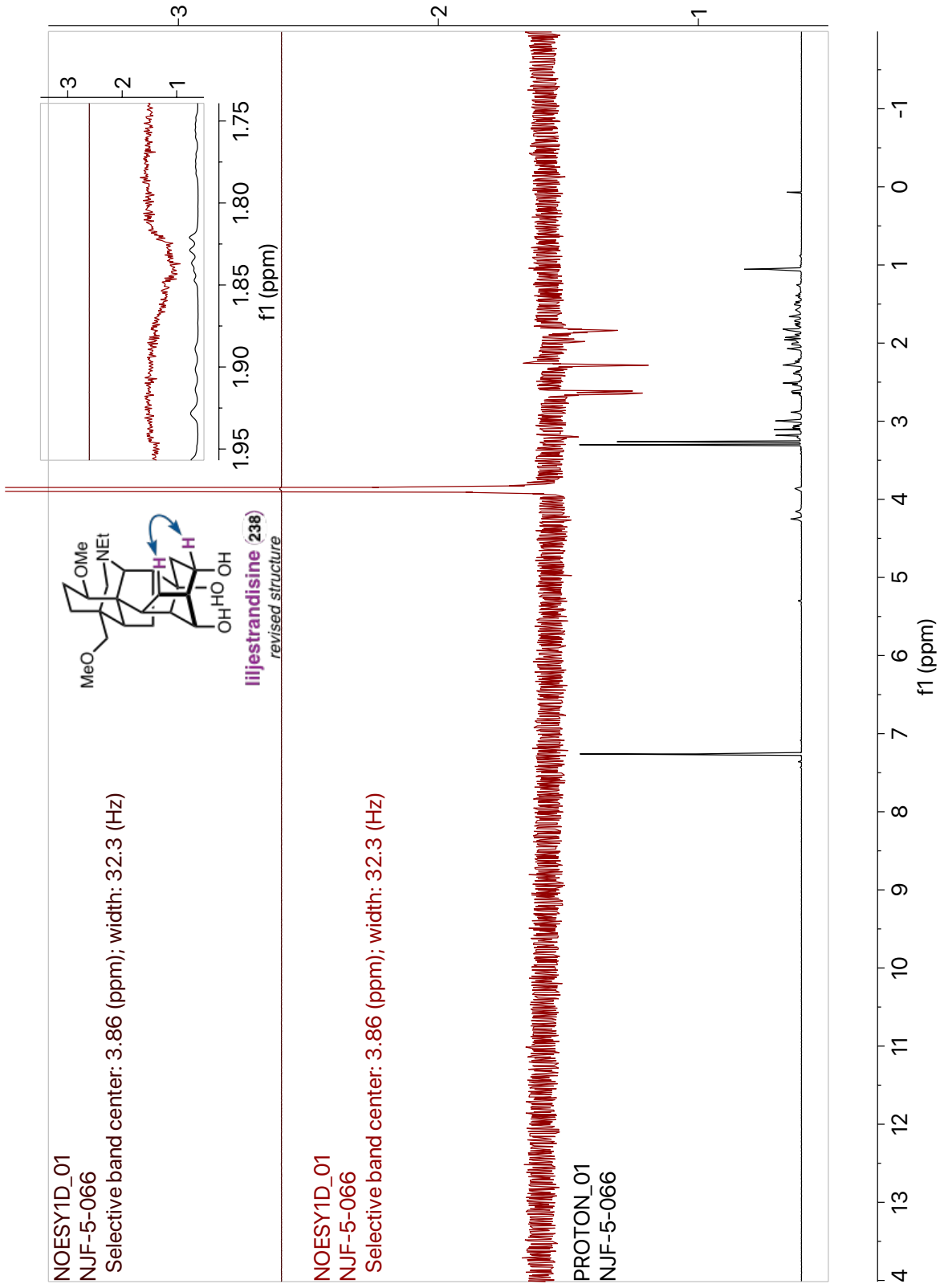

CARBON_01
NJF-5-066
Parameter Value
Title CARBON_01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe penta
Number of Scans 10000
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 6.4875
Acquisition Time 0.8696
Acquisition Date 2021-03-09T02:48:32
Modification Date 2021-03-09T08:00:26
Spectrometer Frequency 150.78
Spectral Width 37682.5
Lowest Frequency -2255.2
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
MeO
OMe
NEt
OH
HO
OH
(–)-liljestrandisine (238)
revised
86.22
79.44
77.00 CDCl3
76.05
73.59
72.63
63.09
59.50
56.34
53.10
49.55
48.63
46.57
46.47
46.08
45.74
42.52
40.89
38.68
32.77
27.92
25.83
24.62
13.69
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

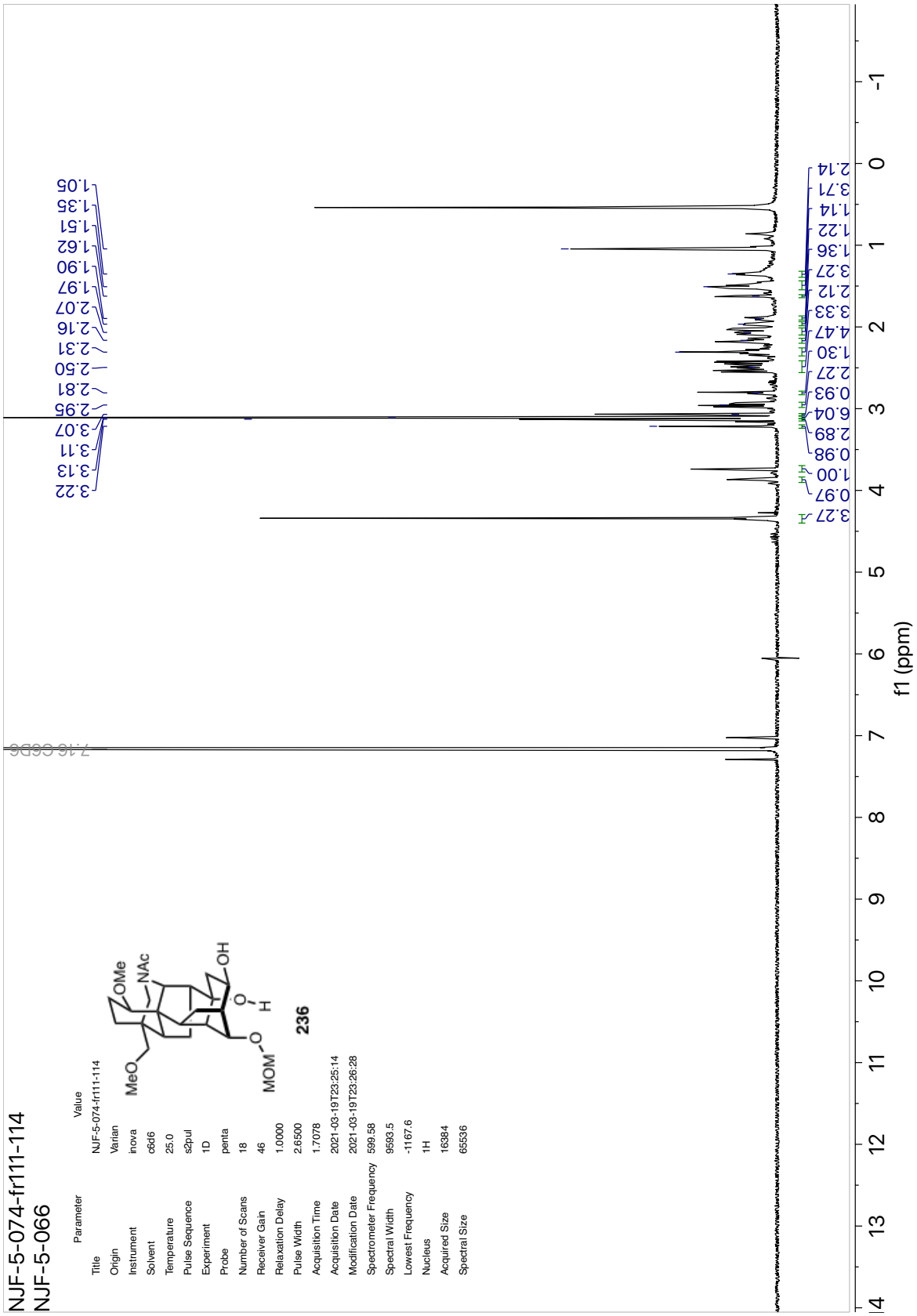

HSQCAD_01
NJF-5-066
Parameter Value
Title HSQCAD_01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence HSQCAD
Experiment HSQC-EDITED
Probe penta
Number of Scans 16
Receiver Gain 40
Relaxation Delay 1.0000
Pulse Width 5.3000
Acquisition Time 0.1500
Acquisition Date 2021-03-08T23:22:32
Modification Date 2021-03-09T00:24:41
Spectrometer Frequency (599.58, 150.78)
Spectral Width (9593.5, 30154.5)
Lowest Frequency (-1193.2, -1507.0)
Nucleus (1H, 13C)
Acquired Size (1439, 96)
Spectral Size (2048, 1024)
MeO
OMe
NEt
OH
HO
OH
(–)-liljestrandisine (238)
revised
f1 (ppm)
f2 (ppm)

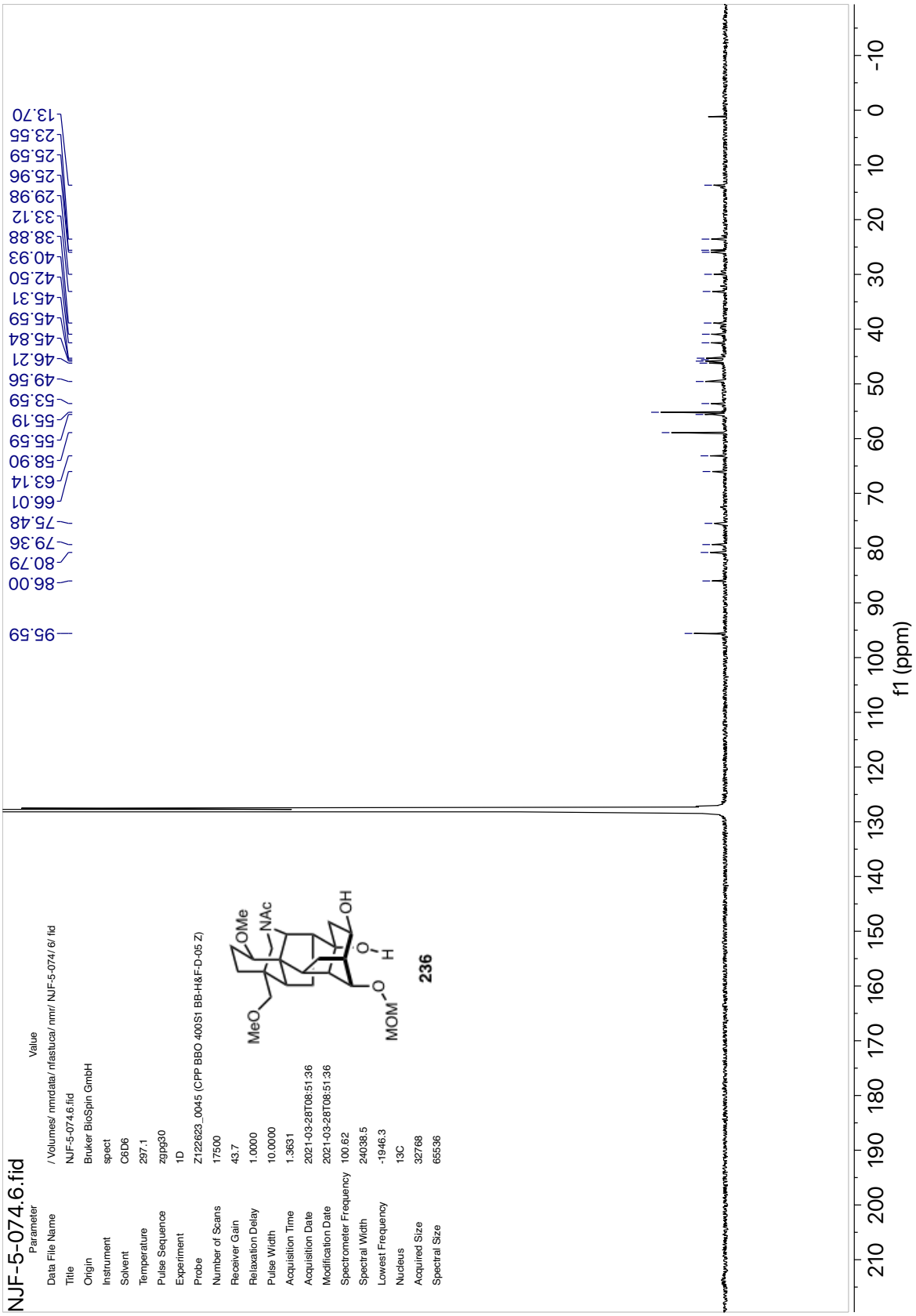

gCOSY_01
NJF-5-066
Parameter Value
Title gCOSY_01
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence gCOSY
Experiment COSY
Probe penta
Number of Scans 4
Receiver Gain 40
Relaxation Delay 1.0000
Pulse Width 5.3000
Acquisition Time 0.1501
Acquisition Date 2021-03-09T02:37:25
Modification Date 2021-03-09T02:48:17
Spectrometer Frequency (599.58, 599.58)
Spectral Width (5377.1, 5377.1)
Lowest Frequency (-442.6, -442.6)
Nucleus (1H, 1H)
Acquired Size (807, 128)
Spectral Size (1024, 1024)
MeO
OMe
NEt
OH
HO
OH
(–)-liljestrandisine (238)
revised
f1 (ppm)
f2 (ppm)

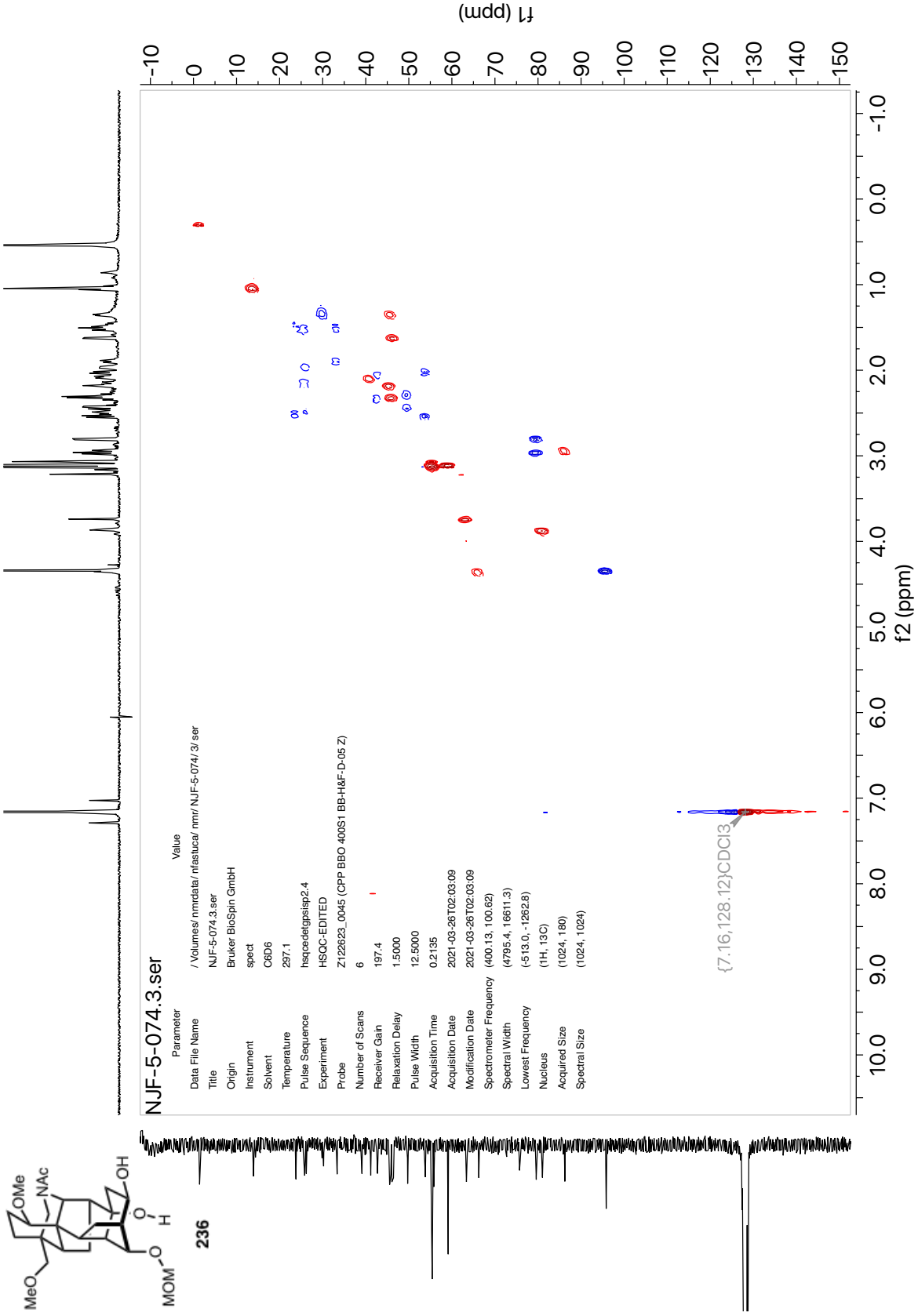


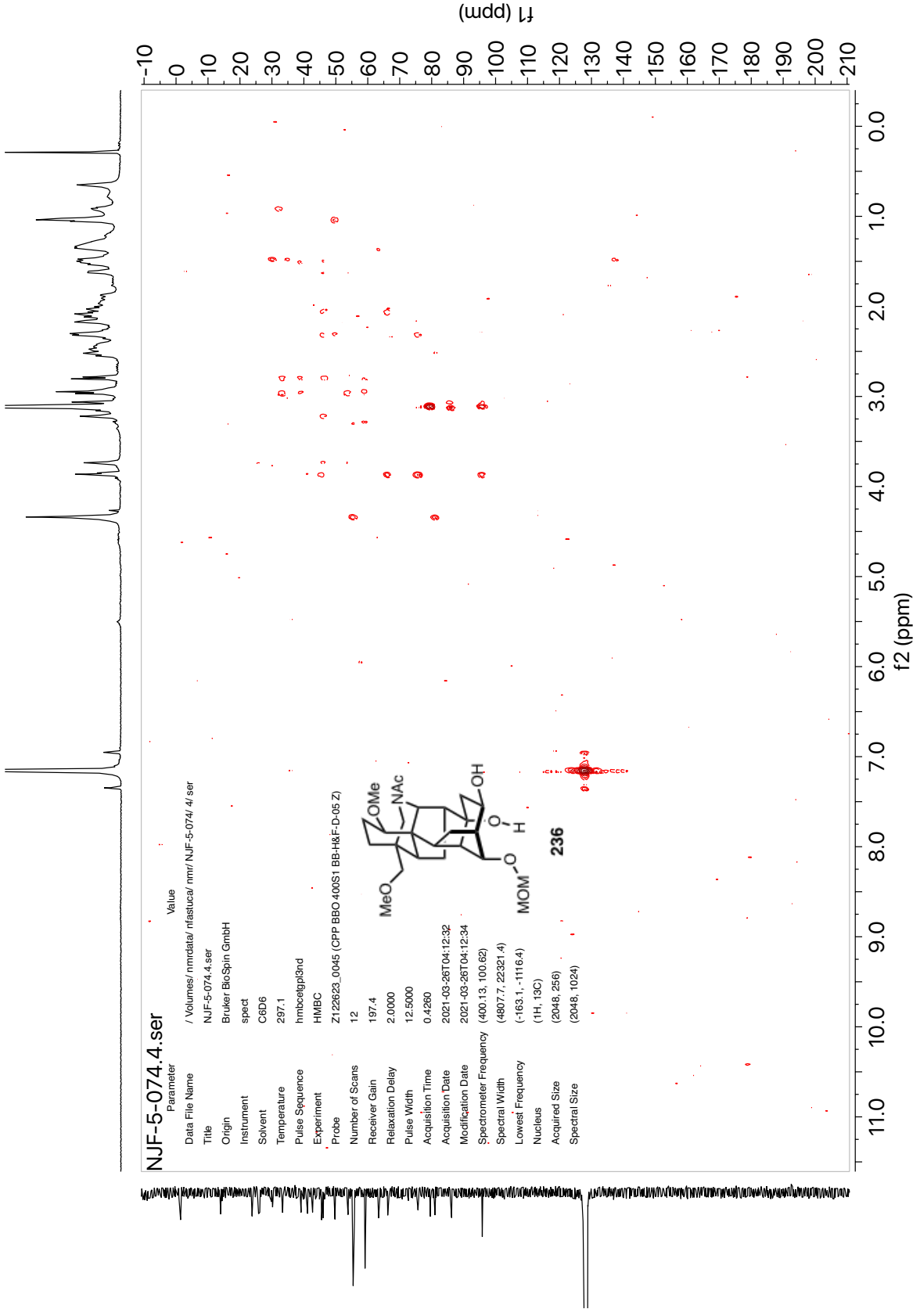
Parameter	Value
Title	gHMBCAD_01
Origin	Varian
Instrument	inova
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	gHMBCAD
Experiment	HMBC
Probe	penta
Number of Scans	16
Receiver Gain	40
Relaxation Delay	1.0000
Pulse Width	5.3000
Acquisition Time	0.1500
Acquisition Date	2021-03-09T00:24:44
Modification Date	2021-03-09T02:37:22
Spectrometer Frequency	(599.58, 150.78)
Spectral Width	(9593.5, 36182.7)
Lowest Frequency	(-1193.2, -2259.6)
Nucleus	(1H, 13C)
Acquired Size	(1439, 200)
Spectral Size	(2048, 2048)

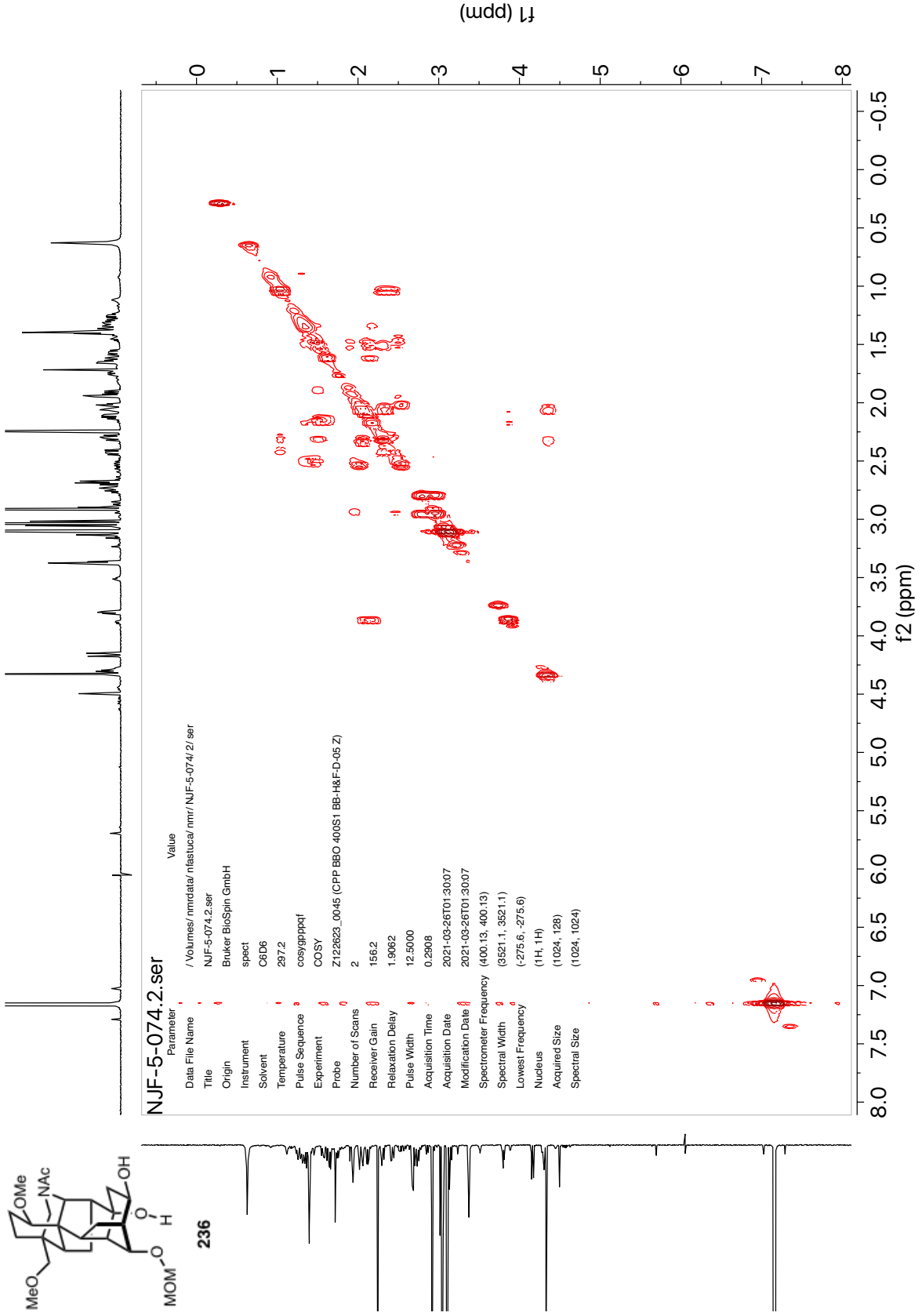

NOESY1D_01
NJF-5-066
Selective band center: 3.86 (ppm); width: 32.3 (Hz)
OMe
NEt
MeO
H
H
OH
HO
OH
liljestrandisine (238)
revised structure
1.95
1.90
1.85
1.80
1.75
f1 (ppm)
NOESY1D_01
NJF-5-066
Selective band center: 3.86 (ppm); width: 32.3 (Hz)
PROTON_01
NJF-5-066
f1 (ppm)

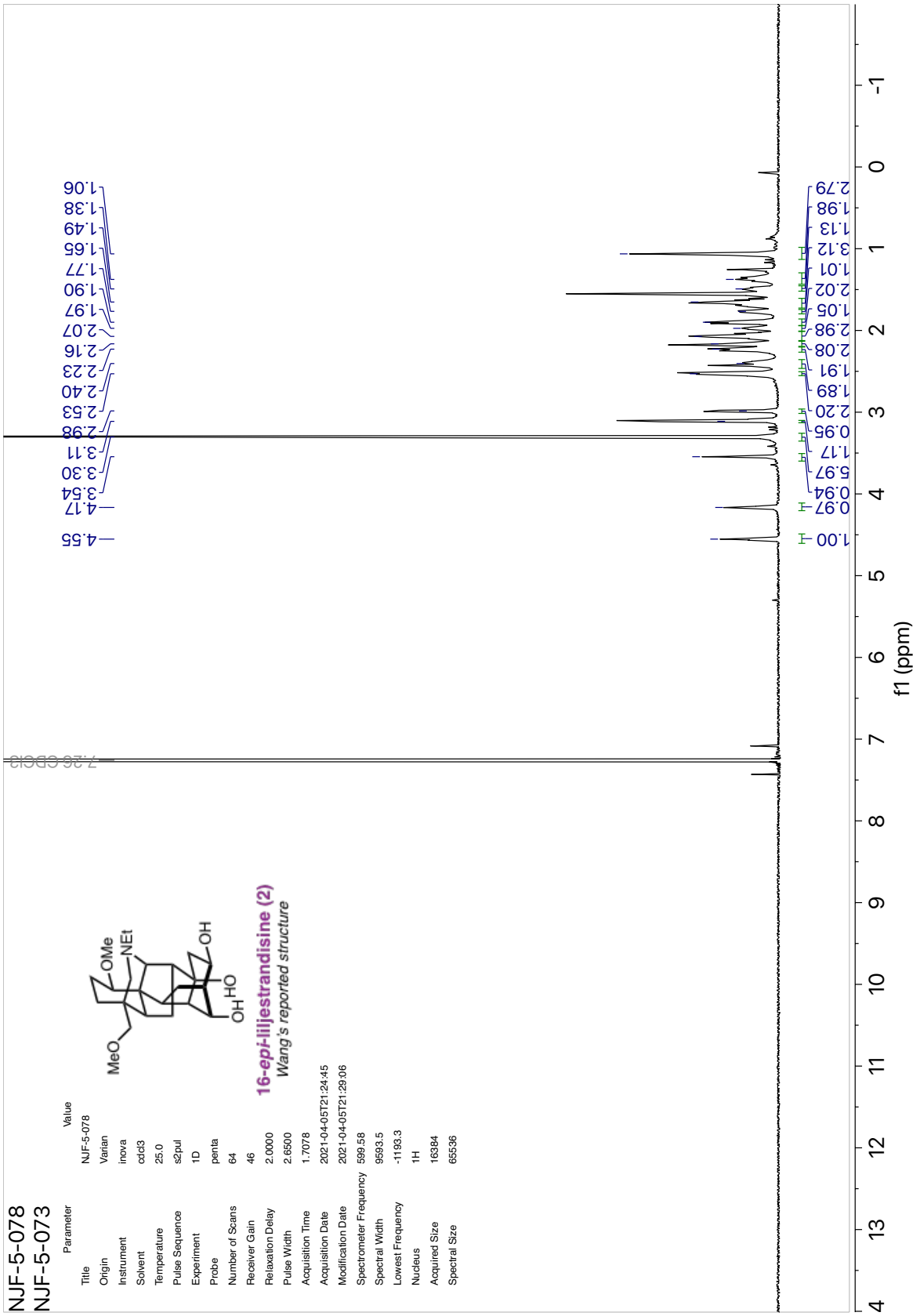

NJF-5-074-fr111-114
NJF-5-066
Parameter Value
Title NJF-5-074-fr111-114
Origin Varian
Instrument inova
Solvent c6d6
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe penta
Number of Scans 18
Receiver Gain 46
Relaxation Delay 1.0000
Pulse Width 2.6500
Acquisition Time 1.7078
Acquisition Date 2021-03-19T23:25:14
Modification Date 2021-03-19T23:26:28
Spectrometer Frequency 599.58
Spectral Width 9593.5
Lowest Frequency -1167.6
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
MeO
OMe
NAc
OH
MOM
236
7.16 C6D6
3.22
3.13
3.11
3.07
2.95
2.81
2.50
2.31
2.16
2.07
1.97
1.90
1.62
1.51
1.35
1.05
3.27
0.97
1.00
0.98
2.89
6.04
0.93
2.27
1.30
4.47
3.33
2.12
3.27
1.36
1.22
1.14
3.71
2.14
f1 (ppm)

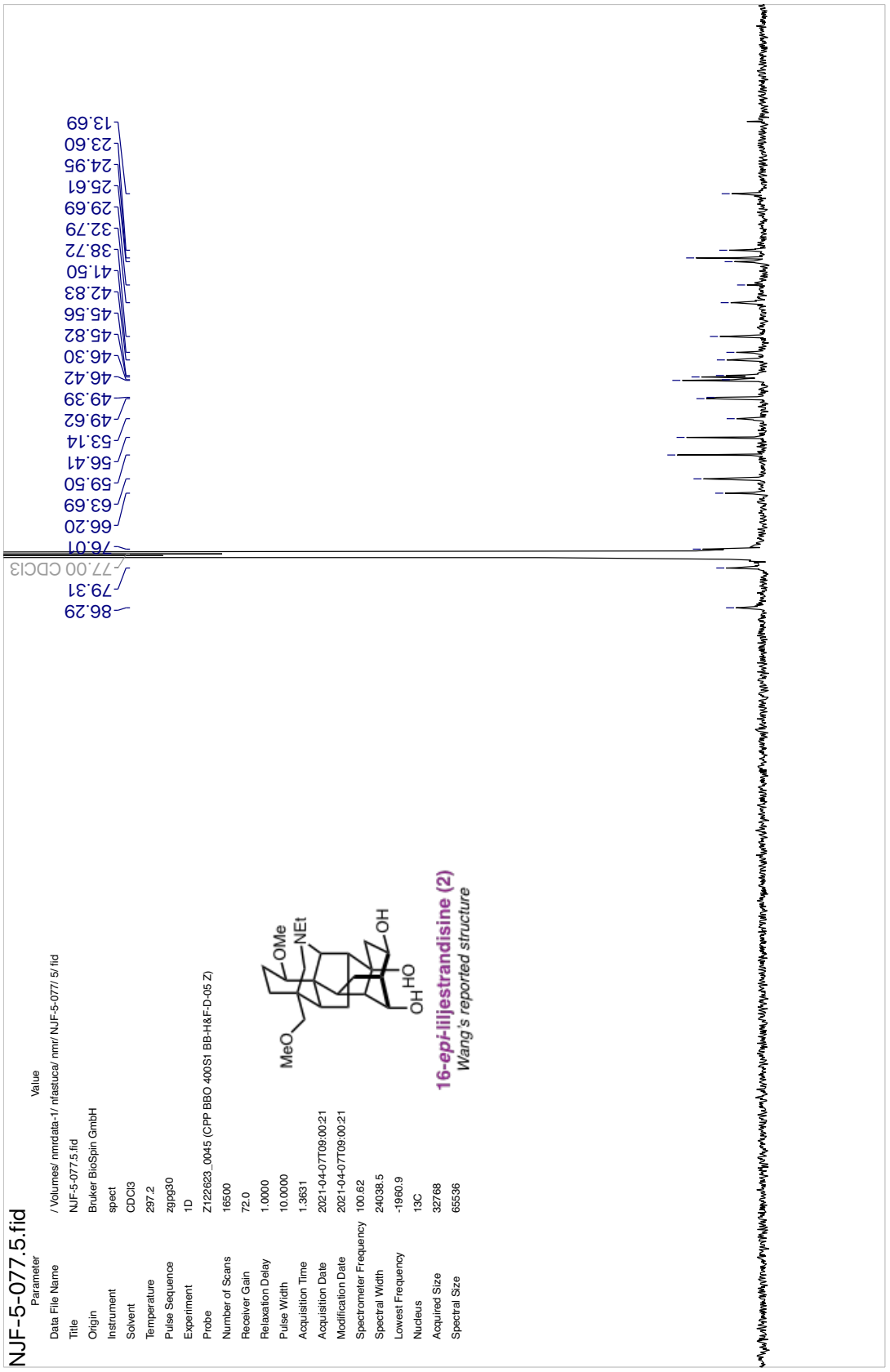

NJF-5-074.6.fid
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-074/ 6/ fid
Title NJF-5-074.6.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent C6D6
Temperature 297.1
Pulse Sequence zgpg30
Experiment 1D
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 17500
Receiver Gain 43.7
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2021-03-28T08:51:36
Modification Date 2021-03-28T08:51:36
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1946.3
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
MeO
OMe
NAc
OH
MOM
236
95.59
86.00
80.79
79.36
75.48
66.01
63.14
58.90
55.59
55.19
53.59
49.56
46.21
45.84
45.59
45.31
42.50
40.93
38.88
33.12
29.98
25.96
25.59
23.55
13.70
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

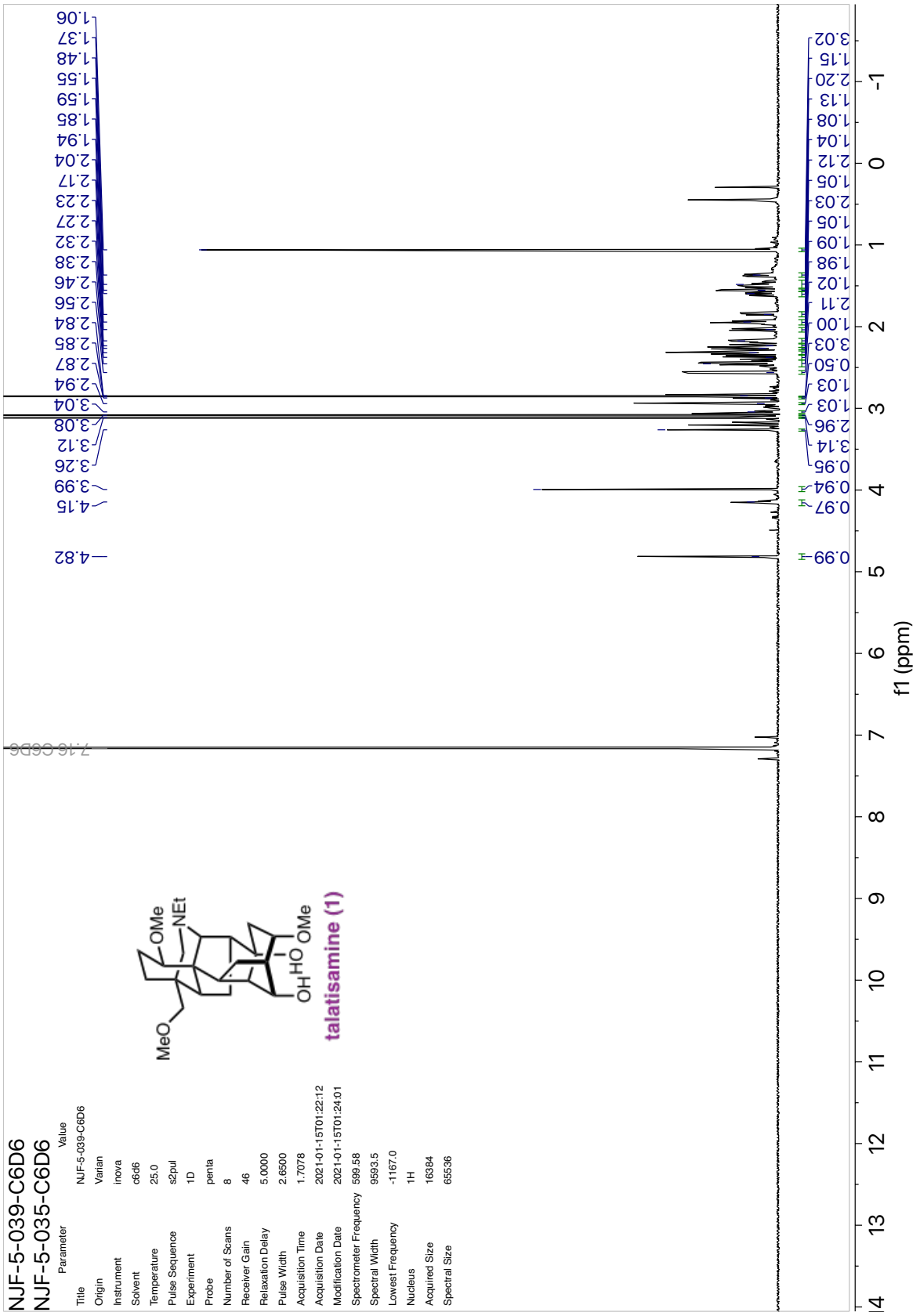

NJF-5-074.3.ser
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-074/ 3/ ser
Title NJF-5-074.3.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent C6D6
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Experiment HSQC-EDITED
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 6
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2021-03-26T02:03:09
Modification Date 2021-03-26T02:03:09
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-513.0, -1262.8)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
{7.16,128.12}CDCl3
f1 (ppm)
f2 (ppm)
OMe
NAc
OH
MeO
MOM
236

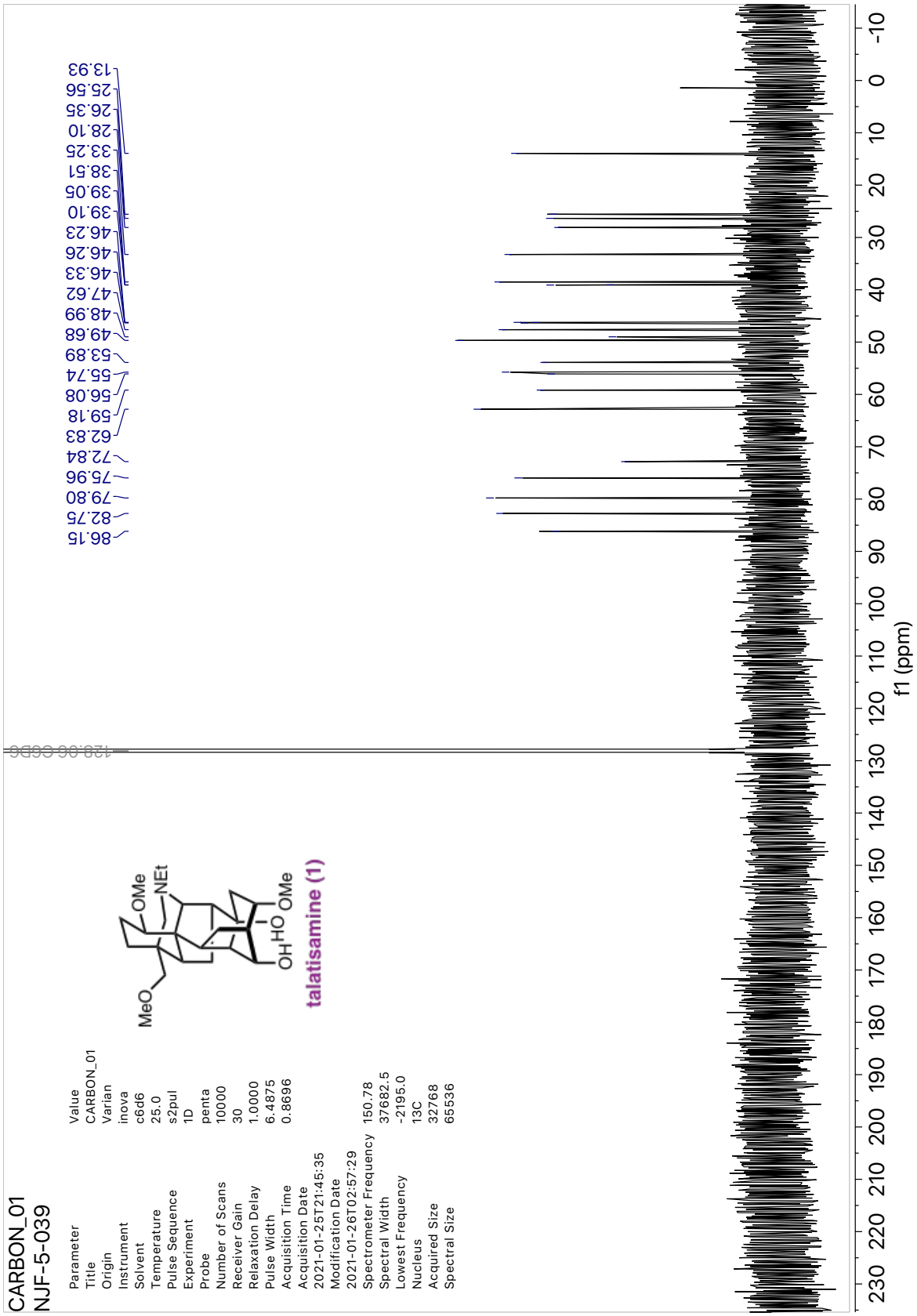

NJF-5-074.4.ser
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-074/ 4/ ser
Title NJF-5-074.4.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent C6D6
Temperature 297.1
Pulse Sequence hmbcetgpl3nd
Experiment HMBC
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 12
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2021-03-26T04:12:32
Modification Date 2021-03-26T04:12:34
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-163.1, -1116.4)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
MeO
OMe
NAc
OH
MOM
236
f1 (ppm)
f2 (ppm)

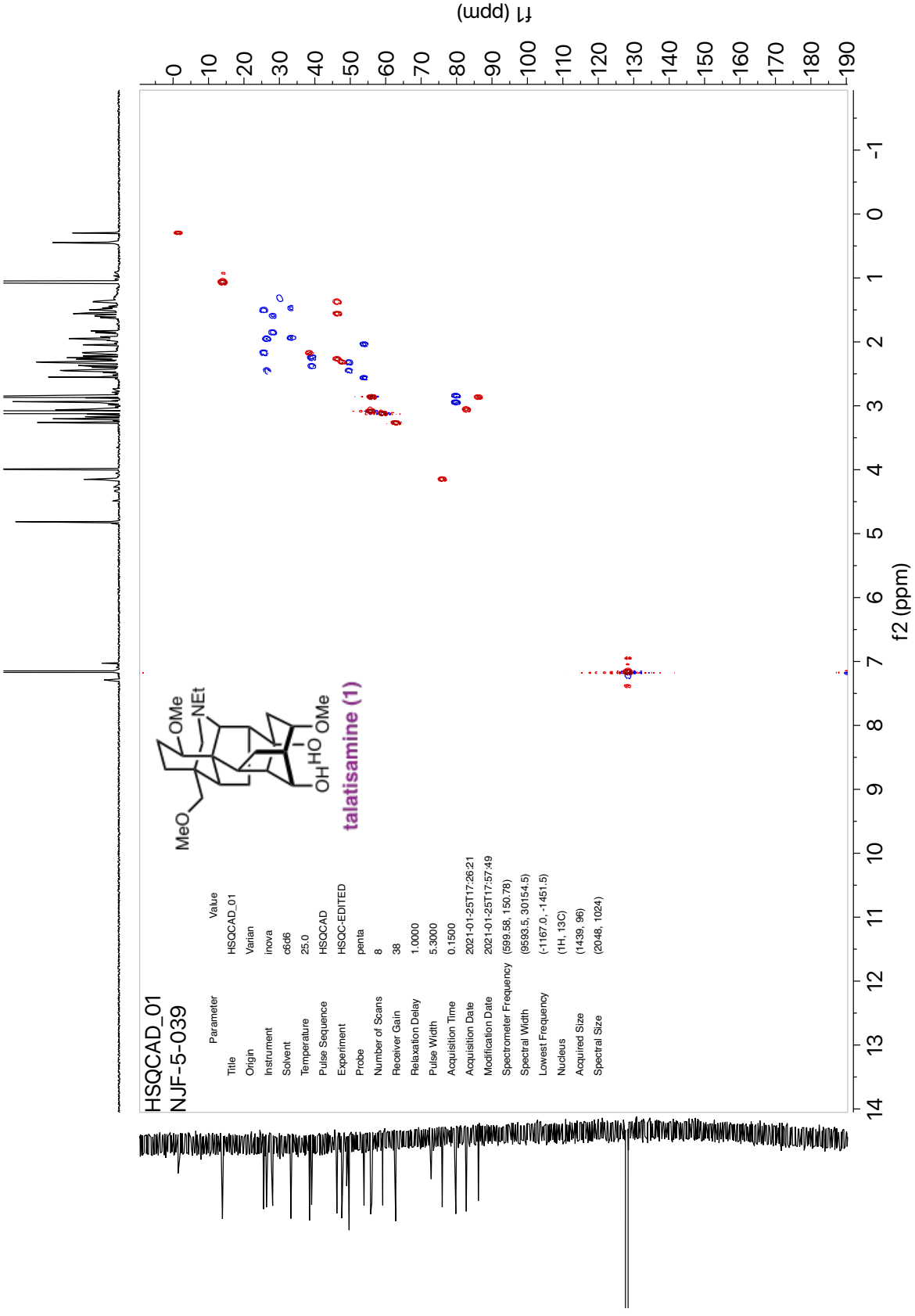

NJF-5-074.2.ser
Parameter Value
Data File Name / Volumes/ nmrdata/ nfastuca/ nmr/ NJF-5-074/ 2/ ser
Title NJF-5-074.2.ser
Origin Bruker BioSpin GmbH
Instrument spect
Solvent C6D6
Temperature 297.2
Pulse Sequence cosygpppqf
Experiment COSY
Probe Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans 2
Receiver Gain 156.2
Relaxation Delay 1.9062
Pulse Width 12.5000
Acquisition Time 0.2908
Acquisition Date 2021-03-26T01:30:07
Modification Date 2021-03-26T01:30:07
Spectrometer Frequency (400.13, 400.13)
Spectral Width (3521.1, 3521.1)
Lowest Frequency (-275.6, -275.6)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
f1 (ppm)
f2 (ppm)
MeO
OMe
NAc
OH
MOM
236


NJF-5-078
NJF-5-073
Parameter Value
Title NJF-5-078
Origin Varian
Instrument inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe penta
Number of Scans 64
Receiver Gain 46
Relaxation Delay 2.0000
Pulse Width 2.6500
Acquisition Time 1.7078
Acquisition Date 2021-04-05T21:24:45
Modification Date 2021-04-05T21:29:06
Spectrometer Frequency 599.58
Spectral Width 9593.5
Lowest Frequency -1193.3
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
16-epi-liljestrandisine (2)
Wang's reported structure
OMe
NEt
MeO
OH
HO
OH
7.26 CDCl3
4.55
4.17
3.54
3.30
3.11
2.98
2.53
2.40
2.23
2.16
2.07
1.97
1.90
1.77
1.65
1.49
1.38
1.06
1.00
0.97
0.94
5.97
1.17
0.95
2.20
1.89
1.91
2.08
2.98
1.05
2.02
1.01
3.12
1.13
1.98
2.79
f1 (ppm)

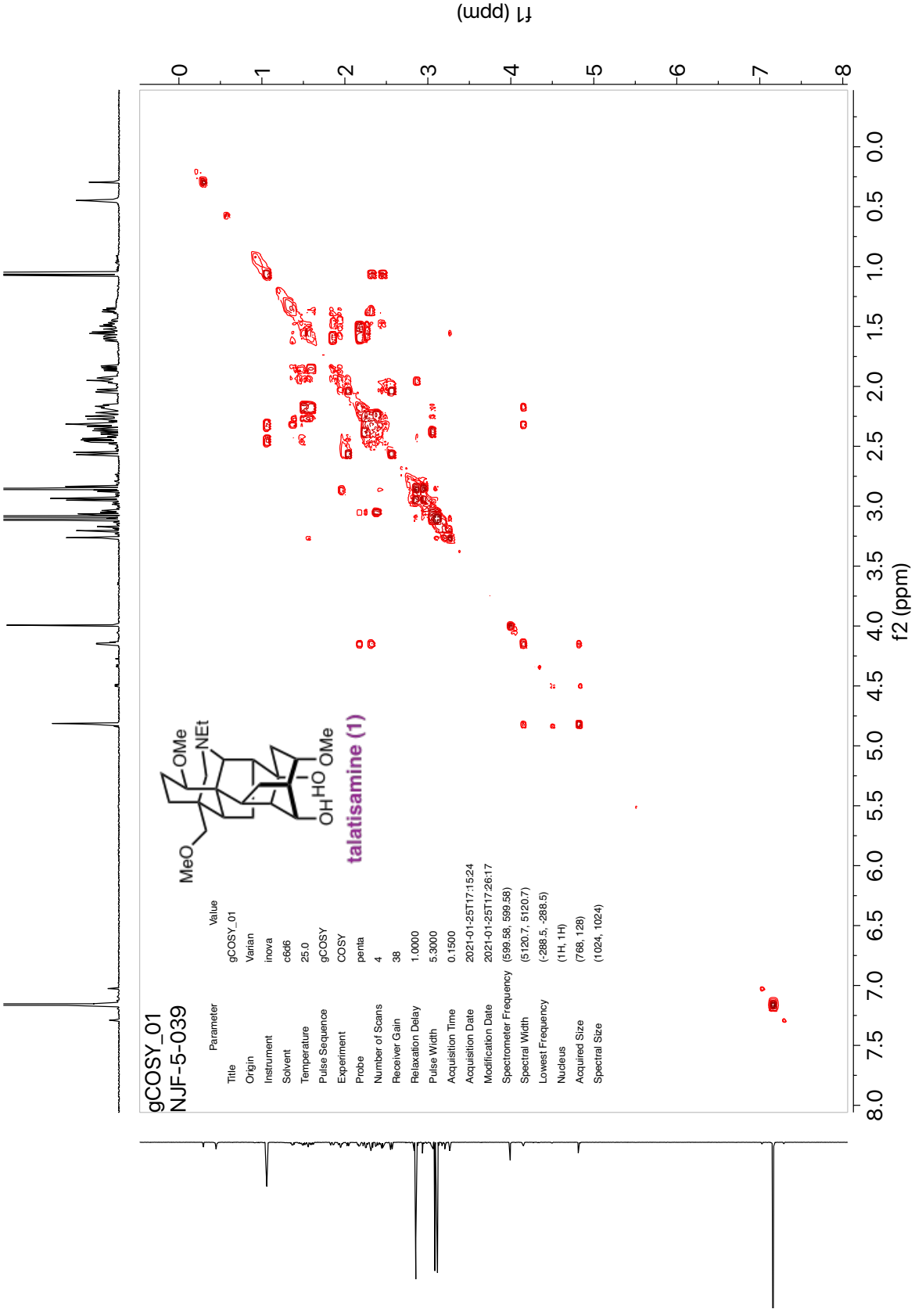

NJF-5-077.5.fid
Parameter
Value
Data File Name
/ Volumes/ nmrdata-1/ nfastuca/ nmr/ NJF-5-077/ 5/ fid
Title
NJF-5-077.5.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
297.2
Pulse Sequence
zgpg30
Experiment
1D
Probe
Z122623_0045 (CPP BBO 400S1 BB-H&F-D-05 Z)
Number of Scans
16500
Receiver Gain
72.0
Relaxation Delay
1.0000
Pulse Width
10.0000
Acquisition Time
1.3631
Acquisition Date
2021-04-07T09:00:21
Modification Date
2021-04-07T09:00:21
Spectrometer Frequency
100.62
Spectral Width
24038.5
Lowest Frequency
-1960.9
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
MeO
OMe
NEt
OH
HO
OH
16-epi-liljestrandisine (2)
Wang's reported structure
86.29
79.31
77.00 CDCl3
76.01
66.20
63.69
59.50
56.41
53.14
49.62
49.39
46.42
46.30
45.82
45.56
42.83
41.50
38.72
32.79
29.69
25.61
24.95
23.60
13.69
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

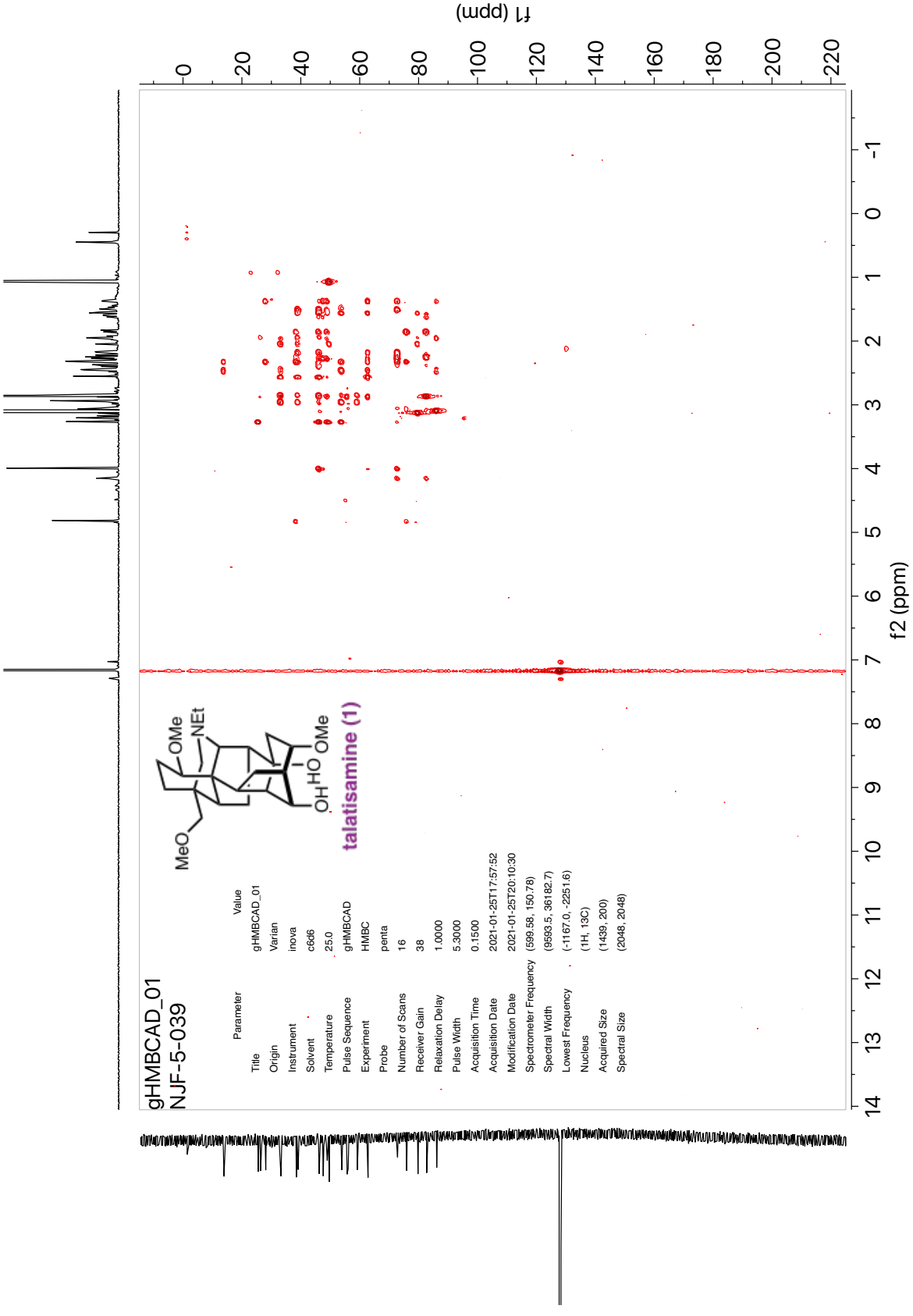

NJF-5-039-C6D6
NJF-5-035-C6D6
Parameter Value
Title NJF-5-039-C6D6
Origin Varian
Instrument inova
Solvent c6d6
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe penta
Number of Scans 8
Receiver Gain 46
Relaxation Delay 5.0000
Pulse Width 2.6500
Acquisition Time 1.7078
Acquisition Date 2021-01-15T01:22:12
Modification Date 2021-01-15T01:24:01
Spectrometer Frequency 599.58
Spectral Width 9593.5
Lowest Frequency -1167.0
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
MeO
OMe
NEt
HO
OH
OMe
talatisamine (1)
7.16 C6D6
4.82
4.15
3.99
3.26
3.12
3.08
3.04
2.94
2.87
2.85
2.84
2.56
2.46
2.38
2.32
2.27
2.23
2.17
2.04
1.94
1.85
1.59
1.55
1.48
1.37
1.06
0.99
0.97
0.94
0.95
3.14
2.96
1.03
1.03
3.03
0.50
1.00
2.11
1.02
1.98
1.09
1.05
2.03
1.05
1.04
2.12
1.08
1.13
2.20
1.15
3.02
f1 (ppm)

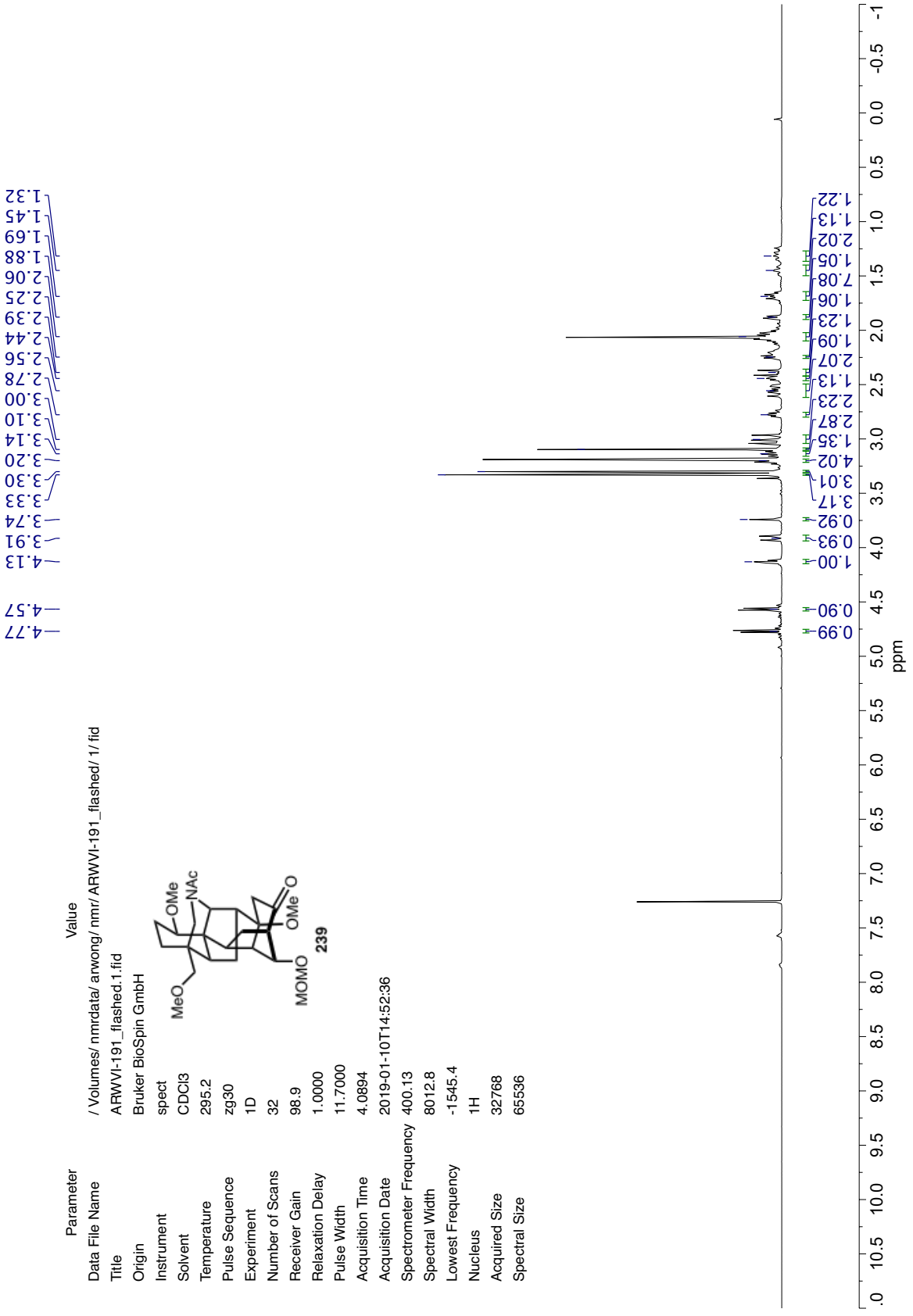

CARBON_01
NJF-5-039
Parameter Value
Title CARBON_01
Origin Varian
Instrument inova
Solvent c6d6
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe penta
Number of Scans 10000
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 6.4875
Acquisition Time 0.8696
Acquisition Date 2021-01-25T21:45:35
Modification Date 2021-01-26T02:57:29
Spectrometer Frequency 150.78
Spectral Width 37682.5
Lowest Frequency -2195.0
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
MeO
OMe
NEt
HO
OH
OMe
talatisamine (1)
128.06 C6D6
86.15
82.75
79.80
75.96
72.84
62.83
59.18
56.08
55.74
53.89
49.68
48.99
47.62
46.33
46.26
46.23
39.10
39.05
38.51
33.25
28.10
26.35
25.56
13.93
f1 (ppm)

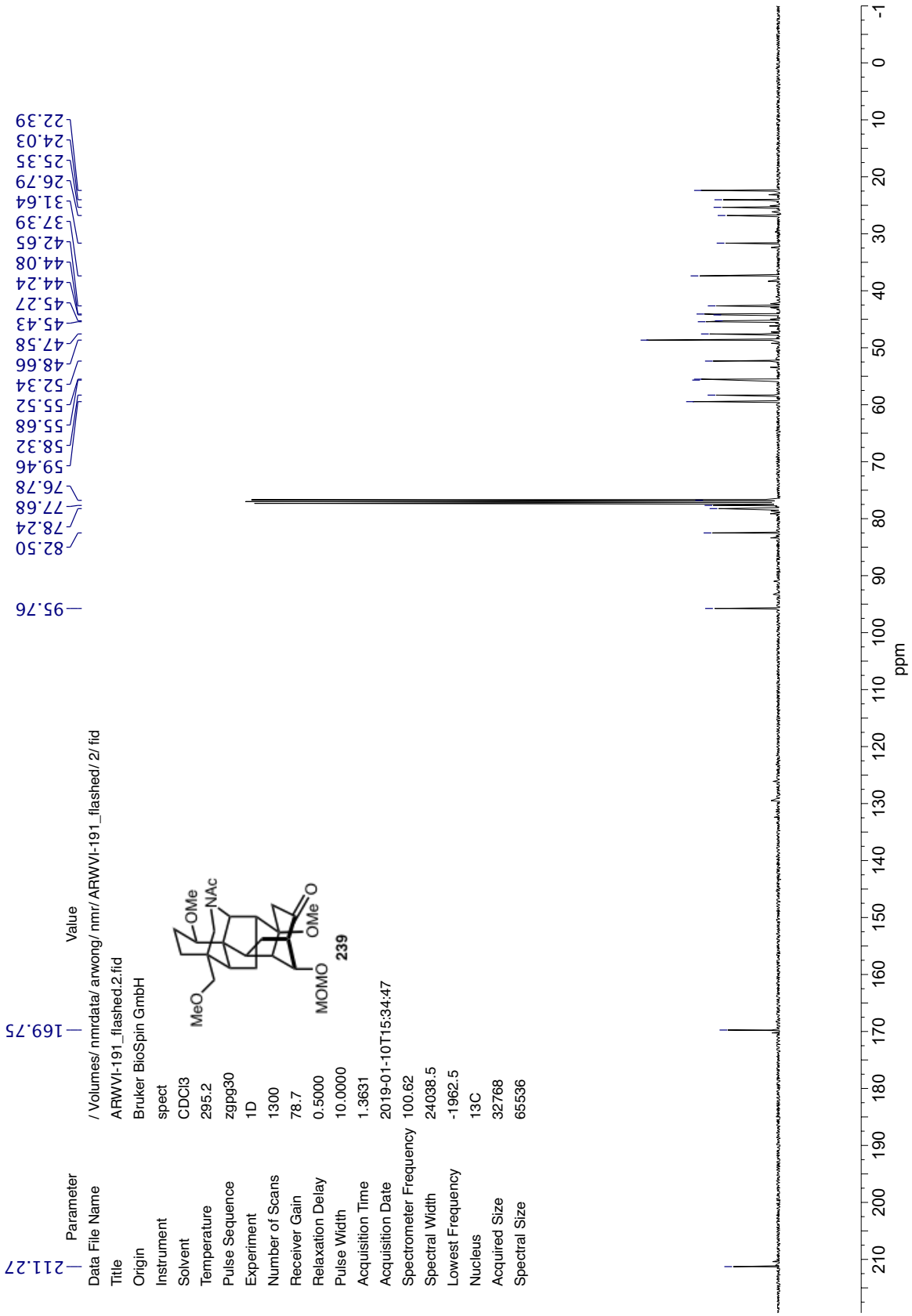


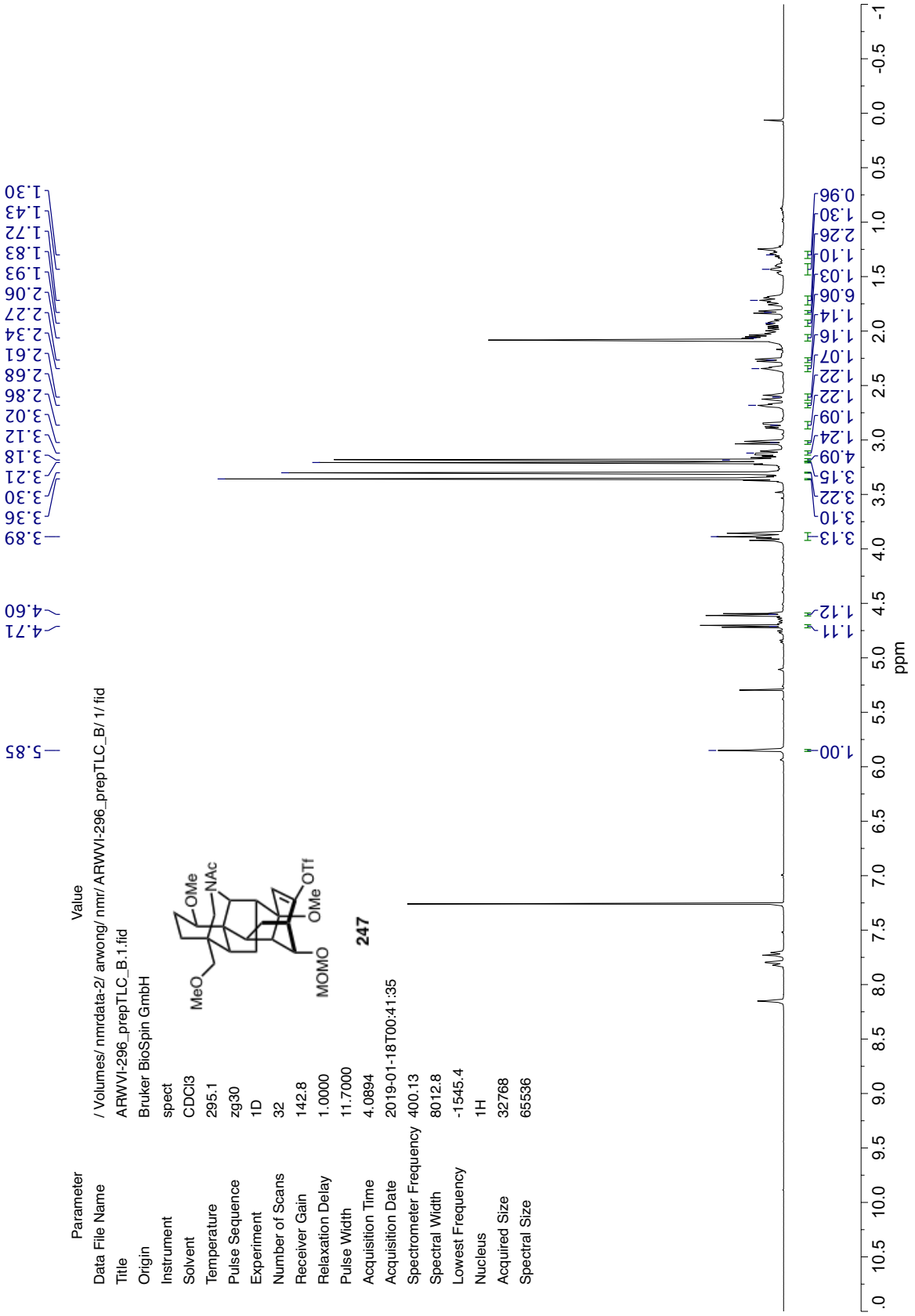
Parameter	Value
Title	HSQCAD_01
Origin	Varian
Instrument	inova
Solvent	c6d6
Temperature	25.0
Pulse Sequence	HSQCAD
Experiment	HSQC-EDITED
Probe	penta
Number of Scans	8
Receiver Gain	38
Relaxation Delay	1.0000
Pulse Width	5.3000
Acquisition Time	0.1500
Acquisition Date	2021-01-25T17:26:21
Modification Date	2021-01-25T17:57:49
Spectrometer Frequency	(599.58, 150.78)
Spectral Width	(9593.5, 30154.5)
Lowest Frequency	(-1167.0, -1451.5)
Nucleus	(1H, 13C)
Acquired Size	(1439, 96)
Spectral Size	(2048, 1024)

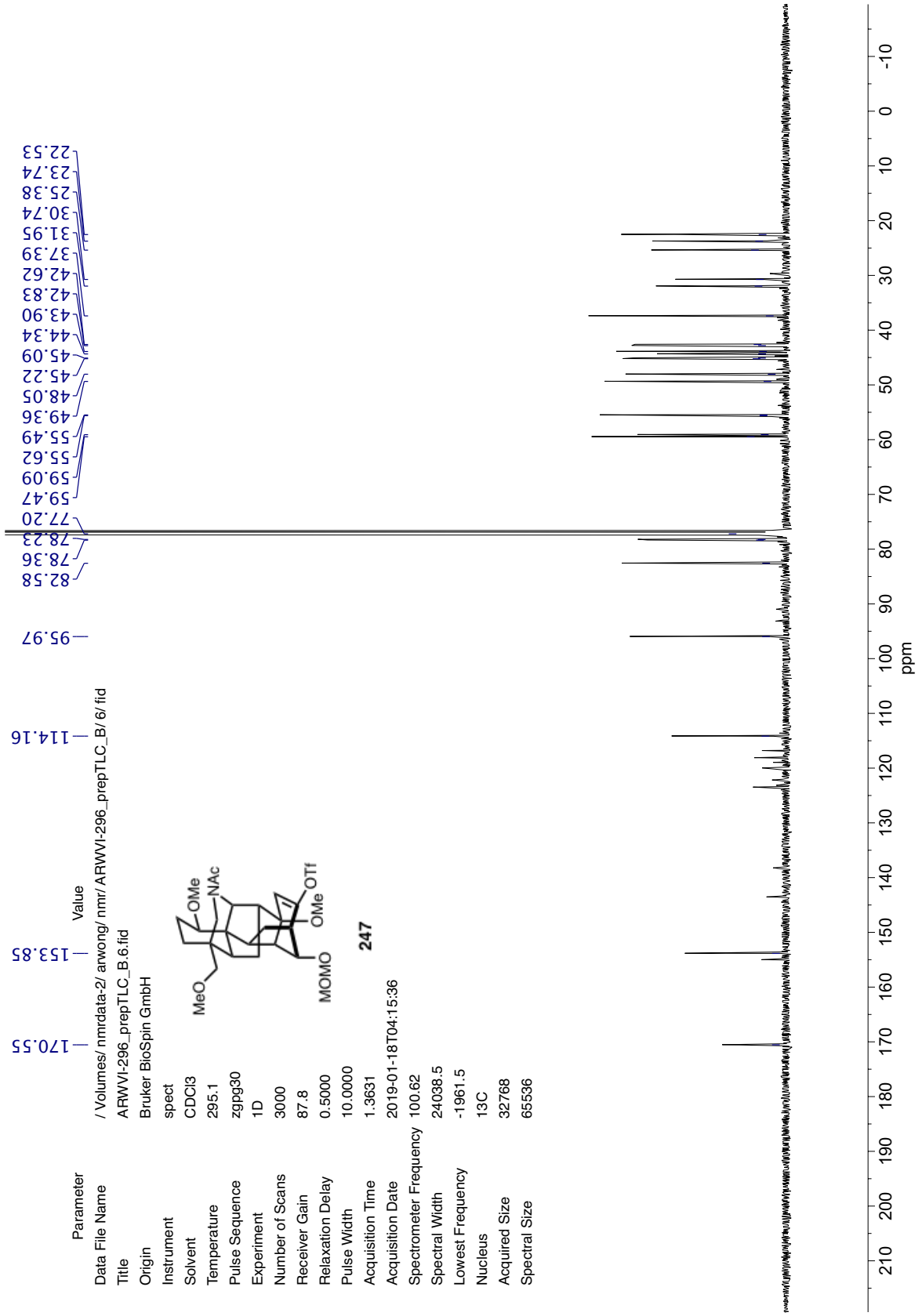

gCOSY_01
NJF-5-039
talatisamine (1)
MeO
OMe
NEt
OH
HO
OMe
Parameter Value
Title gCOSY_01
Origin Varian
Instrument inova
Solvent c6d6
Temperature 25.0
Pulse Sequence gCOSY
Experiment COSY
Probe penta
Number of Scans 4
Receiver Gain 38
Relaxation Delay 1.0000
Pulse Width 5.3000
Acquisition Time 0.1500
Acquisition Date 2021-01-25T17:15:24
Modification Date 2021-01-25T17:26:17
Spectrometer Frequency (599.58, 599.58)
Spectral Width (5120.7, 5120.7)
Lowest Frequency (-288.5, -288.5)
Nucleus (1H, 1H)
Acquired Size (768, 128)
Spectral Size (1024, 1024)
f2 (ppm)
f1 (ppm)

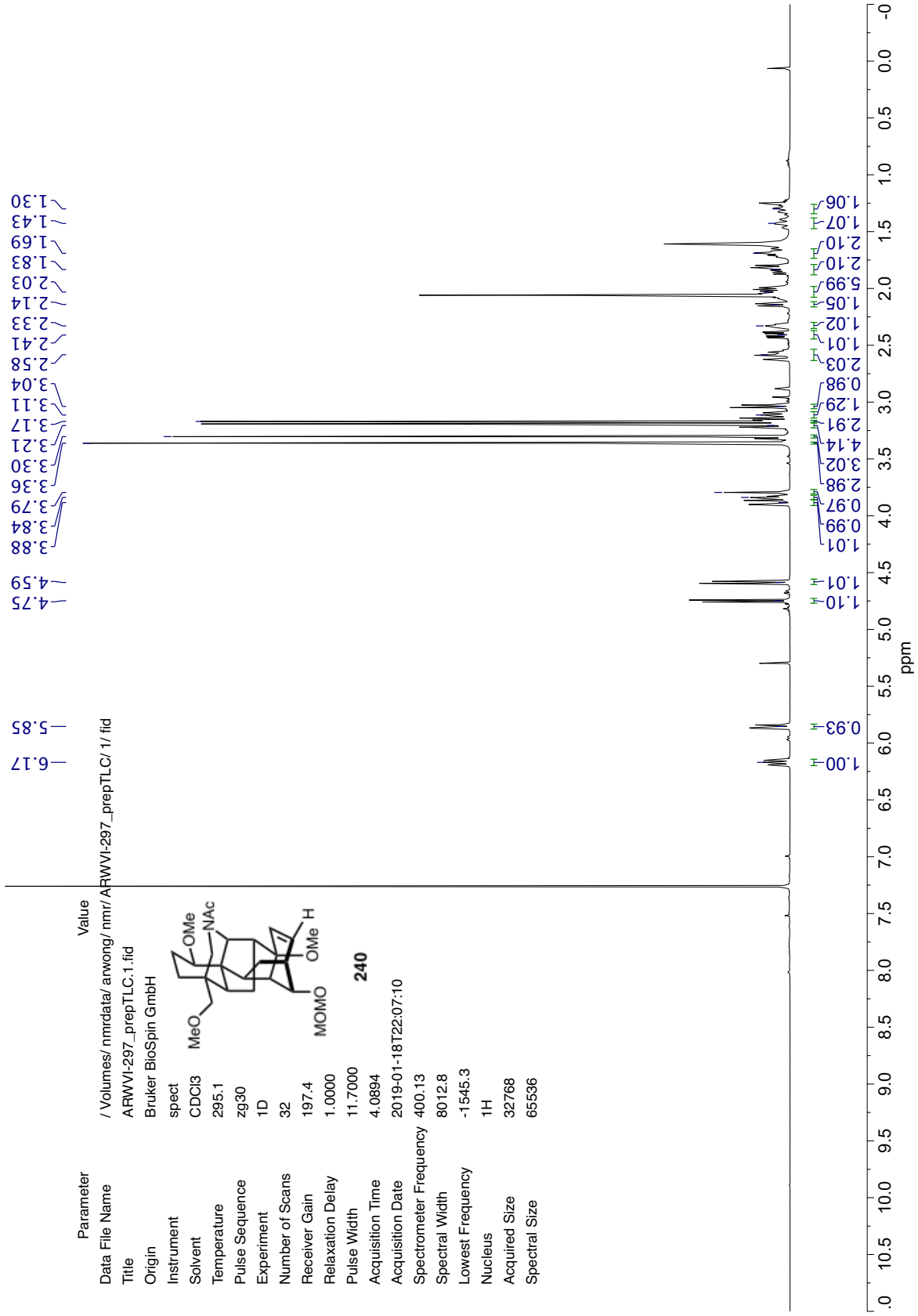

gHMBCAD_01
NJF-5-039
talatisamine (1)
MeO
OMe
NEt
HO
OH
OMe
Parameter Value
Title gHMBCAD_01
Origin Varian
Instrument inova
Solvent c6d6
Temperature 25.0
Pulse Sequence gHMBCAD
Experiment HMBC
Probe penta
Number of Scans 16
Receiver Gain 38
Relaxation Delay 1.0000
Pulse Width 5.3000
Acquisition Time 0.1500
Acquisition Date 2021-01-25T17:57:52
Modification Date 2021-01-25T20:10:30
Spectrometer Frequency (599.58, 150.78)
Spectral Width (9593.5, 36182.7)
Lowest Frequency (-1167.0, -2251.6)
Nucleus (1H, 13C)
Acquired Size (1439, 200)
Spectral Size (2048, 2048)
f1 (ppm)
f2 (ppm)

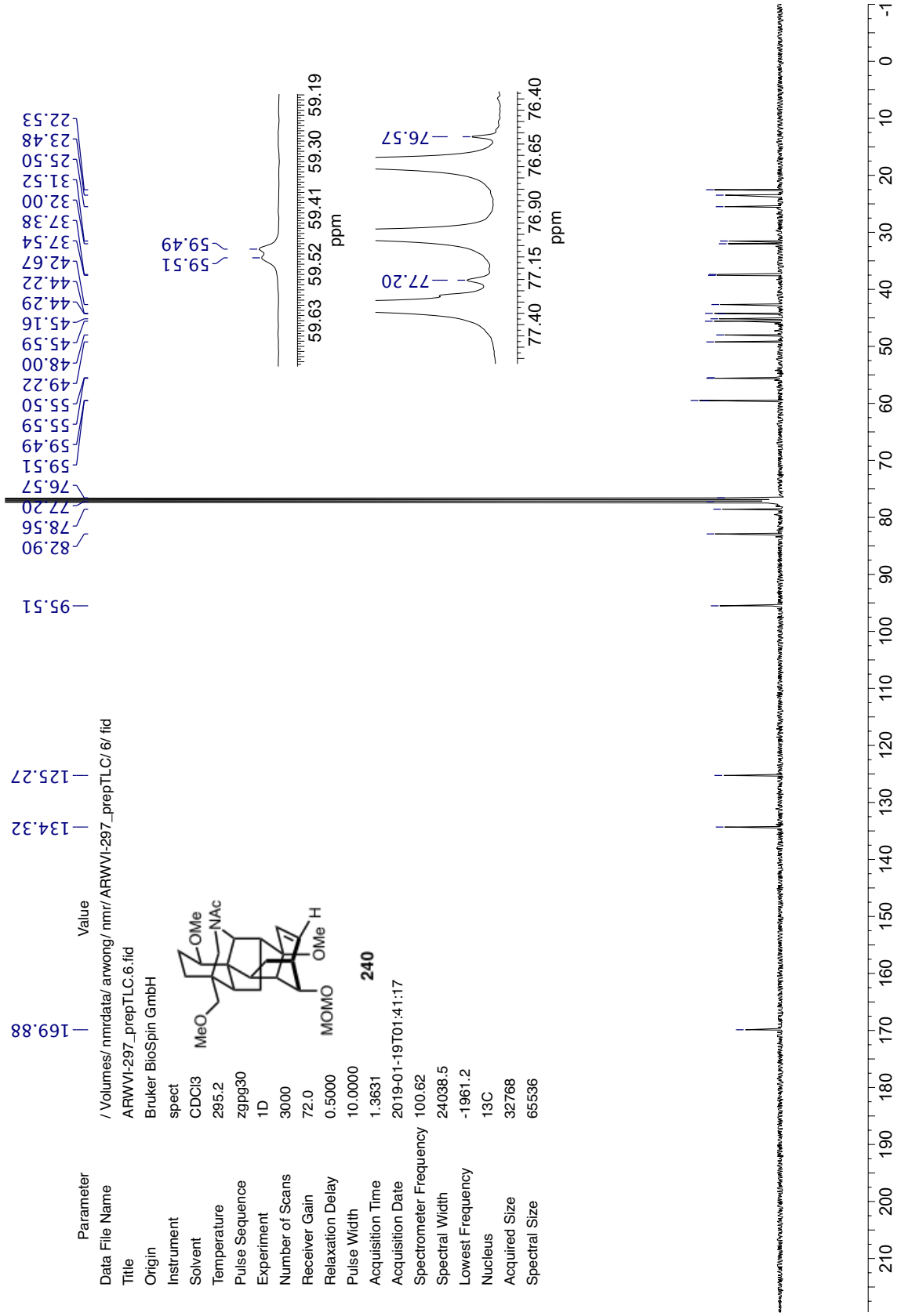

Value
Parameter
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-191_flashed/ 1/ fid
Title ARWVI-191_flashed.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.2
Pulse Sequence zg30
Experiment 1D
Number of Scans 32
Receiver Gain 98.9
Relaxation Delay 1.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Acquisition Date 2019-01-10T14:52:36
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.4
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
OMe
NAc
MeO
OMe
O
MOMO
239
4.77
4.57
4.13
3.91
3.74
3.33
3.30
3.20
3.14
3.10
3.00
2.78
2.56
2.44
2.39
2.25
2.06
1.88
1.69
1.45
1.32
0.90
0.99
1.00
0.93
0.92
3.17
3.01
4.02
1.35
2.87
2.23
1.13
2.07
1.09
1.23
1.06
7.08
1.05
2.02
1.13
1.22
ppm

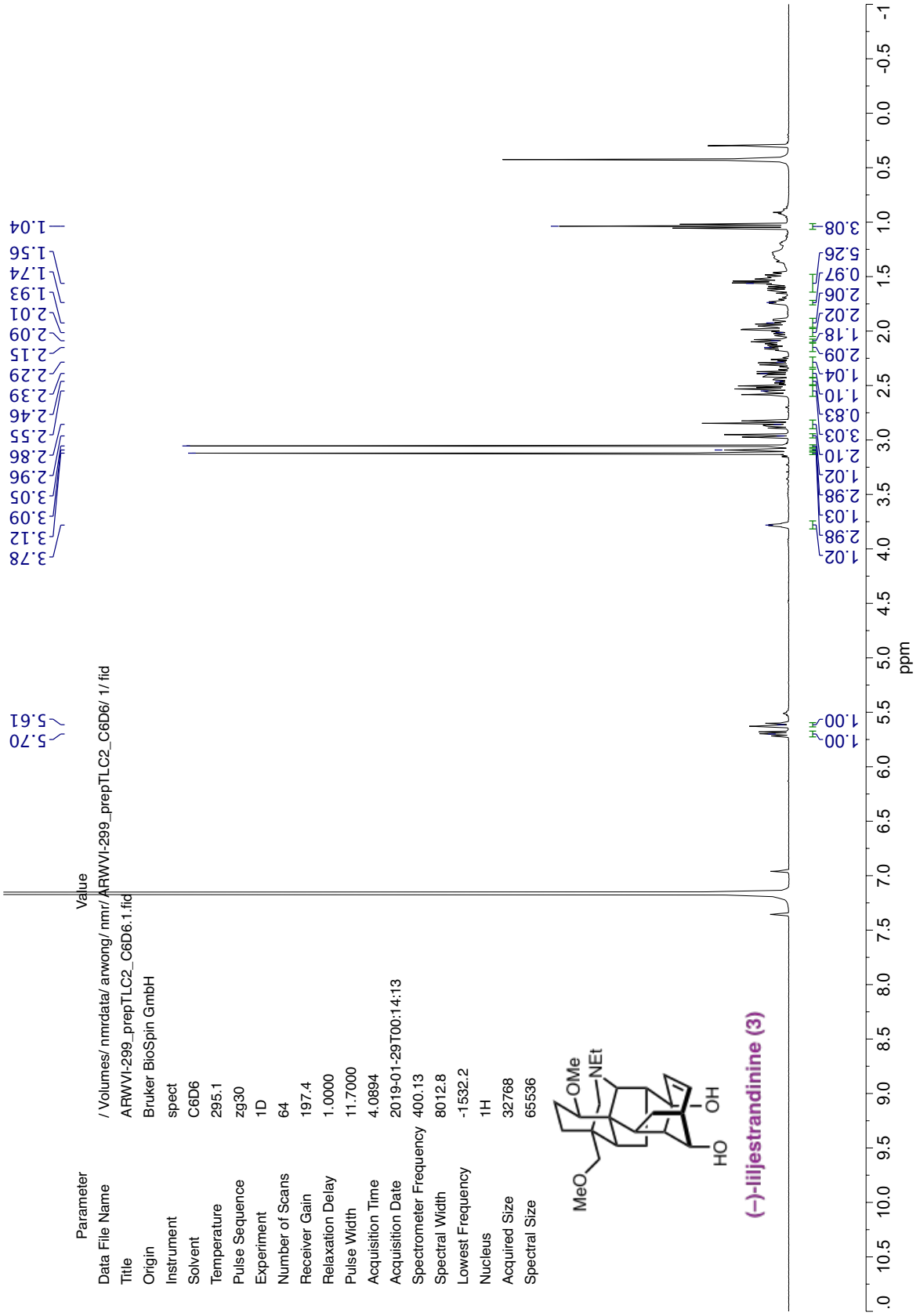

211.27
169.75
95.76
82.50
78.24
77.68
76.78
59.46
58.32
55.68
55.52
52.34
48.66
47.58
45.43
45.27
44.24
44.08
42.65
37.39
31.64
26.79
25.35
24.03
22.39
Parameter
Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-191_flashed/ 2/ fid
Title ARWVI-191_flashed.2.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.2
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 1300
Receiver Gain 78.7
Relaxation Delay 0.5000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2019-01-10T15:34:47
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1962.5
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
OMe
NAc
MeO
OMe
O
MOMO
239
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
ppm

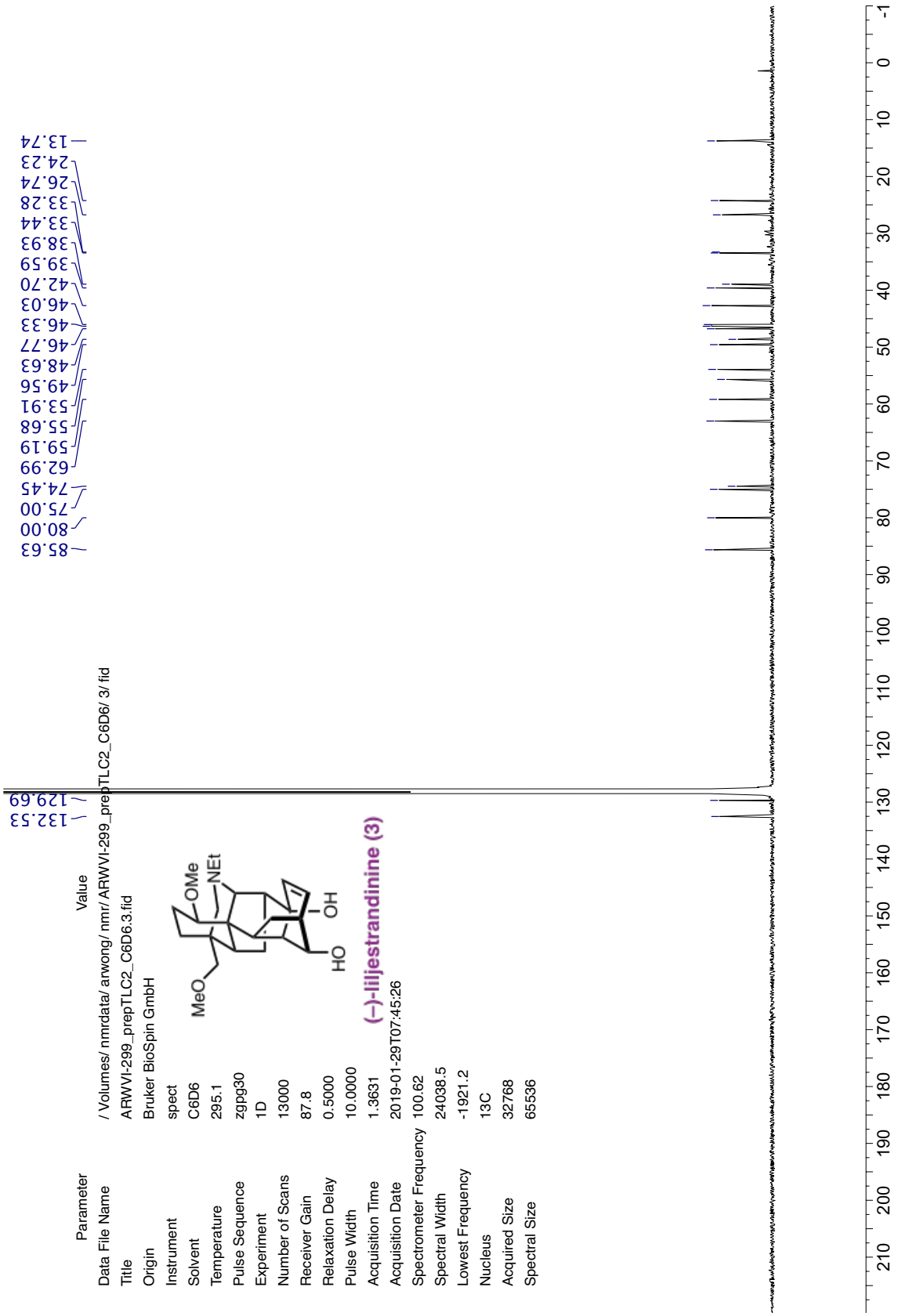

Parameter
Value
Data File Name / Volumes/ nmrdata-2/ arwong/ nmr/ ARWVI-296_prepTLC_B/ 1/ fid
Title ARWVI-296_prepTLC_B.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence zg30
Experiment 1D
Number of Scans 32
Receiver Gain 142.8
Relaxation Delay 1.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Acquisition Date 2019-01-18T00:41:35
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.4
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
MeO
OMe
NAc
MOMO
OMe
OTf
247
5.85
4.71
4.60
3.89
3.36
3.30
3.21
3.18
3.12
3.02
2.86
2.68
2.61
2.34
2.27
2.06
1.93
1.83
1.72
1.43
1.30
1.00
1.12
1.11
3.13
3.10
3.22
3.15
4.09
1.24
1.09
1.22
1.22
1.07
1.16
1.14
6.06
1.03
1.10
2.26
1.30
0.96
ppm


22.53
23.74
25.38
30.74
31.95
37.39
42.62
42.83
43.90
44.34
45.09
45.22
48.05
49.36
55.49
55.62
59.09
59.47
77.20
78.23
78.36
82.58
95.97
114.16
153.85
170.55
MeO
OMe
NAc
MOMO
OMe
OTf
247
Parameter
Value
Data File Name / Volumes/ nmrdata-2/ arwong/ nmr/ ARWVI-296_prepTLC_B/ 6/ fid
Title ARWVI-296_prepTLC_B.6.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.1
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 3000
Receiver Gain 87.8
Relaxation Delay 0.5000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2019-01-18T04:15:36
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1961.5
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


Parameter
Value
Data File Name
/ Volumes/ nmrdata/ arwong/ nmr/ ARWVI-297_prepTLC/ 1/ fid
Title
ARWVI-297_prepTLC.1.fid
Origin
Bruker BioSpin GmbH
Instrument
spect
Solvent
CDCl3
Temperature
295.1
Pulse Sequence
zg30
Experiment
1D
Number of Scans
32
Receiver Gain
197.4
Relaxation Delay
1.0000
Pulse Width
11.7000
240
Acquisition Time
4.0894
Acquisition Date
2019-01-18T22:07:10
Spectrometer Frequency
400.13
Spectral Width
8012.8
Lowest Frequency
-1545.3
Nucleus
1H
Acquired Size
32768
Spectral Size
65536
MeO
OMe
NAc
MOMO
OMe
H
6.17
5.85
4.75
4.59
3.88
3.84
3.79
3.36
3.30
3.21
3.17
3.11
3.04
2.58
2.41
2.33
2.14
2.03
1.83
1.69
1.43
1.30
1.00
0.93
1.10
1.01
1.01
0.99
0.97
2.98
3.02
4.14
2.91
1.29
0.98
2.03
1.01
1.02
1.05
5.99
2.10
2.10
1.07
1.06
ppm


Parameter Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-297_prepTLC/ 6/ fid
Title ARWVI-297_prepTLC.6.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent CDCl3
Temperature 295.2
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 3000
Receiver Gain 72.0
Relaxation Delay 0.5000
Pulse Width 10.0000
Acquisition Time 1.3631
Acquisition Date 2019-01-19T01:41:17
Spectrometer Frequency 100.62
Spectral Width 24038.5
Lowest Frequency -1961.2
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
240
MeO
OMe
NAc
MOMO
OMe
H
169.88
134.32
125.27
95.51
82.90
78.56
77.20
76.57
59.51
59.49
55.59
55.50
49.22
48.00
45.59
45.16
44.29
44.22
42.67
37.54
37.38
32.00
31.52
25.50
23.48
22.53
59.51
59.49
59.63 59.52 59.41 59.30 59.19
ppm
77.20
76.57
77.40 77.15 76.90 76.65 76.40
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
ppm


Parameter
Value
Data File Name / Volumes/ nmrdata/ arwong/ nmr/ ARWVI-299_prepTLC2_C6D6/ 1/ fid
Title ARWVI-299_prepTLC2_C6D6.1.fid
Origin Bruker BioSpin GmbH
Instrument spect
Solvent C6D6
Temperature 295.1
Pulse Sequence zg30
Experiment 1D
Number of Scans 64
Receiver Gain 197.4
Relaxation Delay 1.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Acquisition Date 2019-01-29T00:14:13
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1532.2
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
MeO
OMe
NEt
HO
OH
(–)-liljestrandinine (3)
ppm



Parameter	Value
Data File Name	/ Volumes/ nmrdata/ arwong/ nmr/ ARWVI-299_prepTLC2_C6D6/ 3/ fid
Title	ARWVI-299_prepTLC2_C6D6.3.fid
Origin	Bruker BioSpin GmbH
Instrument	spect
Solvent	C6D6
Temperature	295.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	13000
Receiver Gain	87.8
Relaxation Delay	0.5000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2019-01-29T07:45:26
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1921.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536