AN ABSTRACT OF THE DISSERTATION OF

Somnath Jana for the degree of Doctor of Philosophy in Chemistry presented on February 16, 2012.

Title: Studies Toward the Total Synthesis of (+)-Providencin.

Abstract approved: _____

James D. White

Studies toward the total synthesis of (+)-providencin (**1**), a highly oxygenated cembranoid dipterpene with a unique bicyclo[12.2.0]hexadecane skeleton and pronounced biological activity, are described. These studies resulted in the synthesis of advanced intermediates **320** and **332** which contain all of the carbon atoms of **1**. In a first generation approach toward **1**, a zirconium-mediated deoxygenative ring contraction of furanose **177** was used to furnish enantiopure cyclobutanol **176**. Olefination of furan aldehyde **197** with phosphonate **214** completed cyclobutylfuran segment **215**.

A second generation approach toward cyclobutylfuryl subunit **221** via ring-closing metathesis of diene **237** was unproductive, but the iodolactone subunit **228** needed for **1** was prepared successfully using carbometallation-iodination of alkyne **231**. Nucleophilic substitution of tosylate **230** with the dianion of phenylselenyl acetic acid (**252**) followed by acid-catalyzed lactone formation was employed for construction of the γ-lactone moiety of **228**.

A third generation route to the cyclobutylfuryl subunit of **1** involved a tin(II) chloride-mediated stereoselective allenol synthesis by reaction of aldehyde **302** with propargyllic bromide **264**. A silver-catalyzed allenone-to-furan isomerization of **309** completed the synthesis of cyclobutylfuran subunit **288**. Attempts to couple the two major fragments, **228** and **288**, using palladium-catalyzed C-H activation of the furan component were unsuccessful, but linkage of two major subunits was achieved at the C12-C13 bond via an *inter*molecular aldol reaction to give **332** and at the C6-C7 bond using *inter*molecular palladium-catalyzed cross-coupling to afford **320**.

Studies Toward the Total Synthesis of (+)-Providencin

by

Somnath Jana

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Presented on February 16, 2012.

APPROVED:

Major Professor, representing Chemistry

Chair of the Department of Chemistry

Dean of the Graduate School

I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

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Somnath Jana, Author

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TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

Page

TABLE OF CONTENTS (Continued)

Page

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF TABLES

Dedicated with love to

my parents

CHAPTER 1

Providencin

1.1 Isolation and biological activity

In 2003, the Rodriguez group isolated a highly oxygenated cembranoid from the sea plume *Pseudopterogorgia Kallos* (Bielschowski, 1918), which was collected near Providencia (Old Providence) Island located in the southwestern Caribbean Sea.[1] *Pseudopterogorgia Kallos* and related gorgonian octocorals have proven to be an abundant source of secondary metabolites that possess a diverse range of structural features and biological activities.[2] Dry animal specimens of 1.07 kilograms gave 20.0 milligrams of providencin (**1**) (corresponding to 0.012% yield dry weight) as a colorless amorphous solid.

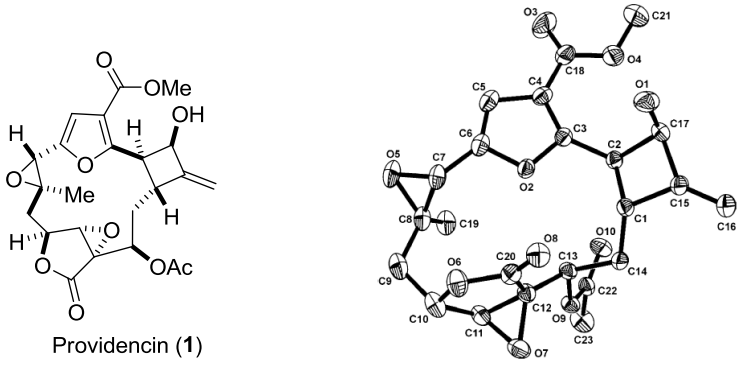


Figure 1.1 Molecular structure and X-ray crystal structure of (+)-providencin (**1**)

The structure and relative configuration of providencin (**1**) was secured through a combination of NMR spectroscopy and single-crystal X-ray analysis. The absolute configuration is still unknown. Providencin (**1**) manifests a unique bicyclo[12.2.0]hexadecane scaffold incorporating a trisubstituted furan linked directly to a tetrasubstituted cyclobutane as well as an unusual α,γ-bridged α,β-epoxy-γ-lactone.[1]

Providencin (**1**) displays modest *in vitro* cytotoxicity against MCF7 breast, NCI-H460 lung, and SF-268 CNS cancer cell lines.[1] The growth inhibition of treated cells to untreated cells was 57%, 39%, and 94% respectively. The natural scarcity of providencin has prevented further biological testing. The intriguing structure as well as the promising biological activity of providencin has stimulated several efforts towards the total synthesis of this natural product.

1.2 Diterpenes Related to Providencin

Rodriguez' group isolated several structurally intriguing diterpenes from *Pseudopterogorgia Kallos*. They proposed that the carbon skeletons represented by providencin and six other compound or classes of compounds share a common biogenic precursor.[3] Cembranoid natural products, the class to which providencin belongs, arise from the cyclization of geranylgeranyl pyrophosphate (GGPP).[3c] Different modes of cyclization or ring contraction can lead to seven novel carbon

skeletons. It has been proposed that a C_2-C_{17} cyclization leads to the providenciane carbon skeleton.

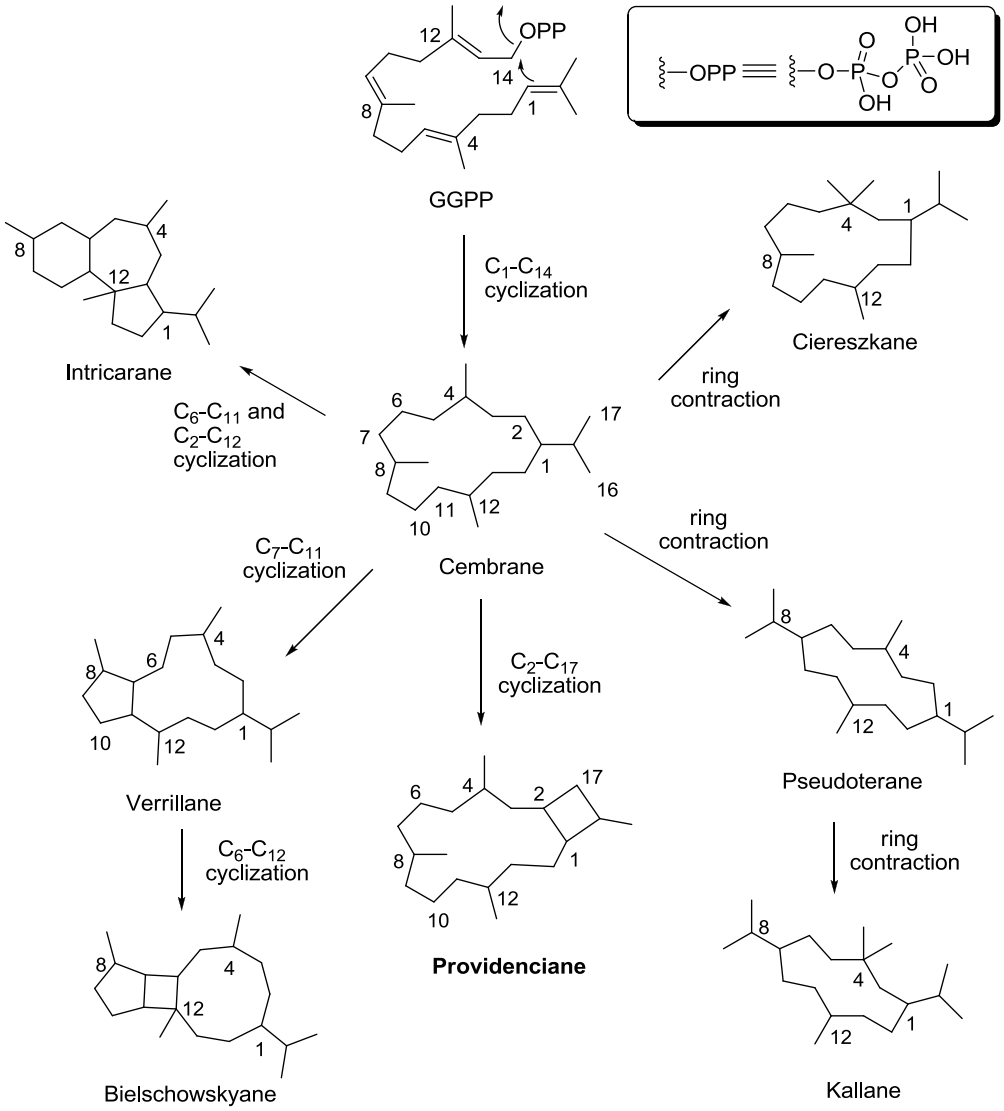


Figure 1.2 Proposed biosynthetic pathway to cembrane and related diterpenes

Providencin (**1**) is closely related to a class of diterpenes with the cembrane-based skeleton known as furanocembranoids. The structure of providencin (**1**) shows a connectivity similar to that of the bipinnatins, a family of diterpenes isolated from the gorgonian *Pseudopterogorgia bipinnata.*[4] The common structural features between these cembranoids include a 2,3,5-substituted furan, a 14-membered macrocycle and a butenolide or epoxidized butenolide.[2] The bipinnatins display inhibition of the nicotinic receptor, as well as anticancer and inflammatory activities.

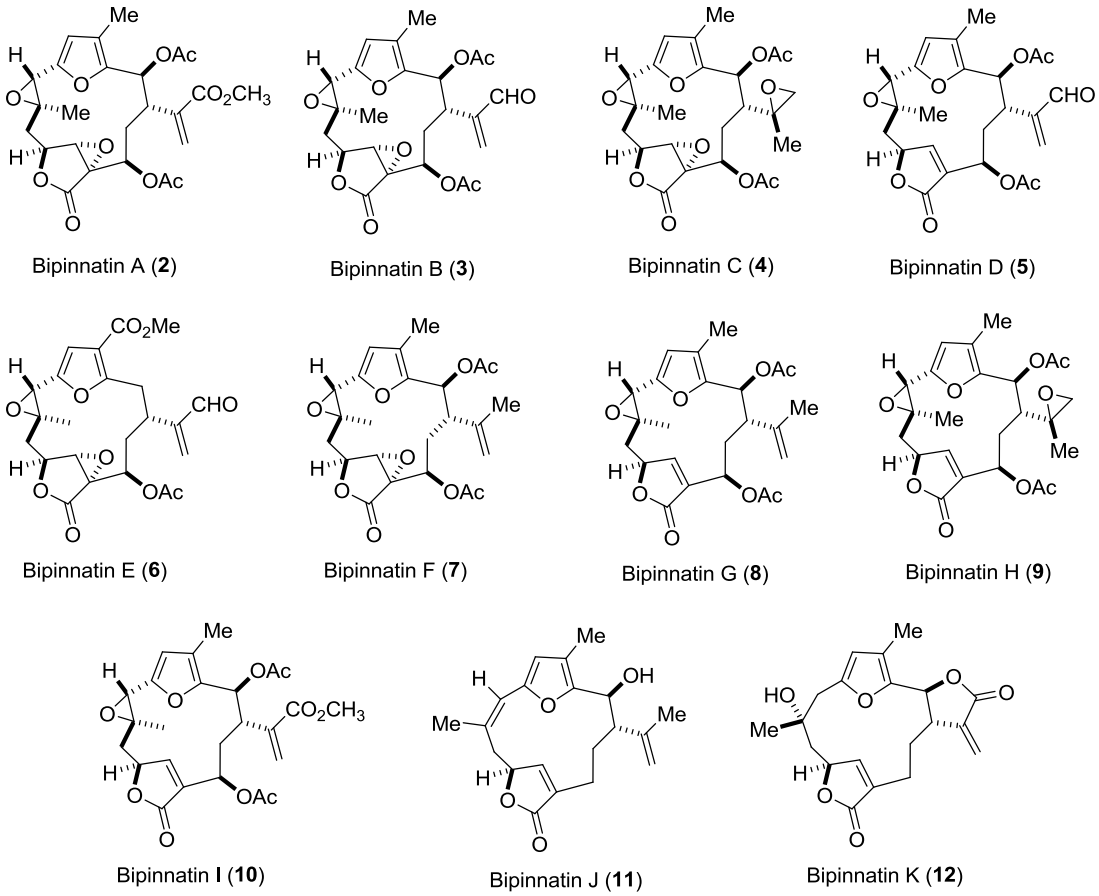


Figure 1.3 Bipinnatin family of natural products

Pseudopterogorgia Kallos has been known to be a source of many other intriguing diterpene natural products.[3,5] These compounds show a wide variety of structural and biological properties and have been the target of numerous synthetic efforts. Kallolide A (**13**), the first and most abundant metabolite isolated from *Pseudopterogorgia Kallos*, shows anti-inflammatory activity, and was synthesized by Marshall and co-workers.[15] A hexacyclic compound, beilschowskysin (**16**), exhibits anitimalarial activity and strong anticancer activity against two cancer cell lines.[3c] Several synthetic studies towards the cyclobutane core of **16** have been reported using intramolecular [2+2] photocycloaddition, but to date there is no total synthesis of this natural product.[7] Intricarene (**17**) was synthesized from its proposed biogenic precursor bipinnatin J (**11**) by both the Trauner[8a] and Pattenden groups.[8b,c] However, no synthetic work has been reported on kallolide E (**14**), kallosin A (**15**), and ciereszkolide (**18**).

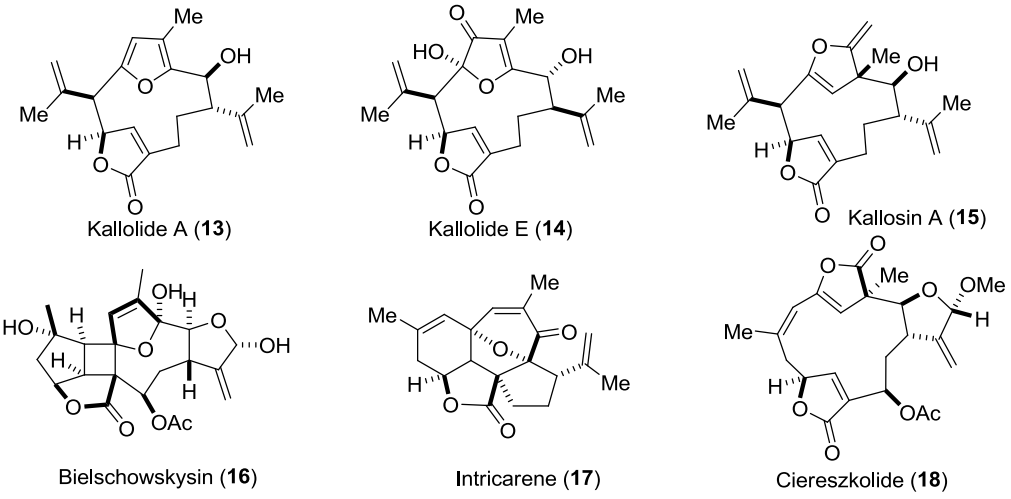


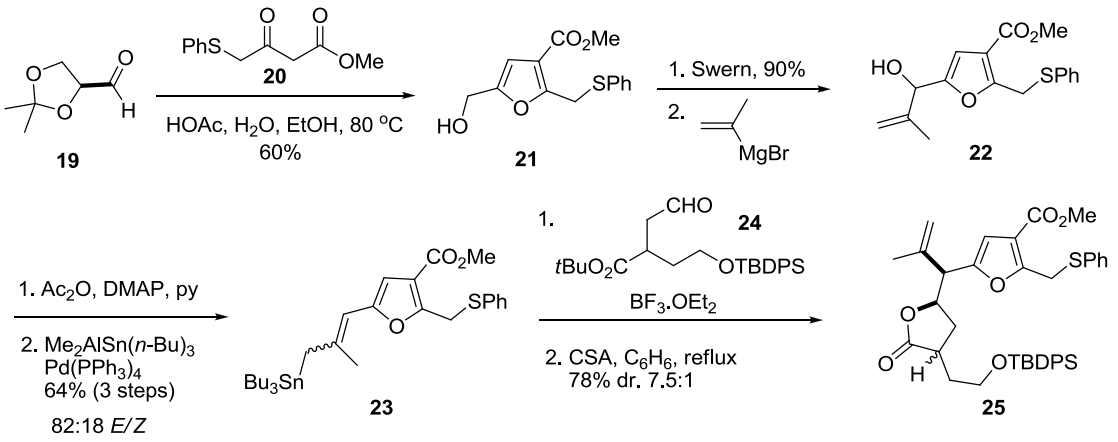
Figure 1.4 Diterpenes isolated from *Pseudopterogorgia Kallos*

1.3 Previous Syntheses of Related Furanocembranoids

Furanocembrane-based diterpenes have been attractive targets for several research groups. Those studies have shown that a variety of approaches can effectively produce the structural moieties found in these molecules.

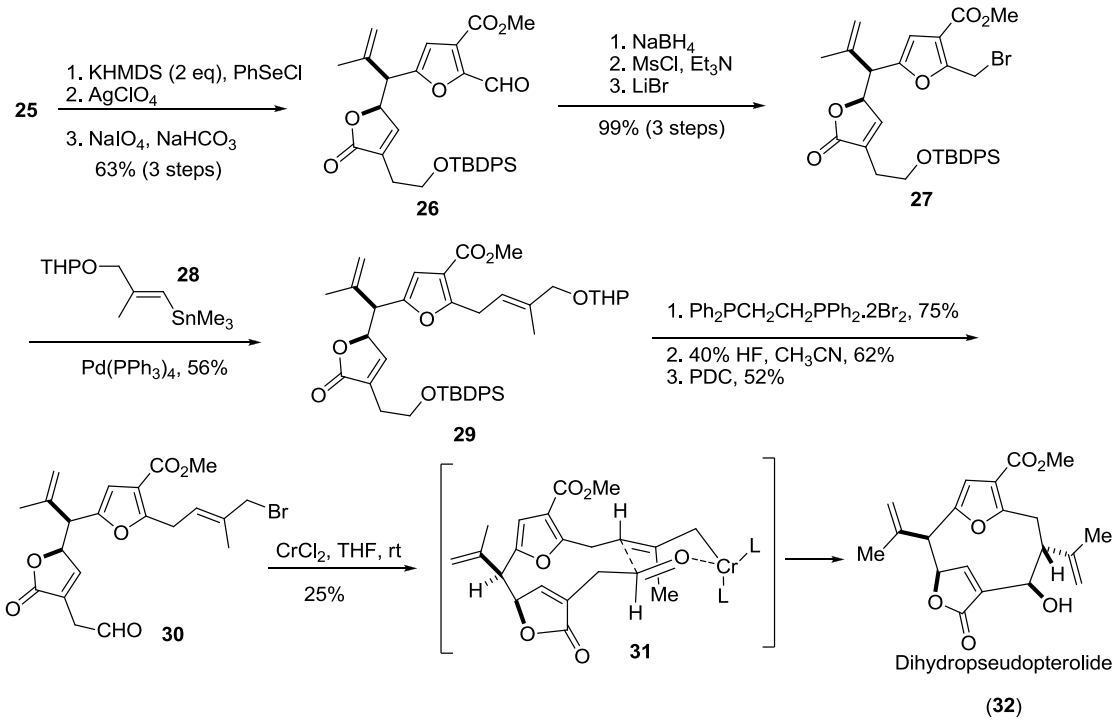
1.3.1 Paquette's Synthesis of Dihydropseudopterolide, Gorgiacerone, and Acerosolide

In 1990, Paquette and co-workers reported a total synthesis of dihydropseudopterolide **32**.[9] Their strategy was to build the furan first and then functionalize the remainder of the macrocycle. The Paquette synthesis began with an aldol reaction between glyceraldehyde acetonide (**19**) and α-thiomalonate **20** (Scheme 1.1). Treatment of the crude with acetic acid in hot ethanol then gave furan **21**. Swern oxidation of **21** to an aldehyde, followed by addition of 2-propenyl magnesium bromide gave allylic alcohol **22**. Acetylation of this alcohol was followed by palladium catalyzed allylic stannylation gave tributylstannane **23** with only modest stereoselectivity. Subsequent treatment of allylic stannane **23** with boron trifluoride etherate in the presence of aldehyde **24** gave predominately the *erythro* product, which was treated with camphorsulfonic acid to afford lactone **25**.



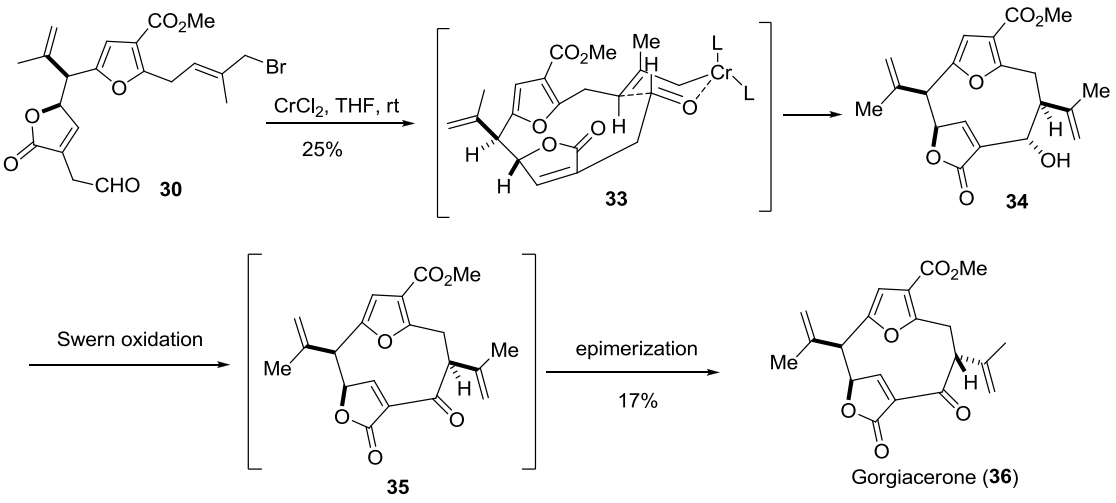
Scheme 1.1 Paquette's synthesis of furanolactone **25**

Formation of a dianion by treating **25** with two equivalents of potassium hexamethyldisilazide and trapping with phenylselenyl chloride gave an α-selenolactone-selenothioacetal that was treated with silver perchlorate to hydrolyze the selenothioacetal to an aldehyde (Scheme 1.2). The selenolactone was oxidatively eliminated with sodium periodate to give butenolide **26**. Sodium borohydride reduction of **26** followed by mesylation and displacement with bromide yielded furyl bromide **27**. Cross-coupling of bromide **27** with vinyl stannane **28** gave **29**, which was converted to bromoaldehyde **30** by a three step sequence. An intramolecular Nozaki-Hiyama-Kishi reaction on **30** in the presence of excess of chromium(II) chloride resulted in stereoselective macrocyclization to afford dihydropseudopterolide **31**, albeit in low yield. The selectivity was explained by an intramolecular π-facially selective attack at the aldehyde carbonyl by the flanking π-bond such that both large groups are equatorially placed on the oxachromium six-membered transition state.



Scheme 1.2 Completion of Paquette's synthesis of dihydropseudopterolide (**32**)

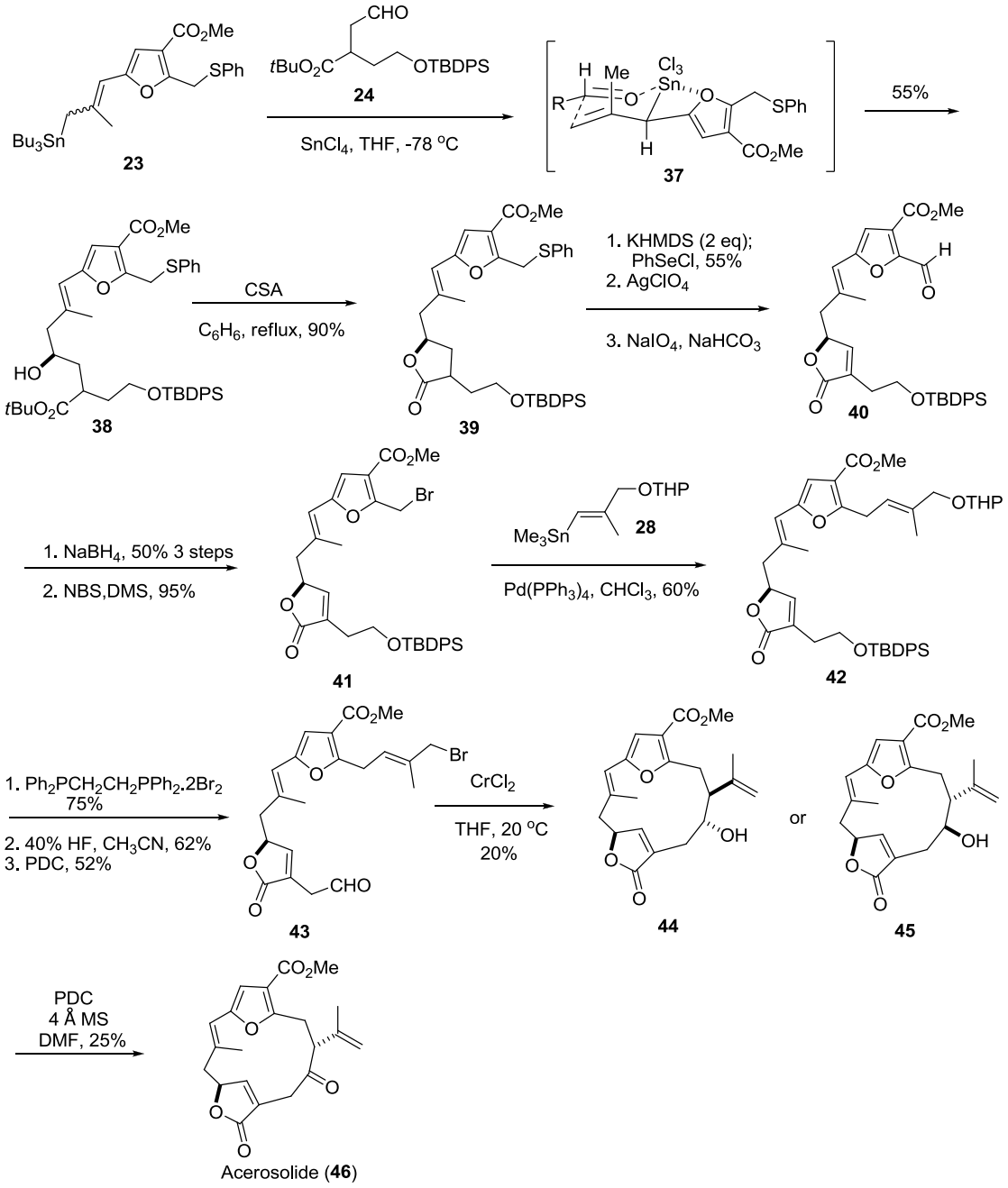
In 1992, Paquette and co-workers published the total synthesis of gorgiacerone (**36**) following the same strategy they used in previous furano-cembranoid syntheses.[10] Exposure of **30** to a large excess of chromium(II) chloride, led to the cyclized product **34** (Scheme 1.3). Finally, Swern oxidation of alcohol **34** and epimerization of the isopropenyl group in the same reaction yielded gorgiacerone (**36**).



Scheme 1.3 Paquette's synthesis of gorgiacerone (**36**)

A year later in 1993, Paquette and Astles completed a synthesis of the furanocembranoid acerosolide (**46**).[11] This synthesis featured similar disconnections to those employed previously yet they were able to tune the reactivity of stannane **23** in order to access the larger ring system. Reaction of (*E*)-allylic stannane **23**, once again with aldehyde **24** in the presence of tin(IV) chloride at low temperature, yielded the desired regioreversed product **38** (Scheme 1.4). This was treated with camphorsulfonic acid to give lactone **39** in good yield. It is believed that primary stannane **23** initially rearranges to a secondary stannane, which then undergoes the metallo-ene bond-forming reaction. A three-step sequence was used to convert the sulfide of **39** to an aldehyde and to oxidize the lactone to a butenolide to yield **40**. The aldehyde was reduced with sodium borohydride, and the resulting alcohol was treated with *N*-bromosuccinimide and dimethyl sulfide to give bromide **41**. An analogous four-step sequence to that used with **27**, including the cross-coupling with **28**, gave allylic

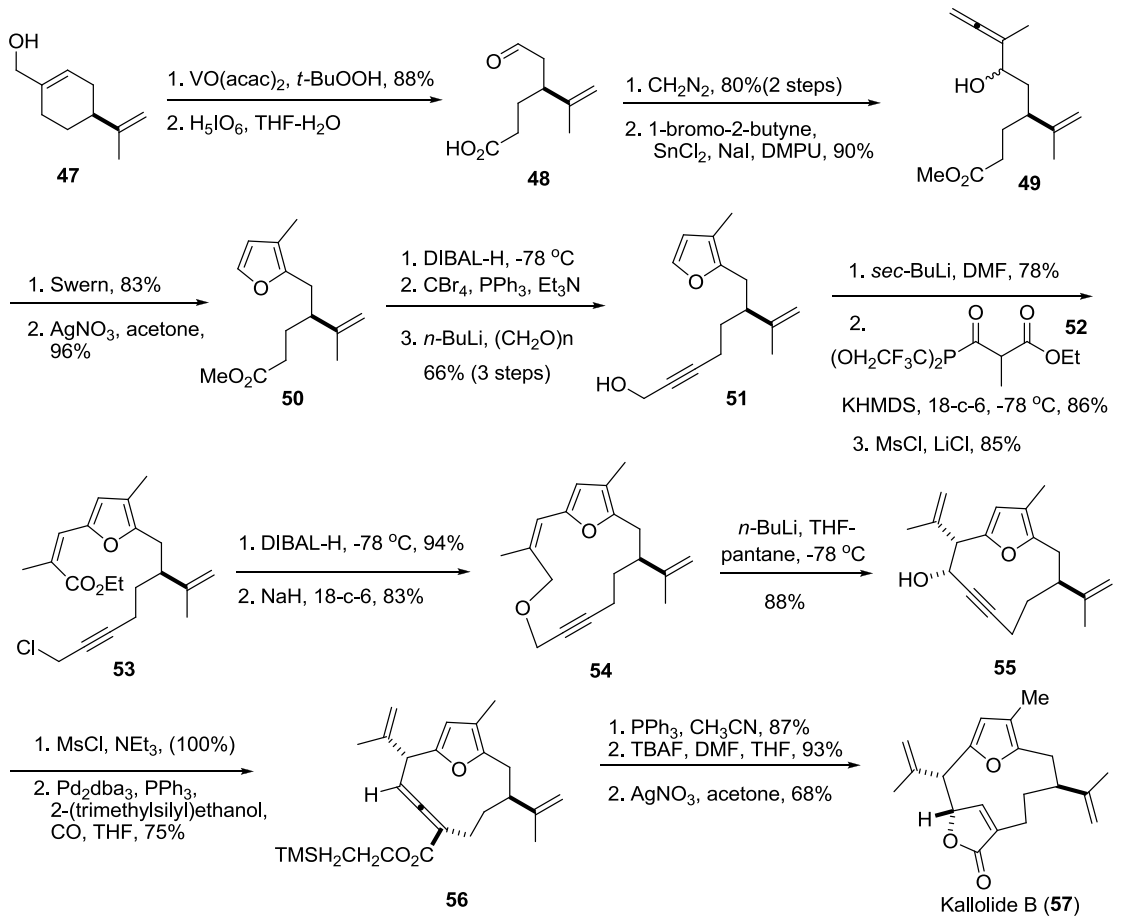
bromide **43**. Finally, chromium-mediated macrocyclization of **43** followed by oxidation of the resulting alcohols **44** and **45** afforded acerosolide (**46**).



Scheme 1.4 Paquette's synthesis of acerosolide (**46**)

1.3.2 Marshall's Synthesis of Kallolide B and Rubifolide

In the 1990's and early 2000's, the Marshall group was one of the key contributors to synthetic efforts towards furanocembranoids and pseudopteranes. In this context, a broad range of novel methodology was investigated to construct key features of these natural products. Marshall developed a new way to isomerize an allenone to a furan as well as an allenoic acid to a butenolide moiety to fabricate the pseudopterane ring system.

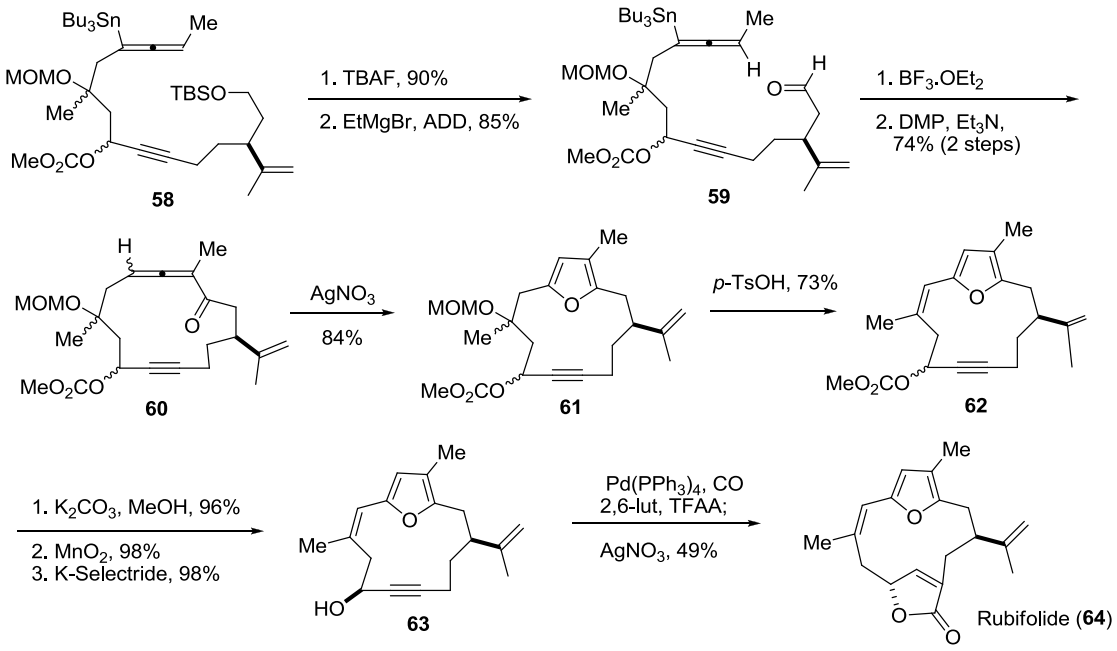


Scheme 1.5 Marshall's synthesis of kallolide B (**57**)

Marshall and co-workers first reported an asymmetric synthesis of the enantiomer of natural kallolide B (**57**) in 1996.[12] They targeted the non-natural enantiomer based on the large cost difference between their starting material (*S*)-(-)-perillyl alcohol (**47**) and its enantiomer. The synthesis began with a directed epoxidation of **47** using vanadyl acetylacetonate and *tert*-butyl hydroperoxide, followed by oxidative cleavage of the resulting epoxide with periodic acid to afford carboxylic acid **48** (Scheme 1.5). Esterification of **48** with diazomethane followed by addition of 1-bromo-2-butyne in the presence of tin(II) chloride and sodium iodide in *N*,*N*'-dimethyl-*N*,*N*'-propylene urea (DMPU) gave allenyl carbinol **49** as a mixture of diastereomers in high yield. Swern oxidation produced an allenone that was treated with a catalytic amount of silver nitrate to affect cyclization to furan **50**. Reduction of the ester to an aldehyde with diisobutylaluminum hydride followed by Corey-Fuchs olefination gave a gem dibromide, which was treated with *n*-butyllithium to afford an acetylide. The latter was trapped with paraformaldehyde to yield propargyllic alcohol **51**. Lithiation of the 5-position of the furan with *sec*-butyllithium followed by addition of dimethylformamide gave a formylated furan, which underwent Stille-Gennari olefination with phosphonate **52**. Subsequent conversion of the propargyllic alcohol to the chloride with mesyl chloride and lithium chloride gave (*Z*)-enoate **53**. The ester was reduced with diisobutylaluminum hydride and the resulting alcohol upon treatment with sodium hydride underwent intramolecular etherification to give a macrocyclic ether **54**. Treatment of allylic ether **54** with *n*-butyllithium effected the key [2,3]-Wittig rearrangement to furnish propargyllic alcohol **55** as the sole product

and in excellent yield. The alcohol was converted to its mesylate which was treated with palladium(0), carbon monoxide, and *β*-trimethylsilylethanol to give allenic ester **56**. The allenoate could be isomerized with triphenylphosphine in hot acetonitrile to yield an equilibrium mixture of separable allenoates. The desired epimer was treated with tetra-*n*-butylammonium fluoride to give an allenoic acid which was exposed to silver nitrate to furnish kallolide B (**57**).

A year later in 1997, Marshall and Sehon reported a synthesis of the enantiomer of rubifolide (**64**).[13] First, the allenyl stannane **58** was prepared from (*S*)-(-)-perillyl alcohol (**47**), using standard protocols. Deprotection of silyl ether **58** with tetrabutylammonium fluoride followed by oxidation and treatment with ethylmagnesium bromide and 1-1'-(azodicarbonyl)dipiperdine (ADD) gave aldehyde **59** (Scheme 1.6). Macrocyclization of **59** using boron trifluoride etherate yielded homopropargyllic alcohol, which was oxidized to allenone **60** using Dess-Martin periodinane. Exposure of the allenone **60** with 10% silver nitrate on silica gel afforded furan **61** in good yield. Treatment of the protected tertiary alcohol of **61** with *p*-toluenesulfonic acid resulted in elimination to give exclusively the (*Z*)-olefin in macrocycle **62**. Saponification of carbonate **62** with potassium carbonate in methanol gave separable epimeric propargyllic alcohols. Oxidation of the mixture with manganese dioxide and subsequent reduction with K-Selectride led exclusively to *syn*-product **63**. Finally, a one-pot reaction of **63** with trifluoroacetic anhydride (TFAA), followed by palladium catalyzed carbonylation and lastly silver nitrate-mediated cyclization yielded rubifolide (**64**).



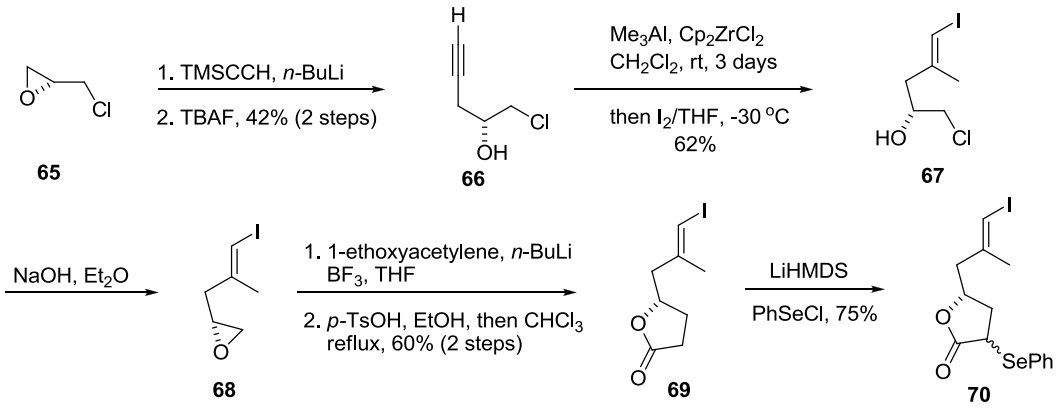
Scheme 1.6 Marshall's synthesis of rubifolide (**64**)

Marshall and co-workers also accomplished the synthesis of deoxypukalide in 2001[14] and kallolide A (**13**) in 1998[15] using their same strategy described earlier.

1.3.3 Pattenden's Synthesis of Lophotoxin

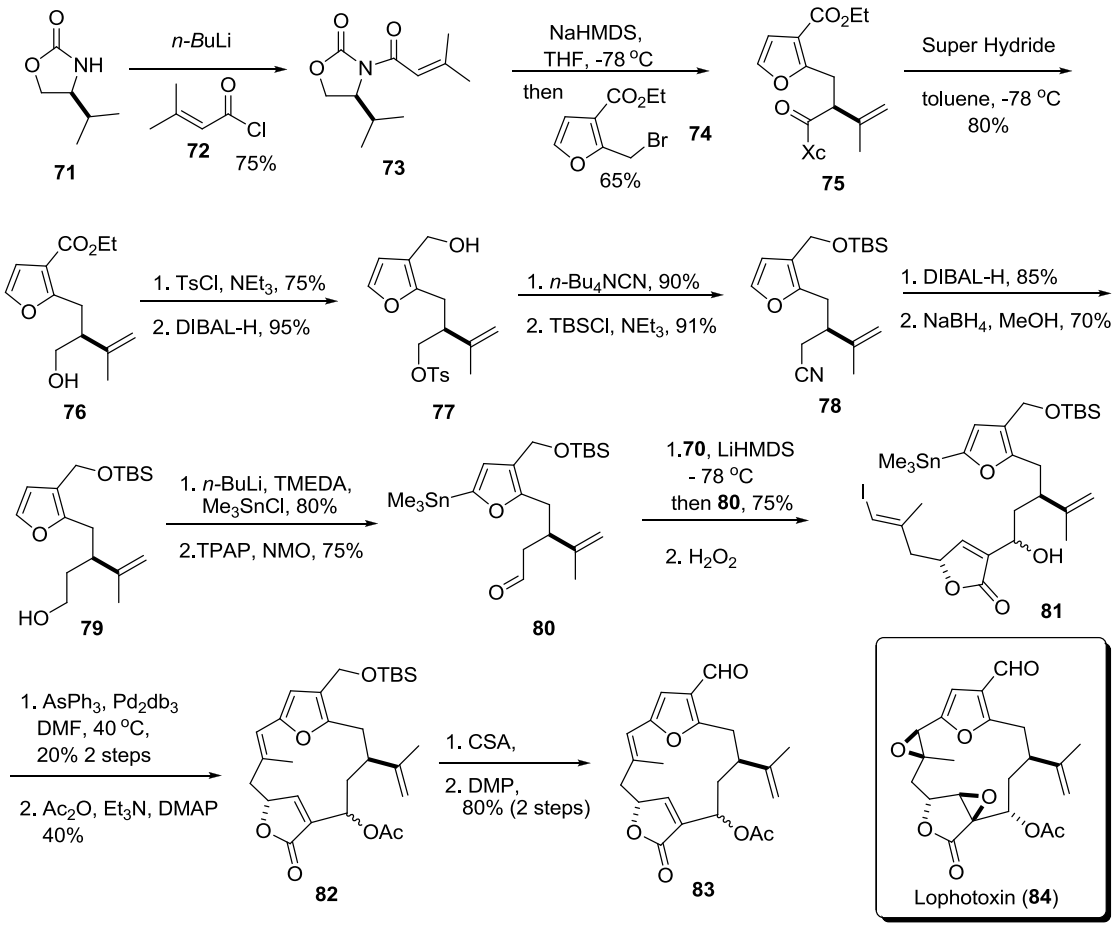
The Pattenden group has been working toward a total synthesis of the elusive target lophotoxin (**84**), and they completed an asymmetric synthesis of bis-deoxylophotoxin (**83**) in 2001.[16] Their approach hinges upon a Stille coupling to close the macrocycle, while the butenolide is formed by unsaturation of a lactone as in Paquette's synthesis. The Pattenden route began with addition of lithiated trimethylsilylacetylene to epichlorohydrin (**65**), followed by alkyne deprotection and carbometallation/iodination to yield vinyl iodide **67** (Scheme 1.7). The chlorohydrin

67 was treated with sodium hydroxide to give an epoxide **68** which was reacted with lithiated ethoxyacetylene to give a secondary alcohol. Acid catalyzed cyclization then yielded lactone **69** which was deprotonated with lithium hexamethyldisilazide and selenated to give *α*-phenylselenolactone **70**.



Scheme 1.7 Pattenden's synthesis of iodolactone **70**

The furan building block of the lophotoxin structure was synthesized from Evans' auxiliary **71** (Scheme 1.8). Oxazolidinone **71** was acylated with 3-methylbuten-2-oyl chloride (**72**) to afford **73**, and allylic deprotonation of **73** with sodium hexamethyldisilazide followed by alkylation with furyl bromide **74** gave **75**. Cleavage of the auxiliary with Super Hydride yielded alcohol **76**, which was converted to its tosylate, subsequent ester reduction afforded alcohol **77**. Displacement of tosylate from **77** with tetrabutylammonium cyanide and silyl protection of the alcohol yielded nitrile **78**.



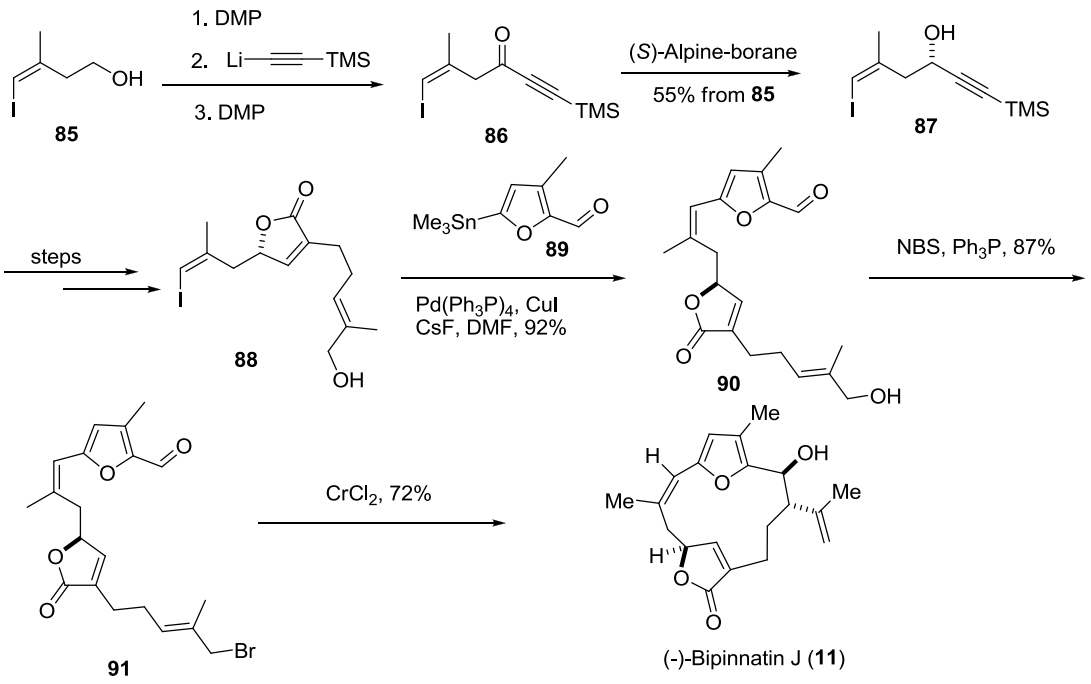
Scheme 1.8 Completion of Pattenden's synthesis of bis-deoxylophotoxin (**83**)

Reduction of nitrile **78** first with diisobutylaluminum hydride and then sodium borohydride gave alcohol **79**. Exposure of furan **70** with excess *n*-butyllithium and trapping with trimethyltin chloride followed by perruthenate oxidation yielded coupling partner **80**. The lithium anion of **70** was treated with aldehyde **80** and then with hydrogen peroxide to give butenolide **81** as a mixture diastereomers. Stille macrocyclization and subsequent acetylation yielded furanocembranoid **82** in low yield. Finally, deprotection of the primary alcohol and oxidation to an aldehyde gave

bis-deoxylophotoxin (**83**). To date, there have been no reports of successful oxidation of this intermediate to yield the lophotoxin (**84**) itself.

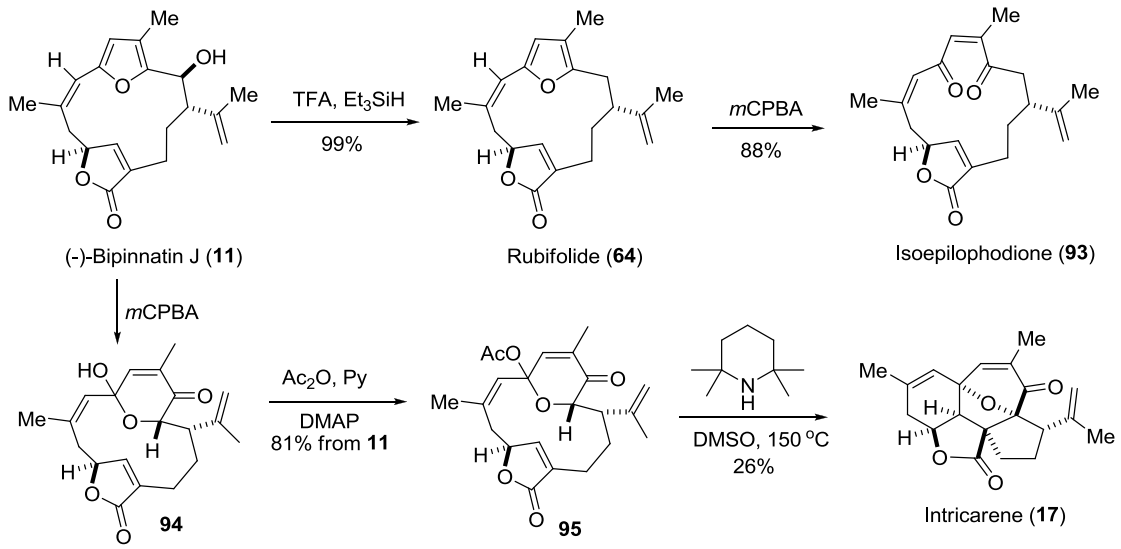
1.3.4 Trauner's Synthesis of (-)-Bipinnatin J, Rubifolide, Isoepilophodione, and Intricarene

In early 2006, Trauner's group reported a racemic and protecting-group-free synthesis of bipinnatin J (**11**).[17] Subsequently, they published an asymmetric synthesis of **11** in order to study its biosynthetic relationship with other furanocembranoids and related natural products such as rubifolide (**64**), isoepilophodione (**93**), and intricarene (**17**).[8a] The Trauner synthesis began with Dess-Martin periodinane oxidation of known vinyl iodide **85** followed by addition of lithiated trimethylsilylacetylene and reoxidation (Scheme 1.9). Asymmetric reduction of the resulting ynone **86** with Midland's (*S*)-Alpine borane gave propargyllic alcohol **87** in 92% ee. The alkyne **87** was elaborated to the butenolide **88** in nine steps, and Stille cross-coupling of **88** with furylstannane **89** afforded linear precursor **90** which was converted to allylic bromide **91** using triphenylphosphine and *N*-bromosuccinimide. Finally, a highly diasteroselective Nozaki-Hiyama-Kishi macrocyclization gave enantiomerically enriched (-)-bipinnatin J (**11**) in good yield.



Scheme 1.9 Trauner's asymmetric synthesis of (-)-bipinnatin J (**11**)

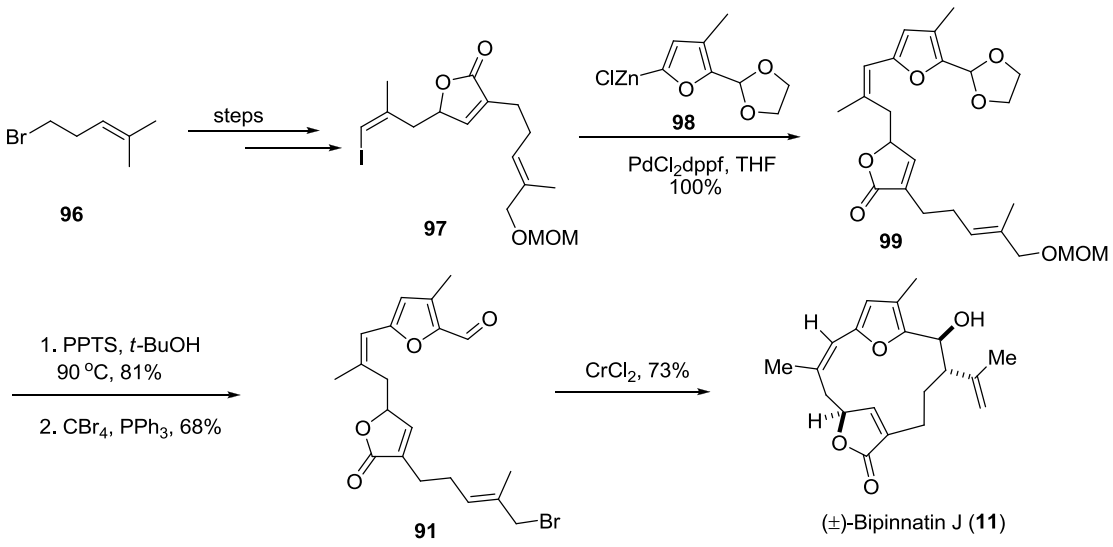
Trauner's group also showed that bipinnatin J (**11**) could be converted into rubifolide (**64**) in essentially quantitative yield by deoxygenation with trifluoroacetic acid and triethylsilane (Scheme 1.10). Rubifolide (**64**) was then oxidized with *m*-chloroperbenzoic acid to isoepilophodione (**93**). In a separate exercise, bipinnatin J (**11**) was oxidized with *m*-chloroperbenzoic acid which promoted an Achmatowicz rearrangement to **94**. Acetylation yielded enone **95** which upon heating with tetramethylpiperidine in dimethyl sulfoxide presumably gave an oxidopyrylium ion that underwent a transannular 1,3-dipolar cycloaddition to afford intricarene (**17**), albeit in low yield.



Scheme 1.10 Trauner's synthesis of rubifolide (**64**), isoepilophodione (**93**) and intricarene (**17**) from bipinnatin J (**11**)

1.3.5 Rawal's Synthesis of (±)-Bipinnatin J

Shortly after Trauner's report on the racemic synthesis of bipinnatin J (**11**), Rawal and Huang also reported a racemic synthesis of **11** using Negishi cross-coupling and Nozaki-Hiyama-Kishi macrocyclization as key reactions.[18] They prepared the butenolide **97** starting from commercially available 5-bromo methylpent-2-ene (**96**) (Scheme 1.11).



Scheme 1.11 Rawal's synthesis of (±)-bipinnatin J (**11**)

Negishi cross-coupling of vinyl iodide **97** with organozinc species **98** derived from 3-methylfurfural yielded coupled product **99** in quantitative yield. Acidic deprotection of **99** and bromination of the allylic alcohol gave the same intermediate, **91** used in Trauner's synthesis. Final diasteroselective Nozaki-Hiyama-Kishi macrocyclization of **91** gave (±)-bipinnatin J (**11**) in good yield.

1.4 References

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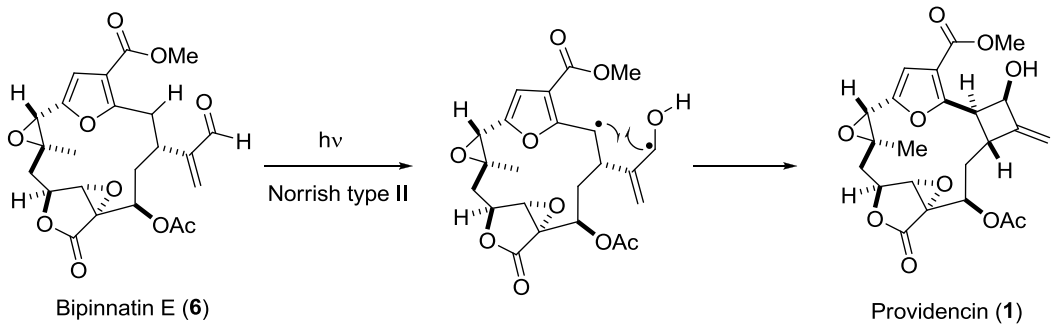
CHAPTER 2

Previous Synthetic Studies Towards Providencin

Three research groups have published their progress towards the synthesis of providencin (**1**). The Pattenden group at the University of Nottingham, the Mulzer group at the University of Vienna, and the Wood group at Colorado State University have explored different approaches toward providencin but neither group has completed a synthesis.

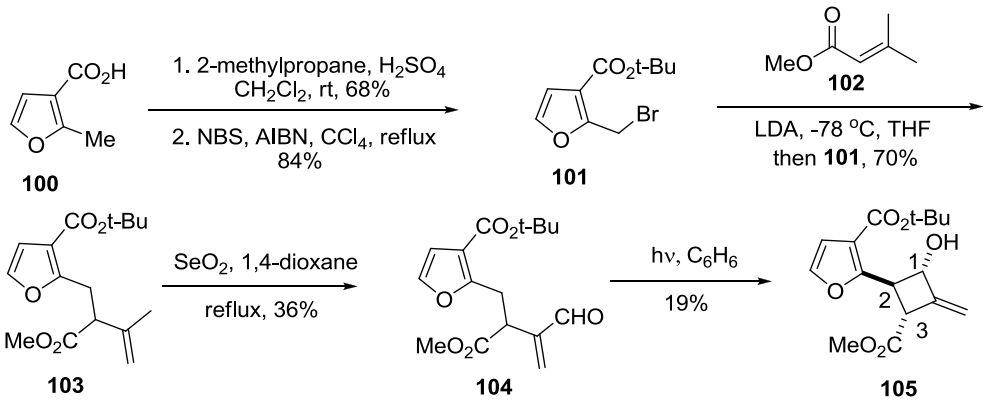
2.1 Pattenden's Synthetic Approach

In 2006, Pattenden and co-workers proposed that the cyclobutanol moiety in providencin (**1**) could be obtained from bipinnatin E (**6**) via a photochemically mediated intramolecular C-H insertion reaction.[1]



Scheme 1.1 Pattenden's proposed biosynthetic pathway to providencin (**1**)

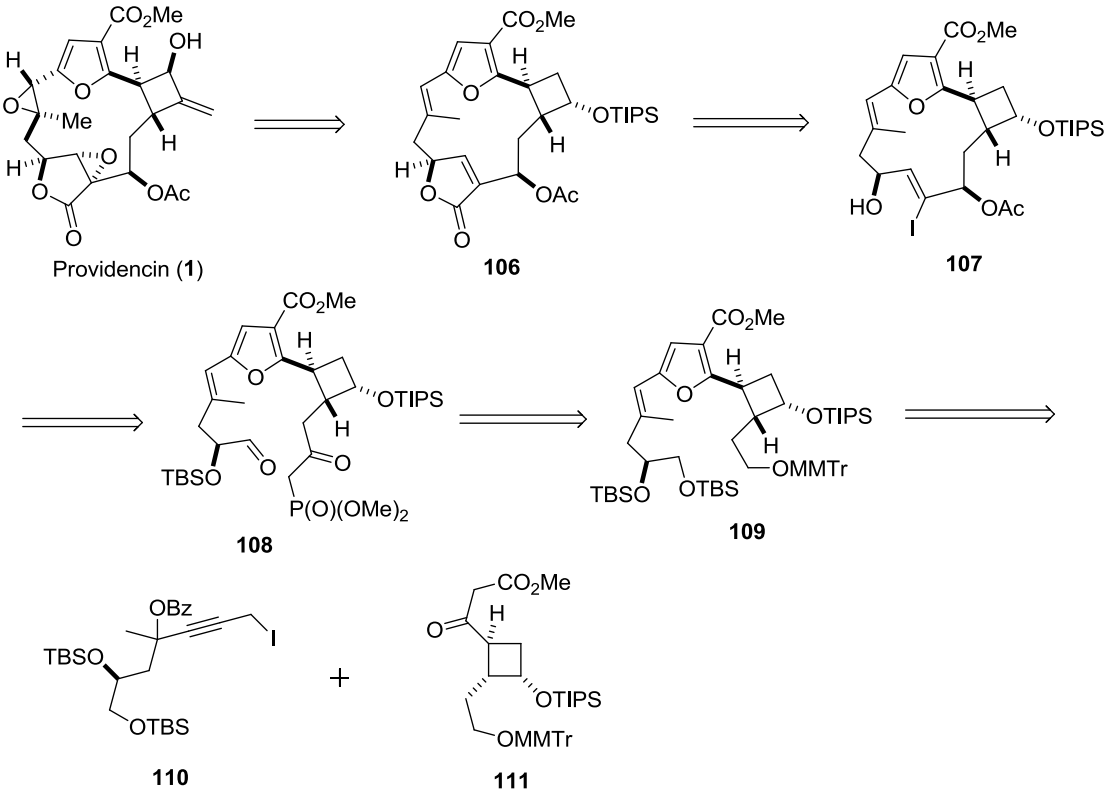
To verify this hypothesis, Pattenden and co-workers prepared a model compound **104**. Commercially available 2-methyl-3-furoic acid (**100**) was esterified and bromination of the resulting ester with *N*-bromosuccinimide gave bromomethyl furan **101**. Deprotonation of 3-methylbut-2-enoate (**102**) using lithium diisopropylamide, followed by alkylation of the resulting α-organolithium species with bromide **101**, gave desired β,γ-unsaturated ester **103**. Allylic oxidation of **103** by selenium oxide furnished α,β-unsaturared aldehyde **104**. Irradiation of a dilute solution of **104** in benzene in a Pyrex photoreactor using light from a 400 Watt medium pressure mercury lamp led to cyclobutanol **105** in a low 19% yield. To make matters worse, NOE experiments showed that **105** possessed the undesired *trans*-1,2-*trans*-2,3-relationship around the cyclobutane ring. Pattenden proposed that the conformational bias imposed by the macrocycle of furanocembrane would promote the formation of the desired cyclobutane diastereomer in the photo product (i.e., *cis*-1,2-*trans*-2,3; cf. **1**) but this idea was never pursued.



Scheme 2.1 Pattenden's synthesis of cyclobutanol **105**

2.2 Mulzer's Synthetic Studies

Mulzer and co-workers have published three reports on their synthetic effort towards providencin (**1**).[2] In his first generation approach, Mulzer envisioned that **1** could be formed by late stage epoxidations of **106** with introduction of the missing hydroxyl group in the cyclobutane moiety.

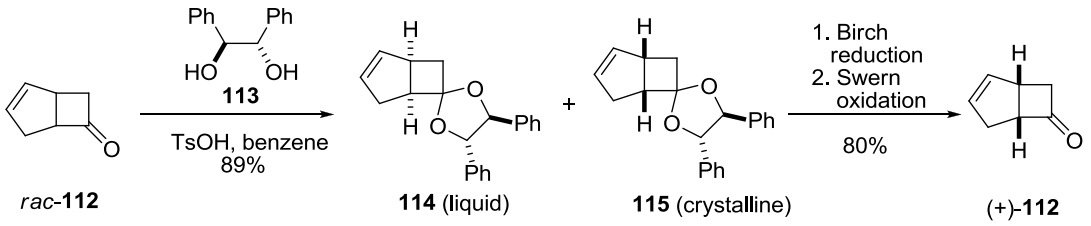


Scheme 2.2 Mulzer's first generation retrosynthetic analysis of providencin (**1**)

Butenolide **106** would be generated by a palladium-catalyzed carbonylation of vinyl iodide **107**, which would be formed by an intramolecular Horner-Wadsworth-Emmons olefination of phosphonate **108**. The aldehyde **108** would be prepared from

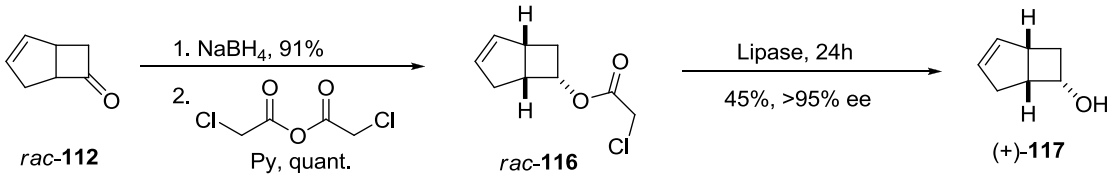
seco-intermediate **109** using standard chemistry. The furan of **109** would arise from two major fragments **110** and **111** via alkylation followed by palladium-catalyzed Wipf furan synthesis.[3]

Mulzer's synthesis began with the preparation of cyclobutanone **112** in optically pure form. Commercially available racemic bicyclic ketone **112** was first resolved via its diastereomeric ketal **114** and **115**, and the crystalline diastereomer **115** was cleaved to enantiomerically pure (+)-**112** by Birch reduction and Swern oxidation (Scheme 2.3).



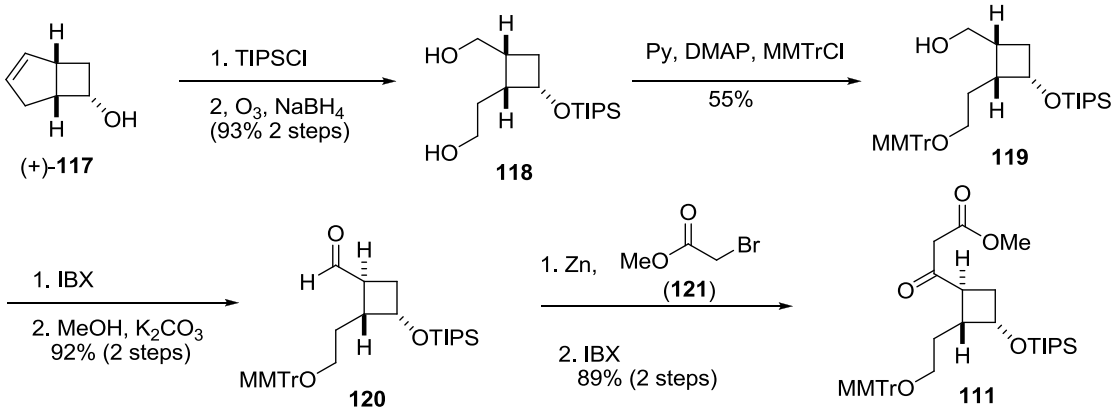
Scheme 2.3 Synthesis of (+)-**112**

In an alternative route, Mulzer used enzymatic resolution to obtain alcohol (+)-**117**. Sodium borohydride reduction and acylation of *rac*-**112** gave *rac*-**116** (Scheme 2.4), after which lipase-catalyzed resolution of *rac*-**116** afforded cyclobutanol (+)-**117** in 45% yield and >95% ee.



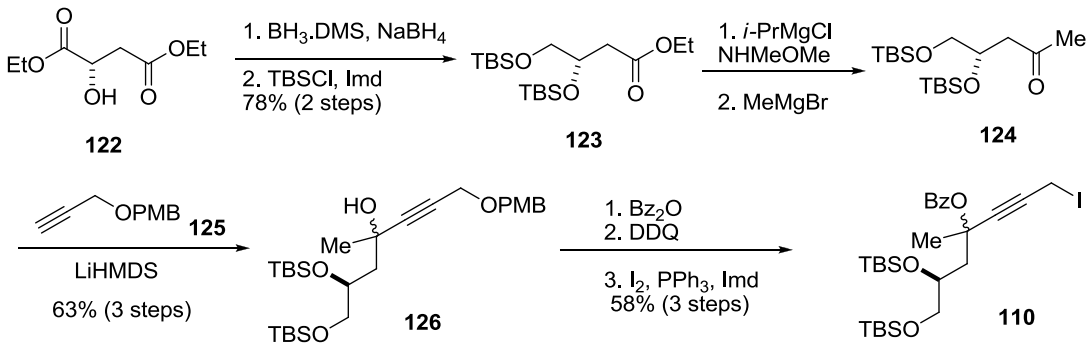
Scheme 2.4 Lipase-catalyzed synthesis of (+)-**117**

Triisopropylsilyl protection of the secondary alcohol of (+)-**117** followed by ozonolysis and reduction gave diol **118** (Scheme 2.5). Monoprotection of **118** with monomethoxytrityl chloride afforded **119**, which was converted to aldehyde **120** by oxidation and subsequent base-catalyzed epimerization. A Reformatsky reaction of aldehyde **120** with methyl bromoacetate (**121**) followed by oxidation yielded β-keto ester **111** in good yield.



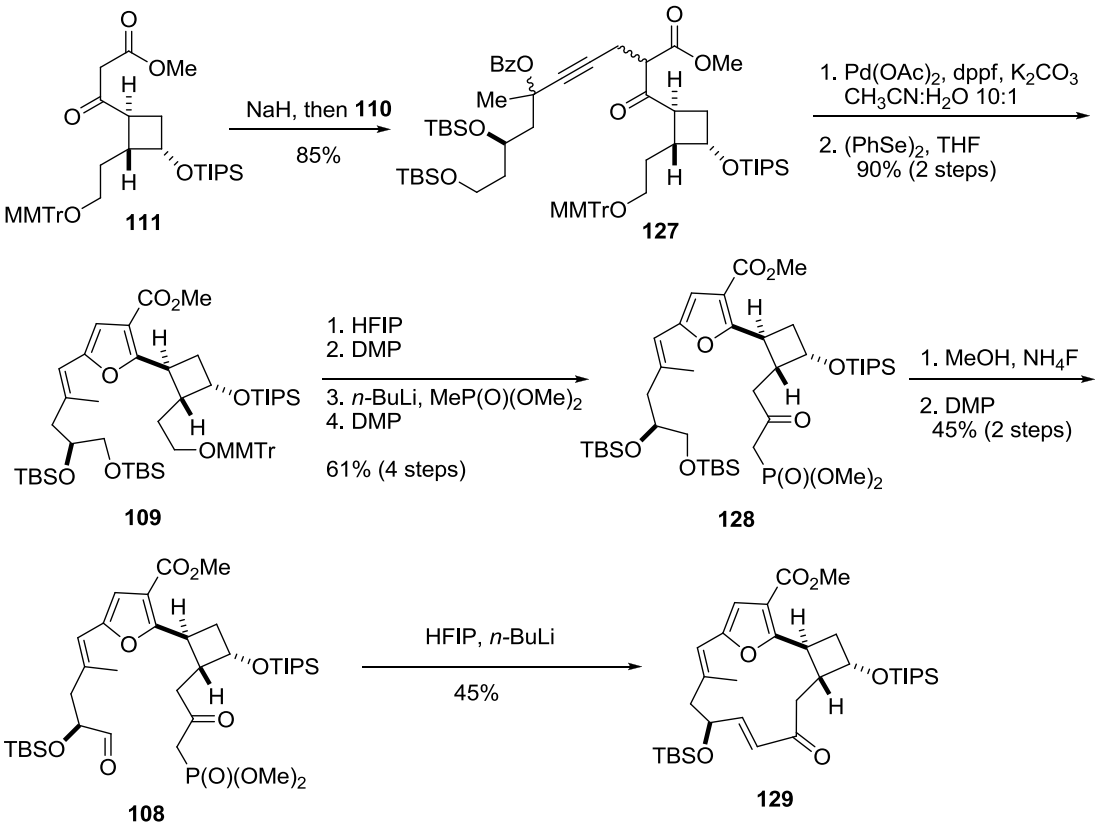
Scheme 2.5 Mulzer's synthesis of cyclobutane fragment **111**

Synthesis of propargyllic iodide **110** commenced with sodium borohydride reduction of (*S*)-malic ester **122** and silyl protection of the resultant diol (Scheme 2.6). Conversion of ester **123** to its Weinreb amide followed by addition of methylmagnesium bromide provided methyl ketone **124**. Addition of deprotonated alkyne **125** to this ketone furnished tertiary alcohol **126**, and after benzoylation, *p*-methoxybenzyl group removal and iodination of the resulting alcohol the coupling partner **110** was produced in 28% overall yield from **122**.



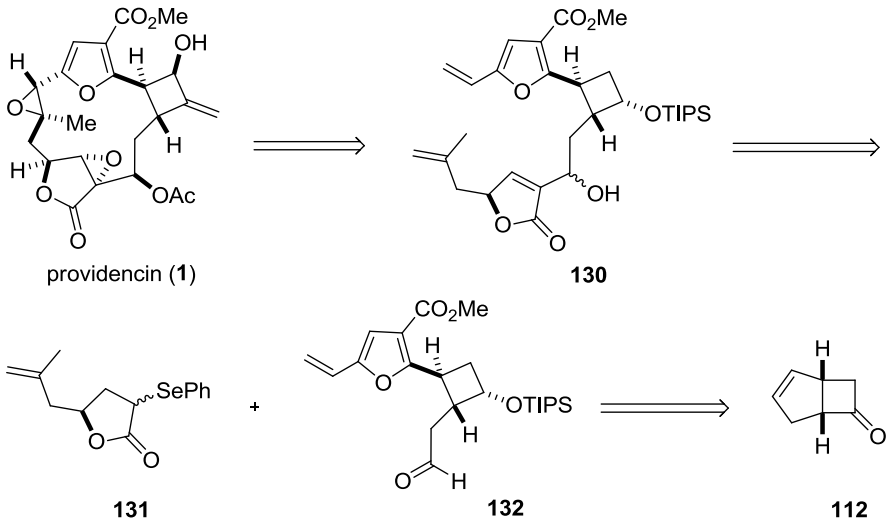
Scheme 2.6 Mulzer's synthesis of propargyllic iodide **110**

The coupling of fragments **110** and **111** was accomplished via alkylation of *β*-keto ester **111** with propargyllic iodide **110** in the presence of sodium hydride (Scheme 2.7). Wipf cyclization of benzoate **127** gave a 1:1 mixture of the corresponding *E*- and *Z*- propenylfurans, which was equilibrated to *E*-isomer **109** using diphenyl diselenide. Detritylation of **109** with hexafluoroisopropyl alcohol (HFIP) and oxidation of the resulting alcohol gave the corresponding aldehyde, which was converted to keto phosphonate **128** in two steps. The primary alcohol of **128** was deprotected and subsequently oxidized to the aldehyde which underwent macrocyclization via Horner-Wadsworth-Emmons olefination to furnish the providencin skeleton **129** in modest yield. No further elaboration of **129** toward providencin (**1**) has been reported to date.



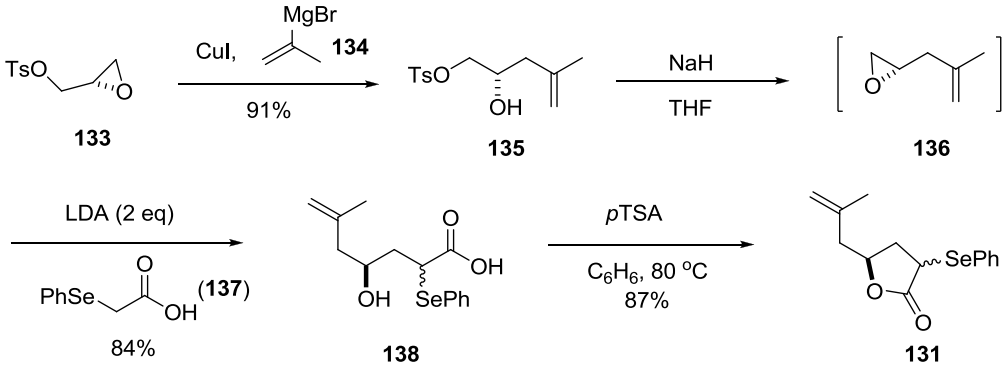
Scheme 2.7 Mulzer's synthesis of macrocycle **129**

In a second generation approach towards providencin (**1**), Mulzer envisioned that ring-closing metathesis (RCM) of **130** would be used to provide the macrocycle of the natural product (Scheme 2.8). Diene **130** would be formed by an aldol reaction between α-seleno lactone **131** and aldehyde **132**, while the furanocyclobutane of **132** segment would be prepared from cyclobutanone **112**.



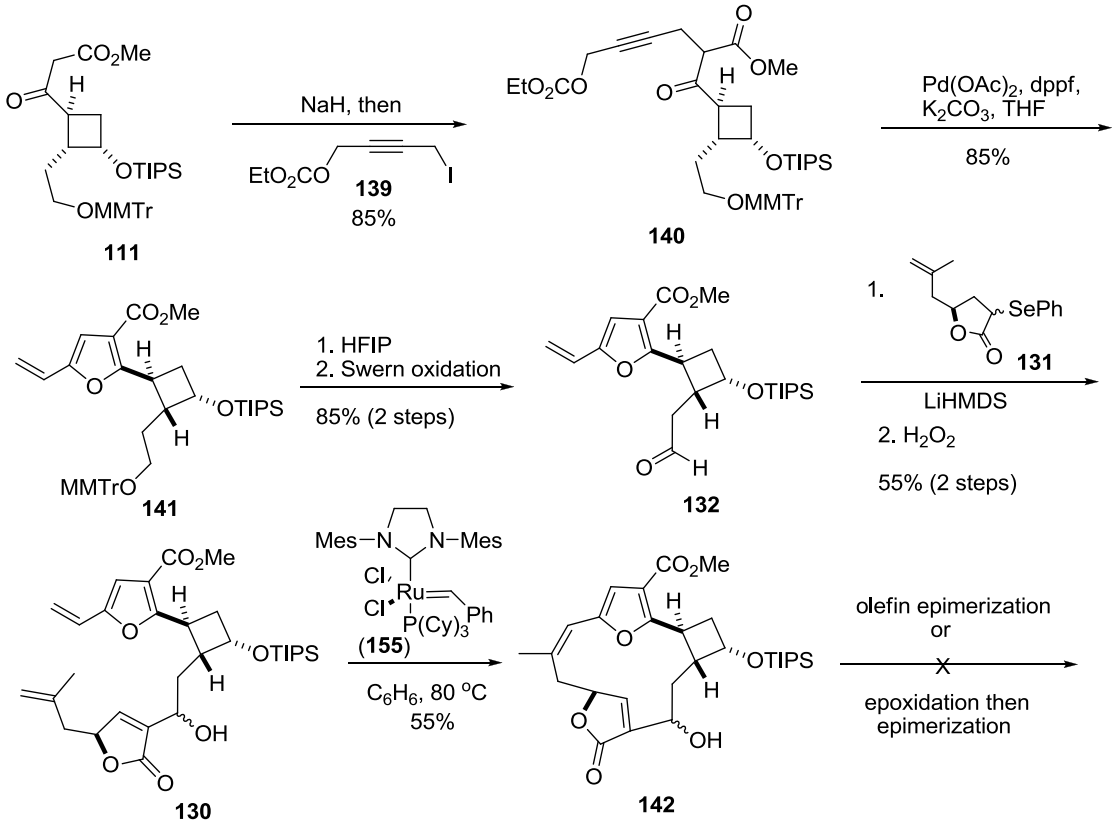
Scheme 2.8 Mulzer's second generation strategy for providencin (**1**)

First, lactone **131** was synthesized in four steps from (*R*)-glycidol tosylate (**133**). Cuprate addition to epoxide **133** provided homoallylic alcohol **135** which was converted to epoxide **136** (Scheme 2.9). The latter was then treated with the dianion of (phenylseleno)acetic acid (**137**) to give hydroxy acid **138**. Acid-catalyzed cyclization of **138** yielded the desired lactone **131** in good overall yield.



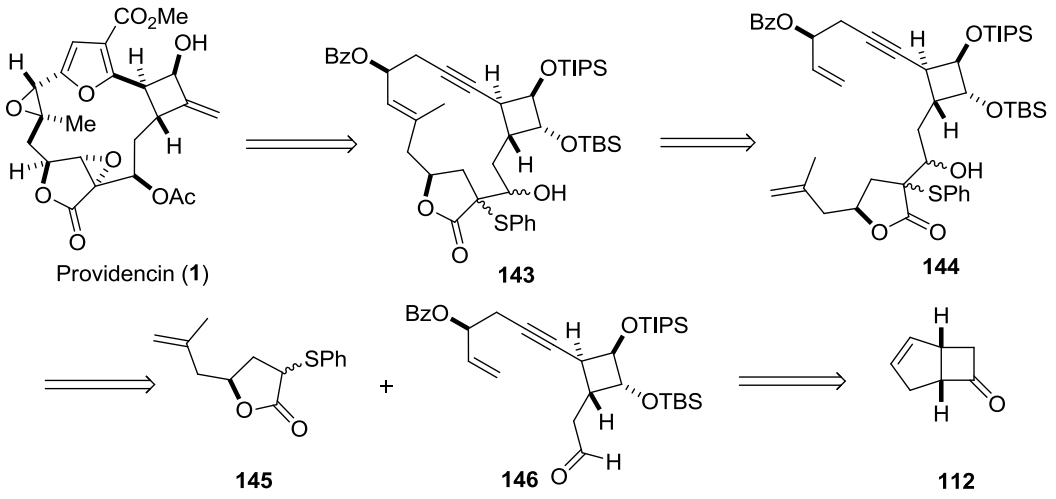
Scheme 2.9 Mulzer's synthesis of α-seleno lactone **131**

Synthesis of cyclobutylfuran **132** began with the alkylation of *β*-ketoester **111** with propargyllic iodide **139** (Scheme 2.10). Wipf cyclization of **140** furnished furan **141** in excellent yield, after which removal of the monomethoxytrityl group followed by oxidation provided aldehyde **132**. Deprotonation of lactone **131** with lithium hexamethyldisilazide and reaction of the anion with aldehyde **132** gave a product, which upon treatment with hydrogen peroxide yielded butenolide **130**. Ring-closing metathesis of diene **130** using Grubbs' II catalyst (**155**) gave *Z*-isomer **142** as a 1:1 mixture of alcohol diastereomers. All the attempts to convert the *Z*-olefin of **142** to the desired *E*-olefin were unsuccessful.



Scheme 2.10 Mulzer's synthesis of macrocycle **142**

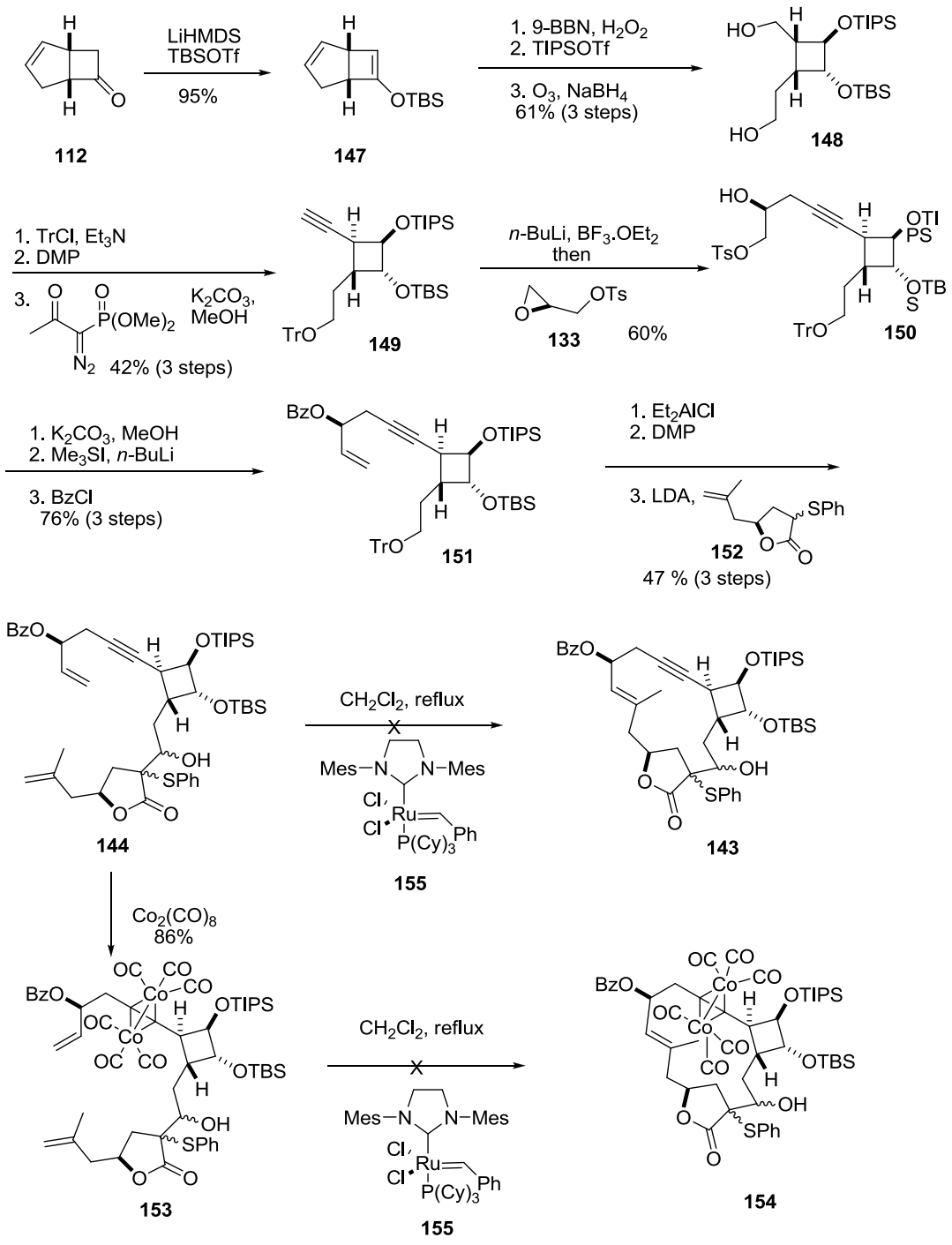
In his third generation approach toward providencin (**1**), Mulzer attempted to build the core structure prior to Wipf cyclization. In this plan, the furan would be introduced into macrocycle **143** by palladium-catalyzed cyclization with the macrocycle again prepared by ring-closing metathesis (Scheme 2.11). The RCM precursor, diene **144**, would be prepared by an aldol reaction between *α*-thiolactone **145** and aldehyde **146** while cyclobutanone **112** would again be the source of the tetrasubstituted cyclobutane **146**.



Scheme 2.11 Mulzer's third generation retrosynthetic plan for providencin (**1**)

In the forward direction, the new route began with conversion of cyclobutanone **112** to *tert*-butyldimethylsilyl enol ether **147** (Scheme 2.12). Hydroboration, triisopropylsilyl ether formation, ozonolysis and subsequent sodium borohydride reduction yielded tetrasubstituted cyclobutane **148**. Mono-protection of diol **148**, oxidation of the remaining alcohol to an aldehyde and epimerization was followed by conversion to alkyne **149**. Deprotonation of alkyne **149** and treatment of

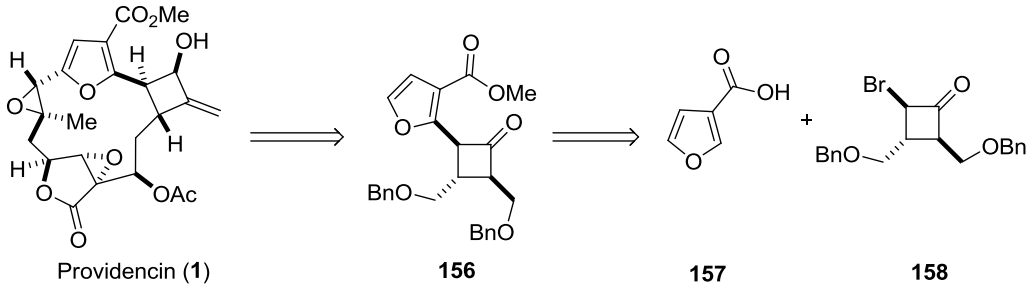
epoxide **133** furnished secondary alcohol **150** which was converted to protected allylic alcohol **151** in three steps. Cleavage of the trityl group from **151** and subsequent oxidation provided an aldehyde, which upon exposure to the anion of lactone **152** afforded the ring-closing metathesis precursor **144**. Unfortunately, all attempts to effect ring-closing metathesis of **144** were unsuccessful; a result that led Mulzer to speculate that the alkyne moiety of this molecule was the source of the problem. However, converting **144** into its cobalt complex **153** also failed to generate macrocycle **154** by ring-closing metathesis. At this stage, Mulzer appears to have abandoned efforts to synthesize providencin and no further work has been published by the Vienna group.



Scheme 2.12 Mulzer's attempted synthesis of macrocycles **143** and **154**

2.3 Wood's Synthetic Approach

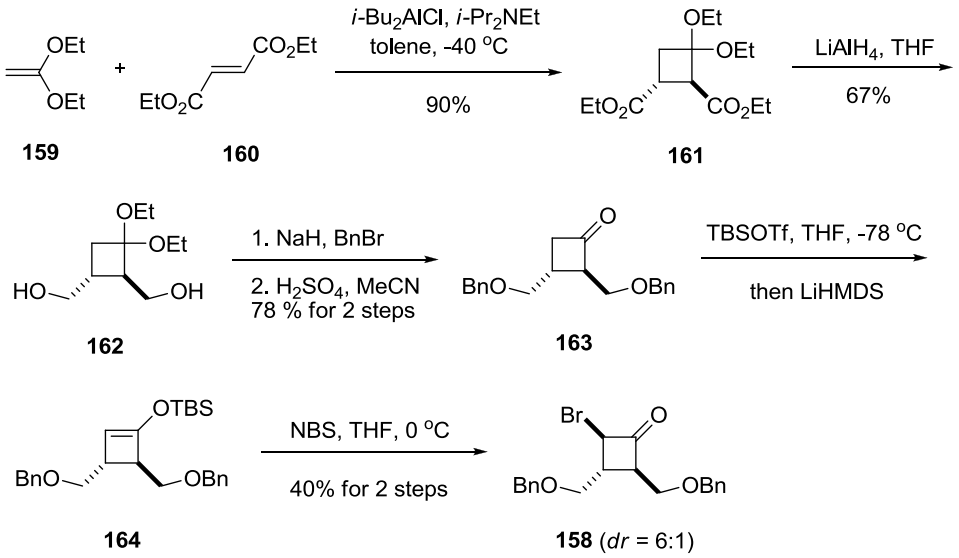
In 2011, Wood's group[4] published their progress towards providencin (**1**), where a route to the furanyl-cyclobutanone fragment of **1** involving a [2+2] photo-cycloaddition and an alkylation reaction was employed. Wood envisioned construction a preassembled furanyl-cyclobutane segment (**156**) that would be derived from coupling of 3-furoic acid (**157**) with bromide **158** (Scheme 2.13).



Scheme 2.13 Wood's strategy for synthesis of the furanyl-cyclobutane segment of providencin (**1**)

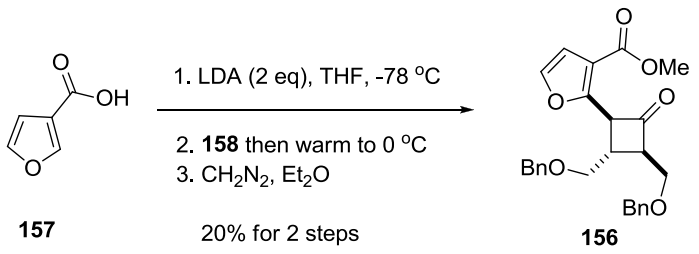
Wood's synthesis of bromocyclobutanone **158** commenced with [2+2] photo-cycloaddition of 1,1-diethoxyethylene (**159**) and diethyl fumarate (**160**) which, under the conditions developed by Brunner,[5] furnished cycloadduct **161** in excellent yield (Scheme 2.14). Reduction of diester **161** to diol **162** and subsequent conversion to the corresponding bis-benzyl ether was followed by removal of acetal hydrolysis to provide cyclobutanone **163** in good overall yield. After extensive experimentation, the most efficient conversion of **163** to **158** was found to be initial transformation to its silyl enol ether **164** and subsequent treatment with *N*-bromosuccinimide. This gave

cyclobutanone **158** as a 6:1 mixture of diastereomers, with the major diastereomer having a trans-trans relationship between the three substituents.



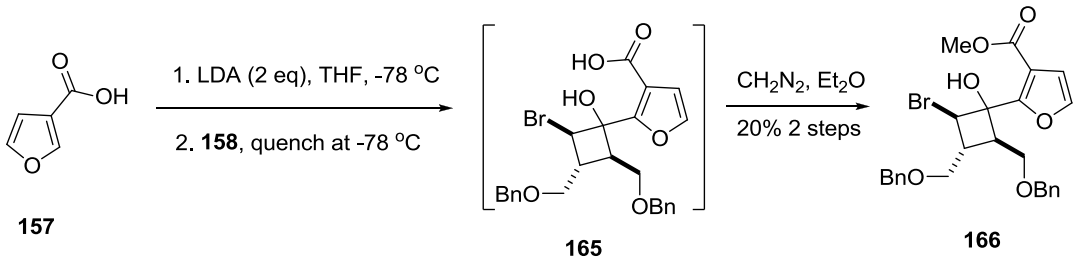
Scheme 2.14 Wood's synthesis of bromocyclobutanone **158**

In an initial reaction of the dianion of 3-furoic acid (**157**) with bromide **158** at low temperature, the crude extract was treated with diazomethane (Scheme 2.14). The desired product **156** was isolated as a single diastereomer in 20 % yield. NMR studies, including 1D NOE and 2D ROESY experiments, confirmed that **156** possessed a trans-trans relationship between substituents.



Scheme 2.15 Wood's initial coupling between **157** and **158**

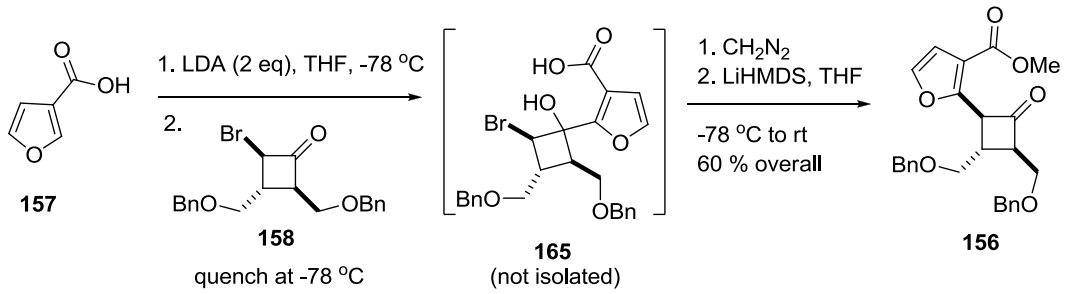
During the course of efforts to improve this yield of the key coupling, Wood observed that quenching the reaction at –78 °C prior to treatment with diazomethane resulted in the formation of tertiary alcohol **165** (Scheme 2.16). This alcohol proved to be very labile and difficult to isolate, but it could be transformed to **156** in an improved yield upon exposure of a base.



Scheme 2.16 Wood's initial synthesis of **166**

Wood and co-workers found that lithium hexamethyldisilazide was the base of choice for promoting the conversion of **165** to **156** and the optimized sequence, wherein addition of the dianion of **157**, esterification and rearrangement were carried out without isolation of intermediates **165** and **166**, yielded the desired cyclobutanone **156** in 60% overall yield (Scheme 2.17). The utilization of key fragment **156** towards

the synthesis of providencin (**1**) is presumably underway in Wood's laboratory although no further progress has been reported.



Scheme 2.17 Wood's optimized synthesis of furanyl-cyclobutanone fragment **156**

2.4 References

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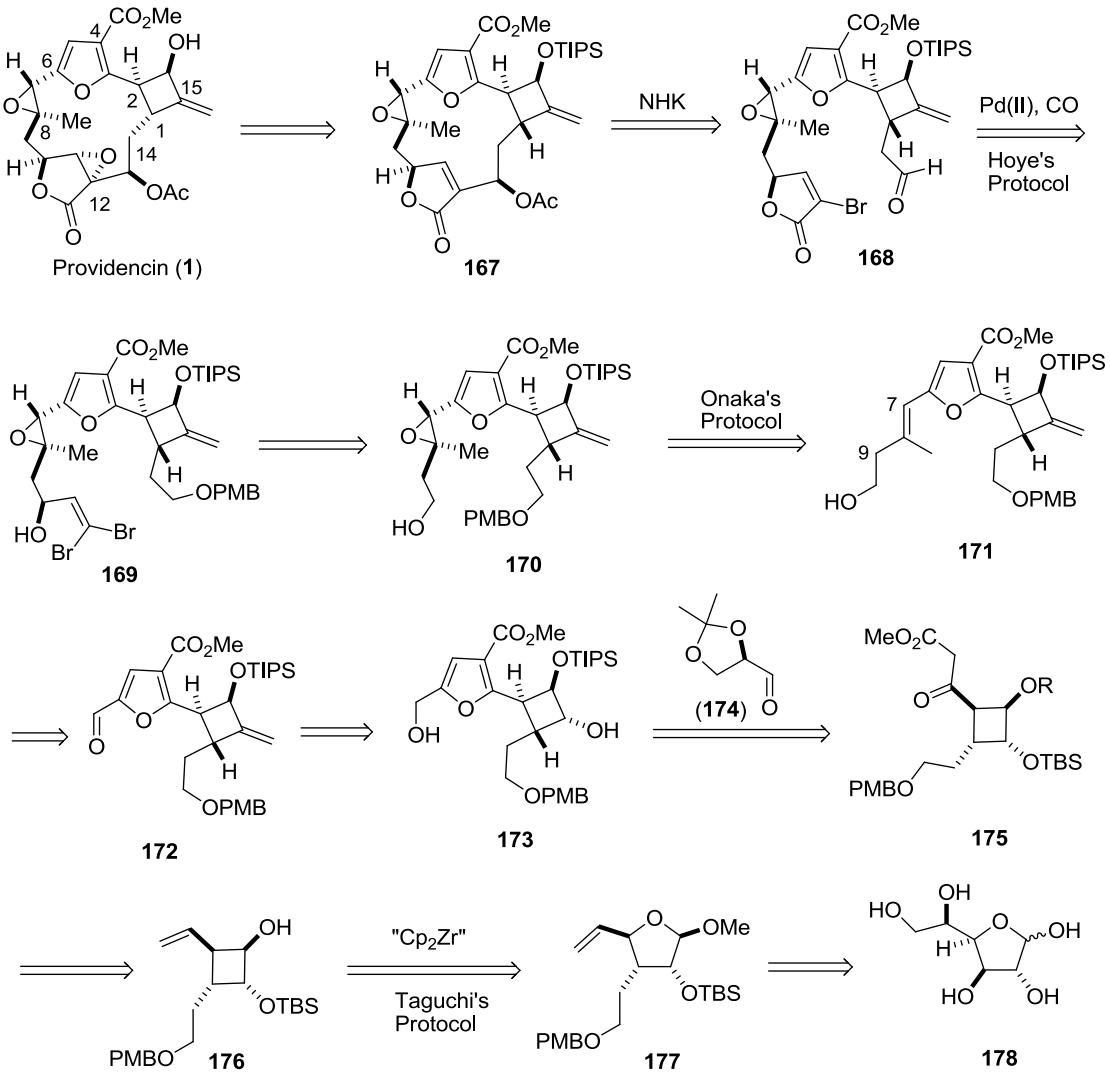
CHAPTER 3

First Generation Approach Towards Providencin

3.1 Retrosynthetic analysis of providencin (1)

In our initial approach, we envisioned that epoxidation of butenolide **167** from the less sterically hindered face would provide providencin (**1**) (Scheme 3.1). The macrocycle **167** would be closed from aldehyde **168** by an intramolecular Nozaki-Hiyami-Kishi reaction,[1] which would be followed by Mitsunobu inversion and acetate formation. Butenolide **168** would be acquired from vinyl dibromide **169** by Hoye's protocol using a palladium catalyst and carbon monoxide.[2] Dibromide **169** would be derived from **170** using standard operations. Asymmetric epoxidation of **171** using Onaka's protocol for *E*-homoallylic alcohols[3] would yield **170**, and alcohol **171** would be prepared via Wittig olefination of aldehyde **172**. Selective protection of the primary alcohol of diol **173**, followed by oxidation of the remaining alcohol to a cyclobutanone and Wittig olefination would yield **161**. The furan ring would be introduced into **173** by Knoevenagel condensation[4] of ester **175** with glyceraldehyde acetonide (**174**) and subsequent acid-catalyzed cyclization. *β*-Ketoester **175** would be prepared from vinyl cyclobutanol **176** using a Wacker oxidation[5] followed by acylation with Mander's reagent.[6] The key transformation of **177** to **176** is predicated upon zirconium-mediated deoxygenative ring contraction of a furanoside, a process first developed by

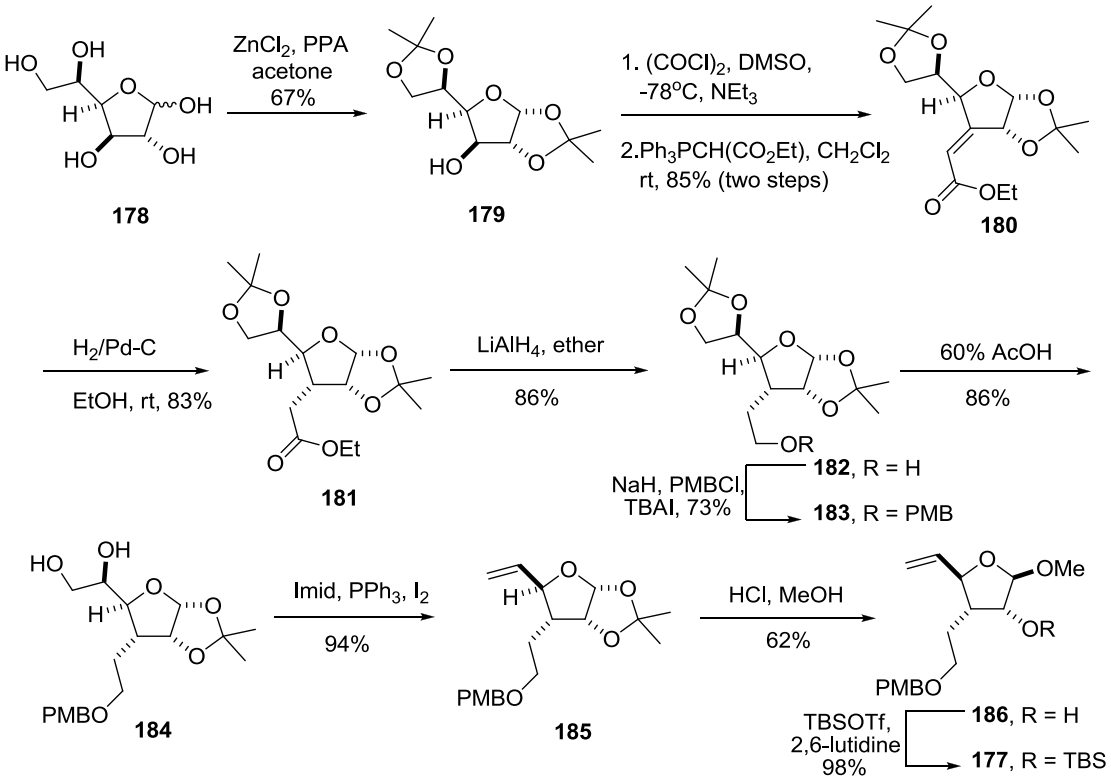
Taguchi[7a,b] and subsequently employed by Paquette[7c,d,e] as an entry to enantiopure cyclobutanols. Furanose **177** would be obtained from readily available D-glucose (**178**).



Scheme 3.1 First generation retrosynthetic analysis of providencin (**1**)

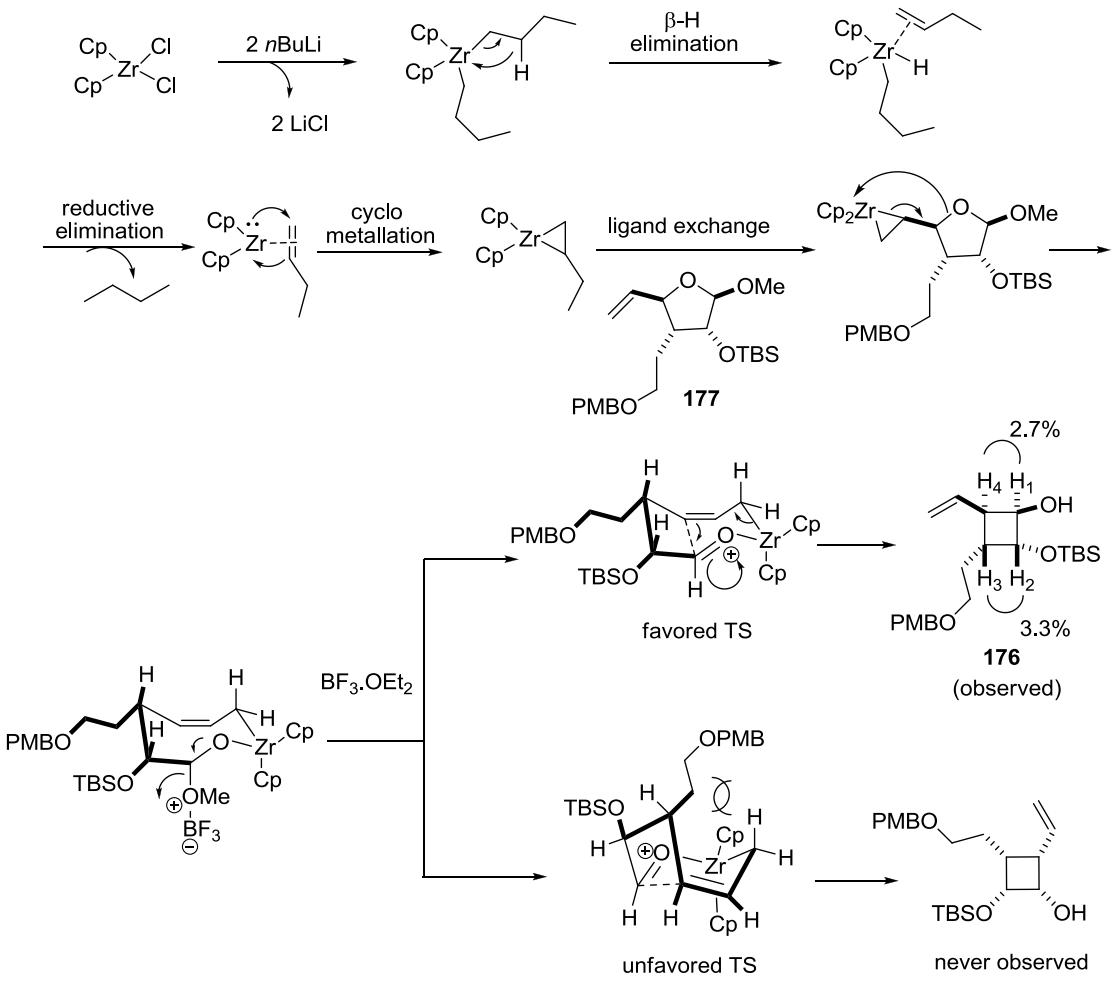
3.2 Synthesis of an enantiopure cyclobutanol via a zirconium-mediated ring contraction of a furanoside

In the forward direction, D-glucose (**178**) was first converted into diacetonide **179** in the presence of anhydrous zinc chloride and polyphosphoric acid in dry acetone (Scheme 3.2).[8a] The secondary alcohol of **179** was oxidized to the corresponding ketone using Swern's conditions and the ketone was subjected to a Wittig reaction to give *α*,*β*-unsaturated ester **180**.[8b] Hydrogenation of alkene **180** over palladium on charcoal gave **181** as a single diasteroisomer and the latter was reduced to alcohol **182**[9] which was protected as its *p*-methoxybenzyl ether **183**.[10] Selective deketalization of **183** using 60% acetic acid gave diol **184** which was converted to the 2-vinyltetrahydrofuran **185** using triphenylphosphine, imidazole, and iodine in hot toluene.[11] The remaining acetonide group in **185** was cleaved in acidic methanol to give a methyl glycoside **186** and the free secondary alcohol in **186** was then protected as its *t*-butyldimethylsilyl ether **177**.



Scheme 3.2 Synthesis of furanoside **177**

The pivotal oxygen atom abstraction from tetrahydrofuran **177** was carried out with dicyclopentadienylzirconium(0), generated by treatment of dicyclopentadienylzirconium(II) dichloride with 2 equivalents of *n*-butyllithium in toluene (Scheme 3.3). That all four stereocenters of **177** had been faithfully transcribed into **176** was confirmed by careful analysis of the ^{1}H NMR spectrum of the cyclobutane which showed NOE's (2.7% and 3.3%) consistent with a cis relationship between H_1 and H_4 and between H_2 and H_3.

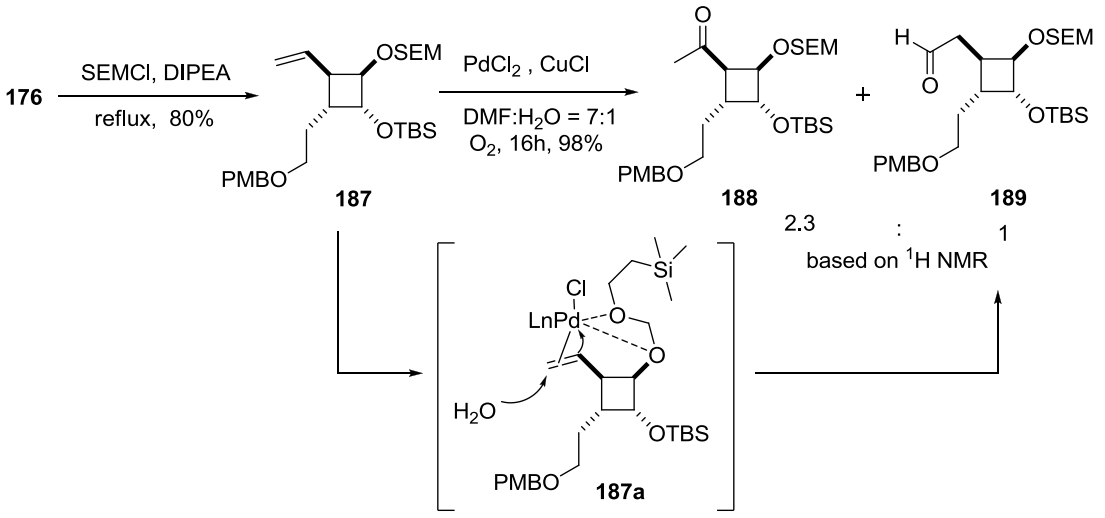


Scheme 3.3 Mechanism for the formation of cyclobutanol **176** from furanoside **177**

3.3 Elaboration of a cyclobutanol into a cyclobutylfuran

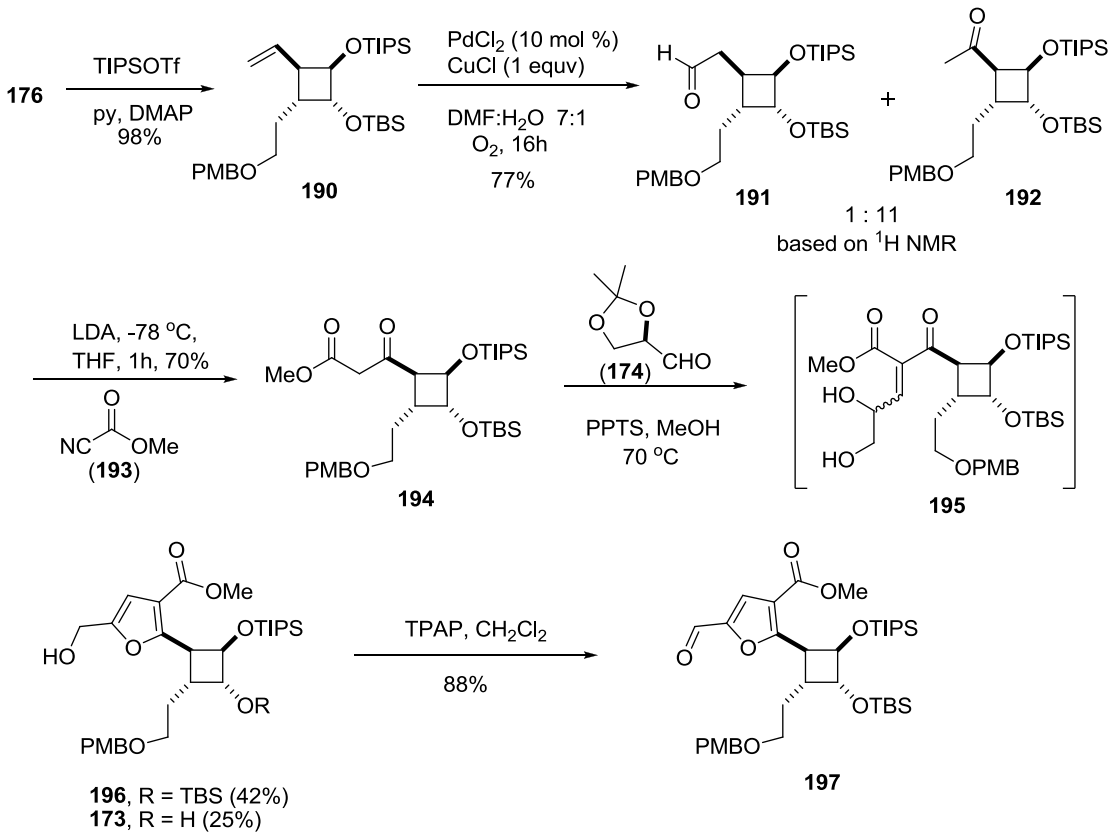
Initially, cyclobutanol **177** was protected as its 2-trimethylsilylethoxymethoxy ether **187** and the latter was subjected to Wacker oxidation conditions (Scheme 3.4). The desired methyl ketone **188** was obtained from this reaction along with substantial amounts of aldehyde **189** (**188**:**189** 2.3:1). The alternate mode of regiochemical oxidation leading to **189** is explained by coordination of the 2-

trimethylsilylethoxymethoxy protecting group of **187** with the palladium metal center leading to complex **187a**. In this complex, water can attack at the more accessible site, leading to the undesired byproduct **189**.[12]



Scheme 3.4 Wacker oxidation of 2-trimethylsilylethoxymethoxy ether **187**

To circumvent this problem, cyclobutanol **176** was converted to its triisopropylsilyl ether **190** (Scheme 3.5) which would be expected to show little tendency to complex with palladium(II). In the event, exposure of **190** to Wacker conditions provided our desired methyl ketone **192** with only a trace amount of aldehyde **191** (**191**:**192** 1:11). Treatment of the kinetically formed lithium enolate of **192** with methyl cyanoformate (**193**) furnished *β*-keto ester **194** which was condensed with 2,3-*O*-isopropylidene–D-glyceraldehyde (**174**)[13] under acid catalysis. The initial Knoevenagel product **195**, detectable by thin-layer chromatography, was converted slowly to a mixture of **196** and desilylated alcohol **173**.[14] Oxidation of **196** with tetra-*n*-propyl perruthenate[15] then yielded aldehyde **197**.

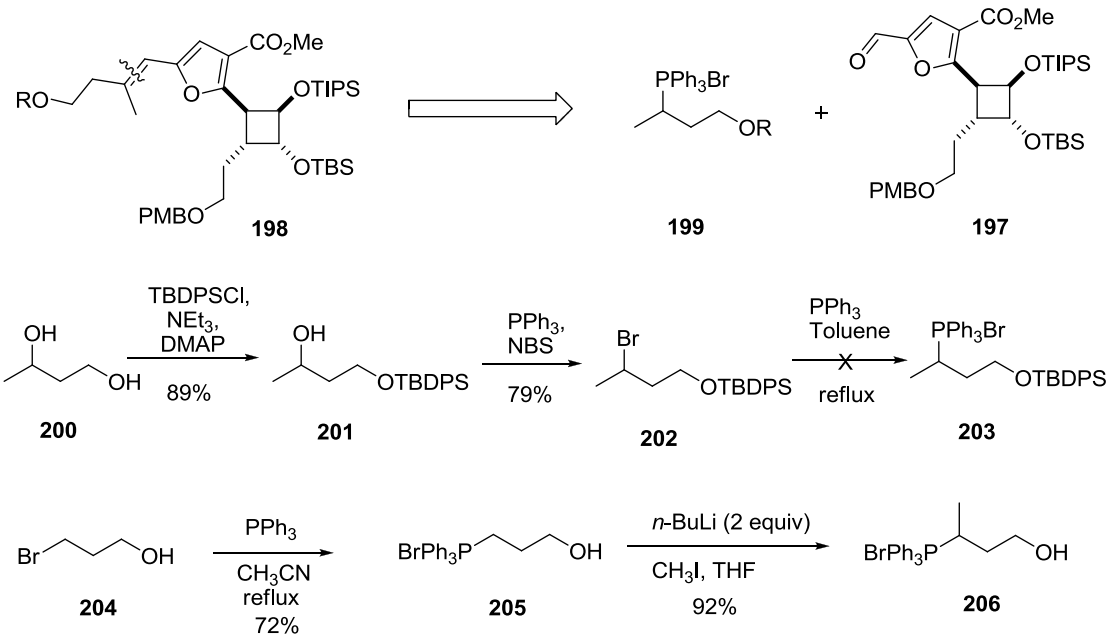


Scheme 3.5 Synthesis of cyclobutylfuranaldehyde **197**

3.4 Installation of an (*E*)-trisubstituted alkene at C7-C8 of providencin

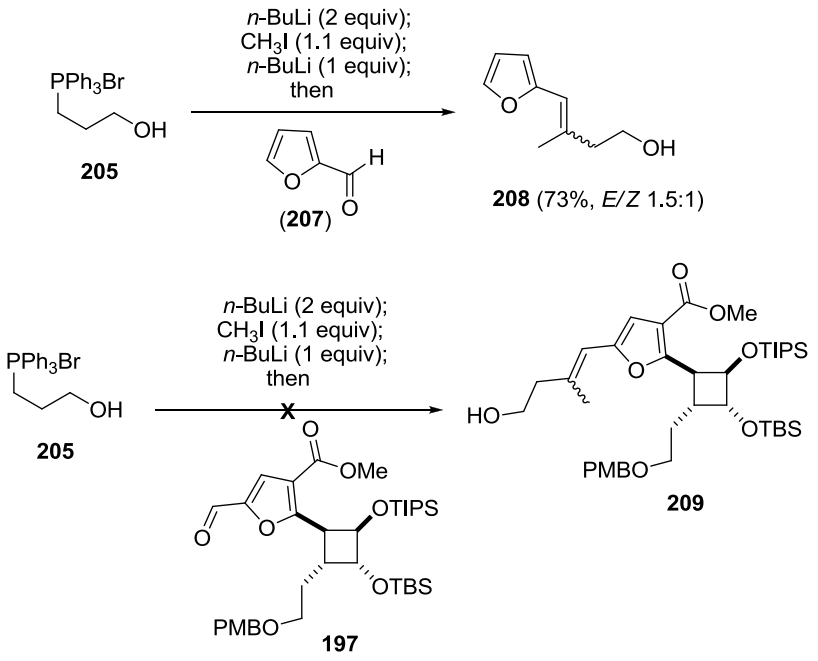
Our initial plan envisioned elaboration of aldehyde **197** to an (*E*)-trisubstituted alkene **198** via Wittig olefination. To make the requisite Wittig salt **199**, diol **200** was selectively protected as the primary *t*-butyldimethylsilyl ether **201**[16] (Scheme 3.6) and the remaining secondary alcohol was converted to the corresponding bromide **202** by *N*-bromosuccinimide.[17] However, when bromide **202** was refluxed with triphenylphosphine in toluene or acetonitrile, no reaction occurred. Fortunately, an

alternative route to **206** was more successful. In this sequence, 3-bromobutanol (**204**) was converted to phosphonium salt **205**[18] which was reacted with *n*-butyllithium and methyl iodide to give phosphonium salt **206** in good yield.[19]



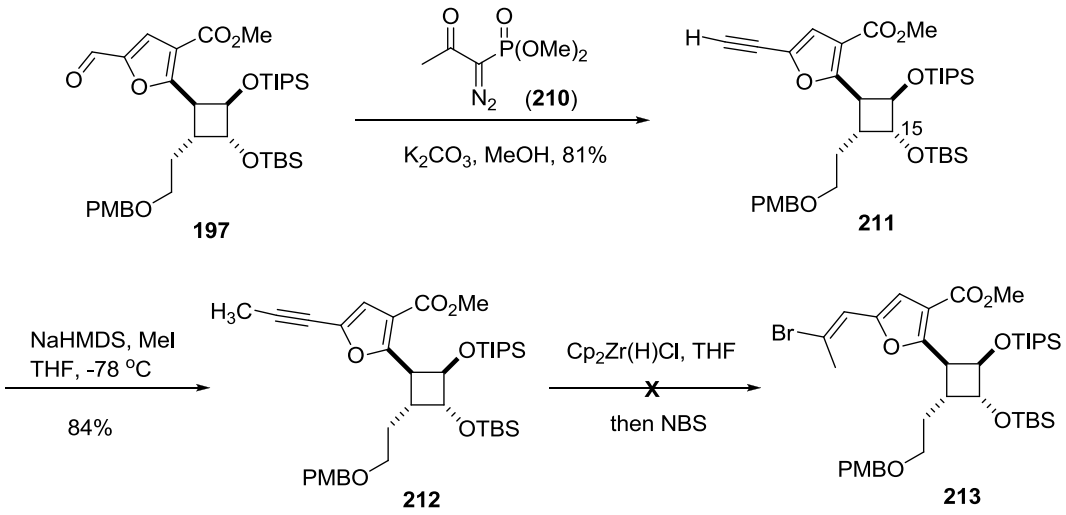
Scheme 3.6 Synthesis of Wittig salt **206**

Before attempting Wittig olefination of aldehyde **197** with phosphonium salt **206**, a model reaction of furfural (**207**) with **206** was investigated. When an excess amount of *n*-butyllithium was used to generate the ylide from **206**, it gave the addition product to furfural but when the phosphonium salt **205** was methylated and reacted in situ with furfural it afforded alkene **208** as an inseparable *E/Z* mixture (1.5:1) in good yield (Scheme 3.7).[20] Unfortunately, when the same reaction conditions were applied to aldehyde **197**, only decomposition occurred. This failure caused us to revise our initial plan for accessing (*E*)-trisubstituted alkene **171**.



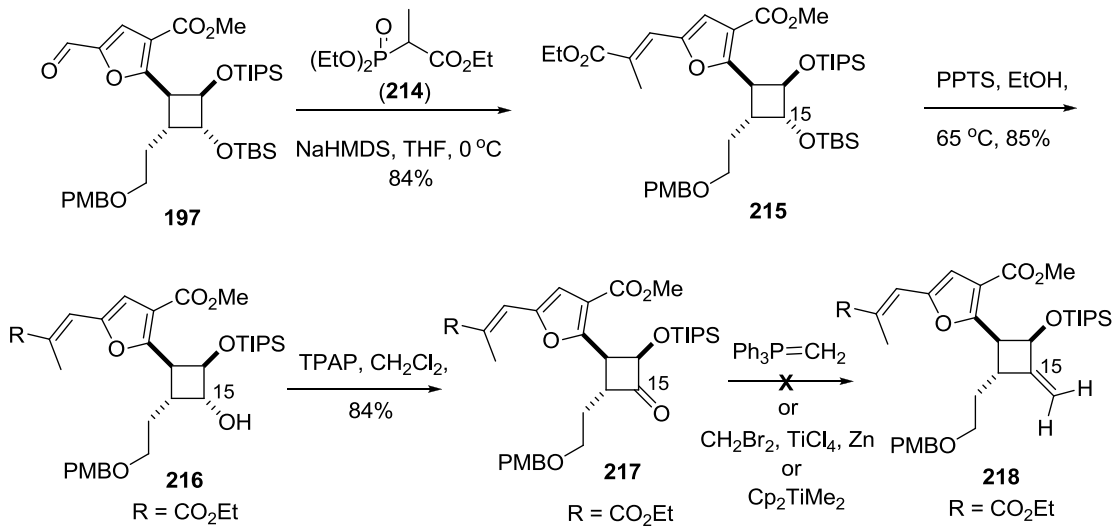
Scheme 3.7 Attempted synthesis of trisubstituted alkene **209**

An alternative plan was envisioned in which conversion of aldehyde **197** to an alkyne could be used to set in place the (*E*)-trisubstituted alkene at C7-C8 of providencin. To this end, aldehyde **197** was reacted with dimethyl 1-diazo-2-oxo-propylphosphonate (**210**)[21] in the presence of base to furnish terminal alkyne **211** (Scheme 3.8). Alkyne **211** was methylated[22] to give disubstituted alkyne **212**, but all attempts to functionalize this alkyne through hydrozirconation with Schwartz reagent[23] returned starting material or destroyed the furan. It is known that zirconium is oxyphilic in nature and since several oxygen atoms including a furan are present in alkyne **212**, we speculate that coordination of a zirconium species with those oxygen atoms could be responsible for destroying the Schwartz reagent.



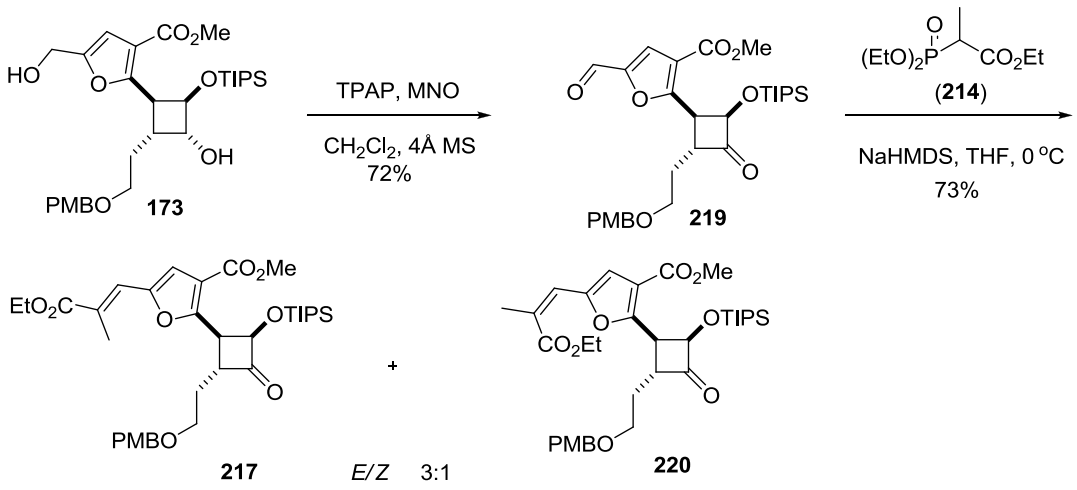
Scheme 3.8 Attempted synthesis of vinyl bromide **213**

The failure to functionalize alkyne **212** prompted a new strategy employing Horner-Wadsworth-Emmons olefination of **197** with ethyl 2-(diethoxyphosphono)propionate (**214**). This reaction produced (*E*)-*α*,*β*-unsaturated ester **215** in excellent yield (Scheme 3.9).[24] At this point, an attempt was made to install the exo methylene function at C15 of providencin. Thus, the *t*-butyldimethylsilyl ether of **215** was cleaved[25] to liberate alcohol **216** which was oxidized to cyclobutanone **217**. However, all attempts to convert **217** to **218** using Wittig olefination,[26] Petasis reagent,[27] or Lombardo reagent[28] resulted only in return of the starting cyclobutanone. It seemed that the steric congestion around the carbonyl moiety of cyclobutanone **217** was responsible for the failure of the methylenation.



Scheme 3.9 Synthesis of (*E*)-*α*,*β*-unsaturated ester **217**

Subsequently, a more direct route to cyclobutanone **217** was found through exhaustive oxidation of diol **173** with tetra-*n*-propylammonium perruthenate to furnish keto aldehyde **219** (Scheme 3.10). Horner-Wadsworth-Emmons olefination of **219** with phosphonate **214** took place exclusively at the aldehyde carbonyl but in this case the result was a 3:1 *E/Z* mixture of **217** and **220**, respectively, which proved difficult to separate.



Scheme 3.10 Alternative route to cyclobutylfuran **217**

At this stage of our approach to providencin,[29] we accepted the fact that our inability to install an exo methylene moiety on cyclobutanone **217** as well as the difficulty elaborating an ethyl ester selectively in the presence of a methyl ester presented serious problems. A viable route to **1** therefore required a revised strategy.

3.5 References

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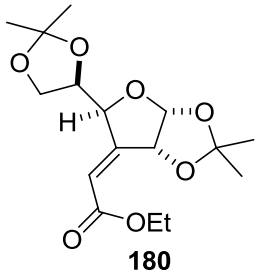
3.6 Experimental Section

General techniques: All reactions requiring anhydrous conditions were conducted in flame dried glass apparatus under an atmosphere of argon. THF, Et_2O, CH_2Cl_2, DMF, benzene and acetonitrile were dried by passage through an activated alumina column under argon. DMSO was distilled from CaH_2 at 15 mm Hg and stored over activated 4Å molecular sieves. Anhydrous MeOH was freshly distilled from calcium hydride. Preparative chromatographic separations were performed on silica gel (35-75 μm); reactions were followed by TLC analysis using silica plates with fluorescent indicator (254 nm) and visualized with a UV lamp or phosphomolybdic acid. All commercially available reagents were purchased from TCI or Aldrich and used as received unless stated otherwise. Optical rotations were measured with a polarimeter using a 1 mL capacity cell with 1 dm path length. Infrared spectra were recorded using a thin film supported on KBr discs or dispersed in a KBr pellet. ^{1}H and ^{13}C NMR spectra were recorded in Fourier transform mode at the field strength specified on either a 300 or 400 or 700 MHz spectrometer. Spectra were obtained on $CDCl_3$ solutions in 5 mm diameter tubes, and chemical shifts in ppm are quoted relative to the residual signals of chloroform (δH 7.26 ppm, or δC 77.0 ppm). Multiplicities in the ^{1}H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constants are reported in Hz. Low (MS) and high (HRMS) resolution mass spectra are reported with ion mass/charge (*m/z*) ratios as values in atomic mass units.



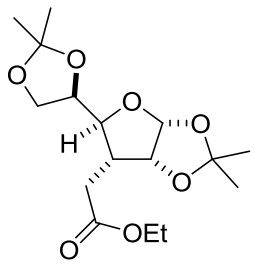
180

Ethyl 2-((3a*R*,5*R*,6a*R*)-5-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethylfuro[2,3-*d*][1,3]dioxol-6(3a*H*,5*H*,6a*H*)-ylidene) Acetate (180)

A solution of DMSO (0.75 mL, 10.04 mmol) in CH_2Cl_2 (1.5 mL) was added to a stirred solution of $(COCl)_2$ (0.39 mL, 4.56 mmol) in CH_2Cl_2 (20.0 mL) at – 78 ^oC. After 20 min, a solution of alcohol **179** (1 g, 3.8 mmol) in CH_2Cl_2 (25 mL) was added over 20 min. The mixture was stirred for 30 min at -78 ^oC, and Et_3N (3.5 mL, 25.84 mmol) was added and warmed to room temperature. After 1 h, the reaction mixture was poured into water (100 mL), the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic extract was dried (Na_2SO_4), filtered and concentrated in vacuo. The crude product was used directly for the next step.

To a stirred solution of the crude product obtained above in CH_2Cl_2 (15 mL) was added $Ph_3P{=}CH(CO_2Et)$ (1.6 g, 4.8 mmol) and the solution was stirred at room temperature for 18 h. The reaction mixture was poured in water (100 mL) and extracted with CH_2Cl_2 (2 x 50 mL), and the combined extract was dried (Na_2SO_4), filtered, and concentrated. The crude residue was purified by silica gel chromatography (9:1 hexanes/ethyl acetate) to afford **180** (1.08 g, 85% from **179**) as a

colorless solid: R_f 0.69 (1:1 hexanes/ethyl acetate); mp 66-70 ^oC (lit.[8b] mp 69-71 ^oC); $[\alpha]^{22}_D$ +116.7 (*c* 1.0, $CHCl_3$) [lit.[8b] $[\alpha]^{29}_D$ +114.0 (*c* 1.15, $CHCl_3$)]; IR (neat) 2983, 2937, 1722, 1373, 1209, 1160, 1055, 1021 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.1 Hz, 3H), 1.37 (s, 3H), 1.43 (s, 3H), 1.46 (s, 3H), 1.54 (s, 3H), 4.00-4.06 (m, 1H), 4.10-4.18 (m, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 4.70 (dt, *J* = 7.0, 1.7 Hz, 5.76 (dt, *J* = 4.2, 1.3 Hz, 1H), 5.86 (d, *J* = 4.2 Hz, 1H), 6.65 (dt, *J* = 7.0, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 25.4, 26.7, 27.1, 60.1, 67.3, 76.7, 78.4, 79.9, 104.9, 110.2, 112.8, 117.9, 151.6, 165.2.

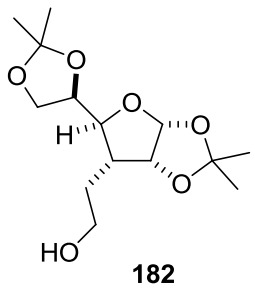


181

Ethyl 2-((3a*R*,5*R*,6*R*,6a*R*)-5-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl tetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl) Acetate (181)

To a 95% ethyl alcohol (201 mL) solution of **180** (16.54 g, 50.42 mmol) was added 10% palladium on carbon (7.47 g, 7.05 mmol). The reaction mixture was purged with hydrogen for 5 min and stirred under a hydrogen atmosphere for 16 h. The reaction mixture was filtered through Celite which was rinsed with ethanol and the filtrate was concentrated. The crude residue was purified by silica gel flash chromatography (9:1 hexanes/ethyl acetate) to give **181** (15.02 g, 90%) as a colorless oil: R_f 0.70 (1:1

hexanes/ethyl acetate); $[\alpha]^{22}_{D}$ +63.7 (*c* 1.15, $CHCl_3$); IR (neat) 2986, 2937, 1735, 1381, 1241, 1214, 1066, 1017 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, *J* = 6.7 Hz, 3H), 1.37 (s, 3H), 1.43 (s, 3H), 1.54 (s, 3H), 2.23-2.39 (m, 1H), 2.65 (dd, *J* = 17.5, 10.2 Hz, 1H), 2.85 (dd, *J* = 17.5, 4.2 Hz, 1H), 3.70 (dd, *J* = 9.8, 7.5 Hz, 2H), 3.95-4.05 (m, 2H), 4.10-4.25 (m, 2H), 4.85 (t, *J* = 4.2 Hz, 1H), 5.80 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 25.2, 26.6, 26.7, 29.9, 44.5, 60.4, 67.8, 77.8, 80.4, 104.9, 109.9, 111.7, 172.2; EI-HRMS calcd for $C_{17}H_{24}O_5$ $[M]^+$ (*m*/*z*) 308.1624, found 308.1634.

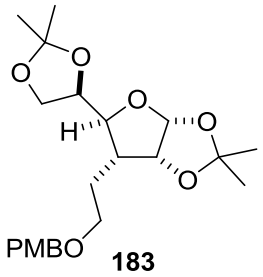


182

2-((3a*R*,5*S*,6*R*,6a*R*)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)ethanol (182)

To a solution of $LiAlH_4$ (3.64 g, 182.2 mmol) in dry Et_2O (364 mL) under argon was added dropwise at 0 ^oC a solution of ester **181** (15.03 g, 45.5 mmol) in dry Et_2O (30 mL). After stirring for 2 h at room temperature, the reaction was quenched with satd aqueous ammonium chloride and extracted with Et_2O (2 x 50 mL). The combined organic extract was washed with brine and dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude mixture was purified by silica gel chromatography (7:3 hexanes/ethyl acetate) to give **182** (11.28 g, 86%) as a

colorless oil: R_f 0.31 (7:3 hexanes/ethyl acetate); $[\alpha]^{23}{}_D$ +49.0 (*c* 1.00, $CHCl_3$); IR (neat) 3412, 2980, 2937, 2887, 2325, 1376, 1212, 1061, 1021, 844 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.34 (s, 3H), 1.36 (s, 3H), 1.45 (s, 3H), 1.55 (s, 3H), 1.70 (s, broad, OH), 1.85-2.1 (m, 4H), 3.75-3.85 (m, 3H), 3.90-4.08 (m, 2H), 4.10-4.20 (m, 2H), 4.75 (t, *J* = 4.1 Hz, 1H), 5.8 (d, *J* = 3.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.3, 26.4, 26.8, 28.0, 45.6, 61.2, 67.6, 77.9, 81.8, 81.9, 105.0, 109.6, 111.7; EI-HRMS calcd for $C_{14}H_{25}O_6$ $[M + H]^+$ (*m/z*) 289.1651, found 289.1648.

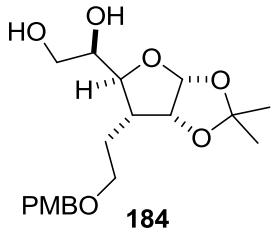


183

(3a*R*,5*S*,6*R*,6a*R*)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-6-(2-(4-methoxybenzyloxy)ethyl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (183)

A cold (0 ^oC) suspension of sodium hydride (4.86 g, 121.96 mmol) in dry THF (125 mL) was treated with a solution of **182** (8.78 g, 30.49 mmol) in dry THF (20 mL) and the mixture was stirred for 20 min at 0 ^oC and for 20 min at room temperature. After cooling the solution to 0 ^oC, *p*-methoxybenzyl chloride (5.37 mL, 39.64 mmol) in THF (10 mL) containing tetra-*n*-butylammonium iodide (1.12 g, 3.04 mmol) was introduced. The reaction mixture was stirred at room temperature for 10 h and the reaction was quenched with satd ammonium chloride solution (50 mL) at 0 ^oC. The separated aqueous layer was extracted with ethyl acetate (2 x 50 mL) and the

combined organic extract was dried (Na_2SO_4), filtered and concentrated, leaving a residue that was chromatographed on silica gel (4:1 hexanes/ethyl acetate) to furnish **183** (10.52 g, 84%) as a colorless oil: R_f 0.50 (1:1 hexanes/ethyl acetate); $[\alpha]^{22}{}_D$ +54.5 (*c* 1.25, $CHCl_3$); IR (neat) 2986, 2933, 2878, 1617, 1515, 1367, 1246, 1212, 1064, 1033, 875, 820, 844 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.34(s, 3H), 1.36 (s, 3H), 1.45 (s, 3H), 1.55 (s, 3H), 1.80-1.88 (m, 1H), 1.89-2.15 (m, 2H), 3.60 (ddd, *J* = 7.3, 4.9, 1.6 Hz, 2H), 3.78-3.80 (m, 1H), 3.86 (s, 3H), 3.95 (dd, *J* = 7.1, 4.7 Hz, 1H), 4.10 (m, 2H), 4.48 (d, *J* = 5.4 Hz, 2H), 4.60 (t, *J* = 3.9 Hz, 1H), 5.76 (d, *J* = 3.5 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.1, 25.3, 26.4, 26.5, 26.8, 45.4, 55.3, 67.3, 68.2, 72.7, 77.7, 81.5, 81.9, 104.9, 109.5, 111.7, 113.7 (2C), 129.3 (2C), 130.6, 159.1; EI-HRMS calcd for $C_{22}H_{32}O_7$ $[M]^+$ *m/z* 408.2148, found *m/z* 408.2143.

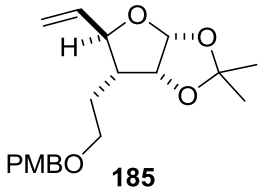


184

(*R*)-1-((3a*R*,5*S*,6*R*,6a*R*)-6-(2-(4-Methoxybenzyloxy)ethyl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)ethane-1,2-diol (184)

A solution of **183** (2.16 g, 5.29 mmol) in 60% AcOH (44 mL) was stirred at room temperature for 18 h, after which toluene (90 mL) was added to the mixture and the solvent was removed under reduced pressure. The residual oil was chromatographed

on silica gel (1:1 hexanes/ethyl acetate) to give **184** (1.60 g, 86%) as a colorless oil: R_f 0.30 (1:4 hexanes/ethyl acetate); $[\alpha]^{23}_D$ +52.1 (*c* 1.15, $CHCl_3$); IR (neat) 3420, 2934, 2869, 1513, 1372, 1247, 1031, 874, 820 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.32 (s, 3H), 1.50 (s, 3H), 1.90 (m, 2H), 2.10 (m, 1H), 2.47 (s, broad, OH), 3.33 (s, broad, OH), 3.55 (dd, *J* = 15.8, 6.8 Hz, 1H), 3.65 (m, 1H), 3.70 (m, 3H), 3.80 (s, 3H), 3.90 (dd, *J* = 9.7, 5.1 Hz, 1H), 4.48 (d, *J* = 6.1 Hz, 2H), 4.60 (t, *J* = 4.0 Hz, 1H), 5.75 (d, *J* = 3.6 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 26.3, 26.7, 44.2, 55.2, 60.4, 63.8, 68.3, 72.7, 73.2, 81.7, 82.7, 104.6, 111.7, 113.8 (2C), 129.8 (2C), 130.0, 159.3; CI-HRMS calcd for $C_{19}H_{28}O_7$ $[M]^+$ *m/z* 368.1835, found *m/z* 368.1838.

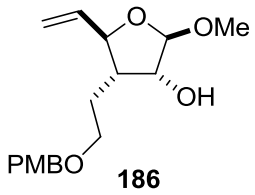


185

(3a*R*,5*S*,6*R*,6a*R*)-6-(2-(4-Methoxybenzyloxy)ethyl)-2,2-dimethyl-5-vinyl-tetrahydrofuro[2,3-*d*][1,3]dioxole (185)

To a stirred solution of **184** (1.50 g, 4.24 mmol) in toluene (36 mL) were added triphenylphosphine (4.46 g, 16.98 mmol) and imidazole (1.15 g, 16.98 mmol) and the mixture was heated at reflux. When reflux started, iodine (3.20 g, 12.72 mmol) was added to the reaction mixture slowly (portion wise). The solution was refluxed for 2.5 h, cooled to room temperature and was washed with satd sodium thiosulphate solution (3 x 30 mL) followed by water (50 mL) and brine (50 mL). The organic layer was

separated and dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by silica gel chromatography (4:1 hexanes/ethyl acetate) to afford **185** (1.33 g, 94%) as a colorless oil: R_f 0.56 (1:1 hexanes/ethyl acetate); $[\alpha]^{20}{}_D$ +34.0 (*c* 1.10, $CHCl_3$); IR (neat) 2911, 1612, 1513, 1248, 1098, 1033, 820 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.32 (s, 3H), 1.52 (s, 3H), 1.65 (m, 1H), 1.90 (m, 2H), 3.55 (t, *J* = 5.1 Hz, 2H), 3.72 (s, 3H), 4.18 (t *J* = 7.8 Hz, 1H), 4.45 (s, 2H), 4.60 (t, *J* = 3.1 Hz, 1H), 5.24 (d, *J* = 9.9 Hz, 1H), 5.35 (d, *J* = 16.9 Hz, 1H), 5.75 (m, 2H), 6.85 (m, 2H), 7.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4, 26.3, 26.7, 46.6, 55.3, 67.9, 72.4, 80.9, 83.0, 104.9, 111.4, 113.7 (2C), 118.7, 129.2 (2C), 130.2, 135.5, 159.1; EI-HRMS calcd for $C_{19}H_{26}O_5$ $[M]^+$ *m*/*z* 334.1780, found *m*/*z* 334.1764.

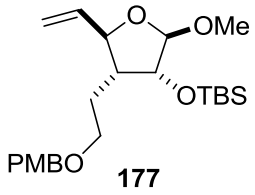


186

(2*R*,3*R*,4*S*,5*R*)-2-Methoxy-4-(2-(4-methoxybenzyloxy)ethyl)-5-vinyltetrahydrofuran-3-ol (186)

A solution of **185** (1.33 g, 4.00 mmol) in HCl-MeOH (1% mol/V) was stirred at room temperature for 16 h. The mixture was neutralized with aq. NaOH (5N) and filtered, and the filtrate was concentrated and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extract was concentrated and the crude residue was purified by chromatography on silica gel (3:1 hexanes/ethyl acetate) to give **186** (0.76 g, 62%) as a colorless oil: R_f 0.62 (1:1 hexanes/ethyl acetate); $[\alpha]^{20}{}_D$ -69.8 (*c* 1.05, $CHCl_3$); IR

(neat) 3443, 2972, 2325, 1614, 1512, 1252, 1101, 1033, 934, 820 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (m, 1H), 1.85 (m, 1H), 2.10 (m, 1H), 3.10 (d, *J* = 3.0 Hz, OH), 3.40 (s, 3H), 3.45 (ddd, *J* = 10.5, 9.6, 2.5 Hz, 1H), 3.68 (ddd, *J* = 8.3, 4.5, 3.3 Hz, 1H), 3.82 (s, 3H), 4.14 (t, *J* = 3.7 Hz, 1H), 4.22 (t, *J* = 8.6 Hz, 1H), 4.40 (s, 2H), 4.90 (s, 1H), 5.14 (d, *J* = 10.0 Hz, 1H), 5.22 (d, *J* = 17.0 Hz, 1H), 5.80 (ddd, *J* = 17.3, 10.1, 7.8 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 47.4, 54.6, 55.3, 69.3, 73.3, 76.9, 85.8, 110.6, 113.9, 116.7, 129.4, 129.5 (3C), 139.1, 159.4; CI-HRMS calcd for $C_{17}H_{24}O_5$ $[M]^+$ *m/z* 308.1624, found *m/z* 308.1634.

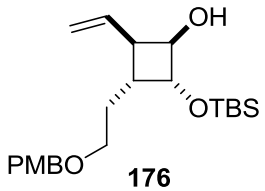


177

***tert*-Butyl((2*R*,3*R*,4*R*,5*R*)-2-methoxy-4-(2-(4-methoxybenzyloxy)ethyl)-5-vinyl-tetrahydrofuran-3-yloxy)dimethylsilane (177)**

To a solution of **186** (586 mg, 1.90 mmol) and 2,6-lutidine (0.3 mL, 2.47 mmol) in CH_2Cl_2 (15 mL) at 0 ^{o}C was added TBSOTf (0.57 mL, 2.47 mmol) and the mixture was stirred at room temperature for 3 h. The reaction was quenched with satd aqueous $NaHCO_3$ solution and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic extract was washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The crude residue was purified by chromatography on silica gel (9:1 hexanes/ethyl acetate) to afford **177** (788 mg, 98%) as a colorless oil: R_f 0.77 (7:3

hexanes/ethyl acetate); $[\alpha]^{23}_{D}$ +32.0 (*c* 1.00, $CHCl_3$); IR (neat) 2953, 2929, 2856, 1523, 1250, 1099, 1039, 835 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 3H), 0.08 (s, 3H), 0.93 (s, 9H), 1.65 (m, 1H), 1.85 (m, 1H), 2.10 (m, 1H), 3.38 (s, 3H), 3.44 (t, *J* = 6.7 Hz, 2H), 3.82 (s, 3H), 4.02 (d, *J* = 3.7 Hz, 1H), 4.22 (t, *J* = 2.3 Hz, 1H), 4.44 (d, *J* = 2.3 Hz, 2H), 4.70 (s, 1H), 5.14 (d, *J* = 10.0 Hz, 1H), 5.24 (d, *J* = 17.1 Hz, 1H), 5.80 (ddd, *J* = 17.8, 10.0, 7.8 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.0, -4.5, 18.1, 24.8, 25.7 (3C), 44.2, 54.5, 55.3, 68.2, 74.3, 76.9, 85.5, 109.1, 113.7 (2C), 117.0, 129.3 (2C), 130.5, 139.2, 159.1; CI-HRMS calcd for $C_{23}H_{39}O_5Si$ $[M + H]^+$ *m/z* 423.2567, found *m/z* 423.2566.

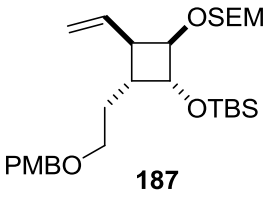


176

(1*R*,2*R*,3*R*,4*R*)-2-(*tert*-Butyldimethylsilyloxy)-3-(2-(4-methoxybenzyloxy)ethyl)-4-vinylcyclobutanol (176)

To a solution of $Cp_2Zr(n\text{-}Bu)_2$, prepared in situ by reaction of zirconocene dichloride (4.49 g, 15.37 mmol) in toluene (30 mL) with *n*-butyllithium in hexane (2 eq) at -78 ^oC for 1.5 h, was added a solution of **177** (2.59 g, 6.15 mmol) in toluene (30 mL) at -78 ^oC. The reaction mixture was stirred for 30 min at -78 ^oC and allowed to warm to ambient temperature. The mixture was stirred for 3 h, a solution of $BF_3.OEt_2$ (3.9 mL, 30.75 mmol) in toluene (5.0 mL) was added at 0 ^oC, and stirring was continued for 2 h at ambient temperature. The reaction was quenched with 1N HCl (50 mL) and the

mixture was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic extract was washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. The crude residue was purified by chromatography on silica gel (9:1 hexanes/ethyl acetate) to give **176** (2.43 g, 86%) as a colorless oil: R_f 0.64 (7:3 hexanes/ethyl acetate); $[\alpha]^{22}_D$ -4.8 (*c* 1.00, $CHCl_3$); IR (neat) 3416, 2985, 2930, 2859, 1509, 1249, 1150, 1095, 1036, 891, 835, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 3H), 0.11 (s, 3H), 0.93 (s, 9H), 1.60 (td, *J* = 14.4, 6.4 Hz, 1H), 1.80 (s, broad, OH), 2.05 (td, *J* = 13.6, 6.9 Hz, 1H), 2.30 (dd, *J* = 7.2, 6.6 Hz, 1H), 2.75 (t, *J* = 8.0 Hz, 1H), 3.50 (ddd, *J* = 16.0, 9.1, 6.8 Hz, 2H), 3.82 (s, 3H), 4.14 (dd, *J* = 11.7, 5.8 Hz, 2H), 4.45 (s, 2H), 5.15 (dd, *J* = 17.3, 2.9 Hz, 1H), 5.25 (dd, *J* = 10.5, 2.5 Hz, 1H), 5.87 (ddd, *J* = 17.1, 10.2, 8.5 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.0, -4.6, 18.1, 25.8 (3C), 29.7, 36.9, 43.7, 55.3, 68.7, 72.6, 75.0, 75.4, 113.7 (2C), 118.0, 129.2 (2C), 130.7, 136.5, 159.1; CI-HRMS calcd for $C_{22}H_{37}O_4Si$ $[M + H]^+$ *m*/*z* 393.2461, found *m*/*z* 393.2455.

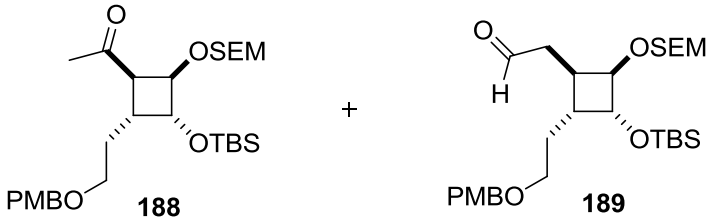


187

***tert*-Butyl((1*R*,2*R*,3*R*,4*R*)-2-(2-(4-methoxybenzyloxy)ethyl)-4-((2-(trimethylsilyl)ethoxy)methoxy)-3-vinylcyclobutoxy)dimethylsilane (187)**

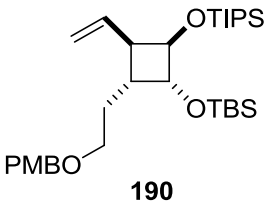
Alcohol **176** (80 mg, 0.20 mmol) was dissolved at room temperature in 2 mL of CH_2Cl_2 containing 62 μL (0.81 mmol) of diisopropylethylamine and 71.8 μL (0.40

mmol) of [2-(trimethylsilyl)]ethoxymethyl chloride (SEM chloride). The reaction mixture was heated at reflux for 10 h, at which point 10 mL of CH_2Cl_2 and 10 mL of 10% aqueous HCl solution were added. The organic layer was separated and washed successively with 10 mL of 10% aqueous HCl, 10 mL of satd aqueous sodium bicarbonate and 20 mL of brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated leaving a reddish oil, which was placed on a silica gel column and eluted with 3% ethyl acetate in hexanes to give **187** (85 mg, 80%) as a colorless oil: R_f 0.64 (9:1 hexanes/ethyl acetate); $[\alpha]^{22}{}_D$ -43.2 (*c* 1.25, $CHCl_3$); IR (neat) 2952, 2928, 2855, 1513, 1249, 1111, 1061, 1039, 1008, 859, 835 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.02 (m, 16H), 0.90 (m, 11H), 1.60-1.70 (m, 1H), 1.88-2.20 (m, 1H), 2.02-2.22 (m, 1H), 2.75 (t, *J* = 8.8 Hz, 1H), 3.40-3.60 (m, 2H), 3.60-3.70 (m, 2H), 3.82 (s, 3H), 4.16 (t, *J* = 7.5 Hz, 1H), 4.34 (t, *J* = 7.8 Hz, 1H), 4.44 (s, 2H), 4.64 (s, 2H), 5.00-5.10 (m, 2H), 5.85-6.00 (m, 1H), 6.85-6.90 (m, 2H), 7.25-7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.0, 4.7, 1.3, 18.0, 18.1, 25.8, 29.2, 37.9, 43.2, 55.3, 65.3, 65.5, 68.7, 72.2, 72.6, 79.2, 93.4, 113.7, 115.7, 129.2, 130.7, 137.8, 159.1; CI-HRMS calcd for $C_{28}H_{51}O_5Si_2$ $[M + H]^+$ (*m*/*z*) 523.3275, found 523.3273.



1-((1*R*,2*R*,3*R*,4*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4-((2-(trimethylsilyl)ethoxy)methoxy)cyclobutyl)ethanone (188)

In a Schlenk flask fitted with an oxygen filled balloon was added a suspension of $PdCl_2$ (2.5 mg, 0.014 mol) and CuCl (14.7 mg, 0.149 mmol) in DMF/H_2O 7:1 (1.00 mL) and the suspension was stirred for 60 min. A solution of **187** (78 mg, 0.149 mmol) in DMF/H_2O 7:1 (0.50 ml) was added and the mixture was stirred for 48 h under an oxygen atmosphere, after which the reaction was quenched by adding ice-cold 3 N HCl (4 mL). The mixture was extracted with Et_2O (2 × 10 mL), and the combined organic extract was dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexanes/ethyl acetate 9:1) to yield 80.0 mg (98%) of inseparable **188** and **189** (2.3:1) as a colorless oil: R_f 0.77 (2:8 hexanes-ethyl acetate); $[\alpha]^{24}{}_D$ – 26.6 (*c* 0.9, $CHCl_3$); IR (neat) 2955, 2927, 2853, 1710, 1614, 1515, 1463, 1113, 1061, 1036, 1005, 835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.30 (s, 9H), 0.60 (s, 3H), 0.65 (s, 3H), 1.55 (m, 1H), 1.90 (m, 1H), 2.70 (m, 1H), 3.24 (dd, *J* = 9.2, 2.6 Hz, 1H), 3.40 (m, 1H), 3.50 (m, 1H), 3.62 (dd, *J* = 9.1, 7.8 Hz, 2H), 3.83 (s, 3H), 4.26 (m, 1H), 4.35 (m, 1H), 4.42 (s, 2H), 4.67 (s, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.9, -4.8, -1.3, 18.0, 25.7, 28.3, 31.5, 34.3, 51.2, 55.2, 65.7, 68.8, 72.6, 79.2, 93.9, 113.7, 129.2, 130.6, 159.1, 201.8, 207.9; EI-HRMS calcd for $C_{28}H_{49}O_6Si_2$ $[M]^+$ (*m/z*) 561.3068, found 561.3061.

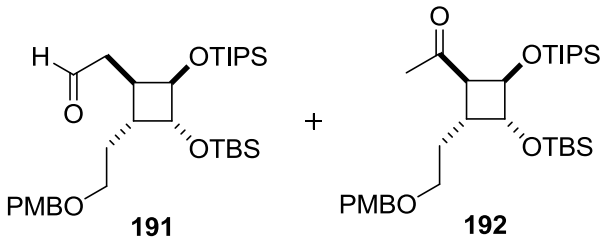


190

***tert*-Butyl((1*R*,2*R*,3*R*,4*R*)-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)-3-vinylcyclobutoxy)dimethylsilane (190)**

To a solution of **176** (409 mg, 1.04 mmol) and DMAP (152.5 mg, 1.25 mmol) in dry pyridine (3.2 mL) was added TIPSOTf (1.1 mL, 4.16) via syringe and the mixture was stirred for 15 h at room temperature. Excess TIPSOTf was consumed by addition of dry MeOH (5 mL) and after 15 min the solution was diluted with Et_2O. The solution was washed with 5% HCl (2 mL) and then with a mixture of satd aqueous $NaHCO_3$ and brine (1:1, 20 mL). The aqueous layer was extracted with Et_2O (2 x 20 mL) and the combined organic extract was dried (Na_2SO_4). Filtration through a short plug of silica gel and concentration of the filtrate in *vacuo* yielded crude product which was purified by chromatography on silica gel (hexanes/ethyl acetate 4:96) to afford **190** (565 mg, 98%) as a colorless oil: R_f 0.65 (2:8 hexanes-ethyl acetate); $[\alpha]^{20}_D$ – 53.9 (*c* 1.15, $CHCl_3$); IR (neat) 2952, 2859, 1642, 1611, 1583, 1515, 1463, 1364, 1302, 1252, 1163, 1101, 996, 777, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 3H), 0.10 (s, 3H), 0.91 (s, 9H), 1.11 (m, 21H), 1.60 (m, 1H), 2.00 (m, 1H), 2.15 (m, 1H), 2.70 (t, *J* = 8.08 Hz, 1H), 3.53 (t, *J* = 6.82 Hz, 2H), 3.82 (s, 3H), 4.24 (t, *J* = 7.78 Hz, 1H), 4.30 (t, *J* = 7.78 Hz, 1H), 4.47 (d, *J* = 3.54 Hz, 2H), 5.05 (d, *J* = 17.3 Hz, 1H), 5.10 (d, *J* = 9.7 Hz, 1H), 6.10 (ddd, *J* = 17.3, 10.2, 8.7 Hz, 1H), 6.90 (m, 2H), 7.25 (m, 2H); ^{13}C

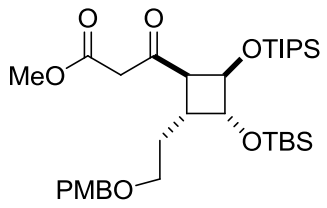
NMR (100 MHz, $CDCl_3$) δ -4.9, -4.7, 12.1, 12.2, 17.9, 18.0 (2C), 25.8, 28.9, 29.2, 37.9, 38.9, 45.0, 45.1, 55.2, 68.7, 68.9, 72.5, 75.1, 75.2, 75.6, 76.0, 113.7 (2C), 115.3, 129.1 (2C), 130.7, 138.4, 138.3, 159.0; EI-HRMS calcd for $C_{31}H_{56}O_4Si_2Na$ $[M + Na]^+$ *m/z* 571.3615, found *m/z* 571.3598.



1-((1*R*,2*R*,3*R*,4*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)ethanone (192)

In a Schlenk flask fitted with an O_2 filled balloon was placed a suspension of $PdCl_2$ (203 mg, 1.15 mol) and CuCl (190.0 mg, 1.92 mmol) in DMF/H_2O 7:1 (4.8 mL). The mixture was stirred for 60 min and a solution of **190** (527.0 mg, 0.96 mmol) in DMF – H_2O (7:1, 4.8 mL) was added. The mixture was stirred at 40 ^oC for 48 h under an O_2 atmosphere and the reaction was quenched by adding ice-cold 3N HCl (4 mL). The mixture was extracted with Et_2O (2 × 10 mL) and the combined organic extract was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude residue was purified by chromatography on silica gel (hexanes/ethyl acetate, 1:9) to yield an inseparable mixture (1:11) of **191** and **192** (417 mg, 77%) as a colorless oil: R_f 0.62 (2:8 hexanes-ethyl acetate); $[\alpha]^{24}_D$ – 56.0 (*c* 1.25, $CHCl_3$); IR (neat) 2940, 2869, 1707, 1617, 1509, 1459, 1357, 1246, 1175, 1107, 888, 838, 773, 681 cm^{-1}; ^1H NMR (400

MHz, $CDCl_3$) δ 0.06 (s, 3H), 0.08 (s, 3H), 0.91 (s, 9H), 1.08 (m, 21H), 1.55 (m, 1H), 1.90 (m, 1H), 2.17 (s, 3H), 2.60 (dd, *J* = 11.6, 8.6 Hz, 1H), 3.20 (dd, *J* = 9.5, 1.7 Hz, 1H), 3.45 (m, 2H), 3.82 (s, 3H), 4.30 (t, *J* = 7.5 Hz, 1H), 4.41 (s, 2H), 4.45 (dd, *J* = 7.1, 6.2 Hz 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.0, -4.5, 12.1 (3C), 17.9 (6C), 18.0, 25.8 (3C), 28.1, 32.0, 33.6, 52.9, 55.9, 58.8, 72.6, 74.8, 75.6, 113.7 (2C), 129.1 (2C), 130.6, 159.1, 208.2; EI-HRMS calcd for $C_{31}H_{56}O_5Si_2Na$ $[M + Na]^+$ *m/z* 578.3564, found *m/z* 578.3571.

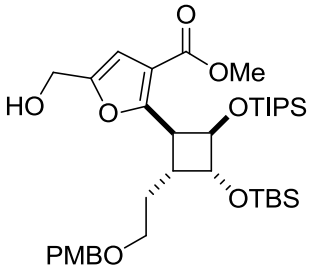


194

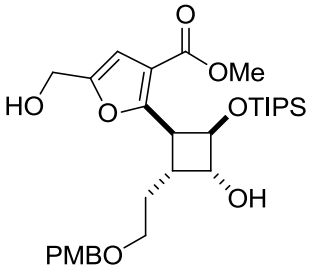
Methyl 3-((1*R*,2*R*,3*R*,4*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)-3-oxopropanoate (194)

To a solution of **191** and **192** (216 mg, 0.38 mmol) in THF (3.8 mL) at -78 ^oC was added a solution of LDA (0.95 mL, 0.95 mmol, freshly prepared as a 1M solution in THF). The pale yellow solution was stirred for 1 h then was treated with methyl cyanoformate (90.4 μL, 1.14 mmol). The resulting solution was stirred for 1 h at -78 ^oC and the reaction was quenched with H_2O (10 mL). The mixture was extracted with Et_2O (3 x 10 mL) and the combined organic extract was washed with H_2O and brine. The extract was dried (Na_2SO_4) and concentrated and the residue was

chromatographed on silica gel (4:96 hexanes/ethyl acetate) to afford **194** (182 mg, 70%) as a colorless oil: R_f 0.71 (7:3 hexanes-ethyl acetate); $[\alpha]^{23}_D$ – 61.2 (*c* 1.2, $CHCl_3$); IR (neat) 2949, 2859, 1747, 1716, 1611, 1459, 1246, 1163, 1104, 882, 835, 780, 681 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 3H), 0.08 (s, 3H), 0.91 (s, 9H), 1.08 (m, 21H), 1.50 (m, 1H), 1.90 (m, 1H), 2.65 (dd, *J* = 11.4, 8.7 Hz, 1H), 3.30 (dd, *J* = 9.5, 1.5 Hz, 1H), 3.45 (m, 2H), 3.50 (s, 2H), 3.72 (s, 3H), 3.82 (s, 3H), 4.30 (t, *J* = 7.7 Hz, 1H), 4.44 (s, 2H), 4.48 (dd, *J* = 8.9, 6.5 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.1, -4.5, 12.1 (3C), 17.9 (6C), 18.0, 25.8 (3C), 27.9, 33.8, 50.8, 52.0, 55.2 (2C), 68.8, 72.6, 74.7, 75.8, 113.7 (2C), 129.1 (2C), 130.5, 159.1, 167.6, 202.3; EI-HRMS calcd for $C_{33}H_{58}O_7Si_2$ $[M]^+$ *m/z* 622.3721, found *m/z* 622.3683.



196



173

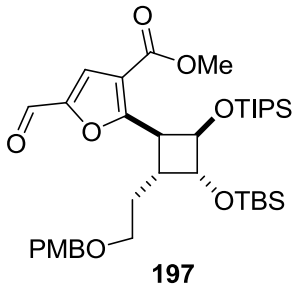
Methyl 2-((1*R*,2*R*,3*R*,4*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)-5-(hydroxymethyl)furan-3-carboxylate (196) and Methyl 2-((1*R*,2*R*,3*R*,4*R*)-3-Hydroxy-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)-5-(hydroxymethyl)furan-3-carboxylate (173)

To a solution of **194** (104 mg, 0.170 mmol) in MeOH (1.7 mL) under argon at room temp was added glyceraldehyde acetonide (**174**, 63.4 μL, 0.510 mmol) followed by PPTS (4.27 mg, 0.017 mmol). The reaction mixture was stirred at 70 ^{o}C for 20 h and quenched with 2% NaOH solution (2 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL) and the combined extract was washed with H_2O, dried (Na_2SO_4) and concentrated. The residue was purified by chromatography on silica gel (14:8 – 40.60 hexanes/ethyl acetate) to afford **196** (47 mg, 42%) along with **173** (23 mg, 25%) as colorless oils.

196: R_f 0.57 (7:3 hexanes-ethyl acetate); $[\alpha]^{22}_D$ – 38.2 (*c* 1.7, $CHCl_3$); IR (neat) 3425, 2930, 2865, 1719, 1614, 1574, 1515, 1466, 1249, 1107, 1070, 900, 835, 773, 684 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 6H), 0.90 (s, 30H), 1.60 (m, 1H), 1.90 (m 1H), 2.6 (m, 1H), 3.50 (m, 2H), 3.76 (s, 3H), 3.82 (s, 3H), 4.20 (dd, *J* = 8.9, 3.4 Hz, 1H), 4.40 (dd, *J* = 8.5, 11.4 Hz, 2H), 4.51 (dd, *J* = 8.7, 6.4 Hz, 1H), 4.60 (dd, *J* = 8.5, 6.1 Hz, 2H), 4.65 (m, 1H), 6.57 (s, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.9, -3.8, 11.8 (3C), 17.7 (6C), 18.0, 25.9 (3C), 29.3, 37.2, 39.2, 51.1, 55.2, 57.3, 68.1, 72.5, 75.3, 76.7, 108.5, 113.6 (2C), 115.4, 129.1 (2C), 130.6, 152.5, 159.0, 161.1, 164.2; EI-HRMS calcd for $C_{36}H_{60}O_8Si_2Na$ [M + Na] $^+$ *m/z* 699.3727, found *m/z* 699.3724.

173: R_f 0.13 (7:3 hexanes-ethyl acetate); $[\alpha]^{22}_D$ + 1.13 (*c* 1.85, $CHCl_3$); IR (neat) 3416, 2941, 2925, 2855, 1719, 1618, 1516, 1466, 1244, 1244, 1065, 882, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (m, 21H), 1.78 (m, 1H), 2.10 (m, 1H), 2.82 (septet, *J* = 4.5

Hz, 1H), 3.43 (ddd, *J* = 12.2, 9.1, 3.4 Hz, 1H), 3.62 (pentet, *J* = 4.5 Hz, 1H), 3.77 (s, 3H), 3.82 (s, 3H), 4.21 (dd, *J* = 4.3, 8.3 Hz, 1H), 4.47 (m, 3H), 4.53 (m, 1H), 4.53 (m, 2H), 6.55 (s, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.8 (3C), 17.6 (6C), 29.4, 37.9, 39.6, 51.2, 55.2, 57.2, 68.7, 73.0, 74.9, 76.0, 108.6, 113.8 (2C), 115.3, 129.4 (3C), 152.4, 159.3, 160.7, 164.3; EI-HRMS calcd for $C_{30}H_{46}O_8SiNa$ $[M + Na]^+$ *m/z* 585.2860, found *m/z* 585.2844.

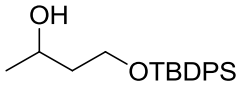


197

Methyl 2-((1*R*,2*R*,3*R*,4*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)-5-formylfuran-3-carboxylate (197)

To a solution of **196** (8.0 mg, 0.011 mmol) in CH_2Cl_2 (0.1 mL) was added tetra-*n*-propylammonium perruthenate (TPAP, 4.63 mg, 0.008 mmol) and the reaction mixture was stirred at room temperature for 1.5 h. The suspension was filtered through a pad of silica gel which was washed with CH_2Cl_2 (10 mL). Evaporation of the filtrate and chromatography of the crude residue on silica gel (93:7 hexanes/ethyl acetate) afforded **197** (7.0 mg, 88%) as a colorless oil: R_f 0.64 (3:7 hexanes-ethyl acetate); $[\alpha]^{16}_D$ – 53.7 (*c* 1.0, $CHCl_3$); IR (neat) 2920, 2858, 1732, 1693, 1456, 1254, 1114, 1075 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 6H), 0.92 (s, 21H), 0.95 (s, 9H),

1.70 (m, 1H), 2.10 (m, 1H), 2.70 (m, 1H), 3.50 (m, 2H), 3.81 (s, 3H), 3.82 (s, 3H), 4.32 (dd, *J* = 8.4, 3.0 Hz, 1H), 4.40 (dd, *J* = 21.5, 11.5 Hz, 2H), 4.60 (dd, *J* = 8.5, 6.4 Hz, 1H), 4.72 (dd, *J* = 8.5, 6.2 Hz, 1H), 6.82 (d, *J* = 8.70Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.45 (s, 1H), 9.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.9, -4.8, 11.6 (3C), 17.6 (6C), 17.7, 25.8 (3C), 29.7, 37.2, 39.9, 51.6, 55.2, 68.0, 72.5, 75.2, 76.7, 113.6 (2C), 117.4, 121.2, 129.1 (2C), 130.5, 150.7, 159.0, 162.9, 166.6, 177.2; HRMS calcd for $C_{36}H_{58}O_8Si_2Na$ $[M + Na]^+$ *m/z* 697.3568, found *m/z* 697.3545.

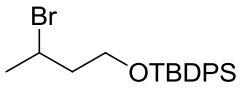


201

4-(*tert*-Butyldiphenylsilyloxy)butan-2-ol (201)

To an ice-cold, stirred solution of **200** (1.0 mL, 11.09 mmol), DMAP (6.77 mg, 0.05 mmol), and NEt_3 (1.68 mL, 12.08 mmol) in dry CH_2Cl_2 (30 mL) was added dropwise a solution of TBDPSCl (2.8 mL, 11.09 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 12 h, and then MeOH (2 mL) was added to the reaction mixture which was stirred for 15 min. The solvent was removed under reduced pressure and the residue was dissolved in Et_2O and the solution was washed with H_2O. The separated Et_2O layer was dried (Na_2SO_4), filtered, and concentrated and the residual oil was purified by silica gel chromatography (hexanes/ethyl acetate, 94:6) to afford **201** (3.25 g, 89%) as a colorless oil: R_f 0.62 (3:7 hexanes-ethyl acetate); IR (neat) 3413, 3067, 1959, 1928, 1858, 1475, 1421, 1110, 1071, 827, 733, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 9H), 1.26 (d, *J* = 6.2 Hz, 3H), 1.69 (m, 1H), 1.80

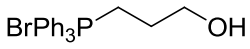
(m, 1H), 3.32 (d, *J* = 2.5 Hz, 1H), 3.90 (m, 2H), 4.15 (m, 1H), 7.46 (m, 6H), 7.74 (d, *J* = 6.9 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0, 23.4, 26.8, 40.1, 63.4, 67.9, 127.8, 129.8, 133.0, 133.1, 135.6; CI-HRMS calcd for $C_{20}H_{29}O_2Si$ $[M + H]^+$ (*m/z*) 329.1936, found 329.1934.



202

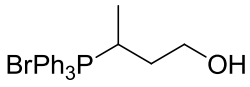
(3-Bromobutoxy)(*tert*-butyl)diphenylsilane (202)

To a solution of **201** (1.066 g, 3.24 mmol) in CH_2Cl_2 (30 mL) was added PPh_3 (1.27 g, 4.86 mmol). The solution was cooled to 0 ^oC and NBS (1.14 g, 6.49 mmol) was added. The reaction mixture was stirred at room temperature for 3 h, and water (20 mL) was added to the mixture. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organic extract was dried (Na_2SO_4), filtered, and concentrated. The crude residue was purified by silica gel chromatography (hexanes/ethyl acetate 3:97) to afford **202** (1.00 g, 79%) as a colorless oil: R_f 0.85 (2:8 hexanes-ethyl acetate); IR (neat) 3071, 3048, 2959, 2924, 1846, 1467, 1429, 1188, 1106, 879, 815 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (s, 9H), 1.86 (d, *J* = 6.7 Hz, 3H), 2.20 (m, 2H), 4.00 (m, 2H), 4.60 (sextet, *J* = 6.7 Hz, 1H), 7.58 (m, 6H), 7.88 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 26.8, 27.0, 43.8, 48.0, 61.9, 127.9, 129.8, 133.6, 133.8, 135.6, 135.7; CI-HRMS calcd for $C_{20}H_{28}O_2Si$ Br $[M + H]^+$ (*m/z*) 391.1092, found 391.1080.



205

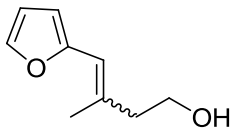
Phophonium salt 205: To a solution of **204** (0.65 mL, 7.2 mmol) in acetonitrile (14.4 mL) was added triphenylphosphine (3.76 g, 14.38 mmol) and the solution was refluxed for 4 h, during which a white precipitate formed. The solid was filtered off and was washed with Et_2O to give **205** as a colorless solid (2.07 g, 72%): IR (neat) 3311, 2890, 2855, 1435, 1120, 746, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.80 (m, 2H), 3.80 (m, 4H), 7.70 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 20.4, 25.8, 25.9, 60.2, 60.4, 130.5, 130.6, 133.4, 135.0, 135.1; EI-HRMS calcd for $C_{21}H_{22}OP$ [M - Br] $^+$ (*m/z*) 321.1408, found 321.1409.



206

Phosphonium salt 206: To a THF (8.26 mL) solution of **205** (500 mg, 1.24 mmol) at 0 ^oC was added *n*-BuLi (1.55 mL, 1.6M in hexane) and the solution was stirred for 1 h at 0 ^oC. Methyl iodide (84.6 μL, 1.36 mmol) was added to the reaction mixture at 0 ^oC which was stirred for 3 h at room temperature. A white precipitate formed which was filtered off and washed with Et_2O to provide **206** (476 mg, 92%) as a yellowish solid: IR (neat) 3355, 1429, 1110, 990, 726, 691, 648 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.12 (m, 1H), 1.44 (dd, *J* = 19.6, 6.7 Hz, 3H), 2.25 (m, 1H), 3.79 (m, 1H), 4.01 (m, 1H), 4.67 (m, 1H), 5.11 (m, 1H), 7.81 (m, 15H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0,

21.8, 22.3, 34.0, 56.8, 56.8, 56.9, 117.4, 118.2, 130.5, 133.7, 133.8, 134.8; EI-HRMS calcd for $C_{22}H_{24}OP$ $[M - Br]^+$ (*m/z*) 335.1565, found 335.1522.

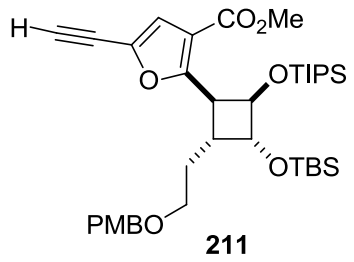


208 (*E/Z* 1.5:1)

5-(Furan-2-yl)-4-methylpent-4-en-1-ol (208)

To a stirred suspension of phosphonium salt **205** (400 mg, 1.00 mmol) in dry THF (10.0 mL) under argon at 0 ^oC was added dropwise *n*-BuLi (1.38 mL, 1.6 M, 2.2 mmol). The initial yellow color turned a dark red color after 10 min. After 15 min, methyl iodide (74.7 μL, 1.2 mmol) was added dropwise at 0 ^oC, producing an immediate white precipitate. After stirring for 15 min at room temperature, *n*-BuLi (0.70 mL, 1.6 M, 1.1 mmol) was added at 0 ^oC, again producing a deep red coloration. After 15 min, a solution of **207** (82.8 μL, 1.0 mmol) in dry THF (1 mL) was introduced and the mixture was stirred for 1 h at 0 ^oC. Water (10 mL) was added and the separated aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic extract was dried (Na_2SO_4), filtered, concentrated and the residue was purified by silica gel chromatography (hexanes/ethyl acetate, 83:17) to afford an inseparable mixture of *E/Z* (1.5:1) of **208** (102 mg, 73%) as a colorless oil: R_f 0.30 (3:7 hexanes-ethyl acetate); IR (neat) 3346, 2933, 2879, 1657, 1493, 1151, 1042, 1014, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.94 (s, 3H), 2.04 (s, 3H), 2.08 (s, broad, 2H), 2.43 (t, *J* = 6.7 Hz, 2H), 2.75 (t, *J* = 6.7 Hz, 2H), 6.77 (t, *J* = 6.5 Hz, 2H), 6.83 (t, *J* = 6.7 Hz,

2H), 6.18 (s, 2H), 6.24 (s, 2H), 6.38 (m, 1H), 6.41 (m, 1H), 7.36 (d, *J* = 1.4 Hz, 1H), 7.38 (d, *J* = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.3, 24.8, 36.8, 43.8, 60.5, 60.9, 107.9, 108.0, 111.0, 116.4, 116.5, 134.3, 134.8, 140.8, 140.9, 152.9, 153.1; EI-HRMS calcd for $C_9H_{12}O_2$ $[M]^+$ (*m/z*) 152.0837, found 152.0836.

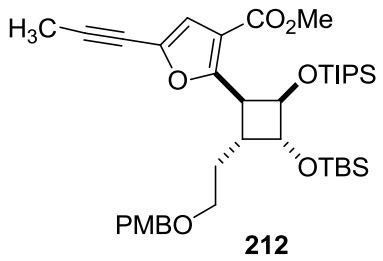


211

Methyl 2-((1*R*,2*R*,3*R*,4*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)-5-ethynylfuran-3-carboxylate (211)

To a solution of **197** (10.0 mg, 0.017 mmol) and K_2CO_3 (15.01 mg, 0.108 mmol) in MeOH (0.20 mL) was added **210** (7.54 mg, 0.039 mmol) and the reaction mixture was stirred for 3.5 h at room temperature. The solution was diluted with Et_2O and washed with satd aqueous $NaHCO_3$. The ethereal layer was dried (Na_2SO_4), filtered and concentrated, and the residue was purified by chromatography on silica gel (hexanes/ethyl acetate 93:7) to give **211** (8.0 mg, 81%) as a colorless oil: R_f 0.65 (2:8 hexanes-ethyl acetate); $[\alpha]^{19}_D$ – 59.8 (*c* 0.65, $CHCl_3$); IR (neat) 3311, 3256, 1960, 2929, 2859, 1719, 1594, 1509, 1462, 1248, 1120, 835, 777, 680 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.11 (s, 6H), 0.90 (m, 30H), 1.70 (m, 1H), 2.00 (m, 1H), 2.60 (m, 1H), 3.41 (s, 1H), 3.50 (m, 2H), 3.75 (s, 3H), 3.81 (s, 3H), 4.22 (dd, *J* = 8.6, 3.2 Hz, 1H),

4.40 (dd, *J* = 25.3, 11.5 Hz, 2H), 4.52 (dd, *J* = 8.7, 6.2 Hz, 1H), 4.64 (dd, *J* = 8.5, 6.0 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.88 (s, 1H), 7.19 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.9, -4.5, 11.9 (3C), 17.6 (6C), 17.7, 25.9 (3C), 29.7, 37.1, 39.5, 51.3, 55.2, 68.1, 72.5, 73.5, 75.2, 76.7, 81.9, 113.6 (2C), 115.5, 116.8, 129.1 (2C), 130.6, 134.5, 159.0, 162.3, 163.4; CI-HRMS calcd for $C_{37}H_{58}O_7Si_2Na$ $[M + Na]^+$ *m/z* 693.3619, found *m/z* 693.3626.

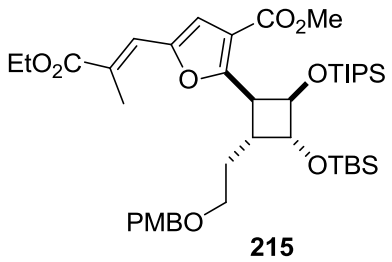


212

Methyl 2-((1*R*,2*R*,3*R*,4*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)-5-(prop-1-ynyl)furan-3-carboxylate (212)

To a solution of **211** (14 mg, 0.02 mmol) in THF (0.20 mL) at –78 °C under argon was added dropwise NaHMDS (0.25M in THF, 0.29 mL, 0.07 mmol). The resulting solution was stirred for 1.5 h at –78 °C, MeI (10.0 μL, 0.16 mmol) was added and the reaction mixture was stirred for an additional 1.5 h at –78 °C. The reaction was quenched with H_2O (10 mL) and the separated aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layer was washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography of the crude residue on silica gel (ethyl acetate: hexanes 7:93) afforded **212** (12 mg, 84%) as a colorless oil: R_f 0.65

(2:8 hexanes-ethyl acetate); $[\alpha]^{20}_{D}$ – 59.7 (*c* 0.40, $CHCl_3$); IR (neat) 2941, 2925, 2859, 2630, 2606, 2489, 1723, 1555, 1513, 1462, 1256, 1116, 1057, 832, 777 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.11 (s, 6H), 0.91 (m, 30H), 1.70 (m, 1H), 2.00 (m, 1H), 2.11 (s, 3H), 2.60 (m, 1H), 3.52 (m, 2H), 3.74 (s, 3H), 3.80 (s, 3H), 4.20 (dd, *J* = 8.7, 3.2 Hz, 1H), 4.40 (dd, *J* = 24.9, 11.3 Hz, 2H), 4.50 (dd, *J* = 8.8, 6.1 Hz, 1H), 4.60 (dd, *J* = 8.7, 6.1 Hz, 1H), 6.68 (s, 1H), 6.81 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.9, -4.5, 4.5, 11.9 (3C), 17.6 (6C), 17.7, 25.8 (3C), 29.3, 37.0, 39.5, 51.1, 55.2, 68.1, 69.8, 72.5, 75.2, 76.5, 97.4, 113.6 (2C), 114.3, 115.4, 129.1 (2C), 130.6, 135.9, 159.0, 161.0, 163.7; CI-HRMS calcd for $C_{38}H_{60}O_7Si_2Na$ $[M + Na]^+$ *m/z* 707.3775, found *m/z* 707.3737.

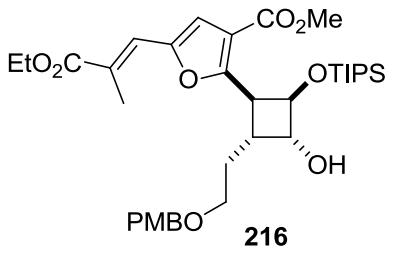


215

Methyl 2-((1*R*,2*R*,3*R*,4*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)-5-((*E*)-3-ethoxy-2-methyl-3-oxoprop-1-enyl)furan-3-carboxylate (215)

To a solution of **214** (11.0 µL, 0.05 mmol) in THF (0.1 mL) at 0 ^oC was added a solution of sodium bis(trimethylsilyl)amide (0.25 mL, 0.06 mmol, 0.25 M in THF). After 15 min, a solution of **197** (17 mg, 0.025 mmol) in THF (0.15 mL) was added dropwise. The reaction mixture was allowed to warm to room temp and was stirred for

1.5 h. The reaction was quenched with a mixture of H_2O and satd NH_4Cl (3:1, 10 mL) and was diluted with Et_2O (20 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic extract was washed with brine (20 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (1:9 hexanes/ethyl acetate) to afford **215** (16 mg, 84%) as a colorless oil: R_f 0.52 (8:2 hexanes-ethyl acetate); $[\alpha]^{24}_D$ – 111.0 (*c* 0.45, $CHCl_3$); IR (neat) 2960, 2925, 2855, 1723 (2), 1641, 1610, 1583, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 6H), 0.90 (m, 30H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.68 (m, 1H), 2.06 (m, 1H), 2.34 (s, 3H), 2.60 (m, 1H), 3.54 (m, 2H), 3.76 (s, 3H), 3.80 (s, 3H), 4.25 (m, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.40 (dd, *J* = 11.4, 33.0 Hz, 2H), 4.58 (dd, *J* = 6.5, 8.4 Hz, 1H), 4.76 (dd, *J* = 6.3, 8.4 Hz, 1H), 6.81 (s, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.9, -4.6, 11.8 (3C), 14.1, 14.3, 17.6 (6C), 18.0, 25.8 (3C), 29.2, 37.2, 39.2, 39.4, 51.3, 55.3, 60.9, 68.0, 72.5, 75.3, 113.6 (2C), 115.6, 116.8, 124.7, 125.3, 129.1 (2C), 130.5, 150.0, 159.0, 162.8, 163.7, 168.5; EI-HRMS calcd for $C_{41}H_{66}O_9SiNa$ $[M + Na]^+$ *m/z* 781.4166, found *m/z* 781.4143.

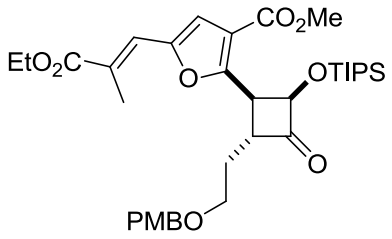


216

Methyl 5-((*E*)-3-Ethoxy-2-methyl-3-oxoprop-1-enyl)-2-((1*R*,2*R*,3*R*,4*R*)-3-hydroxy-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)furan-3-carboxylate (216)

To a solution of **215** (16 mg, 0.02 mmol) in EtOH (0.4 mL) was added PPTS (8 mg, 0.03 mmol) and the mixture was heated for 48 h at 65 ^{o}C. After the solution had cooled by an ice bath, the reaction was quenched with satd aqueous $NaHCO_3$. The separated aqueous layer was extracted with Et_2O (2 x 10 mL) and the combined organic extract was dried (Na_2SO_4), filtered, and concentrated. The crude residue was purified by chromatography on silica gel (15:85 ethyl acetate/hexanes) to furnish alcohol **216** (11 mg, 85%) as a colorless oil: R_f 0.45 (7:3 hexanes-ethyl acetate); $[\alpha]^{24}_D$ – 74.8 (*c* 0.35, $CHCl_3$); IR (neat) 3416, 2941, 2914, 2863, 1723, 1699, 1520, 1454, 1244, 1112, 1073, 878 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (m, 21H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.80 (m, 1H), 2.14 (m, 1H), 2.27 (s, 3H), 2.85 (septet, *J* = 4.5 Hz, 1H), 3.44 (ddd, *J* = 12.4, 9.2, 3.2 Hz, 1H), 3.64 (ddd, *J* = 9.2, 5.3, 3.8 Hz, 1H), 3.81 (s, 3H), 3.83 (s, 3H), 4.28 (m, 3H), 4.50 (m, 3H), 4.58 (dd, *J* = 9.2, 4.7 Hz, 1H), 6.83 (s, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.38 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.8 (3C), 14.2, 14.3, 17.6 (6C), 29.4, 29.7, 37.9, 39.7, 51.3, 55.2, 60.9, 68.6, 73.1, 75.0, 76.4, 113.8 (2C), 115.1, 116.8, 124.9, 125.7, 129.4 (2C), 150.0,

159.3, 162.1, 163.9, 168.4; EI-HRMS calcd for $C_{35}H_{52}O_9SiNa$ $[M + Na]^+$ *m/z* 667.3278, found *m/z* 667.3276.

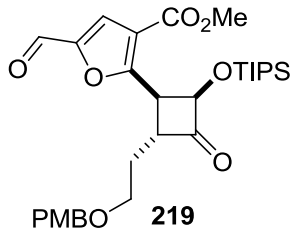


217

Methyl 5-((*E*)-3-Ethoxy-2-methyl-3-oxoprop-1-enyl)-2-((1*R*,2*R*,4*R*)-2-(2-(4-methoxybenzyloxy)ethyl)-3-oxo-4-(triisopropylsilyloxy)cyclobutyl)furan-3-carboxylate (217)

To a solution of **216** (2.0 mg, 0.003 mmol) in CH_2Cl_2 (0.2 mL) was added TPAP (1.2 mg, 0.003 mmol) and the reaction mixture was stirred at room temperature for 2 h. The suspension was filtered through a short pad of silica gel which was washed with CH_2Cl_2 (2 x 10 mL). Evaporation of the filtrate and purification of the crude residue by chromatography on silica gel (14:86 hexanes/ethyl acetate) gave **217** (1.6 mg, 84%) as a colorless oil: R_f 0.62 (3:7 hexanes-ethyl acetate); $[\alpha]^{23}_D$ – 59.6 (*c* 0.32, $CHCl_3$); IR (neat) 2921, 2855, 1797, 1715, 1696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (m, 21H), 1.35 (t, *J* = 7.4 Hz, 3H), 2.10 (m, 2H), 2.17 (s, 3H), 3.57 (m, 2H), 3.70 (m, 1H), 3.81 (s, 3H), 3.83 (s, 3H), 4.27 (q, *J* = 7.3 Hz, 2H), 4.40 (d, *J* = 4.0 Hz, 2H), 4.52 (dd, *J* = 6.1, 9.2 Hz, 1H), 5.32 (dd, *J* = 2.9, 9.2 Hz, 1H), 6.84 (m, 3H), 7.18 (d, J = 8.8 Hz, 2H), 7.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7 (3C), 14.0, 14.3, 17.4 (6C), 29.4, 29.7, 37.6, 51.4, 55.2, 56.4, 61.0, 67.2, 72.7, 84.0, 113.6 (2C), 114.5, 124.5,

126.9, 128.9, 129.1 (2C), 130.0, 150.7, 159.1, 160.0, 163.6, 168.3, 208.1; EI-HRMS calcd for $C_{35}H_{50}O_9SiNa$ $[M + Na]^+$ *m/z* 665.3122, found *m/z* 665.3112.

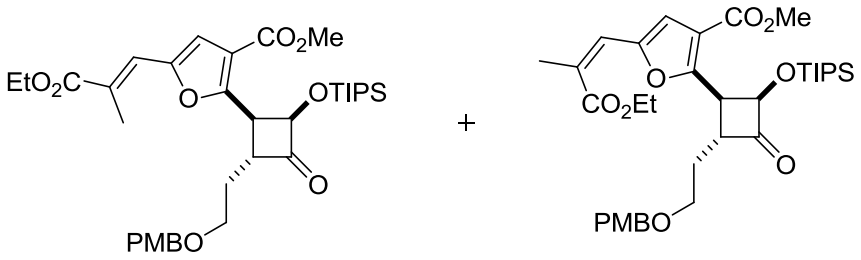


219

Methyl 5-Formyl-2-((1*R*,2*R*,4*R*)-2-(2-(4-methoxybenzyloxy)ethyl)-3-oxo-4-(triisopropylsilyloxy)cyclobutyl)furan-3-carboxylate (219)

A solution of **173** (7.0 mg, 0.017 mmol) in CH_2Cl_2 (0.3 mL) containing activated 4Å molecular sieves, TPAP (0.49 mg, 0.001 mmol) and *N*-methylmorpholine *N*-oxide (3.58 mg, 0.03 mmol) was stirred at room temperature for 1.5 h. The suspension was filtered through a short pad of silica gel which was washed with CH_2Cl_2 (10 mL). Evaporation of the filtrate and purification of the residue by chromatography on silica gel (15:85 hexanes/ethyl acetate) afforded **219** (5.0 mg, 72%) as a colorless oil: R_f 0.65 (6:4 hexanes-ethyl acetate); $[\alpha]^{24}_D$ + 5.2 (*c* 0.5, $CHCl_3$); IR (neat) 2964, 2918, 2859, 1797, 1723, 1684, 1536, 1516, 1443, 1260, 1069, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (m, 21H), 2.1 (m, 2H), 3.57 (t, *J* = 6.1 Hz, 2H), 3.81 (s, 3H), 3.84 (s, 3H), 3.92 (dd, *J* = 7.4, 3.3 Hz, 1H), 4.36 (s, 2H), 4.56 (dd, *J* = 6.9, 8.9 Hz, 1H), 5.30 (dd, *J* = 2.9, 9.1, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.79 (s, 1H), 9.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.8 (3C), 17.4 (6C), 29.9, 38.3, 51.8, 55.2, 56.8, 67.2, 72.7, 84.3, 113.8 (2C), 117.9, 120.5, 129.1 (2C), 130.0, 151.1, 159.1,

162.8, 164.0, 177.4, 207.5; EI-HRMS calcd for $C_{30}H_{42}O_8SiNa$ $[M + Na]^+$ *m/z* 581.2547, found *m/z* 581.2573.



217 *E/Z* 3:1 **220**

(*E* and *Z*) Methyl 5-(3-Ethoxy-2-methyl-3-oxoprop-1-enyl)-2-((1R,2R,4R)-2-(2-(4-methoxybenzyloxy)ethyl)-3-oxo-4-(triisopropylsilyloxy)cyclobutyl)furan-3-carboxylate (217 and 220)

To a solution of **214** (2.17 µL, 0.01 mmol) in THF (0.1 mL) at 0 ^oC was added a solution of sodium bis(trimethylsilyl)amide (55 µL, 0.013 mmol, 0.25M in THF). After 15 min, a solution of **219** (3 mg, 0.005 mmol) in THF (0.1 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 1.5 h. The reaction was quenched with a mixture of H_2O and satd NH_4Cl (3:1, 10 mL) and was diluted with Et_2O (20 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic extract was washed with brine (20 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude mixture was purified by chromatography on silica gel (1:9 hexanes/ethyl acetate) to yield an inseparable mixture of (*E*)-isomer **217** and (*Z*)-isomer **220** (2.5 mg, 73%, *E/Z* 3:1 by NMR) as a colorless oil: R_f 0.52 (8:2 hexanes-ethyl acetate); $[\alpha]^{24}_D$ –

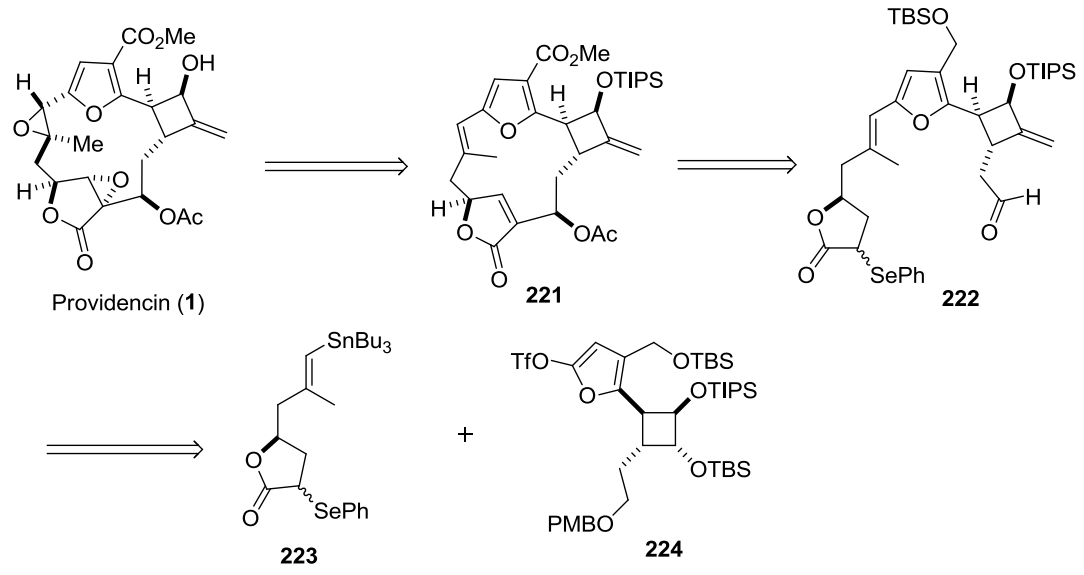
111.0 (*c* 0.45, $CHCl_3$); IR (neat) 2914, 2844, 1789, 1711(2), 1633, 1505, 1466 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (m, 35H), 1.38 (t, *J* = 7.1 Hz, 6H), 2.06 (m, 3H), 2.16 (s, 1H), 2.17 (s, 3H), 3.50 (m, 2H), 3.64 (m, 1H), 3.85 (m, 9H), 4.25 (q, *J* = 7.2 Hz, 3H), 4.40 (m, 3H), 4.53 (dd, *J* = 6.0, 9.1 Hz, 1H), 5.32 (dd, *J* = 2.2, 9.1 Hz, 1H), 6.85 (m, 5H), 7.20 (m, 3H), 7.30 (s, 1H), 7.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7 (3C), 14.0, 14.3, 17.4(6C), 29.7, 30.4, 37.7, 51.5, 55.2, 56.4, 61.0, 67.2, 72.5, 72.7, 84.0, 113.7 (2C), 114.3, 114.5, 124.5, 126.7, 129.1 (2C), 130.0, 150.7, 159.1, 160.0, 163.7, 208.1; EI-HRMS calcd for $C_{35}H_{50}O_9SiNa$ $[M + Na]^+$ *m/z* 665.3122, found *m/z* 665.3112.

CHAPTER 4

Second Generation Approach Towards Providencin

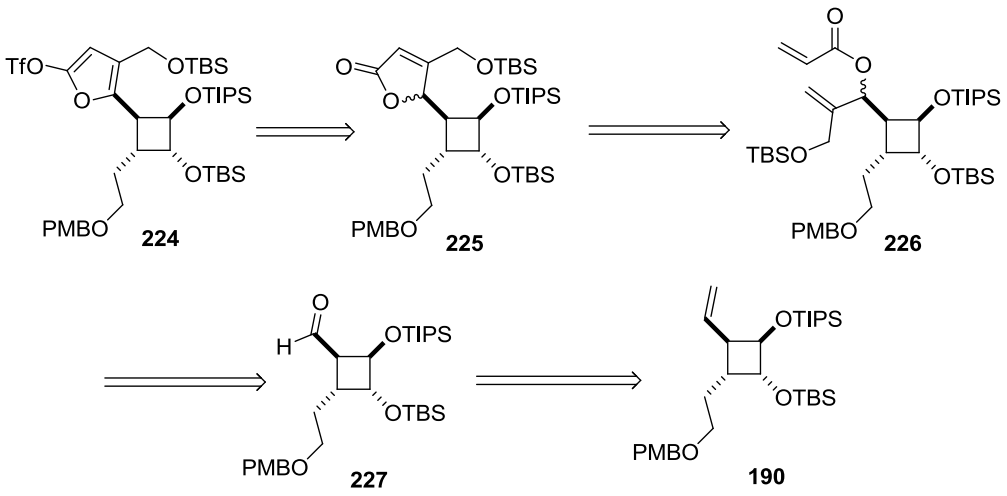
4.1 Second generation strategy for providencin (1)

In a second generation approach toward providencin (**1**), we envisioned that late stage epoxidations of macrocycle **221** would deliver our target molecule (Scheme 4.1). The core structure of providencin in **221** would be generated via an intramolecular aldol reaction of aldehyde **222** which would result from an intermolecular Stille cross-coupling[1] between two major fragments, vinylstannane **223** and furyl triflate **224**.



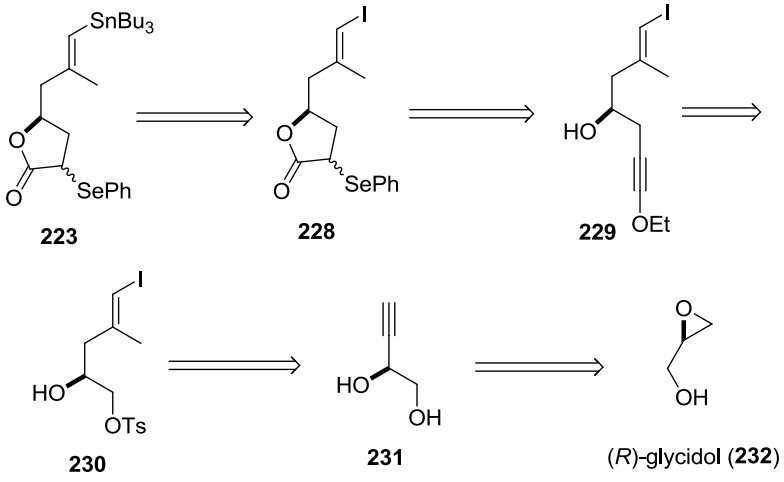
Scheme 4.1 Second generation retrosynthetic analysis of providencin (**1**)

Furyl triflate **224** would result from butenolide **225** by reaction with a base and triflic anhydride (Scheme 4.2).[2] A ring-closing metathesis (RCM) of diene **226** would lead to **225** and RCM precursor **226** would be prepared from aldehyde **227**. The latter would be easily available from cyclobutane **190**.



Scheme 4.2 Retrosynthesis of furyl triflate **224**

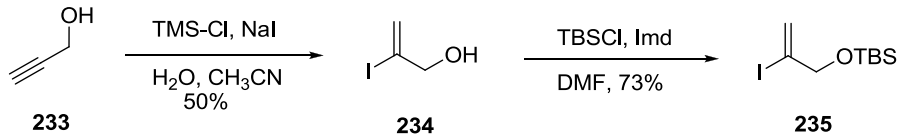
The second component for Stille cross-coupling with **224**, vinyl stannane **223**, would be prepared from the corresponding vinyl iodide **228** by standard chemistry (Scheme 4.3). Following a similar procedure reported by Pattenden and co-workers,[3] *α*-selenolactone **228** would be obtained from hydroxy alkyne **229**, which would be prepared from tosylate **230**. Vinyl iodide **230** would be synthesized from alkyne **231** via Negishi carbometallation-iodination,[4] and the latter would be acquired from commercially available (*R*)-glycidol (**232**).



Scheme 4.3 Retrosynthesis of vinyl stannane **223**

4.2 Preparation of a ring closing metathesis precursor

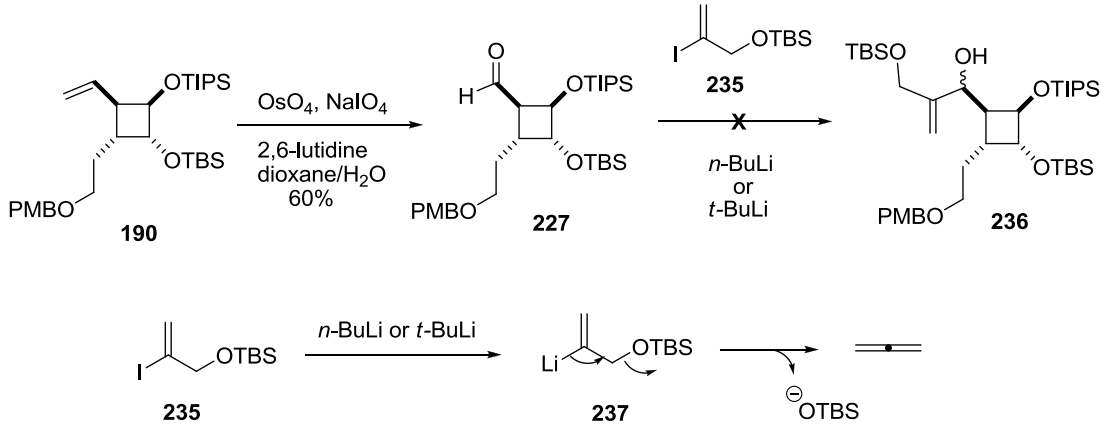
Our new route started with the preparation of vinyl iodide **235** for alkylation of aldehyde **227**. Propargyl alcohol (**233**) was converted to vinyl iodide in the presence of trimethylsilyl chloride and sodium iodide, and alcohol **234** was protected as its *t*-butyldimethylsilyl ether **235** (Scheme 4.4).[5]



Scheme 4.4 Synthesis of vinyl iodide **235**

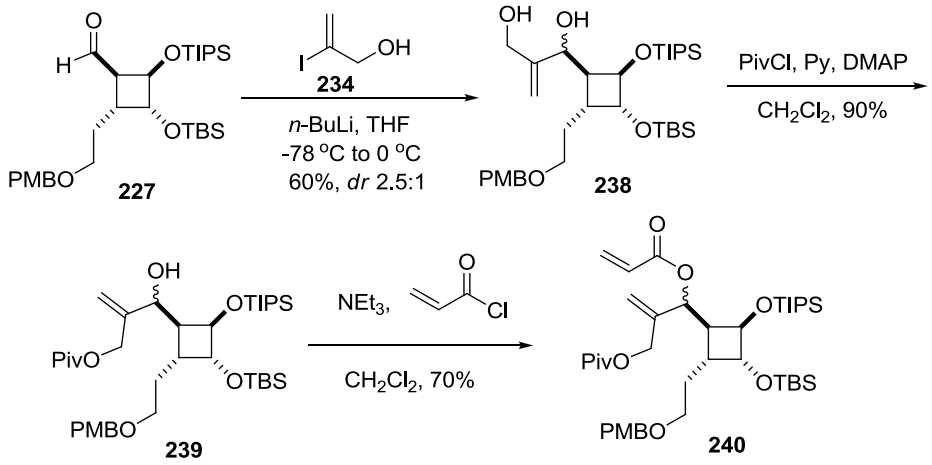
The vinyl moiety of cyclobutane **190** was oxidatively cleaved by osmium tetroxide and sodium periodate to provide aldehyde **227** in moderate yield.[6] Unfortunately, all attempts to alkylate aldehyde **227** with vinyl iodide **235** in the

presence of *n*-butyllithium or *t*-butyllithium resulted only in return of the starting aldehyde.[7] It was surmised that, in the presence of *n*-butyllithium or *t*-butyllithium, the vinyl lithium species **237** was formed but that **237** underwent facile elimination of the *t*-butyldimethylsilyloxy group to give allene which was lost upon evaporative work up (Scheme 4.5).



Scheme 4.5 Attempted synthesis of alcohol **236**

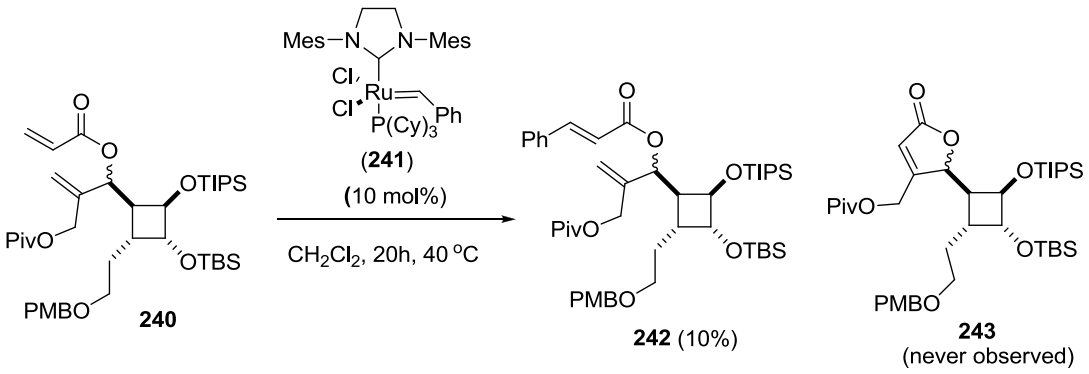
The problem with elimination of the lithio derivative of **235** was avoided by treating iodo alcohol **234** with two equivalents of *n*-butyllithium at low temperature and then reacting the dilithio species with aldehyde **227** (Scheme 4.6).[8] Diol **238** was isolated in moderate yield and as a mixture of diastereomers (2.5:1) from this reaction. After selective protection of the primary alcohol of **238** as its pivaloyl ester **239**,[9] the secondary alcohol of **239** was esterified with acryloyl chloride[9] to provide RCM precursor **240**.



Scheme 4.6 Synthesis of ring closing metathesis precursor **240**

4.3 Attempted Ring closing metathesis of diene 240

When diene **240** was subjected to ring closing metathesis with Grubbs' first generation catalyst,[10,11] even in the presence of titanium(IV) isopropoxide,[12] it returned starting material. However, when Grubbs' second generation catalyst (**241**) was used, cinnamate **242** was observed (10% by ^{1}H NMR) in the reaction mixture (Scheme 4.7) but, no signals for our desired butenolide **243** could be seen in the NMR of the crude mixture. Cinnamate **242** was difficult to separate from starting diene **240**, but the signals due to the phenyl ring as well as the to the *trans*-alkene in the NMR spectra of **242** confirmed its presence. It was found that variation of both the reaction temperature and the solvent gave similar results. It appears that the combination of electron deficiency in the conjugated double bond and steric hindrance due to *gem*-disubstitution in the allylic alkene moiety of **240** contributed to the failure of this ring closing metathesis.

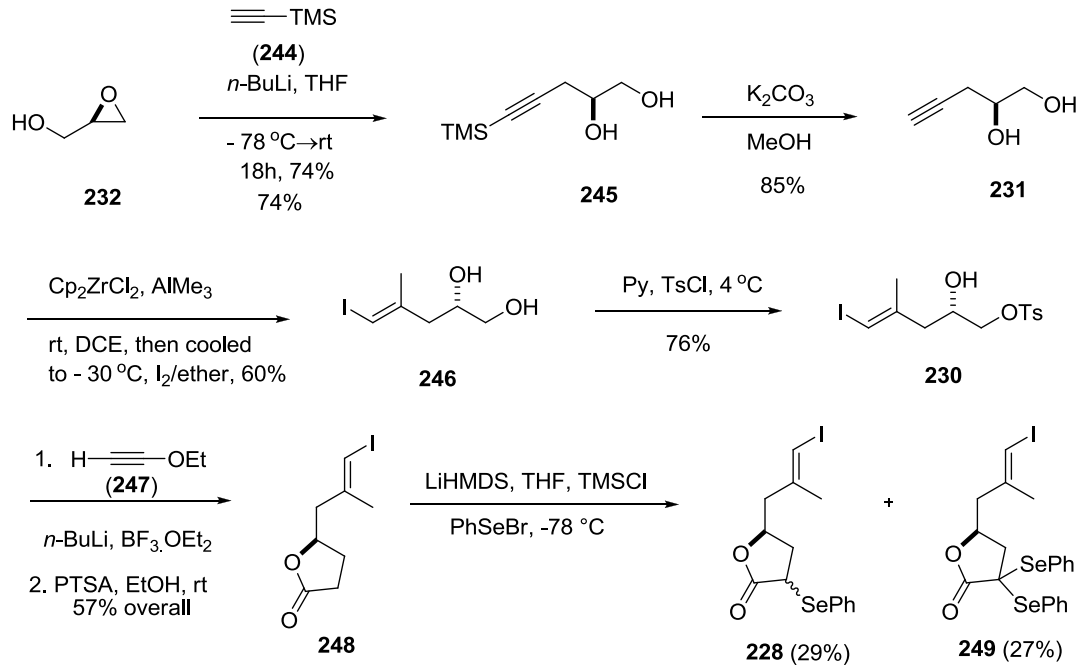


Scheme 4.7 Attempted ring closing metathesis of **240**

4.4 Synthesis of vinyl iodide 225

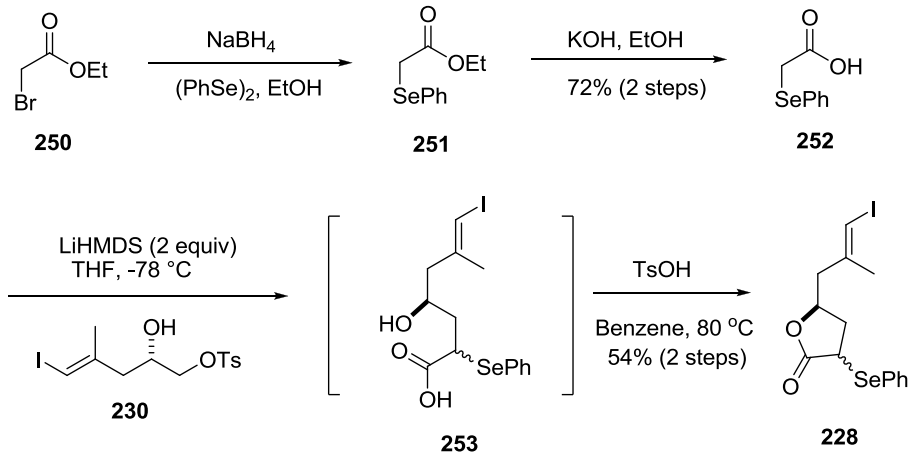
Alongside experiments focused on synthesis of the furylcyclobutane segment of providencin, a route to vinyl iodide **228** was developed starting from (*R*)-glycidol (**232**). The epoxide of **232** was opened by reaction with the lithiated derivative of trimethylsilylacetylene (**244**) to afford diol **245** which was treated with potassium carbonate in methanol to release alkyne **231** (Scheme 4.8).[13] Negishi carbometallation-iodination[14] of alkyne **231** yielded *E*-iodoalkene **246** with a trace amount of the alternate regioisomer. The primary alcohol of **246** was converted selectively to tosylate **230** which was treated with an excess of the lithium salt of ethoxyacetylene (**247**). The product was immediately hydrolyzed using *p*-toluenesulfonic acid as a catalyst to yield lactone **248**. Finally, deprotonation of **248** using lithium hexamethyldisilazide at -78 ^{o}C, followed by trapping of the enolate with trimethylsilyl chloride and then quenching of the resultant silyl ether with phenylselenyl bromide gave substituted lactone **228**. Although **228** was formed in low yield and was

accompanied by bis-selenelated lactone **249**, these lactones were easily separated by chromatography.



Scheme 4.8 Synthesis of vinyl iodide **228**

In view of the mixture of **228** and **249** obtained by selenylation of **248**, an alternative route to our desired lactone **228** was devised. First phenylseleno acetic acid (**252**) was prepared from ethyl bromoacetate (**250**) in two steps (72% overall yield).[15] Treatment of carboxylic acid **252** with two equivalents of lithium hexamethyldisilazide at -78 °C followed by addition of tosylate **230** yielded hydroxy acid **253** which underwent acid-catalyzed cyclization in hot benzene.[16] This sequence afforded vinyl iodide **228** as a mixture of two diastereomers (1.4:1) in 54% overall yield based on **230** (Scheme 4.9).



Scheme 4.9 Alternative route to vinyl iodide **228**

Although our retrosynthetic plan called for conversion of vinyl iodide **228** to its corresponding vinyl stannane **223**, our failure to synthesize its furyl triflate coupling partner **224** caused us to delay this transformation. At this stage of our approach, we realized that we required an improved route to our cyclobutylfuran segment, specifically one that would allow us to use our already prepared vinyl iodide fragment **228**. This new route to the cyclobutylfuran segment of providencin is discussed in Chapter 5.

4.5 References

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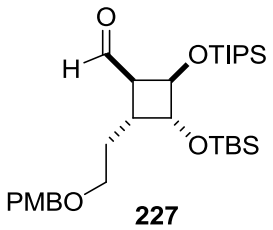
4.6 Experimental Section

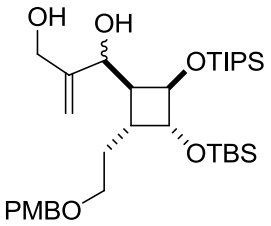


227

(1*R*,2*R*,3*R*,4*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutanecarbaldehyde (227)

To a solution of **190** (118 mg, 0.21 mmol) in dioxane-water (3:1, 2.1 mL) were added 2,6-lutidine (48.6 μL, 0.42 mmol), OsO_4 (86 mg, 0.008 mmol), and $NaIO_4$ (179 mg, 0.84 mmol, 2.5% in 2-methyl-2-propanol) an the reaction mixture was stirred at room temperature for 15 h. Water (10 mL) and CH_2Cl_2 (10 mL) were added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic extract was washed with brine, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under vacuum and the crude residue was purified by silica gel chromatography (1:9 ethyl acetate/hexanes) to afford **227** (65 mg, 60%) as a colorless oil: R_f 0.52 (9:1 hexanes-ethyl acetate); $[\alpha]^{22}_{D}$ – 56.7 (*c* 1.35, $CHCl_3$); IR (neat) 2937, 2859, 1715, 1606, 1509, 1462, 1240, 1104 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 6H), 0.90 (s, 9H), 1.20 (m, 21H), 1.51 (m, 1H), 2.00 (m, 1H), 2.65 (m, 1H), 3.02 (m, 1H), 3.45 (m, 2H), 3.82 (m, 3H), 4.33 (m, 1H), 4.41 (s, 2H), 4.52 (m, 1H), 6.89 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 9.85 (d, *J* = 3.57 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.0, -4.7, 11.8, 12.4 (3C),

17.8(6), 25.8 (3C), 18.0, 32.4, 52.7, 55.7, 55.2, 68.4, 72.6, 75.2, 76.8, 113.7 (2C), 129.1 (2C), 130.4, 159.1; EI-HRMS calcd for $C_{30}H_{54}O_5SiNa$ [M + Na] $^+$ (*m/z*) 573.3408, found 573.3401.

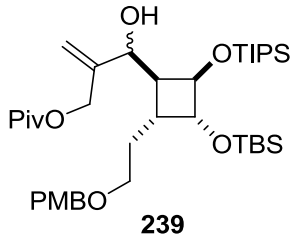


238 (*dr* 2.5:1)

1-((1*S*,2*R*,3*R*,4*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)-2-methylenepropane-1,3-diol (**238**)

To a solution of **234** (103.2 mg, 0.56 mmol) in 3.35 mL of Et_2O at -78 ^oC was added slowly 0.2 mL of 2.6 M *n*-butyllithium in hexanes. The solution was quickly warmed to 0 ^oC and stirred for 2 h at 0 ^oC. A solution of **227** (103 mg, 0.187 mmol) in 1 mL of Et_2O was added to the reaction mixture which was stirred for 1 h at 0 ^oC. The mixture was hydrolyzed with MeOH (4 mL) and water (1 mL), the layers were separated and the aqueous phase was extracted with Et_2O (2 x 10 mL). The combined organic extract was dried (anhydrous Na_2SO_4), filtered, and concentrated. Purification of the crude residue by silica gel chromatography (6:4 hexanes-ethyl acetate) afforded **238** (68 mg, 60%, *dr* 2.5:1) as a brown oil: R_f 0.24 (8:2 hexanes-ethyl acetate); $[\alpha]^{19}{}_D$ – 49.6 (*c* 0.50, $CHCl_3$); IR (neat) 3443, 2925, 1516, 1462, 1248, 835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 3H), 0.07 (s, 3H), 0.91 (s, 9H), 1.10 (m, 21H), 1.50 (m, 1H), 1.93 (m, 1H), 2.29 (m, 1H), 2.36 (m, 1H), 3.40 (m, 2H), 3.82 (s, 3H), 4.04 (s, 2H), 4.30

(dd, *J* = 6.3, 9.2 Hz, 1H), 4.39 (s, 2H), 4.49 (m, 1H), 4.65 (s, 1H), 5.15 (s, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.0, -4.5, 11.9 (3C), 17.9 (6C), 18.0, 25.8 (3C), 28.7, 32.5, 44.9, 55.3, 63.7, 65.0, 68.9, 70.0, 72.4, 76.3, 111.7, 113.7 (2C), 129.3 (2C), 130.2, 147.9, 159.2; EI-HRMS calcd for $C_{33}H_{60}O_6Si_2Na$ $[M + Na]^+$ (*m/z*) 631.3826, found 631.3817.

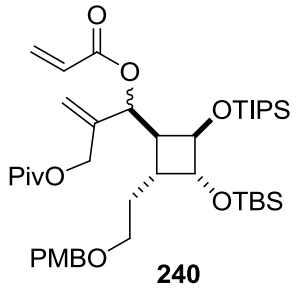


239

2-(((1*S*,2*R*,3*R*,4*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4(triisopropylsilyloxy)cyclobutyl)(hydroxy)methyl)allyl pivalate (239)

To a solution of **238** (10.0 mg, 0.016 mmol) in dry CH_2Cl_2 (0.2 mL) at 0°C was added pyridine (5.3 µL, 0.065 mmol), trimethylacetyl chloride (8.0 µL, 0.065 mmol) and *N*,*N*-dimethylaminopyridine (0.4 mg, 0.0032 mmol). The resultant mixture was stirred for 2 h at 0 ^{o}C and then quenched with satd aqueous NH_4Cl (10 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (silica gel, 15:85 ethyl acetate/hexanes) to provide **239** (10 mg, 90%) as a colorless oil: R_f 0.75 (8:2 hexanes-ethyl acetate); $[\alpha]^{20}_{D}$ – 42.3 (*c*

0.80, $CHCl_3$); IR (neat) 3517, 2960, 2937, 1867, 1731, 1614, 1520, 1466, 1252, 1147, 905, 843 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 3H), 0.07 (s, 3H), 0.90 (s, 9H), 1.09 (m, 21H), 1.21 (s, 9H), 1.50 (m, 1H), 1.92 (m, 1H), 2.30 (m, 2H), 3.34 (m, 2H), 3.82 (s, 3H), 4.30 (dd, *J* = 6.4, 9.2 Hz, 1H), 4.39 (s, 2H), 4.48 (m, 1H), 4.51 (s, 2H), 4.59 (s, 1H), 5.21 (s, 1H), 5.33 (s, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.0, -4.5, 11.9 (3C), 17.9 (6C), 18.0, 25.8 (3C), 27.1 (3C), 29.1, 29.7, 32.1, 38.8, 43.8, 55.2, 65.3, 68.4, 68.7, 72.5, 76.0, 76.3, 113.5, 113.7 (2C), 129.1 (2C), 130.6, 142.9, 159.0, 178.0; EI-HRMS calcd for $C_{38}H_{69}O_7Si_2$ $[M + H]^+$ (*m/z*) 693.4582, found 693.4604.

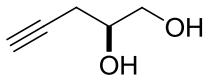


240

1-((1*S*,2*R*,3*R*,4*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)-2-(pivaloyloxymethyl)allyl acrylate (240)

To a CH_2Cl_2 (0.3 mL) solution of **239** (17 mg, 0.024 mmol) at 0 ^oC were added triethylamine (10.24 µL, 0.073 mmol), acryloyl chloride (4.0 µL, 0.048 mmol), and *N*,*N*-dimethylaminopyridine (0.58 mg, 0.2 mmol). The mixture was stirred at room temperature for 15 h. The reaction was quenched with satd aqueous NH_4Cl solution. The separated aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL) and the combined organic extract was dried (Na_2SO_4), filtered, and concentrated. Purification of the

crude residue by silica gel chromatography (hexanes-ethyl acetate, 94:6) furnished **240** (12.8 mg, 70%) as a colorless oil: R_f 0.55 (8.5:1.5 hexanes-ethyl acetate); $[\alpha]^{20}{}_D$ – 38.0 (*c* 0.15, $CHCl_3$); IR (neat) 2935, 2868, 1732, 1512, 1460, 1146, 1105, 840 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 3H), 0.06 (s, 3H), 0.91 (s, 9H), 1.05 (m, 21H), 1.21 (s, 9H), 1.50 (m, 1H), 1.95 (m, 1H), 2.37 (m, 2H), 3.37 (m, 2H), 3.82 (s, 3H), 4.37 (m, 4H), 4.55 (d, *J* = 13.8 Hz, 1H), 4.60 (d, *J* = 13.8 Hz, 1H), 5.16 (s, 2H), 5.54 (s, 1H), 5.85 (dd, *J* = 1.2, 10.3 Hz, 1H), 6.15 (dd, *J* = 10.4, 17.3 Hz, 1H), 6.40 (dd, *J* = 1.2, 17.2 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.0, -4.6, 12.1 (3C), 17.9 (6C), 18.0, 25.8 (3C), 27.2 (3C), 29.2, 29.7, 32.9, 38.8, 42.9, 55.2, 64.7, 68.6, 70.0, 72.5, 74.9, 75.6, 113.4, 113.7 (2C), 128.8, 129.1 (2C), 130.1, 130.4, 142.5, 159.0, 164.1, 178.0; EI-HRMS calcd for $C_{41}H_{70}O_8Si_2Na[M + Na]^+$ (*m/z*) 769.4507, found 769.4487.



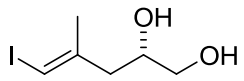
231

(*S*)-Pent-4-yne-1,2-diol (231)

To a solution of (trimethylsilyl)acetylene (**244**, 2.80 mL, 20.23 mmol) in THF (10 mL) at –78 °C was added dropwise *n*-butyllithium in hexane (2.5M, 8.10 mL, 10.23 mmol). After 30 min, the mixture was added to a stirred solution of (*R*)-glycidol (**232**, 0.89 mL, 13.49 mmol) and *n*-butyllithium in hexane (5.90 mL, 14.83 mmol) in THF (20 mL) at -78 °C. The reaction mixture was allowed to warm to ambient temperature and was stirred for 18 h. The reaction was quenched by addition of satd aqueous NH_4Cl

solution (50 mL), the layers were separated and the aqueous layer was extracted with Et_2O (2 x 20 mL). The combined organic layer was washed with brine, dried (Na_2SO_4) and concentrated. The crude residue (1.72 g) was used directly for the next step.

The crude residue (1.72 g) obtained above was dissolved in MeOH (25 mL) and to the solution was added K_2CO_3 (4.12 g, 29.9 mmol). The reaction mixture was stirred at room temperature for 15 h, then filtered and concentrated. The crude residue was purified by silica gel chromatography (6:4, ethyl acetate/hexanes) to give **231** (0.85 g, 85%) as a colorless sticky oil: R_f 0.25 (3:7 hexanes-ethyl acetate); $[\alpha]^{21}_D$ + 6.5 (*c* 1.0, $CHCl_3$) [lit.[13b] $[\alpha]^{23}_D$ + 7.1 (*c* 1.01, CH_2Cl_2)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.08 (t, *J* = 2.6 Hz, 1H), 2.45 (ddd, *J* = 1.2, 2.6, 6.3 Hz, 2H), 3.61 (dd, *J* = 6.5, 11.3 Hz, 1H), 3.77 (dd, *J* = 3.4, 11.3 Hz, 1H), 3.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.3, 65.3, 70.1, 70.8, 80.1.

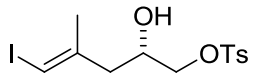


246

(*S*,*E*)-5-Iodo-4-methylpent-4-ene-1,2-diol (246)

To a suspension of Cp_2ZrCl_2 (334.4 mg, 1.14 mmol) in DCE (1.0 mL) at room temperature was added slowly $AlMe_3$ (0.3 mL, 3.12 mmol) and the mixture was stirred for 15 min. The solution was cooled to 0 ^{o}C and a solution of **231** (105.0 mg, 1.04 mmol) in DCE (1.1 mL) was added via cannula. The mixture was stirred for 41 h at room temperature, then was cooled to – 30 ^{o}C and a solution of I_2 in Et_2O (3.0 mL)

was added. The mixture was stirred for 45 min – 30 ^{o}C, then was allowed to warm to 0 ^{o}C and the reaction was quenched with satd sodium potassium tertarate solution (30 mL) and pentane (20 mL). The layers were separated and the aqueous layer was extracted with EtOAc (6 x 30 mL). The combined organic extract was dried (Na_2SO_4), filtered and concentrated, and the crude residue was purified by silica gel chromatography (55:45 ethyl acetate/hexanes) to give **246** (154 mg, 60%) as a colorless oil: R_f 0.25 (3:7 hexanes-ethyl acetate); $[\alpha]^{21}_{D}$ – 10.4 (*c* 0.65, $CHCl_3$); IR (neat) 3361, 2921, 2871, 1271, 1151 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.91 (d, *J* = 0.8 Hz, 3H), 2.39 (dd, *J* = 8.3, 11.1 Hz, 2H), 3.46 (dd, *J* = 10.6, 6.9 Hz, 1H), 3.88 (m, 1H), 6.06 (q, *J* = 0.8 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.2, 43.2, 66.2, 69.6, 77.6, 144.6; EI-HRMS calcd for $C_6H_{11}O_8IO_2[M]^+$ (*m/z*) 241.9804, found 241.9910.

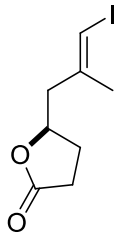


230

(*S*,*E*)-2-Hydroxy-5-iodo-4-methylpent-4-enyl 4-methylbenzenesulfonate (230)

To a solution of **246** (2.53 g, 10.45 mmol) in pyridine (25.0 mL) at 0 ^{o}C was added *p*-tolylsulfonyl chloride (2.19 g, 11.50 mmol) and the mixture was stirred at 4 ^{o}C for 20 h. The reaction was quenched with water (100 mL), the layers were separated and the aqueous layer was extracted with EtOAc (4 x 50 mL). The combined organic extract was dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by silica gel chromatography (22:88 ethyl acetate/hexanes) to afford **230** (3.18 g, 76%) as a colorless oil: R_f 0.66 (7:3 hexanes/ethyl acetate); $[\alpha]^{18}_{D}$ + 5.8 (*c* 0.85, $CHCl_3$); IR

(neat) 3517, 2910, 2848, 1361, 1170, 1096, 976 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.86 (d, *J* = 0.8 Hz, 3H), 2.38 (d, *J* = 6.1 Hz, 2H), 2.48 (s, 3H), 3.92 (dd, *J* = 5.6, 9.4 Hz, 1H), 4.03 (m, 2H), 6.00 (s, 1H), 7.39 (d, *J* = 8.06 Hz, 2H), 7.82 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 24.0, 42,7, 67.1, 72.7, 78.4, 128.0 (2C), 130.0 (2C), 132.4, 143.1, 145.2; CI-HRMS calcd for $C_{13}H_{18}O_4SI$ $[M + H]^+$ *m/z* 396.9971, found *m/z* 396.9956.

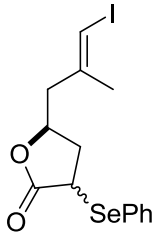


248

(*R*,*E*)-5-(3-Iodo-2-methylallyl)dihydrofuran-2(3H)-one (248)

To a stirred solution of ethoxyacetylene (**247**, 40% solution w/w in hexanes, 78.9 µL, 0.33 mmol) in THF (2.0 mL) at – 78 ^{o}C was added a solution of *n*-BuLi (2.5 M) in hexanes (0.13 mL, 0.32 mmol). The mixture was stirred at – 78 ^{o}C for 1 h and a solution of **230** (22.0 mg, 0.05 mmol) in THF (1.0 mL) was added dropwise. The reaction mixture was stirred at – 78 ^{o}C for 2 h, then was warmed to 0 ^{o}C and $BF_3.OEt_2$ (27.9 µL, 0.22 mmol) was added. The mixture was stirred at 0 ^{o}C for 1 h, after which the reaction was quenched by addition of a satd aqueous solution of $NaHCO_3$. The resulting mixture was diluted with Et_2O (10 mL) and water (10 mL), and the separated aqueous phase was extracted with Et_2O (2 x 20 mL). The combined organic extract was dried (Na_2SO_4), filtered, and concentrated to leave a crude oil.

To an EtOH (1.00 mL) solution of the crude oil obtained above was added *p*-toluenesulfonic acid (10.0 mg) and the mixture was stirred at room temperature for 18 h. The reaction was quenched with satd aqueous $NaHCO_3$ and the mixture was diluted with EtOAc (5 mL). The separated aqueous phase was extracted with EtOAc (2 x 10 mL) and the combined organic extract was dried (Na_2SO_4), filtered, and concentrated. Chromatographic purification (silica gel, 25:75 ethyl acetate/hexanes) of the residue gave **248** (8.0 mg, 57%) as a colorless oil: R_f 0.4 (6:4 hexanes-ethyl acetate); $[\alpha]^{20}{}_D$ -82.8 (*c* 0.85, $CHCl_3$); IR (neat) 2923, 2851, 1768, 1456, 1174 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.86-1.90 (m, 1H), 1.92 (d, *J* = 1.0 Hz, 3H), 2.28-2.38 (m, 1H), 2.51 (dd, *J* = 8.7, 14.1 Hz, 1H), 2.56 (dd, *J* = 6.9, 9.5 Hz, 2H), 2.66 (dd, *J* = 7.2, 14.3 Hz, 1H), 4.63 (m, 1H), 6.11 (q, *J* = 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4, 27.6, 28.5, 44.9, 78.3, 78.6, 142.7, 176.6; EI-HRMS calcd for $C_8H_{11}O_2I$ $[M]^+$ (*m/z*) 265.9804, found 265.9799.



228 (*dr* 1.4:1)

(*S*,*E*)-5-(3-Iodo-2-methylallyl)-3-(phenylselenyl)dihydrofuran-2(3*H*)-one (228)

To a solution of α-selenoacetic acid (**252**, 4.48 g, 20.74 mmol) in anhydrous THF (20 mL) was added slowly LiHMDS (45.6 mL, 45.65 mmol, 1M solution in THF) at -78 ^oC. The mixture was stirred at – 78 ^oC for 1 h and a solution of **230** (3.18 g, 8.01

mmol) in THF (20 mL) was added. The reaction mixture was stirred at -78 ^{o}C for 30 min and then at 0 ^{o}C for 1 h. The mixture was warmed to room temperature and was stirred at room temperature for 2 h. To the mixture was added 1N NaOH (85 mL) and the layers were separated. The organic layer was discarded and the aqueous layer was acidified with 1N HCl (125.0 mL) and extracted with Et_2O (3 x 50 mL). The combined organic extract was dried (Na_2SO_4), filtered and concentrated to give a crude oil.

The crude oil obtained above was immediately dissolved in dry benzene (20 mL) and TsOH.H_2O (180 mg, 0.94 mmol, 10 mol%) was added to the solution. The mixture was refluxed for 16 h and the reaction was quenched with satd aqueous $NaHCO_3$ solution. The aqueous layer was extracted with Et_2O (2 x 30 mL) and the organic extract was dried (Na_2SO_4), filtered and concentrated. Purification of the crude residual oil by silica gel chromatography (15:85 ethyl acetate: hexanes) gave an inseparable mixture (1.4:1) of stereoisomers **228** (1.82 g, 54% based on **230**) as a viscous yellow oil: R_f 0.31 (8:2 hexanes/ethyl acetate); IR (neat) 2918, 2847, 1767, 1434 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ **major**: 1.85 (s, 3H), 2.35 (dd, *J* = 5.4, 7.5 Hz, 2H), 2.45 (dd, *J* = 5.8, 14.4 Hz, 1H), 2.61 (dd, *J* = 7.1, 14.2 Hz, 1H), 3.96 (t, *J* = 5.4 Hz, 1H), 4.40 (m, 1H), 6.06 (s, 1H), 7.40 - 7.50 (m, 3H), 7.65 – 7.75 (2H); **minor**: 1.83 (d, *J* = 1.0 Hz, 3H), 1.96 (ddd, *J* = 7.9, 9.1, 13.7 Hz, 1H), 2.29 – 2.36 (m, 1H), 2.48 (dd, *J* = 7.1, 14.4 Hz, 1H), 2.75 (ddd, *J* = 6.7, 9.4, 13.7 Hz, 1H), 4.02 (t, *J* = 9.3 Hz, 1H), 4.55 – 4.65 (m, 1H), 6.01 (q, *J* = 1.0 Hz, 1H), 7.40 – 7.50 (m, 3H), 7.65 – 7.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ **major**: 24.2, 36.4, 36.7, 44.5, 76.9,

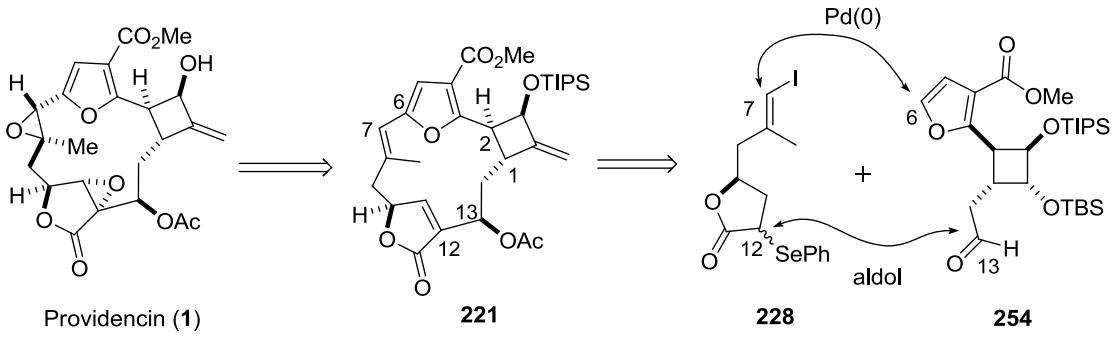
78.7, 126.5, 129.3, 129.5 (2C), 135.9 (2C), 142.3, 175.2; **minor**: 24.5, 35.2, 36.9, 44.8, 76.9, 78.8, 126.8, 129.1, 129.4 (2C), 135.9 (2C), 142.3, 175.2; CI-HRMS calcd for $C_{14}H_{16}O_2SeI$ $[M + H]^+$ *m/z* 422.9361, found *m/z* 422.9350.

CHAPTER 5

Third Generation Approach Towards Providencin

5.1 Third generation retrosynthetic analysis of providencin

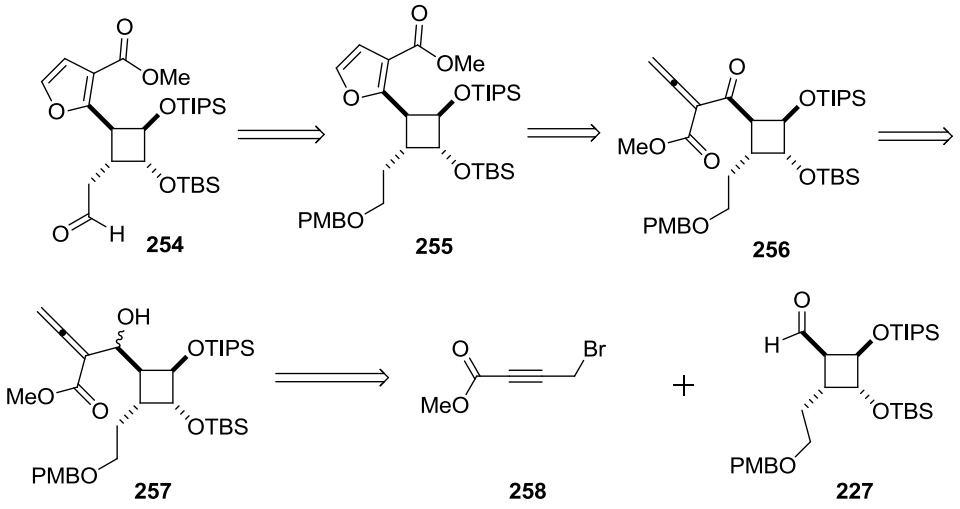
In a variant of our previous strategy, we foresaw that the core structure **221** of providencin could be assembled in principle from two major fragments, vinyl iodide **228** and cyclobutylfuran **254**. We envisioned that the C_6-C_7 bond of **221** could be forged either via palladium-catalyzed C-H activation[1] at C6 of furan **254** or by Stille cross-coupling[2] between vinyl iodide **228** and a 6-stannyl derivative of **254**. In this scenario, the C_{12}-C_{13} bond would be acquired by an aldol coupling (Scheme 5.1).



Scheme 5.1 Third generation strategy for providencin (**1**)

Since synthesis of the α-seleno lactone fragment **228** had already been accomplished in our second generation synthesis, we now focused on synthesis of the

cyclobutylfuran subunit **254**. We envisioned that aldehyde **254** would be available from **255** and that the furan ring of this moiety would be installed from **256** using Marshall's allenone-to-furan isomerization[3] protocol (Scheme 5.2). Allenic ketone **256** would be prepared from allenic alcohol **257** which would be obtained from alkynyl bromide **258** and aldehyde **227** using Harada's procedure.[4] The latter was already in hand from our second generation approach to providencin.

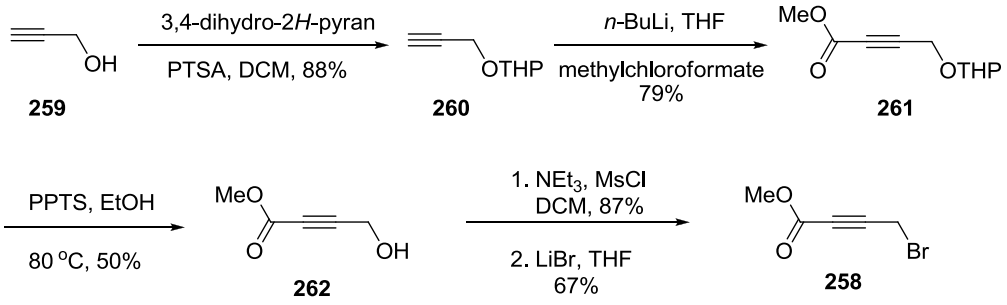


Scheme 5.2 Retrosynthetic analysis of cyclobutylfuran fragment **254**

5.2 Synthesis of the cyclobutylfuran fragment of providencin

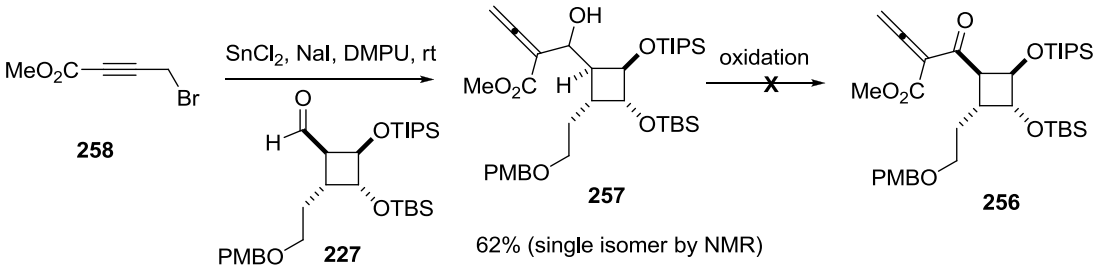
This third generation approach commenced with the preparation of bromide **258** from propargyl alcohol (**259**). Formation of the tetrahydropyranyl ether of **260** and subsequent deprotonation of alkyne **260** with *n*-butyllithium was followed by reaction with methyl chloroformate to afford ester **261**. Acid-catalyzed cleavage of the

tetrahydropyranyl ether of **261** gave alcohol **262** which was converted to the corresponding bromide **258**.[5]



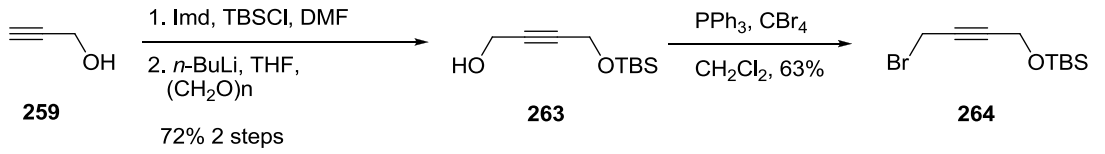
Scheme 5.3 Synthesis of alkynyl bromide **258**

When the organostannane derived from alkyne **258** in the presence of tin(II) chloride and sodium iodide was treated with aldehyde **227**, we were pleased to find that allenol **257** was formed in 62% yield and as a single diastereomer (Scheme 5.4). The configuration at the secondary alcohol center of **257** was not determined due to the fact that it would be oxidized at the next step to a ketone. However, all attempts to oxidize this alcohol to allenone **256** using Dess Martin reagent, tetra-*n*-propylammonium perruthenate or Swern conditions led to a complex mixture of unknown compounds. We speculate that since allenone **256** possesses an allenic moiety conjugated with two different carbonyl groups, it would be a highly reactive Michael acceptor and could lead to a complex mixture of products under these oxidation conditions.

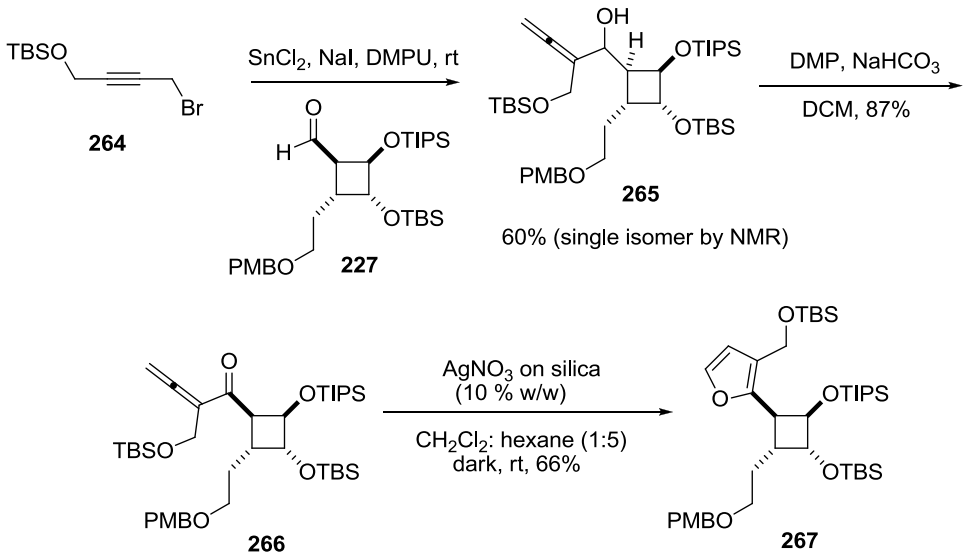


Scheme 5.4 Synthesis of allenol **257**

This oxidation problem was solved by using a modified alkynyl bromide **264**[6] as the alkylating partner for aldehyde **227**. First, propargyl alcohol (**259**) was protected as its *t*-butyldimethylsilyl ether, after which deprotonation of the alkyne with *n*-butyllithium followed by addition of paraformaldehyde gave alcohol **263**. This alcohol was converted to bromide **264** with carbon tetrabromide and triphenylphosphine in good overall yield (Scheme 5.5).

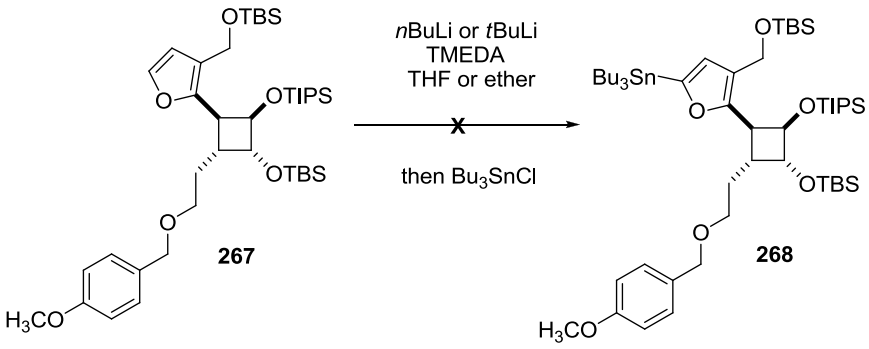


Scheme 5.5 Synthesis of alkynyl bromide **264**



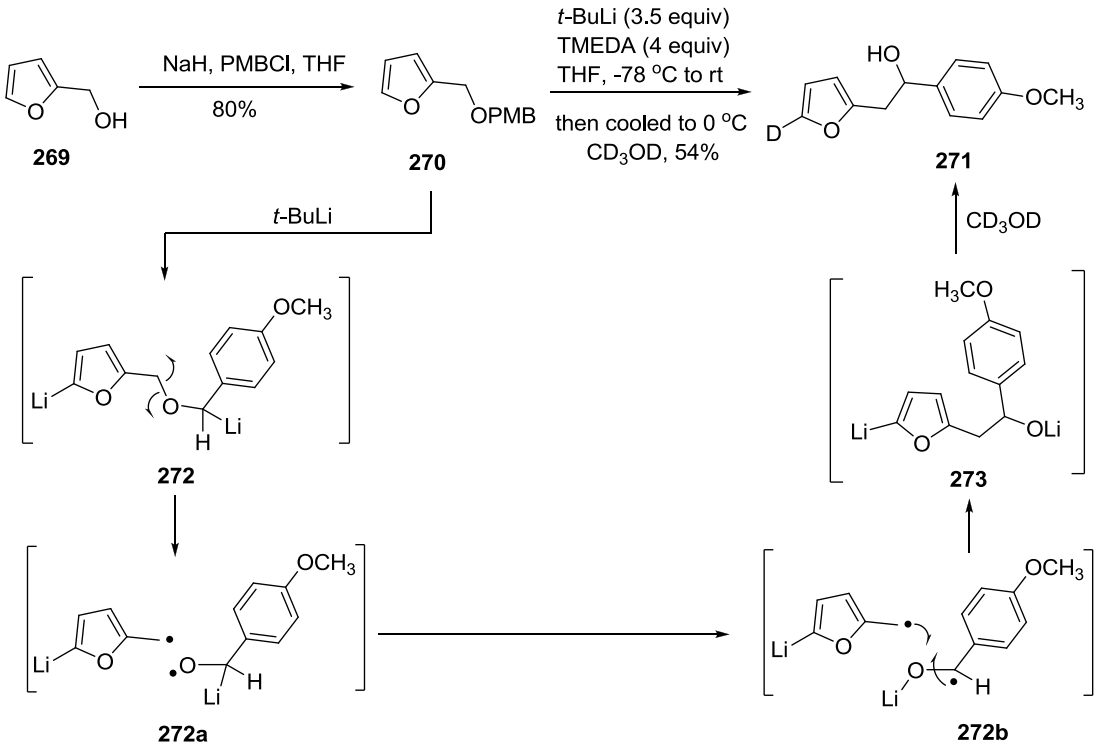
Scheme 5.6 Synthesis of cyclobutylfuran **267**

Treatment of the organostannane species prepared from **264** with aldehyde **227** afforded a single diastereomer of allenol **265** in 60% yield (Scheme 5.6). Oxidation of **265** with Dess-Martin periodinane smoothly converted the alcohol to allenone **266**, and exposure of this ketone to 10% silver nitrate on silica gel in a mixed solvent system furnished our desired furan **267**. The overall yield of **267** from **227** was 35%.



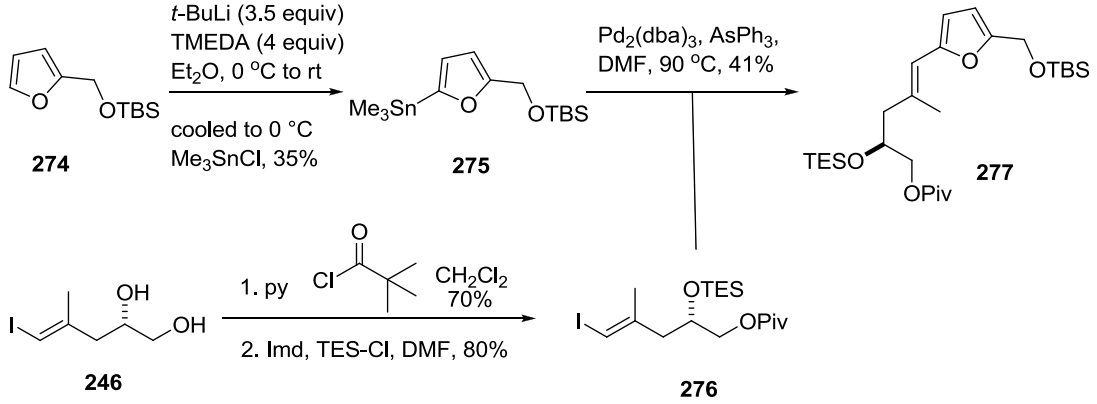
Scheme 5.7 Attempted synthesis of furylstannane **268**

Our initial intention was to convert furan **267** to the stannane derivative **268** so that we could link **268** with vinyl iodide **228** via a Stille cross-coupling experiment. Unfortunately, all efforts to functionalize the C-5 position of furan **267** with either *n*-butyllithium or *t*-butyllithium and tri-*n*-butyltin chloride led to a complex mixture of unknown compounds (Scheme 5.7). We speculated that the *p*-methoxybenzyl protecting group in **267** was interfering with deprotonation of the furan in these experiments and to prove this hypothesis we used the same reaction conditions on model furan **270**.



Scheme 5.8 Rearrangement of furan **270** with *t*-butyllithium

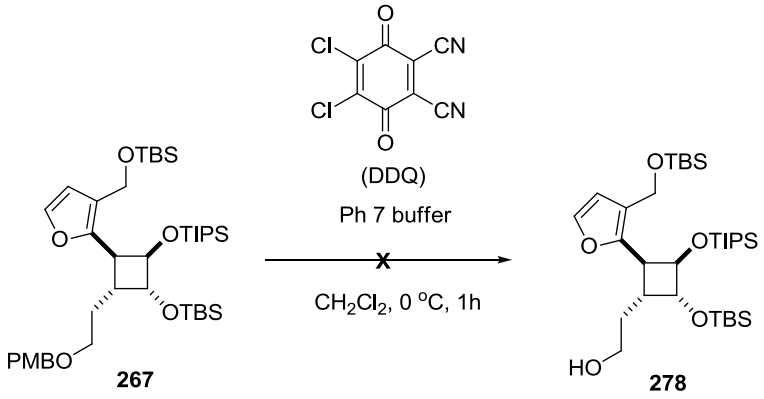
When *p*-methoxybenzyl ether **270** was treated with *t*-butyllithium and tetramethylethylenediamine (TMEDA) at low temperature and the mixture was quenched with deuterated methanol, rearranged product **271** was isolated in 54% yield. The structure of **271** was established by NMR analysis and mass spectrometry (Scheme 5.8). A [1,2]-Wittig rearrangement[7] of dianion **272** would generate **273** which was trapped by deuterated methanol.



Scheme 5.9 Synthesis of furyl stannane **275** and a model Stille coupling with **276**

Since the presence of a *p*-methoxybenzyl group in **270** turned out to be the problematic actor in the deprotonation of this furan, we explored analogous chemistry with *t*-butyldimethylsilyl ether **274**. When furan **274** was allowed to react with *t*-butyllithium and tetramethylethylenediamine (TMEDA) at -78 ^{o}C and then with trimethyltin chloride, we were pleased to obtain furyl stannane **275** after purification on neutral alumina, albeit in low yield (Scheme 5.9). With furyl stannane **275** in hand, we attempted a model Stille cross-coupling with vinyl iodide **276**. Vinyl iodide **276** was prepared from diol **246** in two steps, first by selective formation of the pivaloyl

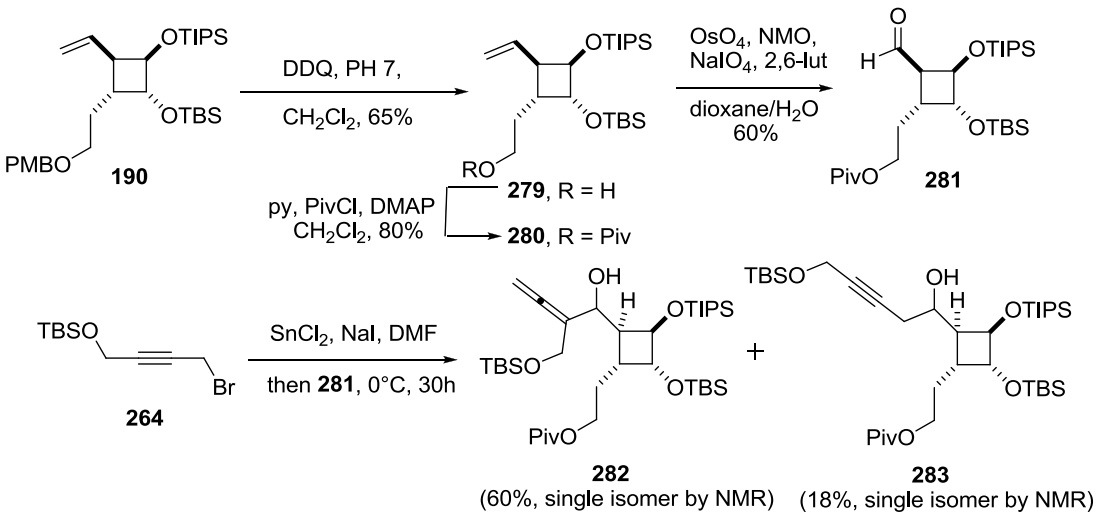
ester of the primary alcohol (yield 70%) and then trimethylsilyl protection of the remaining secondary alcohol (yield 80%). Coupling of stannane **275** with **276** in the presence of tris(dibenzylideneacetone)dipalladium(0) and triphenylarsine in hot dimethylformamide produced (*E*)-alkene **277** in an unoptimized 41% yield, a result that gave confidence to our plan for the final stage assembly of the complete providencin skeleton.



Scheme 5.10 Attempted cleavage of *p*-methoxybenzyl ether **267**

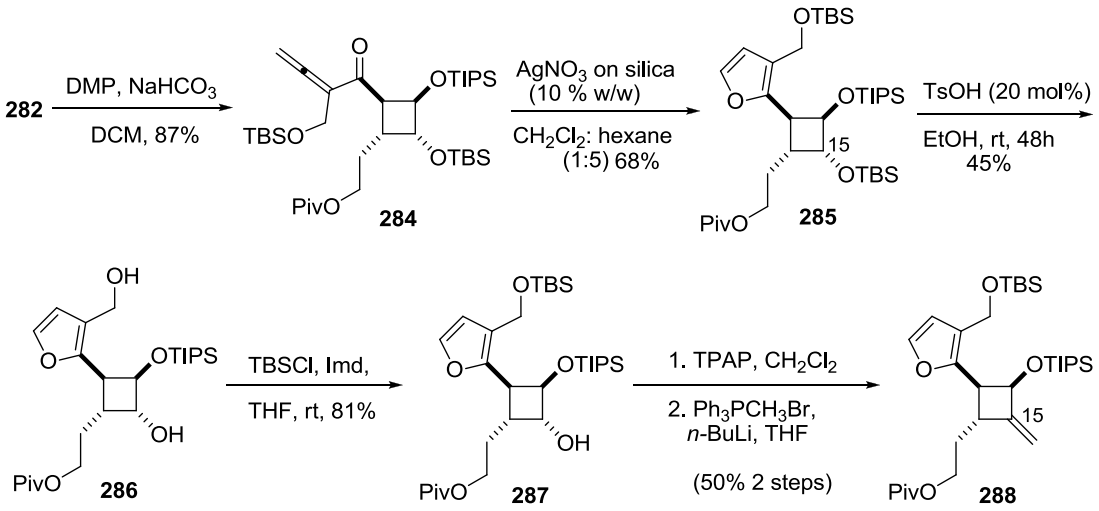
However, when **267** was treated with 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ) to cleave the *p*-methoxybenzyl ether, a complex mixture of compounds was obtained. Proton NMR of the crude reaction mixture showed the presence of *p*-methoxybenzyl aldehyde, the expected byproduct from oxidation of the *p*-methoxybenzyl group of **267**, along with many unknown compounds. We suspected that the electron-rich disubstituted furan ring of **267**, acting as a potential diene, might undergo Diels-Alder cycloaddition with 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ) along with other side reactions,

generating a complex mixture. In light of this disappointing result, we adopted a modified route to the cyclobutylfuran portion of providencin. The important modification made in this revision was removal of the *p*-methoxybenzyl ether before furan formation and its replacement by a pivaloyl group.



Scheme 5.11 Synthesis of allenol **282** and alkynol **283**

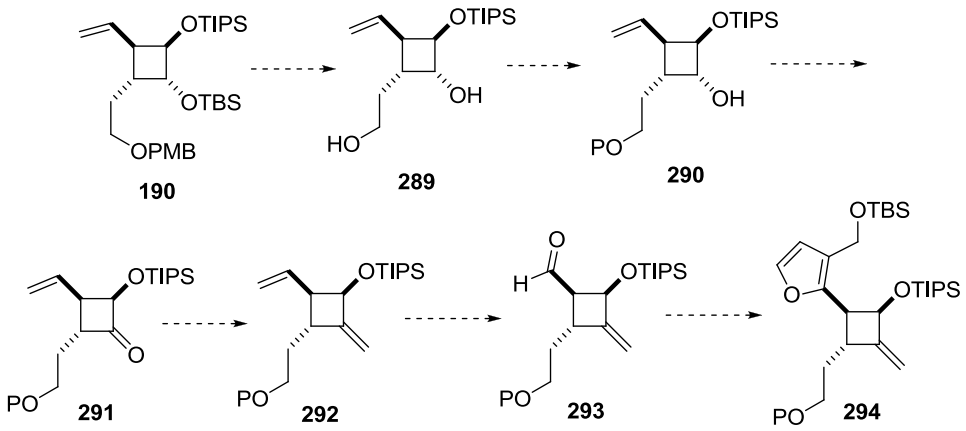
The new route began with removal of the *p*-methoxybenzyl group from **190** with 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ) and subsequent esterification of alcohol **279** with pivaloyl chloride to afford **280** (Scheme 5.11). Oxidative cleavage of the vinyl moiety of **280** then gave aldehyde **281** in moderate yield. Addition of the organostannane, prepared in situ from bromide **264**, to aldehyde **281** at 0 ^{o}C gave **282** and **283** with the desired allenic alcohol **282** as the major product.



Scheme 5.12 Synthesis of "northern sector" of providencin

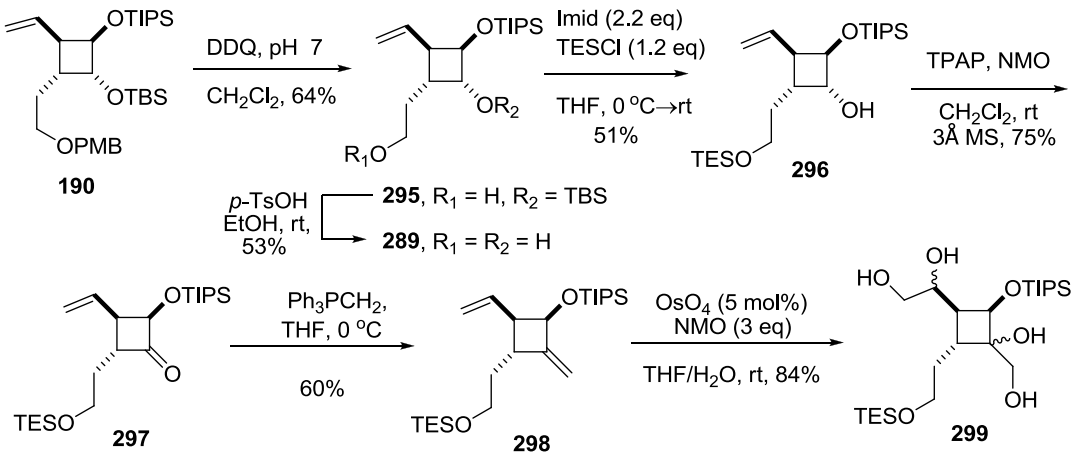
After chromatographic purification, allenol **282** was oxidized to allenic ketone **284** with Dess-Martin reagent, and the ketone was treated with silver nitrate in the dark to furnish furan **285** (Scheme 5.12). At this stage, we attempted to install the exo methylene moiety at C15 of providencin and thus **285** was treated with catalytic amount of *p*-toluenesulfonic acid in ethanol to cleave both *t*-butyldimethylsilyl ethers. Monitoring this reaction by thin layer chromatography revealed that the cleavage of the primary *t*-butyldimethylsilyl group of **285** was a relatively fast process and that cleavage of the more hindered secondary silyl ether was very slow at room temperature. Heating the reaction mixture at 60 ^{o}C to accelerate silyl ether cleavage led to decomposition. The best result was obtained when **285** was allowed to react with 20 mol% of *p*-toluenesulfonic acid for 48 hours at room temperature to give a 45% yield of diol **286** after which the primary alcohol of **286** was reprotected selectively as its *t*-butyldimethylsilyl ether **287**. Oxidation of secondary alcohol **287**

by tetra-*n*-propylammonium perruthenate to a ketone and Wittig olefination[8] of this cyclobutanone yielded **288**, thus completing a route to the "northern sector" of providencin. However, the low efficiency (yield 45%) of the deprotection step (**285→286**) caused us to change the protecting group at C15 in an earlier stage of the synthesis.



Scheme 5.13 A modified route to the cyclobutylfuran segment of providencin

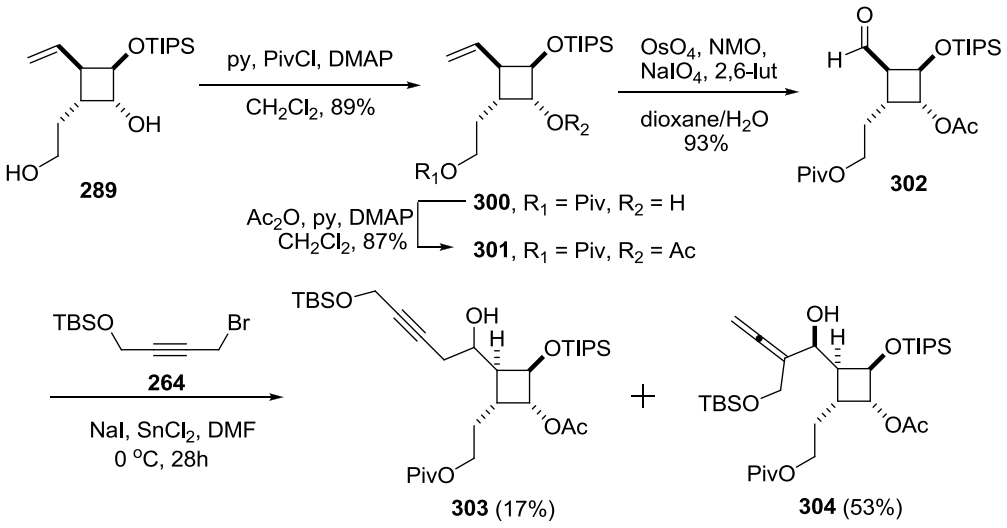
In this revised plan, we intended to install the exo-methylene moiety of the cyclobutane at an early stage of our synthesis after removal of both the *p*-methoxybenzyl and *t*-butyldimethylsilyl groups from **190**. This would deliver diol **289** (Scheme 5.13), the primary alcohol of which would be selectively protected as **290**. Oxidation of the secondary alcohol to a ketone followed by Wittig olefination would then afford diene **292**. Selective oxidative cleavage of the more exposed alkene functionality of **292** would provide aldehyde **293** which would be transformed into the desired cyclobutylfuran **294** following the protocol used earlier.



Scheme 5.14 Preparation of diene **298**

In the forward direction, cleavage of the *p*-methoxybenzyl ether[9] of **190** by 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ) to alcohol **295** was followed by acid-catalyzed removal of the *t*-butyldimethylsilyl group to afford diol **289** (Scheme 5.14). The primary alcohol of **289** was selectively protected as its triethylsilyl ether **296**, and subsequent oxidation of the remaining secondary alcohol gave cyclobutanone **297**. Wittig olefination of **297** with methylenetriphenylphosphorane smoothly installed the exo methylene function in **298** to yield diene **298**. However attempts, to react the more exposed vinyl moiety of **298** with either osmium tetraoxide-sodium periodate[10] or with potassium osmate, or with AD-mix-β[11] returned only starting material. When catalytic osmium tetraoxide and *N*-methylmorpholine *N*-oxide (NMO) were used with **298**, tetraol **299** was isolated in 84% yield. The lack of selectivity in osmylation of **298** and consequently our inability to transform diene **298** into aldehyde **293** caused us to abandon this strategy. Instead of installing the exo methylene group at this early stage of our synthesis, it was

decided to defer this step. Also, the labile nature of the triethylsilyl protection in **296** made it advisable to replace this entity with a more robust protecting group.



Scheme 5.15 Synthesis of alkynol **303** and allenol **304**

In this revised plan, the primary hydroxyl group of diol **289** was selectively converted[12] to its pivalate ester **300** and the secondary alcohol was protected as an acetate[13] to afford diester **301** (Scheme 5.15). Osmium tetraoxide-sodium periodate[14] mediated cleavage of alkene **301** yielded aldehyde **302** and then the latter was treated with the organostannane species prepared in situ from alkynyl bromide **264**. The desired allenol **304** was obtained as a single diastereoisomer along with alkynol **303** which was separated from **304** by silica gel chromatography.

5.3 Mosher ester analysis of allenol 304

Although the hydroxyl configuration of **304** is inconsequential from the viewpoint of access to cyclobutylfuran **310**, we nevertheless decided to determine the

stereochemistry at the secondary alcohol center of this allenol. In order to accomplish that, the method of Mosher was used.[15] The Mosher method employs esterification of a chiral secondary alcohol with (*R*) and (*S*)-2-methoxy-2-trifluoromethylphenylphenylacetyl chloride, analysis of chemical shift differences in NMR spectra of the resultant diastereoisomer provides a reliable means for assigning their absolute configuration.

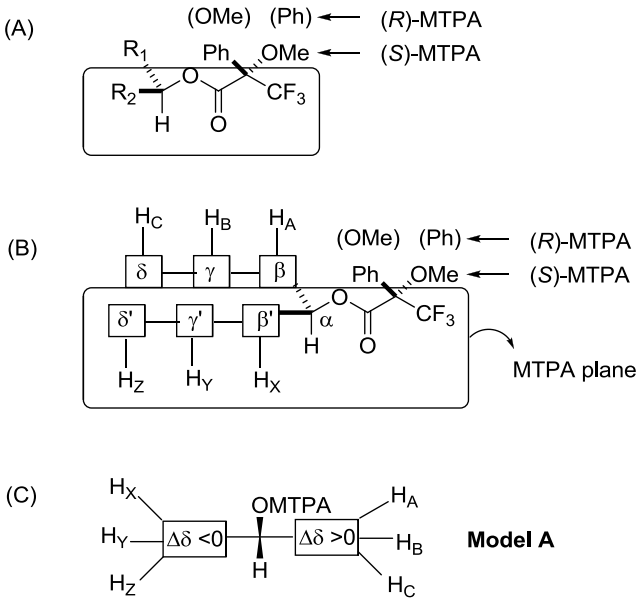


Figure 5.1 Mosher model for determination of the absolute configuration of a secondary alcohol

Figure 5.1 shows the concept underlying the Mosher method (A), including its extended application (B) using high-field NMR measurements of proton chemical shifts. An idealized conformation of a Mosher ester is depicted in Figure 5.1B (for convenience, the plane and the conformation of the *α*-methoxy-*α*-

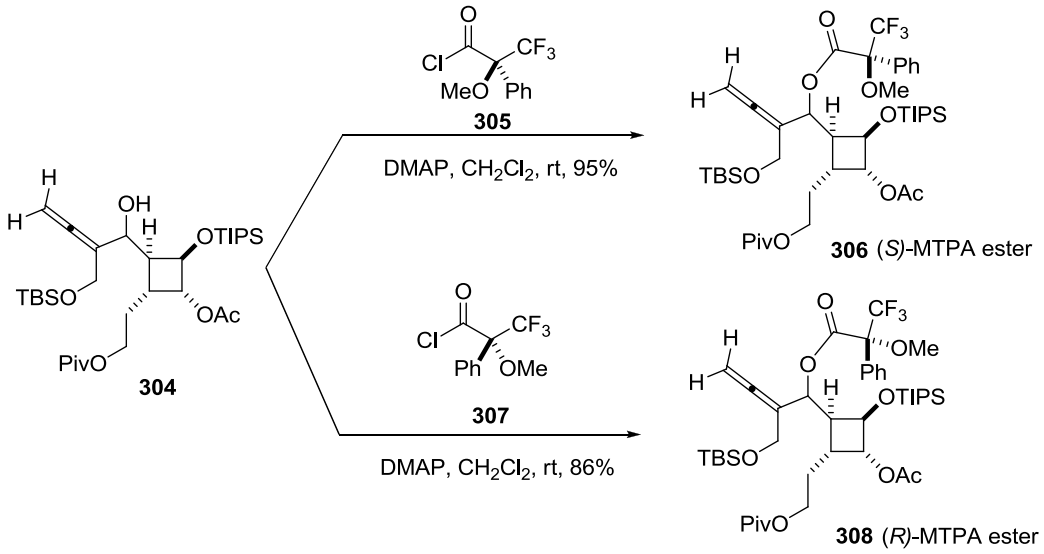
trifluoromethylphenylacetyl (MTPA) group will be called the MTPA plane and the ideal conformation, respectively). Due to the diamagnetic shielding effect of the phenyl ring, the $H_{A,B,C,...}$ NMR signals of the (*R*)-MTPA ester should appear upfield relative to those of the (*S*)-MTPA ester. The reverse should hold true for $H_{X,Y,Z}$. Therefore, if $\Delta\delta = \delta S - \delta R$, protons on the right side of the MTPA plane (Figure 5.1B) should have positive values ($\Delta\delta > 0$) and protons on the left side of the plane should have negative values ($\Delta\delta < 0$). This is illustrated in Figure 5.1C. Now, Mosher's method can be extended using the following protocol:

(1) Assign as many proton chemical shifts as possible with respect to each of the (*R*)- and (*S*)-MTPA esters.

(2) Obtain $\Delta\delta$ values for those protons.

(3) Put the protons with positive $\Delta\delta$ on the right side and those with negative $\Delta\delta$ on the left side of model A (Figure 5.1C).

(4) Construct a molecular model of the compound in question and confirm that all the assigned protons with positive and negative $\Delta\delta$ values are actually found on the right side and left side of the MTPA plane, respectively. The absolute values of $\Delta\delta$ must be proportional to the distance from the MTPA moiety.



Scheme 5.16 Preparation of (*S*)- and (*R*)-MTPA esters of **304**

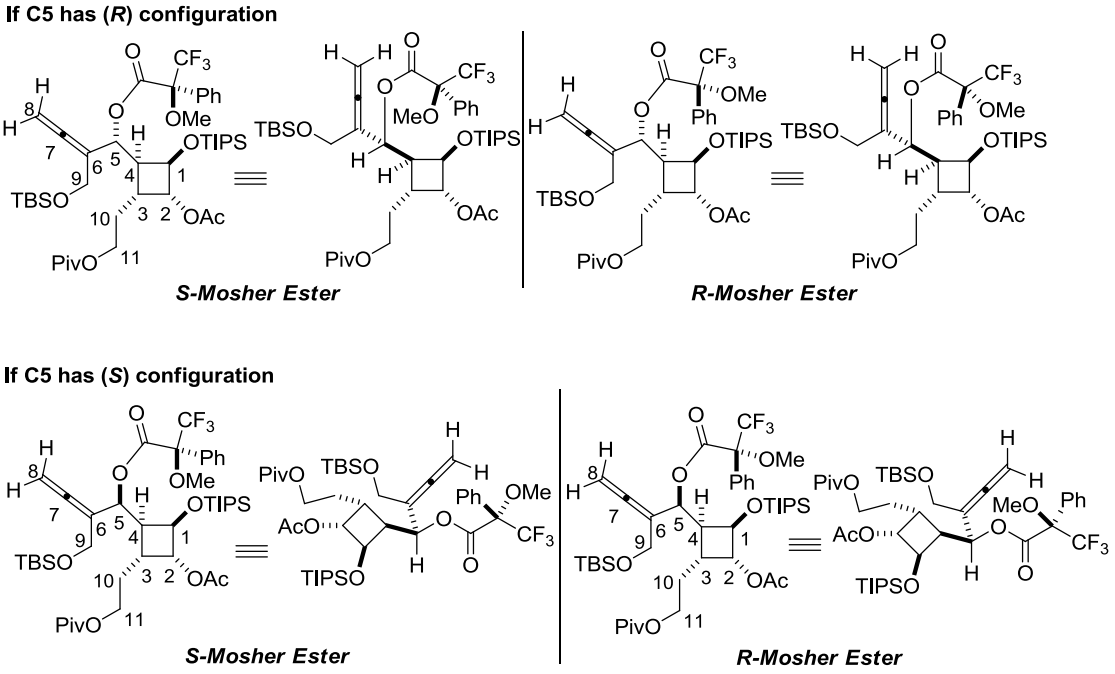
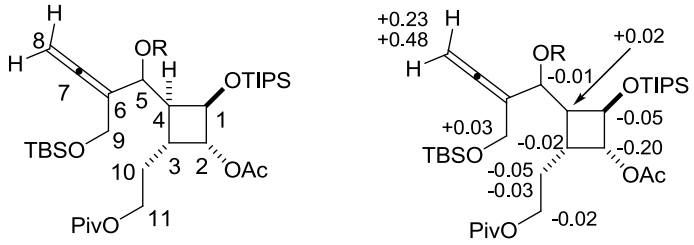


Figure 5.2 Conformations of MTPA esters of **304** with (5*R*)- and (5*S*)-configuration

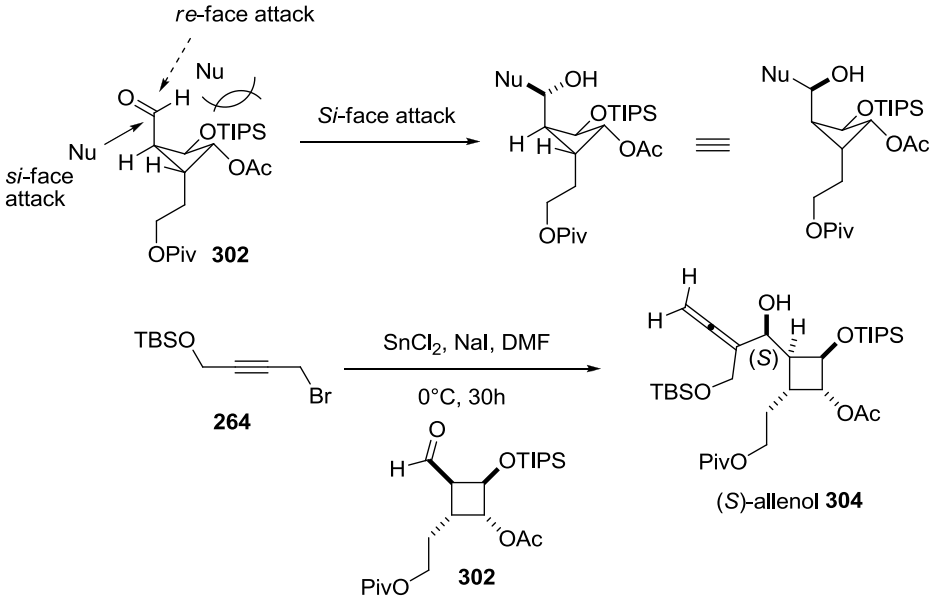
Thus, (*R*)- and (*S*)-MTPA esters were prepared from allenol **304** by reaction with (*R*)- and (*S*)-*α*-methoxy-*α*-trifluoromethylphenylacetyl chloride (**305** and **307** respectively) and 4-dimethylaminopyridine (DMAP) (Scheme 5.16). In Figure 5.2, the conformations of MTPA esters with possible (*R*)- and (*S*)-C5 configuration have been depicted. In the case where C5 has (*R*) configuration, the $\Delta\delta = \delta S - \delta R$ values for the cyclobutane substituent would be positive and those for the allene substituent would be negative. On the other hand, if C5 has (*S*) configuration, the $\Delta\delta = \delta S - \delta R$ values for the cyclobutane substituent would be negative and those for the allene substituent would be positive. Comparison of proton NMR spectra of (*S*)-MTPA ester **306** and (*R*)-MTPA ester **308** proved that allenol **304** has (*S*) configuration at the alcohol center.



Chemical Shift (ppm)	H_1	H_2	H_3	H_4	H_{10}	H_{11}	H_5	H_8	H_9
δS	4.50	5.14	2.62	2.67	1.71 1.54	3.91	5.52	4.95 4.86	4.36
δR	4.55	5.34	2.65	2.65	1.76 1.57	3.93	5.53	4.72 4.38	4.33
Δδ(δS-δR)	-0.05	-0.20	-0.02	+0.02	-0.05 -0.03	-0.02	-0.01	+0.23 +0.48	+0.03

Table 5.1 Measured δ values of protons in the NMR spectra of (*R*)- and (*S*)- MTPA esters of **304**

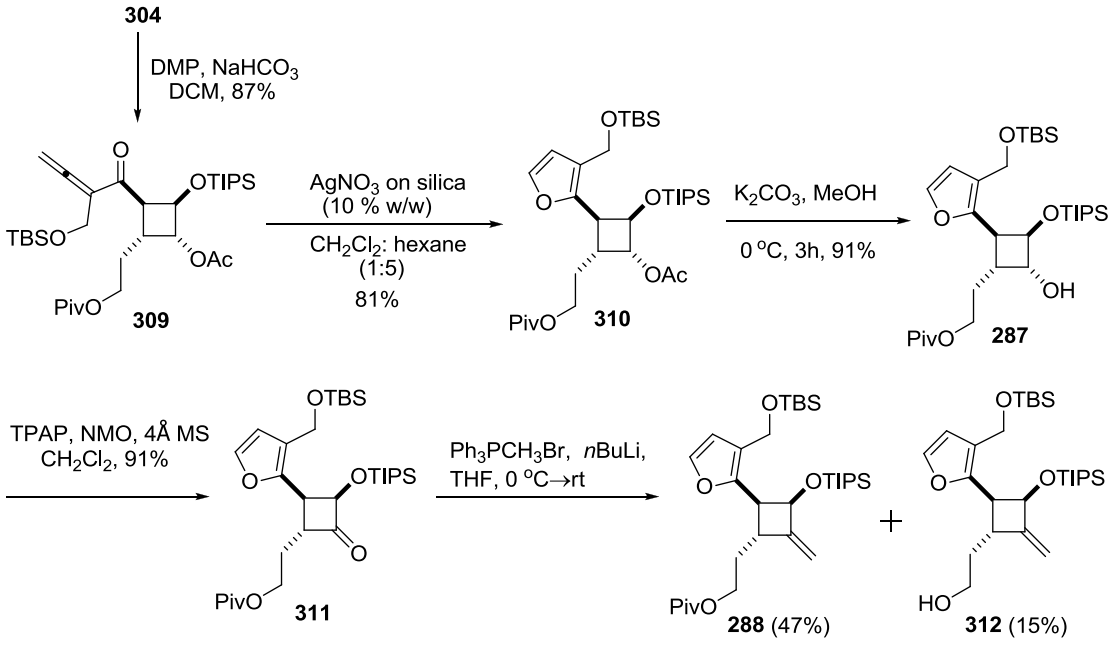
This conclusion mandates that attack of the stannane nucleophile at the aldehyde carbonyl of **302** takes place from the *si*-face. A molecular model shows that attack at the *re*-face of aldehyde **302** would be hindered by the bulky triisopropylsilyl group whereas approach of the stannane from the *si*-face is opposed only by a hydrogen atom. The much more favorable attack at the aldehyde of **302** from its *si*-face thus leads to (*S*)-allenol **304**, exclusively (Scheme 5.17).



Scheme 5.17 Stereoelectronic explanation for the formation of (*S*)-allenol **304**

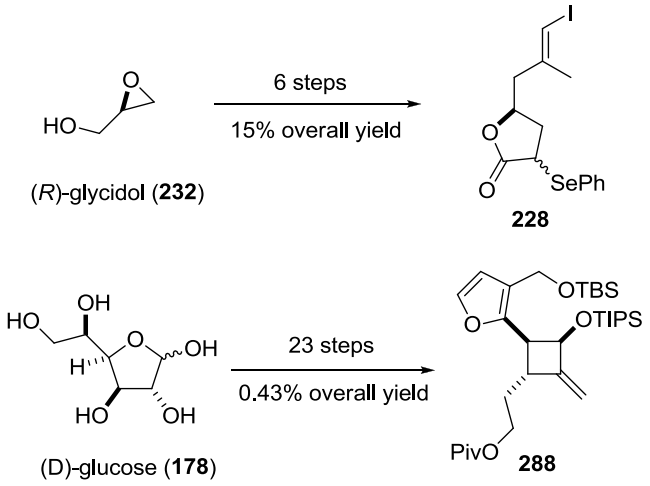
5.4 Completion of the synthesis of the "northern sector" of providencin

With pure allenol **304** in hand, oxidation to allenone **309** followed by isomerization to furan **310** in the presence of silver nitrate proceeded in excellent yield (70% over two steps, Scheme 5.18). Exposure of **310** to potassium carbonate in methanol[16] smoothly cleaved the acetate to give free alcohol **287** which was oxidized to cyclobutanone **311** with tetra-*n*-propylammonium perruthenate. Wittig olefination of ketone **311** using standard conditions yielded **288**, the "northern sector" of providencin, along with a minor amount **312** in which the pivalate was cleaved.



Scheme 5.18 Synthesis of the cyclobutylfuran portion of providencin

At this stage, two major fragments required for providencin, iodolactone **228** and cyclobutylfuran **288** had been synthesized. Specifically, lactone **228** had been prepared from (*R*)-glycidol (**232**) in six steps and 15% overall yield while furan **288** was obtained from (D)-glucose (**178**) in 23 steps and 0.43% overall yield (Scheme 5.19). We now turned into our attention to strategies for coupling these two fragments. These are discussed in the following section.

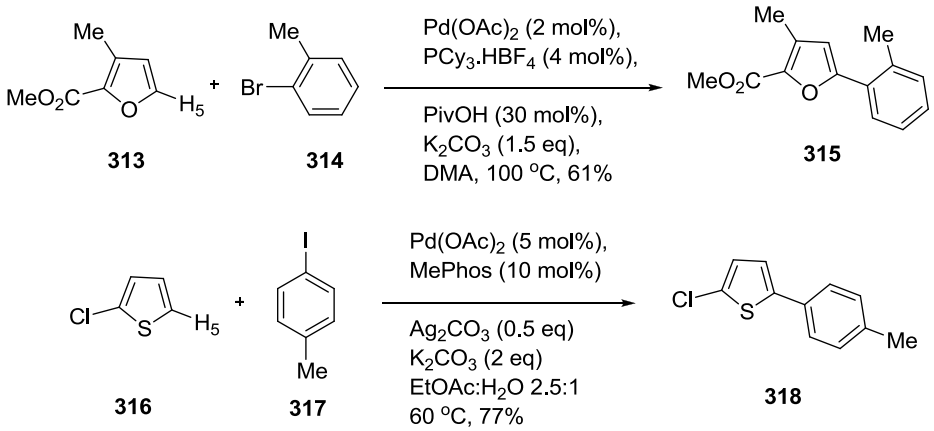


Scheme 5.19 Summary of the preparation of major fragments **228** and **288**

5.5 Coupling of vinyl iodide and cyclobutylfuran segments 228 and 288 or 312

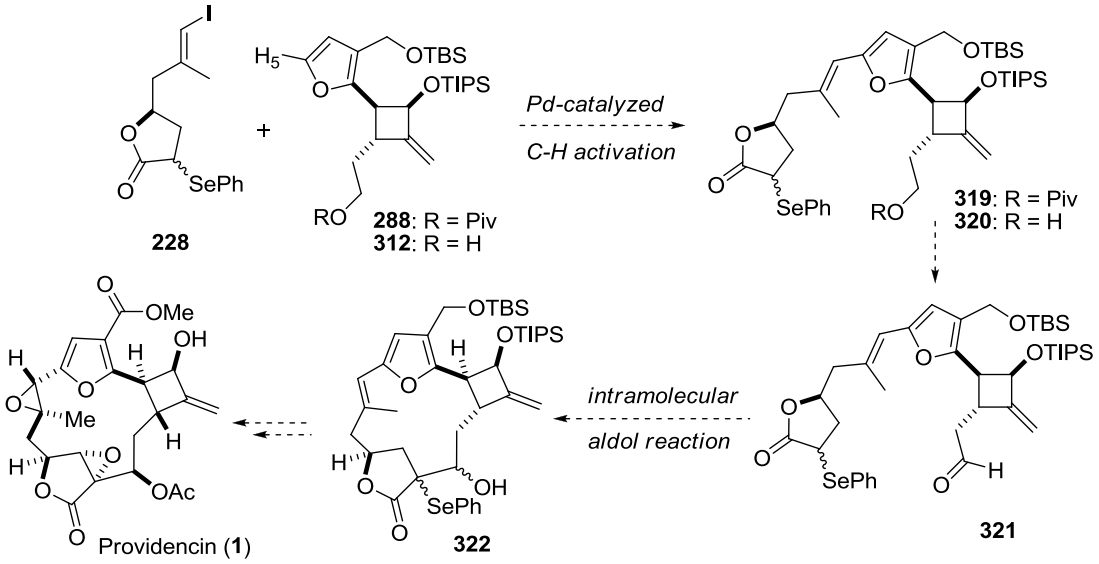
5.5.1 Palladium-catalyzed C-H activation

Transition-metal-catalyzed C-H bond functionalization of arenes and hetero arenes is a very powerful tool for forming new C-C bonds.[17] In particular, palladium-catalyzed arylation via C-H bond activation using aryl halides to prepare biaryls has undergone intensive development over the past decade. The Fagnou research group developed a variety of reaction conditions to couple hetero aromatics with aryl halides.[18] For example, when 2,3-disubstituted furan **313** and aryl bromide **314** were treated with a catalytic amount of palladium acetate and tricyclohexylphosphonium tetrafluoroborate in *N*,*N*-dimethyl acetamide (DMA) at elevated temperature (100 ^{o}C), C-H activation at the C-5 position of furan **313** took place to give trisubstituted furan **315** in 61% yield (Scheme 5.20).



Scheme 5.20 Fagnou's protocol for arylation of heteroarenes via C-H activation

The Fagnou group also reported that 2-chlorothiophene **316** could be coupled with aryl iodide **317** in the presence of palladium acetate under biphasic conditions at 60 ^{o}C to yield 2,5-disubstituted thiophene **318** in good yield.

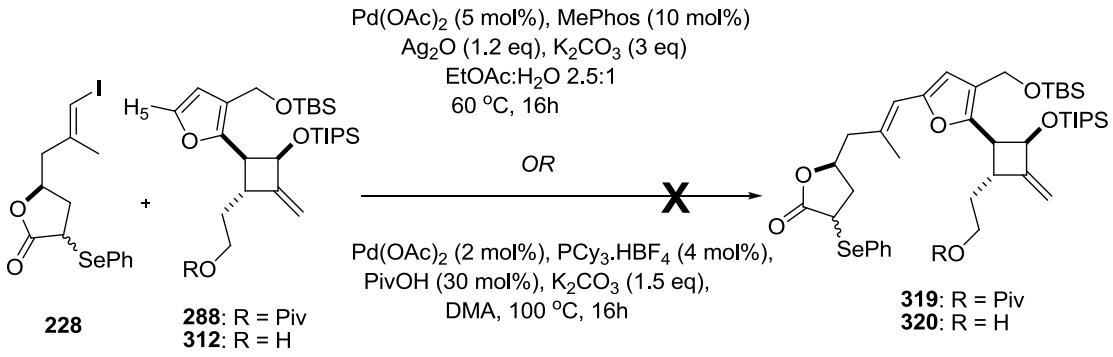


Scheme 5.21 Initial strategy for segment coupling using palladium-catalyzed C-H activation

Inspired by Fagnou's work on C-H activation of hetero aromatics, our initial coupling strategy envisioned linkage of either furan **288** or **312** with vinyl iodide **228** via palladium-catalyzed C-H activation at the C-5 position of the furan. In principle, this would lead to (*E*)-trisubstituted alkene **319** or **320** (Scheme 5.21). Either pivaloyl ester **319** or alcohol **320** would be transformed into aldehyde **321** which would be our candidate for an *intra*molecular aldol coupling to create the macrocycle **322**.

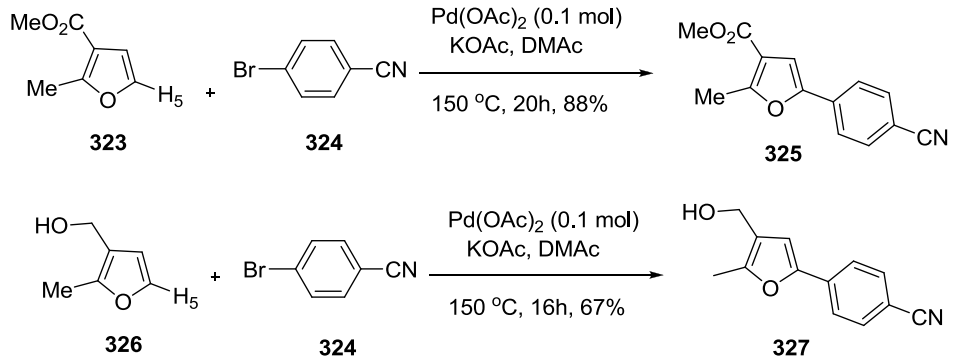
Thus, vinyl iodide **228** and either furan **288** or **312** were treated with a substoichiometric amount of palladium acetate in either a biphasic medium at 60 ^{o}C or

in *N*,*N*-dimethyl acetamide at 100 ^{o}C (Scheme 5.22). Only starting materials remained after 16 hours at 60 ^{o}C, and when the reaction mixture was heated for a longer period of time (30 hours) at 60 ^{o}C decomposition of the starting materials was observed with no evidence for the formation of either **319** or **320**. The same result was observed when the reaction was run at 100 ^{o}C for 16 hours.



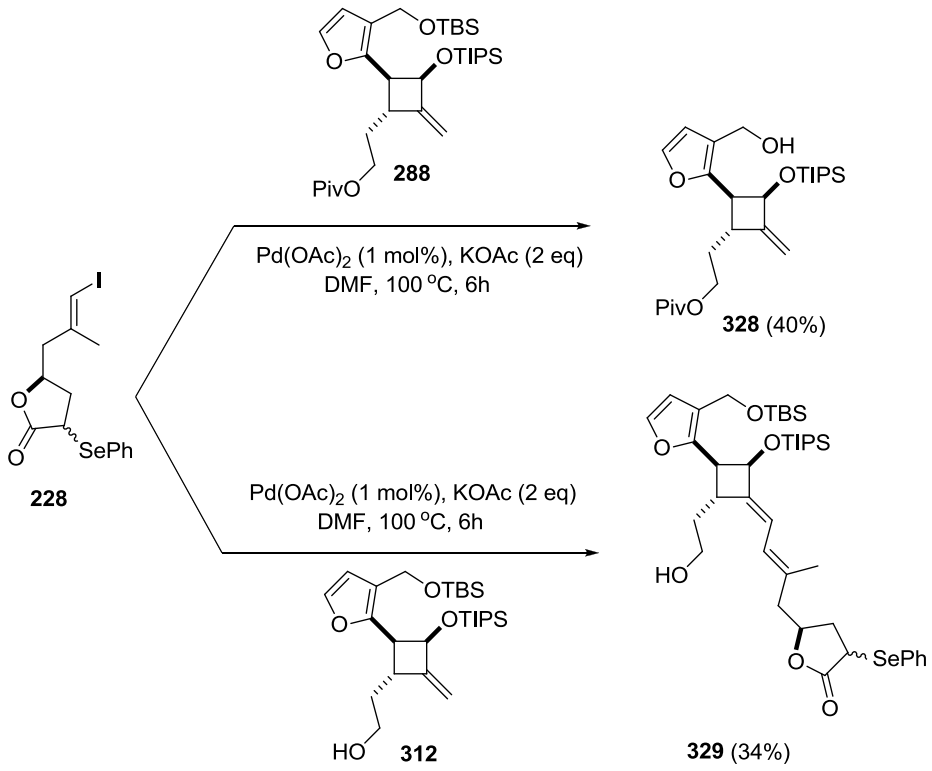
Scheme 5.22 Attempted coupling of **228** and **288** or **312** using palladium-catalyzed C-H activation

Our failure to couple **228** with **288** using Fagnou's protocol prompted us to investigate a related procedure published by the Doucet group.[19] Doucet reported that coupling 2,3-disubstituted furan **323** with aryl bromide **324** in the presence of a substoichiometric amount of palladium acetate and potassium acetate under phosphine-free conditions yielded trisubstituted furan **325** in good yield (Scheme 5.23). He also showed that furan **326** which contains a free hydroxyl group coupled with **324** under the same reaction conditions to produce **327** in 67% yield.



Scheme 5.23 Doucet's procedure for C-H activation and coupling of hetero arenes

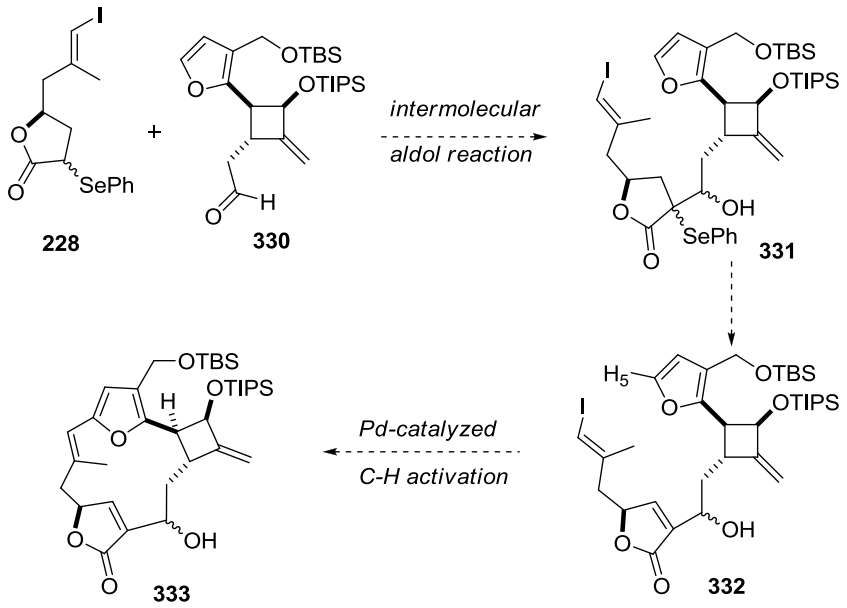
When furan **288** was treated with vinyl iodide **228** in the presence of a catalytic amount of palladium acetate and a stoichiometric quantity of potassium acetate in hot dimethylformamide, only cleavage of the *t*-butyldimethylsilyl ether of **288** occurred to give alcohol **328** along with unreacted vinyl iodide **228** (Scheme 5.24). However, when furan **312** containing a free hydroxyl group and **288** were subjected to the Doucet reaction conditions, a Heck coupling[20] took place to produce **329**. The structure of **329** was established by extensive 1D, 2D NMR experiments and mass spectroscopy. We surmise that the free hydroxyl group in **312** coordinated with the palladium complex formed from **228** and directed coupling with the exo methylene function of **312** to give conjugated diene **329**.



Scheme 5.24 Synthesis of trisubstituted alkene **329**

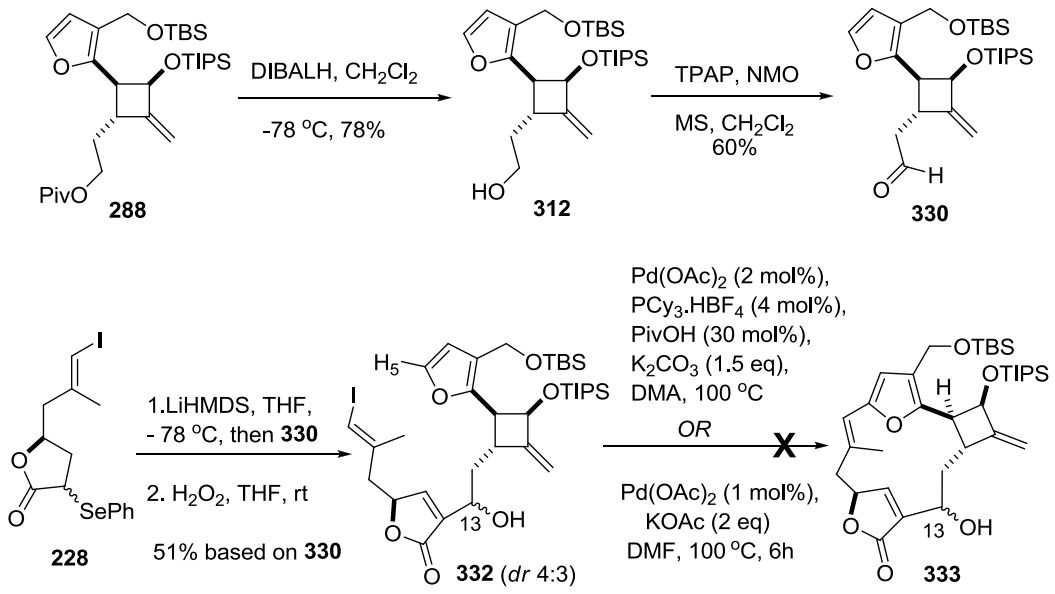
5.5.2 Aldol coupling of subunits 228 and 330

Alongside experiments directed toward *inter*molecular coupling of **228** with **288** or **312** via palladium-catalyzed C-H activation at the C-5 position of the furan, we also foresaw the possibility of an *intra*molecular coupling of seleno lactone **228** and a cyclobutylfuran unit. In principle, this could be effected if **228** were first linked to aldehyde **330** via an *inter*molecular aldol reaction. This would lead to **331** which could then undergo oxidative elimination of the phenylselenyl subunit to give **332**. *Intra*molecular palladium-catalyzed C-H activation of the furan in **332** at the C-5 position would then furnish the macrocycle **333** (Scheme 5.25).



Scheme 5.25 Alternative strategy for coupling subunits **228** and **330**

In the forward direction, reduction of pivaloyl ester **288** using diisobutylaluminum hydride yielded alcohol **312** which was oxidized with tetra-*n*-propylammonium perruthenate to aldehyde **330** (Scheme 5.26). Exposure of the lithium enolate of α-seleno lactone **228** to aldehyde **330** at low temperature gave an aldol product which was immediately treated with hydrogen peroxide. We were pleased to observe that this sequence afforded hydroxy butenolide **332** in acceptable overall yield as a 4:3 diastereomeric mixture at the C-13 alcohol center. However, all attempts to close the macrocycle **333** from **332** using an *intra*molecular palladium-catalyzed C-H activation of the furan under either Fagnou's or Doucet's conditions led only to decomposition of **332**.

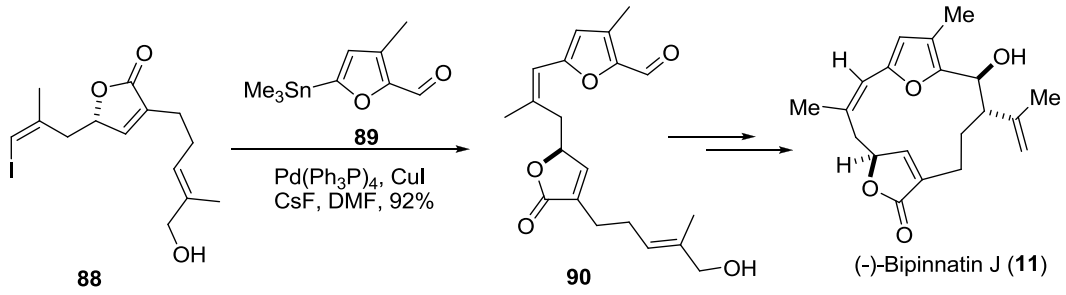


Scheme 5.26 Synthesis of hydroxy butenolide **332**

At this stage, we realized that a coupling strategy for our two principal subunits involving either *inter*molecular or *intra*molecular palladium-catalyzed C-H activation at the C-5 position of the furan component using either Fagnou's or Doucet's protocol were destined for failure. On the other hand, we had proved that aldol coupling of the two subunits, lactone **228** and aldehyde **328**, was feasible. It was clear that we needed to modify our coupling strategy by first connecting vinyl iodide **228** to C-5 of furan **288**, for which a transition metal-mediated cross-coupling seemed the best option. An *intra*molecular aldol reaction would then be employed to close the macrocycle **333** along lines demonstrated with the formation of **332**. This strategy is discussed in the following section.

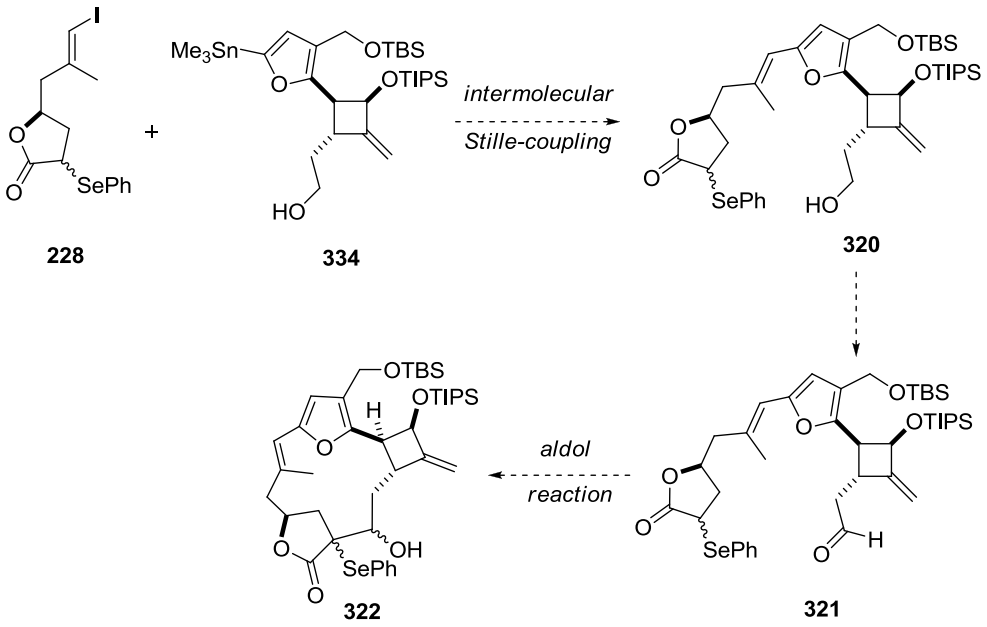
5.5.3 Stille cross-coupling of subunits 228 and 334

In light of our failed coupling of **228** with furans **288** or **312** via C-H activation at the C-5 position of the furan, we decided to explore linkage of the 5-stannyl derivative of furan **312** with vinyl iodide **228** using a Stille cross-coupling.[21] Trauner's group, in their synthesis of bipinnatin J (**11**), successfully employed Stille cross-coupling of 5-furyl stannane **89** with vinyl iodide **88** to give **90** in high yield using a catalytic amount of tetrakis(triphenylphosphine)palladium, cuprous iodide and cesium fluoride (5.27).[22]



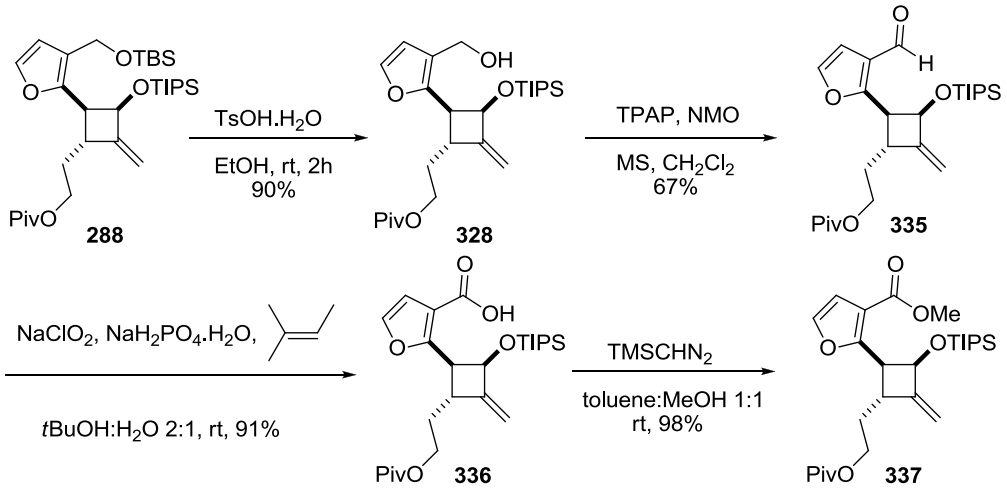
Scheme 5.27 Trauner's Stille cross-coupling of vinyl iodide **88** with furyl stannane **89** to give **90**

Inspired by Trauner's result, we hypothesized that Stille cross-coupling of vinyl iodide **228** with furyl stannane **334** would afford (*E*)-trisubstituted alkene **320** which could then be oxidized to aldehyde **321**. An *intra*molecular aldol reaction of **321** would then lead to the macrocycle **322** (Scheme 5.28).



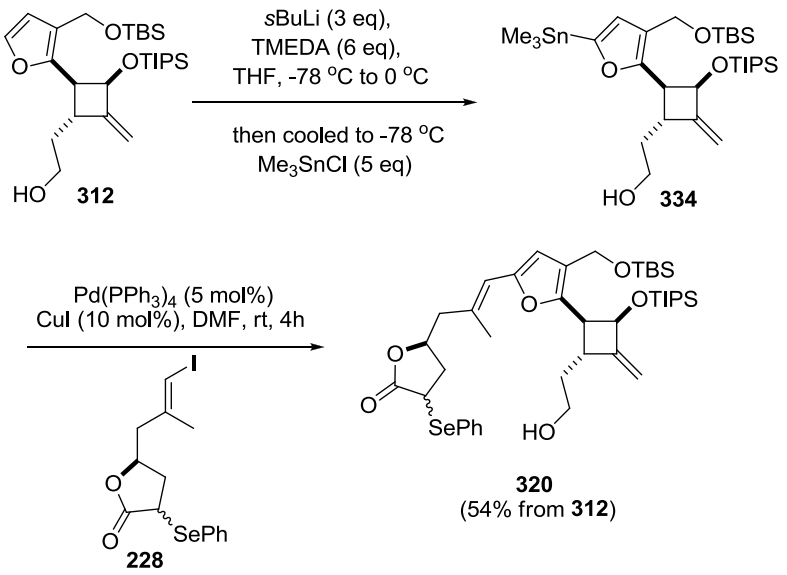
Scheme 5.28 Strategy for coupling using a Stille cross-coupling

Initial efforts to prepare furyl stannane **334** from furan **312** were unproductive and all attempts to functionalize the C-5 position of furan **312** with *n*-butyllithium or with *t*-butyllithium and trimethyltin chloride led only to the return of starting material. This suggested that the H-5 proton of furan **312** was so weakly acidic that it could not be abstracted even by a strong base. Conceivably, the acidity of H-5 could be enhanced by an electron-withdrawing group at C-3 of furan **312** and this idea was pursued with furan **288**. Acid-catalyzed hydrolysis of the *t*-butyldimethylsilyl ether of **288** gave alcohol **328** which was oxidized to aldehyde **335** with tetra-*n*-propylammonium perruthenate (Scheme 5.29). Pinnick oxidation of **335** to carboxylic acid **336** followed by esterification of **336** provided methyl ester **337**.



Scheme 5.29 Synthesis of ester **337**

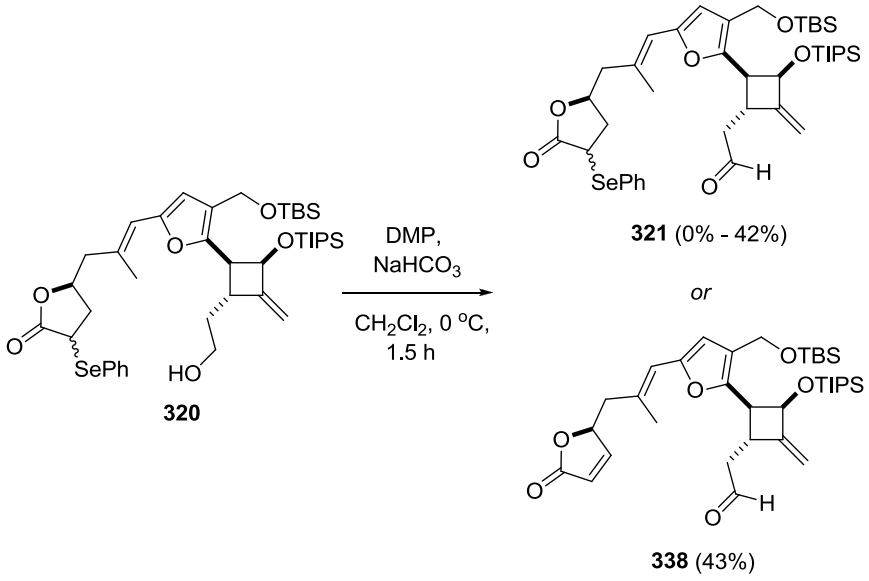
Although neither lithium diisopropylamide nor lithium diethylamide were able to deprotonate the C-5 position of furan **337**, the reaction of *s*-butyllithium with alcohol **312** was found to be more promising. When furan **312** was treated with an excess of *s*-butyllithium and freshly distilled tetramethylethylenediamine (TMEDA) in tetrahydrofuran and then with trimethyltin chloride, furyl stannane **334** was obtained in good yield as determined by proton NMR (Scheme 5.30). Attempts at purification of **334** using deactivated silica gel or neutral alumina chromatography led to substantial destannylation, hence the crude furyl stannane was reacted directly with vinyl iodide **228**. This Stille cross-coupling, carried out in the presence of tetrakis(triphenylphosphine)palladium and cuprous iodide in degassed dimethylformamide, furnished (*E*)-trisubstituted alkene **320** in 54% yield based on furan **312**.



Scheme 5.30 Synthesis of furyl stannane **334** and Stille coupling with **228**

With **320** in hand, our goal was to oxidize this alcohol to aldehyde **321**. An initial attempt to oxidize **320** was made with Dess-Martin reagent under buffered conditions which gave aldehyde **321** in low yield. This oxidation was capricious, however and when the same conditions were repeated on **320**, we invariably obtained the butenolide **338** as the major product with only a trace amount of aldehyde **321**. It was found that oxidation and subsequent elimination of the phenylselenyl oxide from **320** was competing with oxidation of the primary alcohol under Dess-Martin oxidation conditions. In the hope of avoiding overoxidation of **320**, other oxidants were investigated but Swern oxidation produced a complex mixture of compounds, whereas tetra-*n*-propylammonium perruthenate led to a less polar compound that underwent decomposition upon attempted purification. At this stage, it seemed that aldehyde **321** retaining the phenylselenyl substituent would not be available by oxidation of **320**, and

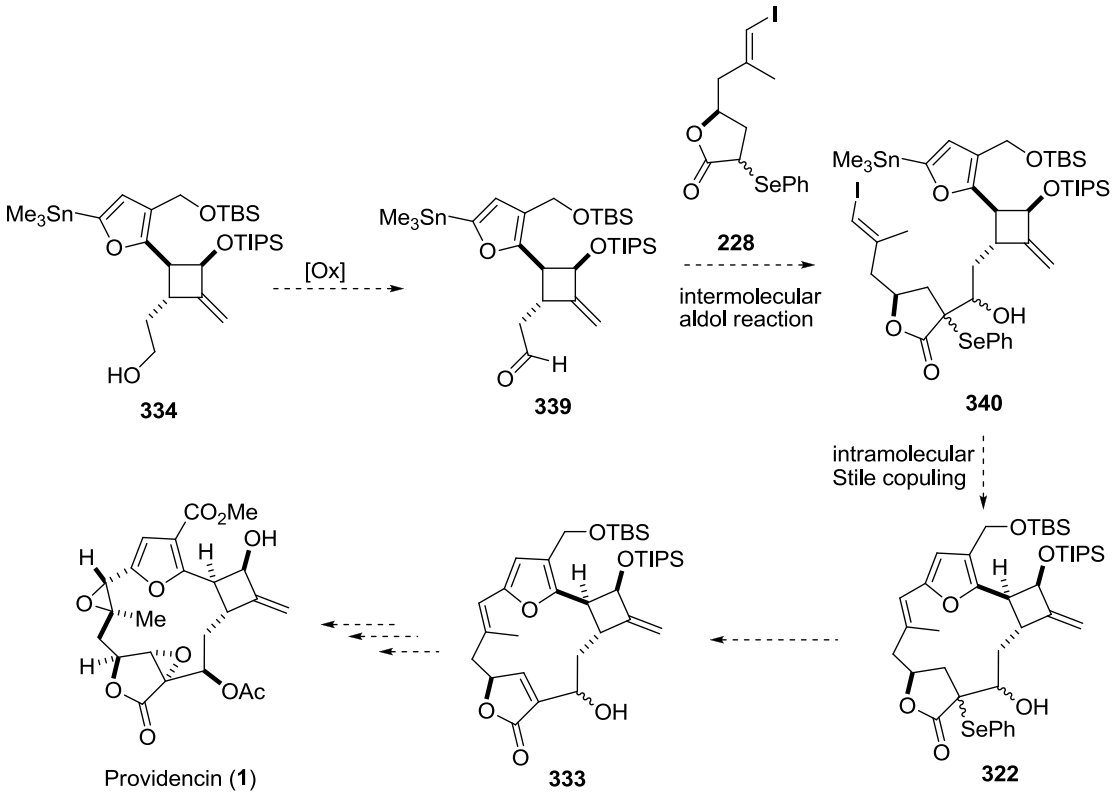
having exhausted the supply of precursors to **320** no further attempt was made to complete the synthesis of providencin from **320**. An attempt to generate the enolate of enone **338** via a Morita-Baylis-Hillman reaction using magnesium iodide, tetramethylethylenediamine (TMEDA) and 4-dimethylaminopyridine to close the macrocycle was unsuccessful.



Scheme 5.31 Oxidation of alcohol **320**

A possible solution to difficulties associated with oxidation of **320** to aldehyde **321** is depicted in Scheme 5.32. Since furyl stannane **334** is already in hand, oxidation of this alcohol to aldehyde **339** would open the door to its coupling with *α*-seleno lactone **228** via an *inter*molecular aldol reaction. This would lead to aldol adduct **340** which would be subjected to an intramolecular Stille coupling to yield macrocycle **322**. Oxidation and elimination of the phenylselenyl substituent of **322** would provide **333**, after which chemoselective and diastereoslective epoxidations, functional group

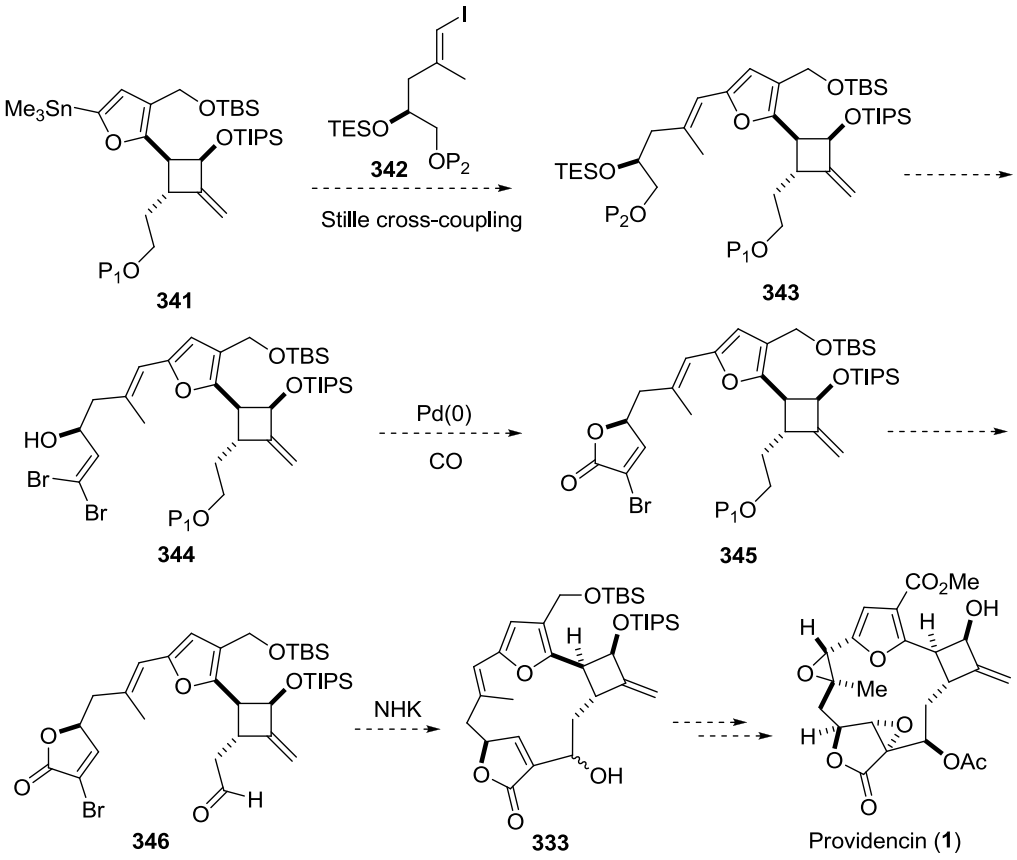
interconversions and final removal of triisopropylsilyl ether would lead to (+)-providencin (**1**).



Scheme 5.32 A plan for completion of the total synthesis of providencin (**1**)

In an alternative plan, we envisioned that Stille cross-coupling of a modified furyl stannane **341** with vinyl iodide **342** could provide **343** which could be transformed into hydroxy bromide **344** using standard conditions (Scheme 5.33). Butenolide **345** would be obtained from dibromide **344** via Hoye's protocol using a palladium catalyst and carbon monoxide. The protected primary alcohol of **345** would be converted to aldehyde **346** which would be subjected to an intramolecular Nozaki-

Hiyami-Kishi reaction to close the macrocycle **333**. The later would lead to providencin (**1**).



Scheme 5.33 An alternative strategy for the completion of total synthesis of providencin (**1**)

In summary, a route to advanced intermediates **320** and **332**, which possess all the required carbons for providencin (**1**), has been developed. The enantiopure cyclobutane moiety of **1** was synthesized using a zirconium-mediated ring contraction of a furanose, while the furan unit was obtained by isomerization of an allenone. Assembly of the two major subunits was accomplished via an *inter*molecular aldol

reaction and by means of Stille cross-coupling but all attempts to close the macrocycle nucleus of providencin form these advanced systems failed.

5.6 References

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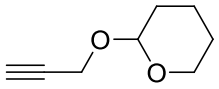
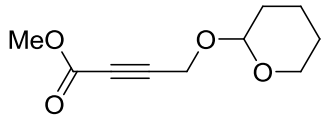
5.7 Experimental Section



260

2-(Prop-2-ynyloxy)tetrahydro-2H-pyran (**260**)

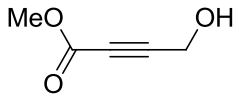
To a CH_2Cl_2 (356 mL) solution of propargyl alcohol (**259**, 10.0 g, 178.3 mmol) at 0 ^oC were added dihydropyran (19.4 mL, 214.0 mmol) and *p*-toluenesulfonic acid (1.69 g, 8.91 mmol) and the mixture was stirred for 1.5 h at 0 ^oC. A satd solution of $NaHCO_3$ was added slowly to the mixture which was stirred until gas evolution ceased. The separated aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL) and the combined organic extract was dried over Na_2SO_4. After filtering, the organic phase was concentrated to leave a crude oil that was purified by distillation (head temperature 73 ^oC at 10 mmHg) to afford **260** as a colorless oil (21.2 g, 88%): R_f 0.50 (8:2 hexanes/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 1.50-1.90 (m, 6H), 2.43 (t, *J* = 2.4 Hz, 1H), 3.53-3.57 (m, 1H), 3.83-3.88 (m, 1H), 4.28 (dd, *J* = 11.2, 2.3 Hz, 2H), 4.84 (t, *J* = 3.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9, 20.3, 30.2, 53.9, 61.9, 73.9, 79.7, 96.8.



261

Methyl 4-(Tetrahydro-2H-pyran-2-yloxy)but-2-ynoate (261)

To a solution of **260** (2.052 g, 14.64 mmol) in THF (55.0 mL) was added *n*-BuLi (6.77 mL, 2.6 M solution in hexane) at – 78 ^{o}C and the reaction mixture was allowed to warm to – 20 ^{o}C slowly (15 min) and then was cooled to – 78 ^{o}C. A solution of methyl chloroformate (2.26 mL, 29.28 mmol) in THF (45 mL) was added slowly to the reaction mixture and the solution was stirred for 15 min at – 78 ^{o}C and then warmed to 0 ^{o}C. After stirring the solution for 1.5 h at 0 ^{o}C, the reaction was quenched with a satd solution of NH_4Cl and the separated aqueous layer was extracted with Et_2O (2 x 25 mL). The combined organic extract was dried over Na_2SO_4 (anhydrous) and concentrated, and the crude residue was distilled under reduced pressure (head temperature 140 ^{o}C, 12 mmHg) to give **261** as a colorless oil (2.29 g, 79%): R_f 0.50 (8:2 hexanes/ethyl acetate); IR (neat) 2239, 1713 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 1.52-1.93 (m, 6H), 3.54-3.59 (m, 1H), 3.80 (s, 3H), 3.81-3.86 (m, 1H), 4.40 (s, 2H), 4.82 (t, *J* = 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 25.8, 30.0, 52.7, 53.6, 61.9, 77.3, 83.9, 97.1, 153.6.

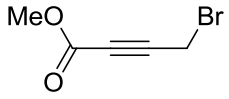


262

Methyl 4-Hydroxybut-2-ynoate (262)

To a solution **261** (303 mg, 1.52 mmol) in 95% ethanol (16 mL) was added pyridinium *p*-toluenesulfonate (28.0 mg, 0.15 mmol) and the solution was refluxed at 80 ^{o}C for 2 h. The mixture was poured into a satd solution of $NaHCO_3$ (20 mL) and the separated aqueous layer was extracted with Et_2O (3 x 20 mL). The combined

organic extract was dried over anhydrous Na_2SO_4, filtered, and concentrated and the crude residue was purified by chromatography (silica gel, 2:8 ethyl acetate/hexanes) to afford **262** (88 mg, 50%) as a colorless oil: R_f 0.37 (7:3 hexanes/ethyl acetate); IR (neat) 3408, 2233, 1715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 4.42 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.6, 52.9, 77.3, 85.6, 153.7.



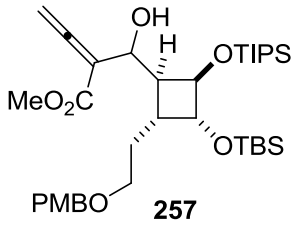
258

Methyl 4-Bromobut-2-ynoate (258)

To a CH_2Cl_2 (30.0 mL) solution of **262** (1.658 g, 14.5 mmol) At 0 ^oC were added triethylamine (5.0 mL, 36.3 mL) and mesyl chloride (2.8 mL, 36.5 mmol). The reaction mixture was stirred for 3 h at 0 ^oC and the reaction was quenched with aqueous satd NH_4Cl solution. The separated aqueous layer was extracted with CH_2Cl_2 and the combined organic layer was dried (anhydrous Na_2SO_4), filtered, and concentrated. The crude residue was used for next reaction without further purification.

To an ice-cold solution of the crude oil obtained above (1.002 g, 5.21 mmol) in THF (14.0 mL) was added LiBr (0.906 g, 10.43 mmol) and the mixture was allowed to stir for 10 h at room temperature. Water (20 mL) was added to the reaction mixture and the separated aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic extract was dried over anhydrous Na_2SO_4, filtered, and concentrated under

reduced pressure. The crude residue was chromatographed (silica gel, 7:93 ethyl acetate/hexanes) to give **258**[5b] (609 mg, 67%) as a colorless oil: R_f 0.67 (7:3 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 4.97 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.5, 52.9, 77.3, 81.7, 153.4. CI-HRMS calcd for $C_5H_6O_2Br$ $[M + H]^+$ *m/z* 176.9551, found *m/z* 176.9543.

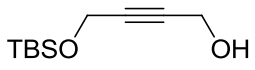


257

Methyl 2-(((1*S*,2*R*,3*R*,4*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4(triisopropylsilyloxy)cyclobutyl)(hydroxy)methyl)buta-2,3-dienoate (257)

To a solution of **258** (40.8 mg, 0.23 mmol) in 1.1 mL of DMPU at room temperature under argon were added simultaneously $SnCl_2$ (53.0 mg, 0.27 mmol) and NaI (40.4 mg, 0.27 mmol) and the resulting mixture was stirred for 2.5 h while protected from light. The bright yellow solution was cooled to 0 °C and a solution of **227 (**32 mg, 0.28 mmol) in DMPU (1.0 mL) was added over a 10 min period. After 20 h at room temperature in the absence of light, the reaction mixture was diluted with Et_2O (10.0 mL) and a satd aqueous solution of NH_4Cl (10 mL) with efficient stirring. The separated aqueous layer was extracted with Et_2O (3 x 10 mL) and the combined organic extract was washed satd aqueous $NaHCO_3$ and brine, dried over anhydrous

Na_2SO_4, filtered, and concentrated. Flash chromatographic purification of the crude residue on silica gel (9:91 ethyl acetate:hexanes) afforded **257** (23 mg, 62%) as a light yellow oil: R_f 0.42 (8:2 hexanes/ethyl acetate); $[\alpha]^{29}{}_D$ – 13.6 (*c* 1.1, $CHCl_3$); IR (neat) 3527, 2941, 2857, 1960, 1711, 1608, 1517, 1253, 1085 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.90 (s, 9H), 1.11 (s, 21H), 1.41-1.50 (m, 1H), 1.89-1.96 (m, 1H), 2.35-2.40 (m, 1H), 2.49-2.51 (m, 1H), 3.33-3.37 (m, 2H), 3.38 (d, *J* = 2.4 Hz, OH), 3.74 (s, 3H), 3.82 (s, 3H), 4.29 (dd, *J* = 5.8, 9.0 Hz, 1H), 4.36 (d, *J* = 1.4 Hz, 2H), 4.47 (dd, *J* = 6.1, 9.1 Hz, 1H), 4.91 (t, *J* = 2.5 Hz, 1H), 5.24 (dd, *J* = 2.5, 14.1 Hz, 1H), 5.38 (dd, *J* = 3.0, 14.1 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.1, -4.5, 11.9, 17.8, 25.8, 29.0, 29.7, 31.7, 44.4, 52.1, 55.2, 65.9, 68.4, 72.4, 76.1, 76.3, 81.2, 101.6, 113.7, 129.1, 130.7, 159.0, 166.2, 214.1; CI-HRMS calcd for $C_{35}H_{60}O_7Si_2Na$ $[M + Na]^+$ *m/z* 671.3775, found *m/z* 671.3766.



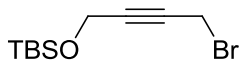
263

4-(*tert*-Butyldimethylsilyloxy)but-2-yn-1-ol (263)

To a DMF (45 mL) solution of propargyl alcohol (**259**, 2.1 mL, 35.6 mmol) were added imidazole (3.64 g, 53.5 mmol) and TBSCl (6.45 g, 42.8 mmol) at room temperature. The reaction mixture was stirred at room temperature for 16 h and was diluted with water (100 mL) and Et_2O (50 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 25 mL). The combined organic extract was

dried over anhydrous Na_2SO_4, filtered, and concentrated to leave a crude oil (6.36 g) which was used directly for the next reaction.

To a THF (64.2 mL) solution of the crude oil (6.56 g, 38.5 mmol) obtained above at -78 ^oC was added slowly *n*-BuLi (22.3 mL, 2.6 M in hexane) and the reaction mixture was stirred for 20 min at – 78 ^oC. A solution of paraformaldehyde (2.31 g, 77.0 mmol) in THF (10.0 mL) was added to the mixture at – 78 ^oC and the solution was warmed to room temperature and stirred for 3 h. Aqueous NH_4Cl solution (25 mL) was added to the reaction mixture and the layers were separated. The aqueous layer was extracted with Et_2O (2 x 25 mL) and the combined organic extract was dried (Na_2SO_4), filtered, and concentrated. The crude residue was purified by silica gel chromatography (1:9 ethyl acetate/hexane) to afford **263** (6.32 g, 80%, 2 steps) as a colorless oil: R_f 0.22 (9:1 hexanes/ethyl acetate); IR (neat), 3369, 2956, 2929, 2885, 1466, 1256, 1139 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 6H), 0.93 (s, 9H), 1.62 (t, *J* = 5.6 Hz, OH), 4.32 (td, *J* = 1.5, 5.9 Hz, 2H), 4.37 (t, *J* = 1.7 Hz, 2H); δ ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) -5.1, 18.3, 25.8, 51.2, 51.7, 82.9, 84.5.

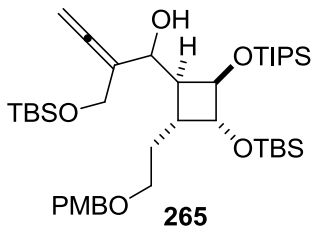


264

(4-Bromobut-2-ynyloxy)(*tert*-butyl)dimethylsilane (264)

To a solution of **263** (1.00 g, 4.99 mmol) in 9.98 mL of CH_2Cl_2 was added triphenylphosphine (1.74 g, 6.63 mmol) and the mixture was cooled in an ice bath. To this solution at 0 ^oC was added portionwise CBr_4 (2.19 g, 6.63 mmol) over 10 min and

the brown reaction mixture was stirred for 16 h at room temperature. The solvent was removed in vacuo and the crude residue was purified by silica gel chromatography (5:95 ethyl acetate/hexanes) to provide **264** (819 mg, 63%) as a colorless oil: R_f 0.8 (85:15 hexanes/ethyl acetate); IR (neat), 2960, 2929, 2863 1474, 1365, 1260, 1151 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 6H), 0.93 (s, 9H), 3.96 (t, *J* = 1.9 Hz, 2H), 4.39 (t, *J* = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.1, 14.4, 18.3, 25.8, 51.8, 79.7, 85.5.

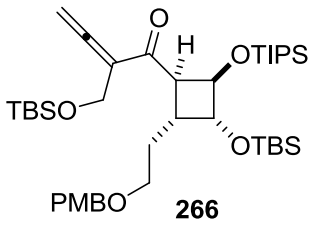


265

1-((1*S*,2*R*,3*R*,4*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)-2-((*tert*-butyldimethylsilyloxy)methyl)buta-2,3-dien-1-ol (265)

To a solution of **264** (28.5 mg, 0.10 mmol) in DMPU (1 mL) at room temperature under argon were added $SnCl_2$ (24.6 mg, 0.12 mmol) and NaI (19.3 mg, 0.12 mmol), and the resulting mixture was stirred for 2 h in a flask wrapped with aluminum foil to protect the contents from light. The foil was removed, the bright yellow solution was cooled to 0 °C, and a solution of **227 (**15 mg, 0.027 mmol) in DMPU (0.5 mL) was added over a 10 min period. After 20 h at room temperature in the absence of light, the reaction mixture was diluted with Et_2O and a satd aqueous solution of NH_4Cl was

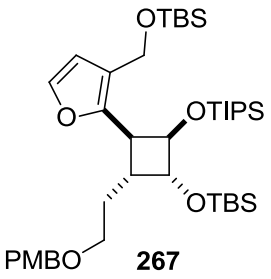
added with efficient stirring. The separated aqueous layer was extracted with Et_2O (3 x 10 mL) and the combined organic extract was washed with satd aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concentrated. Flash chromatography of the crude residue on silica gel (9:91 ethyl acetate:hexanes) afforded **265** (12.0 mg, 60%) as a colorless oil: R_f 0.50 (8:2 hexanes/ethyl acetate); $[\alpha]^{26}_{D}$ – 25.1 (*c* 0.35, $CHCl_3$); IR (neat) 3536, 2937, 2859, 1964, 1727, 1610, 1509, 1458, 1248, 1096, 1069 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 3H), 0.05 (s, 3H), 0.07 (s, 6H), 0.90 (s, 18H), 1.07-1.10 (m, 21H), 1.54-1.57 (m, 1H), 1.93-2.02 (m, 1H), 2.32-2.44 (m, 2H), 3.18 (d, *J* = 2.6 Hz, OH), 3.37-3.48 (m, 2H), 3.82 (s, 3H), 4.13 (td, *J* = 2.3, 11.6 Hz, 1H), 4.22 (td, *J* = 2.1, 11.8 Hz, 1H), 4.32 (dd, *J* = 5.9, 8.5 Hz, 1H), 4.42 (d, *J* = 1.4 Hz, 2H), 4.45 (m, 1H), 4.65 (t, *J* = 2.6 Hz, 1H), 4.84 (qd, *J* = 2.3, 10.3 Hz, 4.93 (qd, *J* = 2.3, 10.5 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.3, -5.2, -5.0, -4.5, 11.9, 17.9, 18.2, 25.8, 29.4, 29.7, 32.1, 44.4, 55.2, 63.0, 66.4, 72.5, 76.0, 77.5, 104.4, 113.7, 129.1, 130.7, 159.0, 205.8; CI-HRMS calcd for $C_{40}H_{74}O_6Si_3Na$ $[M + Na]^+$ *m/z* 757.4691, found *m/z* 757.4681.



266

1-((1*R*,2*R*,3*R*,4*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)-2-((*tert*-butyldimethylsilyloxy)methyl)buta-2,3-dien-1-one (266)

To a solution of **265** (7.0 mg, 0.009 mmol) in 0.2 mL of CH_2Cl_2 at 0 ^oC was added $NaHCO_3$ (3.2 mg, 0.038 mmol) and Dess-Martin periodinane (8.0 mg, 0.019 mmol). The slurry was stirred for 2.5 h at 0 ^oC and the reaction mixture was diluted with CH_2Cl_2 (1.0 mL) and satd $Na_2S_2O_3$ solution (10 mL). After stirring the biphasic mixture vigorously for 20 min, the layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extract was washed with satd $NaHCO_3$, water, and brine and dried over anhydrous Na_2SO_4. The drying agent was removed by filtration and the filtrate was concentrated in vacuo. The crude mixture was purified by silica gel chromatography (9:1 pentane/ethyl acetate) to yield **266** (6 mg, 87%) as a colorless oil: R_f 0.50 (9:1 hexanes/ethyl acetate); $[\alpha]^{26}_D$ – 39.4 (*c* 1.5, $CHCl_3$); IR (neat), 2925, 2859, 1933, 1731, 1664, 1474, 1244, 1108, 843 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 12H), 0.90 (s, 18H), 1.03 (s, 21H), 1.47-1.55 (m, 1H), 1.91-1.96 (m, 1H), 2.43 (m, 1H), 3.43 (m, 2H), 3.82 (s, 3H), 3.85 (dd, *J* = 1.8, 8.9 Hz, 1H), 4.29 (td, *J* = 3.6, 13.5 Hz, 1H), 4.36-4.42 (m, 3H), 4.46 (td, *J* = 3.4, 13.5 Hz, 1H), 4.52 (dd, *J* = 6.8, 8.2 Hz, 1H), 5.16 (ddd, *J* = 3.2, 4.2, 7.2 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.3 (2), -5.0, -4.5, 12.1, 17.9, 18.3, 25.8 (2), 28.5, 19.7, 35.2, 48.7, 55.2, 58.4, 68.8, 72.6, 74.9, 76.2, 81.9, 112.2, 113.7, 129.1, 130.6, 159.1, 199.5, 216.2; CI-HRMS calcd for $C_{40}H_{72}O_6Si_3$ $[M]^+$ *m/z* 733.4715, found *m/z* 733.4733.

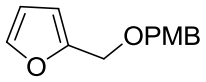


267

***tert*-Butyl((2-((1*R*,2*R*,3*R*,4*R*)-3-(*tert*-butyldimethylsilyloxy)-2-(2-(4-methoxybenzyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)furan-3-yl)methoxy)dimethylsilane (267)**

To a solution of **266** (30.0 mg, 0.04 mmol) in 0.5 mL of hexane and 0.1 mL of CH_2Cl_2 at room temperature was added 34.0 g of $AgNO_3$ on SiO_2 (10 wt%, 0.02 mmol) in a single portion. The suspension was stirred at room temperature in the absence of light for 2 h and the mixture was diluted with Et_2O (5 mL) and filtered through a short pad of Celite which was washed with Et_2O (10 mL). The filtrate was concentrated in vacuo and the crude oil was purified by silica gel chromatography (96/4, hexanes/ethyl acetate) to give **267 (**20 mg, 66%) as a pale yellow oil: R_f 0.76 (9:1 hexanes/ethyl acetate); $[\alpha]^{26}{}_D$ – 25.8 (*c* 0.35, $CHCl_3$); IR (neat) 2912, 2851, 1738, 1618, 1505, 1458, 1248 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 3H), 0.08 (s, 3H), 0.10 (s, 3H), 0.11 (s, 3H), 0.9-1.0 (m, 39H), 1.60-1.72 (m, 1H), 2.02-2.06 (m, 1H), 2.41-2.48 (m, 1H), 3.29 (dd, *J* = 2.6, 8.7 Hz, 1H), 3.46-3.50 (m, 2H), 3.81 (s, 3H), 4.41 (s, 2H), 4.43-4.47 (m, 3H), 4.63 (dd, *J* = 6.6, 8.7 Hz, 1H), 6.32 (d, *J* = 1.7 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.2 (2C), -4.9, -4.6, 11.9, 14.1, 17.7 (2C), 18.0, 18.4, 22.7, 25.9 (2C), 29.7, 30.3, 37.4,

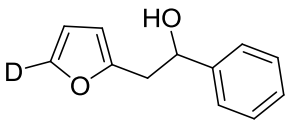
38.7, 55.2, 57.3, 68.9, 72.5, 75.3, 110.6, 113.7, 121.0, 129.1, 130.6, 140.5, 19.4, 159.0; CI-HRMS calcd for $C_{40}H_{72}O_6Si_3$ $[M]^+$ *m/z* 732.4637, found *m/z* 732.4606.



270

2-((4-Methoxybenzyloxy)methyl)furan (270)

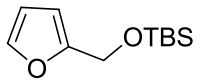
To a cold (0 ^oC) suspension of sodium hydride (0.61 g, 15.3 mmol) in dry THF (10.2 mL) was added a solution of **269** (0.44 mL, 30.49 mmol) in dry THF (3 mL) and the mixture was stirred for 30 min at 0 ^oC and for 20 min at room temperature. To this mixture at 0 ^oC was added a solution of *p*-methoxybenzyl chloride (1.0 mL, 7.63 mmol) in THF (5 mL) and the reaction mixture was stirred at room temperature for 10 h. The reaction was quenched with satd ammonium chloride solution (30 mL) and the separated aqueous layer was extracted with Et_2O (2 x 30 mL). The combined organic extract was dried (Na_2SO_4), filtered, and concentrated and the crude residue was chromatographed on silica gel (4:1 hexanes/ethyl acetate) to furnish **270** (0.87 g, 80%) as a colorless oil: R_f 0.46 (1:1 hexanes/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 4.48 (s, 2H), 4.51 (s, 2H), 6.34-6.38 (m, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 63.5, 71.5, 109.2, 110.2, 113.8, 129.5, 130.0, 142.7, 151.9, 159.3.



271

2-((5'-Deutero)furan-2-yl)-1-phenylethanol (271)

To a stirred THF (1.6 mL) solution of **270** (35.0 mg, 0.164 mmol) at -78 ^{o}C were added slowly *t*-BuLi (0.2 mL, 0.33 mmol, 1.73 M solution in hexane) and freshly distilled TMEDA (0.1 mL, 0.65 mmol). The solution turned yellow and was allowed to warm to room temperature and was stirred for 4 h during which the color changed yellow to brown. The mixture was cooled to -78 ^{o}C and the reaction was quenched with CD_3OD (1.0 mL). The mixture was poured into water (5 mL), the layers were separated and the aqueous layer was extracted with Et_2O (2 x 5 mL). The combined organic extract was washed with brine, dried (Na_2SO_4), filtered, and concentrated. The crude residue was purified by silica gel chromatography (95:5 hexanes/ethyl acetate) to afford **271** (19 mg, 54%) as a colorless oil: R_f 0.25 (9:1 hexanes-ethyl acetate); IR (neat) 3424, 2921, 2836, 1618, 1516 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 (dd, *J* = 4.4, 7.8 Hz, 1H), 3.82 (s, 3H), 4.97 (dd, *J* = 5.8, 7.6 Hz, 1H), 6.08 (d, *J* = 3.1 Hz, 1H), 6.31 (d, *J* = 3.1, 1H), 6.80 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.2, 55.2, 72.5, 107.2, 110.1, 113.8, 126.9, 135.5, 152.4, 159.1; EI-HRMS calcd for $C_{13}H_{13}O_3D$ $[M]^+$ *m/z* 219.1006, found *m/z* 219.1010.

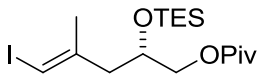


274

***tert*-Butyl(furan-2-ylmethoxy)dimethylsilane (274)**

To a stirred solution of **269** (0.44 mL, 5.09 mmol) in dry DMF (10.0 mL) at room temperature were added imidazole (0.46 g, 7.12 mmol) and TBSCl (0.84 g, 5.59 mmol). The reaction mixture was stirred at room temperature for 3 h and was poured

into water (25 mL). The separated aqueous layer was extracted with Et_2O (2 x 50 mL) and the combined organic extract was dried over Na_2SO_4, filtered, and concentrated. Purification of the crude oil by silica gel chromatography gave **274** (0.7 g, 65%) as a colorless oil: R_f 0.82 (9:1 hexanes-ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 6H), 0.92 (s, 9H), 4.66 (s, 2H), 6.24 (d, *J* = 3.2 Hz, 1H), 6.33 (dd, *J* = 1.8, 3.1 Hz, 1H), 7.39 (dd, *J* = 0.8, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.2 (2C), 18.4, 25.8(3C), 58.1, 107.2, 110.1, 142.0, 154.3.



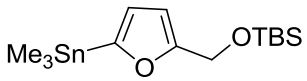
276

(*S*,*E*)-5-Iodo-4-methyl-2-(triethylsilyloxy)pent-4-enyl Pivalate (276)

To a CH_2Cl_2 solution (0.3 mL) of **246** (18 mg, 0.074 mmol) at 0 ^{o}C was added slowly pyridine (59.7 µL, 0.74 mmol) and trimethylacetyl chloride (10.0 µL, 0.081 mmol). The reaction mixture was allowed to warm to room temperature and was stirred for 18 h. The reaction was quenched by addition of a saturated aqueous $NaHCO_3$ solution, the separated aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL) and the combined organic extract was dried (Na_2SO_4), filtered, and concentrated. The crude mixture was used for the next reaction without further purification.

To a solution of the crude oil (19 mg, 0.058 mmol) obtained above in DMF (0.5 mL) at room temperature were added imidazole (11.9 mg, 0.17 mmol) and TESCl (28.46 µL, 0.17 mmol). The reaction mixture was stirred at room temperature for 15 h,

when MeOH (3 mL) was added. The solution was stirred for 10 min, then was poured into a mixture of H_2O (3 mL) and Et_2O (10 mL). The separated aqueous layer was extracted with Et_2O (2 x 20 mL) and the combined organic extract was dried (Na_2SO_4), filtered and concentrated. The crude mixture was purified by silica gel chromatography (2:98 ethyl acetate/hexanes) to give **276** (20 mg, 56% 2 steps) as a colorless oil: R_f 0.60 (95:5 hexanes/ethyl acetate); $[\alpha]^{20}_D$ - 5.5 (*c* 0.80, $CHCl_3$); IR (neat) 2960, 2877, 1729, 1475, 1453, 1281, 1150 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 0.61 (q, *J* = 7.8 Hz, 6H), 0.97 (t, *J* = 7.9 Hz, 9H), 1.24 (s, 9H), 1.88 (s, 3H), 2.40 (dd, *J* = 4.7, 7.7 Hz, 2H), 3.95 (m, 3H), 6.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.8 (3C), 6.8 (3C), 24.5, 27.2 (3C), 38.7, 44.7, 67.4, 68.7, 77.9, 143.9, 178.3. EI-HRMS calcd for $C_{17}H_{34}O_3SiI$ $[M + H]^+$ (*m/z*) 441.1322, found 441.1329.

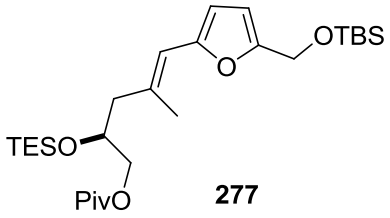


275

***tert*-Butyldimethyl((5-(trimethyllstannyl)furan-2-yl)methoxy)silane (275)**

To an Et_2O (1.5 mL) solution of **274** (56.0 mg, 0.26 mmol) and TMEDA (0.15 mL, 1.04 mmol) at 0 ^oC was added dropwise *n*-BuLi (0.3 mL, 0.52 mmol, 1.73M in pentane). The solution turned brown and was warmed to room temperature. After stirring at room temperature for 1 h, the reaction mixture was cooled to 0 ^oC and Me_3SnCl (1.28 mL, 1.3 mmol, 1M in THF) was added. The mixture was warmed to room temperature and was stirred for overnight. Water (10.0 mL) was added to the reaction mixture, the layers were separated and the aqueous layer was extracted with

Et_2O (3 x 10 mL). The combined organic extract was dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified by neutral alumina chromatography (pentane) to provide **275** (35 mg, 35%) as a colorless oil: R_f 0.65 (5:95 Et_2O-hexanes on neutral alumina); IR (neat) 2956, 2925, 2855, 1478,1252 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 6H), 0.33 (s, 9H), 0.92 (s, 9H), 4.70 (s, 2H), 6.26 (d, *J* = 3.0 Hz, 1H), 6.52 (d, *J* = 3.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -9.2 (3C), -5.1 (2C), 18.4, 25.9 (3C), 58.3, 107.1, 121.5, 158.8, 160.2.

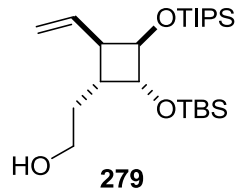


277

(*S*,*E*)-5-(5-((*tert*-Butyldimethylsilyloxy)methyl)furan-2-yl)-4-methyl-2-(triethylsilyloxy)pent-4-enyl Pivalate (277)

Furyl stannane **275** (9.0 mg, 0.023 mmol) and vinyl iodide **276** (12.3 mg, 0.028 mmol) were dissolved in 0.3 mL of DMF and the mixture was degassed three times. Then $Pd_2(dba)_3$ (6.3 mg, 0.006 mmol) and $AsPh_3$ (7.0 mg, 0.023 mmol) were added to the reaction mixture under argon and the mixture was heated at 95 ^oC for 5 h. The mixture was diluted with Et_2O (10 mL) and water (10.0 mL), and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layer was dried (anhydrous Na_2SO_4), filtered and concentrated, and the crude residue was purified by silica gel chromatography (3% Et_2O in pentane) to afford **277** (5.0 mg, 41%) as a pale yellow oil: R_f 0.29 (95:5 hexanes-Et_2O); $[\alpha]^{28}{}_D$ – 1.2 (*c* 0.4, $CHCl_3$); IR (neat) 2959, 2924,

2880, 2851,1732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 6H), 0.63 (q, *J* = 7.6 Hz, 6H), 0.93 (s, 9H), 0.97 (t, *J* = 7.6 Hz, 9H), 1.24 (s, 9H), 2.03 (d, J = 0.9 Hz, 3H), 2.37 (dd, *J* = 5.7, 9.9 Hz, 2H), 4.01-4.09 (m, 3H), 4.65 (s, 2H), 6.11 (s, 1H), 6.14 (d, *J* = 3.3 Hz, 1H), 6.24 (d, *J* = 3.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.2 (2C), 4.9, 6.7, 18.4, 19.3, 25.8, 27.2, 29.6, 30.3, 38.7, 46.3, 58.3, 67.7, 69.0, 108.6, 108.7, 117.2, 133.6, 152.6, 152.8, 178.3; EI-HRMS calcd for $C_{28}H_{52}O_5Si_2Na$ $[M + Na]^+$ (*m/z*) 547.3251, found 547.3231.

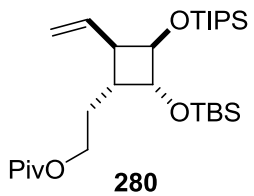


279

2-((1*R*,2*R*,3*R*,4*R*)-2-(*tert*-Butyldimethylsilyloxy)-3-(triisopropylsilyloxy)-4-vinylcyclobutyl)ethanol (279)

To a stirred solution of **190** (44.0 mg, 0.08 mmol) in CH_2Cl_2 (1.0 mL) and pH 7 buffer (0.05 mL) at 0 ^{o}C was added DDQ (22.0 mg, 0.096 mmol). The solution was stirred at 0 ^{o}C for 1 h, after which the mixture was diluted with pH 7 buffer (50.0 µL). The aqueous layer was separated and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extract was dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude residue was purified by silica gel chromatography (6:94 ethyl acetate:hexanes) to yield **279** (22.0 mg, 64%,) as a pale yellow oil: R_f 0.43 (9:1 hexanes-ethyl acetate); $[\alpha]^{22}{}_D$ – 39.5 (*c* 1.0, $CHCl_3$); IR (neat) 3330, 2943, 2863, 1478 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 3H), 0.09 (s, 3H), 0.90 (s, 9H), 1.06 (m, 21H), 1.59-1.68 (m, 1H),

1.86-1.95 (m, 1H), 2.10-2.19 (m, 1H), 2.65 (t, *J* = 8.3 Hz, 1H), 3.63-3.74 (m, 2H), 4.22 (dd, *J* = 6.9, 8.3 Hz, 1H), 4.31 (dd, *J* = 6.3, 7.5 Hz, 1H), 5.05 (dd, *J* = 6.3, 7.5 Hz, 1H), 5.05 (dd, *J* = 9.5, 10.2 Hz, 2H), 6.01 (ddd, *J* = 8.8, 10.2, 17.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.7, -4.6, 12.1 (3C), 18.0 (6C), 25.9 (3C), 29.7, 32.4, 38.4, 45.1, 61.3, 75.1, 75.6, 115.6, 138.1; CI-HRMS calcd for $C_{23}H_{49}O_3Si_2$ [M + H] $^+$ *m/z* 428.3164, found *m/z* 428.3145.

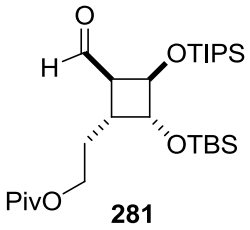


280

2-((1*R*,2*R*,3*R*,4*R*)-2-(*tert*-Butyldimethylsilyloxy)-3-(triisopropylsilyloxy)-4-vinylcyclobutyl)ethyl Pivalate (280)

To a CH_2Cl_2 solution (1.5 mL) of **279** (67 mg, 0.156 mmol) at 0 ^{o}C was added slowly pyridine (25.2 µL, 0.312 mmol) followed by trimethylacetyl chloride (38.4 µL, 0.312 mmol) and DMAP (1.9 mg, 0.015 mmol). The mixture was allowed to warm to room temperature and was stirred for 12 h. The reaction was quenched by addition of satd aqueous $NaHCO_3$ solution and the separated aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extract was washed with satd $CuSO_4$ solution, dried (Na_2SO_4), filtered, and concentrated. The crude mixture was purified by silica gel chromatography (4:96 ethyl acetate/hexanes) to afford **280** (64 mg, 80%) as a colorless oil: R_f 0.69 (9:1 hexanes/ethyl acetate); $[\alpha]^{22}{}_D$ – 55.8 (*c* 1.9, $CHCl_3$); IR (neat) 2964, 2867, 1734, 1470 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 3H), 0.07

(s, 3H), 0.90 (s, 9H), 1.06 (m, 21H), 1.20 (s, 9H), 1.59 (m, 1H), 1.97 (m, 1H), 2.10 (m, 1H), 2.68 (t, *J* = 8.7 Hz, 1H), 4.10 (q, *J* = 6.4 Hz, 2H), 4.20 (dd, *J* = 6.7, 8.5 Hz, 1H), 4.28 (dd, *J* = 6.2, 7.4 Hz, 1H), 5.04 (m, 2H), 6.00 (ddd, *J* = 8.5, 10.5, 17.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.0, -4.8, 11.9 (3C), 17.9 (6C), 25.8 (3C), 27.2 (3C), 28.1, 31.9, 38.7, 44.8, 63.0, 75.0, 75.6, 115.5, 137.9, 178.5; CI-HRMS calcd for $C_{28}H_{64}O_4Si_2$ $[M]^+$ *m/z* 512.3757, found *m/z* 512.3769.

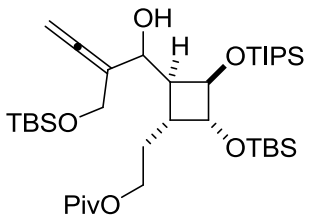


281

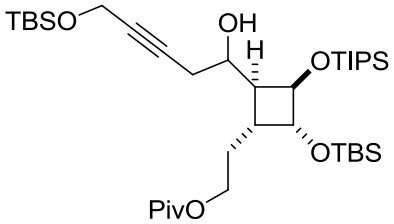
2-*((1R,2R,*3*R,4R*)-2-(*tert*-Butyldimethylsilyloxy)-4-formyl-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (281)

To a solution of **280** (64 mg, 0.124 mmol) in dioxane-water (3:1, 1.24 mL) were added 2,6-lutidine (28.8 µL, 0.248 mmol), OsO_4 (0.12 mL, 0.006 mmol, 0.05M in 2-methyl-2-propanol), and $NaIO_4$ (106.0 mg, 0.50 mmol). The reaction mixture was stirred at room temperature for 15 h and was diluted with water (10 mL) and CH_2Cl_2 (10 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extract was washed with aqueous $CuSO_4$ solution and brine, dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude mixture was purified by silica gel chromatography (5:95 ethyl acetate/hexanes) to afford **281** (38.5 mg, 60%) as a colorless oil: R_f 0.5 (9:1 hexanes-

ethyl acetate); $[\alpha]^{23}_{D}$ – 68.6 (*c* 1.15, $CHCl_3$); IR (neat) 2953, 2863, 1731(2), 1147 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 6H), 0.91 (s, 9H), 1.06 (s, 21H), 1.19 (s, 9H), 1.55 (m, 1H), 1.99 (m, 1H), 2.65 (m, 1H), 3.04 (d, *J* = 8.9 Hz, 1H), 4.07 (m, 2H), 4.31 (dd, *J* = 6.2, 7.7 Hz, 1H), 4.52 (dd, *J* = 6.6, 9.2 Hz, 1H), 9.87 (d, *J* = 2.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.0, -4.7, 11.8 (3C), 17.9 (6C), 25.7 (3C), 27.1 (4C), 30.3, 31.9, 38.7, 52.4, 62.7, 75.1, 76.8, 178.4, 202.2; EI-HRMS calcd for $C_{27}H_{55}O_5Si_2$ [M + H] $^+$ (*m/z*) 515.3588, found 515.3581.



282
(single isomer by NMR)



283
(single isomer by NMR)

2-((1*R*,2*R*,3*R*,4*S*)-2-(*tert*-Butyldimethylsilyloxy)-4-(5-(*tert*-butyldimethylsilyloxy)-1-hydroxypent-3-ynyl)-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (282) and 2-((1*R*,2*R*,3*R*,4*S*)-2-(*tert*-Butyldimethylsilyloxy)-4-(2-((*tert*-butyldimethylsilyloxy)methyl)-1-hydroxybuta-2,3-dienyl)-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (283)

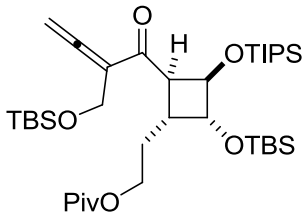
To a solution of **264** (51.0 mg, 0.19 mmol) in 1.0 mL of DMF at room temperature under nitrogen were added $SnCl_2$ (44.3 mg, 0.23 mmol) and NaI (34.4 mg, 0.23 mmol), and the resulting mixture was stirred for 3 h while protected from light in a flask wrapped with aluminum foil. The foil was removed, the bright yellow solution

was cooled to 0 °C, and a solution of **281 (**40 mg, 0.077 mmol) in 1.0 mL of DMF was added to the mixture over a 10 min period. After 30 h at 0 ^{o}C in the absence of light, the reaction mixture was diluted with Et_2O and a satd aqueous solution of NH_4Cl while being stirred. The separated aqueous layer was extracted with Et_2O (3 x 10 mL) and the combined organic extract was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure after which flash chromatography of the crude residue on silica gel (3:97 ethyl acetate: hexanes) afforded **282** (32.0 mg, 60%) and **283** (10.0 mg, 18%) as colorless oils.

282: R_f 0.44 (9:1 hexanes-ethyl acetate); $[\alpha]^{29}{}_{D}$ – 61.0 (*c* 1.0, $CHCl_3$); IR (neat) 3539, 2957, 2931, 2872, 1729, 1470, 1460, 1247, 1147 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.10 (s, 6H), 0.91 (s, 18H), 1.09 (m, 21H), 1.20 (s, 9H), 1.49 (m, 1H), 1.98 (m, 1H), 2.36 (m, 4H), 3.02 (s, 1H), 3.98 (m, 1H), 4.15 (m, 1H), 4.22-4.29 (m, 2H), 4.31 (t, *J* = 1.7 Hz, 2H), 4.46 (dd, *J* = 6.0, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.3, -5.2, -5.0, -4.6, 11.9 (3C), 17.9 (6C), 25.8 (6C), 27.2 (3C), 28.7, 30.3 (2C), 31.7, 38.6, 44.2, 63.0 (2C), 66.4, 75.9, 76.5, 77.9, 104.4, 178.4, 205.6; CI-HRMS calcd for $C_{37}H_{74}O_6Si_3$ $[M]^+$ (*m/z*) 699.4872, found 699.4899.

283: R_f 0.58 (9:1 hexanes-ethyl acetate); $[\alpha]^{24}{}_{D}$ – 38.2 (*c* 1.15, $CHCl_3$); IR (neat) 3539, 2954, 2928, 1726, 1475, 1460, 1262, 1153 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.07 (s, 6H), 0.90 (s, 18H), 1.08 (21H), 1.19 (s, 9H), 1.57 (m, 1H), 1.97 (m, 1H), 2.39 (m, 2H), 3.18 (d, *J* = 2.6 Hz, 1H). 3.97 (m, 1H), 4.12 (m, 1H), 4.16 (td, *J*

= 1.9, 13.6 Hz, 1H), 4.27 (td, *J* = 1.9, 13.6 Hz, 1H), 4.34 (dd, *J* = 5.2, 7.9 Hz, 1H), 4.48 (dd, *J* = 6.0, 8.9 Hz, 1H), 4.69 (m, 1H), 4.88 (qd, *J* = 2.4, 10.5 Hz, 1H), 4.96 (qd, *J* = 2.4, 10.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.1 (2C), -4.6 (2C), 11.9 (3C), 17.9 (6C), 23.3, 25.8 (6C), 27.2 (3C), 28.3, 30.3 (2C), 31.2, 38.7, 43.9, 51.9, 62.2, 68.1, 75.8, 76.3, 80.5, 81.4, 178.3; CI-HRMS calcd for $C_{37}H_{74}O_6Si_3$ $[M]^+$ (*m/z*) 698.4793, found 698.4820.

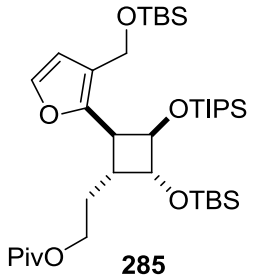


284

2-((1*R*,2*R*,3*R*,4*R*)-2-(*tert*-Butyldimethylsilyloxy)-4-(2-((*tert*-butyldimethylsilyloxy)methyl)buta-2,3-dienoyl)-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (284)

To a solution of **282** (24.0 mg, 0.034 mmol) in 0.4 mL of CH_2Cl_2 at 0 ^oC was added $NaHCO_3$ (11.0 mg, 0.131 mmol) and Dess-Martin periodinane (28.0 mg, 0.065 mmol). The slurry was stirred at 0 ^oC for 2.5 h and the mixture was diluted with CH_2Cl_2 (1.0 mL) and 10 mL of satd $Na_2S_2O_3$ solution. After stirring the biphasic mixture vigorously for 20 min, the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extract was washed with satd $NaHCO_3$ and brine, and dried over Na_2SO_4. The drying agent was removed by filtration, and the solvent was removed in vacuo. Purification of the crude oil by silica

gel chromatography (98:2 hexane/ethyl acetate) provided **284** (23 mg, 96%) as a yellow oil: R_f 0.65 (9:1 hexanes/ethyl acetate); $[\alpha]^{25}{}_D$ – 24.0 (*c* 1.2, $CHCl_3$); IR (neat) 2958, 2928, 2864, 1932, 1736, 1667, 1474, 1455, 1255, 1153, 1111 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.07 (s, 6H), 0.9 (s, 18H), 1.34 (s, 21H), 1.18 (s, 9H), 1.53 (m, 1H), 1.97 (m, 1H), 2.45 (m, 1H), 3.83 (dd, *J* = 1.8, 9.0 Hz, 1H), 3.95-4.11 (m, 2H), 4.28 (td, *J* = 3.7, 13.5 Hz, 1H), 4.41 (dd, *J* = 6.6, 9.7 Hz, 1H), 4.44 (td, *J* = 3.7, 13.5 Hz, 1H), 4.51 (dd, *J* = 7.2, 8.3 Hz, 1H), 5.26 (td, *J* = 3.5, 14.1 Hz, 1H), 5.36 (td, *J* = 3.5, 14.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.4, -5.3, -5.0, -4.6, 12.1 (3C), 17.9 (6C), 25.8 (6C), 27.1 (3C), 27.5, 30.3 (2C), 34.3, 38.6, 48.4, 58.4, 62.6, 74.7, 76.2, 82.1, 112.1, 178.4, 198.9, 216.2; CI-HRMS calcd for $C_{37}H_{72}O_6Si_3$ $[M]^+$ *m/z* 696.4637, found *m/z* 696.4653.

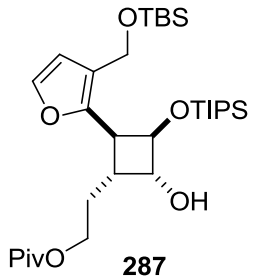


285

2-((1*R*,2*R*,3*R*,4*R*)-2-(*tert*-Butyldimethylsilyloxy)-4-(3-((*tert*-butyldimethylsilyloxy)methyl)furan-2-yl)-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (285)

To a solution of **284** (23.0 mg, 0.04 mmol) in 2.74 mL of hexane and 0.54 mL of CH_2Cl_2 at room temperature was added 28.0 mg of $AgNO_3$ on SiO_2 (10 wt%, 0.016 mmol) in a single portion. The suspension was stirred at room temperature in the

absence of light for 2.5 h, then was diluted with Et_2O and filtered through a short pad of Celite which was washed with Et_2O (20 mL). The solvent was removed in vacuo and the crude mixture was purified by silica gel chromatography (98/2, hexanes/ethyl acetate) to give **285 (**17.0 mg, 74%) as a pale yellow oil: R_f 0.62 (9:1 hexanes/ethyl acetate); $[\alpha]^{25}{}_D$ – 36.3 (*c* 0.65, $CHCl_3$); IR (neat) 2954, 2924, 2856, 1729, 1460, 1251 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 3H), 0.08 (s, 3H), 0.10 (s, 6H), 0.90 (m, 39 H), 1.17 (s, 9H), 1.67 (m, 1H), 2.04 (m, 1H), 2.47 (m, 1H), 3.30 (dd, *J* = 2.7, 9.0 Hz, 1H), 4.02 (m, 1H), 4.14 (m, 1H), 4.45 (dd, *J* = 6.7, 8.6 Hz, 1H), 4.49 (d, *J* = 2.3 Hz, 2H), 4.64 (dd, *J* = 6.5, 8.5 Hz, 1H), 6.32 (d, *J* = 1.7 Hz, 1H), 7.31 (d, *J* = 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.2, -5.1, -4.9, -4.7, 11.9 (3C), 17.7 (6C) 25.8 (3C), 25.9 (3C), 27.1 (4C), 29.7, 30.3 (2C), 36.9, 38.6 (2C), 57.3, 62.8, 75.2, 76.6, 110.6, 121.1, 140.5, 149.0, 178.3; CI-HRMS calcd for $C_{37}H_{72}O_6Si_3$ $[M]^+$ *m/z* 697.4715, found *m/z* 697.4744.



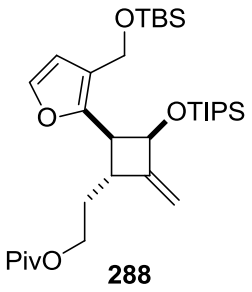
287

2-((1*R*,2*R*,3*R*,4*R*)-2-(3-((*tert*-Butyldimethylsilyloxy)methyl)furan-2-yl)-4-hydroxy-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (287)

To a solution of **285** (11 mg, 0.015 mmol) in EtOH (0.2 mL) was added PPTS (1.0 mg, 0.005 mmol) and the mixture was stirred for 48 h at room temperature. The

reaction was quenched with satd aq $NaHCO_3$ solution and the separated aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic extract was dried (Na_2SO_4), filtered, and concentrated. The crude oil was used for the next step without further purification.

The crude residue (4.0 mg) obtained above was dissolved in 0.2 mL of THF, and imidazole (1.74 mg, 0.025 mmol) and TBSCl (3.20 mg, 0.021 mmol) were added to the solution. The mixture was stirred at room temperature for 16 h and the reaction was quenched with satd aqueous $NaHCO_3$ solution. The separated aqueous layer was extracted with Et_2O (2 x 10 mL) and the combined organic extract was dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified by silica gel chromatography (7:93 ethyl acetate:hexanes) to afford **283** (4.0 mg, 36%, 2 steps) as a colorless oil: R_f 0.68 (8:2 hexanes/ethyl acetate); $[\alpha]^{20}{}_D$ – 6.0 (*c* 1.45, $CHCl_3$); IR (neat) 3466, 2933, 2871, 1734, 1711, 1454 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 3H), 0.09 (s, 3H), 0.95 (s, 30H), 1.20 (s, 9H), 1.72-1.81 (m, 1H), 2.06-2.14 (m, 1H), 2.16 (d, *J* = 4.7 Hz, 1H), 2.64 (dd, *J* = 3.6, 8.0 Hz, 1H), 3.34 (dd, *J* = 6.2, 8.4 Hz, 1H), 4.06-4.22 (m, 2H), 4.44 (dd, *J* = 6.2, 8.4 Hz, 1H), 4.49 (d, *J* = 2.0 Hz, 2H), 4.66 (dd, *J* = 5.7, 9.4 Hz, 1H), 6.32 (d, *J* = 1.5 Hz, 1H), 7.29 (d, *J* = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.2 (2C), 11.9 (3C), 17.6 (6C), 25.9 (3C), 27.1 (3C), 28.8, 29.7, 38.6, 57.2, 63.1, 75.3, 76.0, 110.7, 121.3, 121.3, 140.6, 148.7, 178.6; CI-HRMS calcd for $C_{33}H_{57}O_6NaSi_2$ $[M + Na]^+$ *m/z* 605.3670, found *m/z* 605.3654.



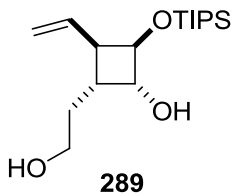
288

2-((1*R*,2*R*,3*R*)-2-(3-((*tert*-Butyldimethylsilyloxy)methyl)furan-2-yl)-4-methylene-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (288)

To a solution of **287** (4.0 mg, 0.0068 mmol) in CH_2Cl_2 (0.1 mL) was added TPAP (2.9 mg, 0.0082 mmol) and the reaction mixture was stirred at room temperature for 1 h. The suspension was filtered through a short pad of silica gel which was washed with CH_2Cl_2 (2 x 5 mL). Evaporation of the filtrate gave a crude residue which was used immediately for the next reaction.

To a solution of the crude residue (3.2 mg, 0.0065 mmol) obtained above in dry THF (0.1 mL) at 0 ^oC was added $Ph_3P{=}CH_2$ (0.3 mL, 0.022 mmol, 0.076 M in THF, freshly prepared from Ph_3PCH_3Br (100.0 mg, 0.28 mmol) and *n*-BuLi (95.6 μL, 0.23 mmol, 2.5 M solution in hexane) in THF (3.0 mL) at 0 ^oC) and the mixture was stirred at 0 ^oC for 10 min. The solution was warmed to room temperature and was stirred for 30 min. The reaction was quenched with satd NH_4Cl (10 mL) solution, the layers were separated, and the aqueous layer was extracted by Et_2O (2 x 5 mL). The combined organic extract was dried, filtered and concentrated, and the crude residue was purified by silica gel chromatography (3:97 Et_2O:pentane) to provide **288** (2.0 mg, 50%, 2 steps) as a colorless oil: R_f 0.8 (9:1 hexanes/ethyl acetate); $[\alpha]^{19}{}_D$ – 4.1 (*c*

0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 3H), 0.09 (s, 3H), 0.95 (m, 30H), 1.18 (s, 9H), 1.94 (dd, *J* = 6.9, 7.5 Hz, 2H), 3.53 (m, 1H), 3.46 (dd, *J* = 5.9, 7.8 Hz, 1H), 4.10 (t, *J* = 6.7 Hz, 2H), 4.54 (d, *J* = 2.6 Hz, 2H), 5.03 (s, 1H), 5.08 (m, 1H), 5.22 (s, 1H), 6.33 (d, *J* = 1.5 Hz, 1H), 7.30 (d, *J* = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.2 (2C), 12.0 (3C), 17.7 (6C), 25.9 (3C), 27.1 (3C), 29.6, 33.4, 38.6, 41.6, 43.1, 57.3, 62.3, 72.7, 77.1, 107.3, 110.8, 121.4, 148.8, 154.9, 178.4; CI-HRMS calcd for $C_{32}H_{58}O_5Si_2$ $[M]^+$ *m/z* 578.3823, found *m/z* 578.3815.

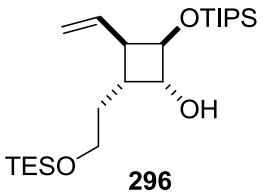


289

(1*R*,2*R*,3*R*,4*R*)-2-(2-Hydroxyethyl)-4-(triisopropylsilyloxy)-3-vinylcyclobutanol (285)

To an EtOH (absolute) solution (0.3 mL) of **279** (24.0 mg, 0.056 mmol) was added *p*-toluenesulfonic acid (1.0 mg, 0.0056 mmol) at room temperature and the mixture was stirred for 4 h. When TLC showed that all the starting material had been consumed, the reaction was quenched with satd aqueous $NaHCO_3$ solution. The aqueous layer was extracted with EtOAc (3 x 5 mL) and the combined organic extract was dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude oil was purified by silica gel chromatography (6:4 hexanes:ethyl acetate) to afford **289** (9.0 mg, 53%) as a colorless oil: R_f 0.28 (6:4 hexanes-ethyl acetate); $[\alpha]^{22}_D$ – 29.0 (*c* 0.40, $CHCl_3$); IR (neat) 3302, 2920, 2868, 1455, 1154 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (m, 21H), 1.68-1.75

(m, 1H), 1.93-2.03 (m, 1H), 2.25-2.32 (m, 1H), 2.65 (dt, *J* = 2.8, 7.9 Hz, 1H), 3.14 (bs, 2OH), 3.63 (ddd, *J* = 7.8, 11.7, 17.5 Hz, 1H), 3.76-3.83 (m, 1H), 4.26 (t, *J* = 7.7 Hz, 2H), 5.00-5.08 (m, 2H), 6.00 (ddd, *J* = 8.6, 10.3, 17.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.9 (3C), 17.9 (6C), 32.3, 39.6, 45.7, 62.1, 74.6, 75.3, 115.3, 137.8; EI-HRMS calcd for $C_{17}H_{35}O_3Si$ $[M]^+$ (*m/z*) 315.2356, found 315.2328.

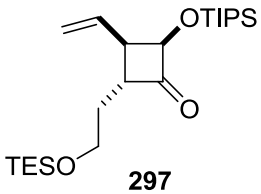


296

(1*R*,2*R*,3*R*,4*R*)-2-(2-(Triethylsilyloxy)ethyl)-4-(triisopropylsilyloxy)-3-vinylcyclobutanol (296)

To a THF (0.5 mL) solution of **289** (23.0 mg, 0.073 mmol) at 0 ^{o}C was added imidazole (10.9 mg, 0.161 mmol) and TESCl (14.6 μL, 0.087 mmol). The reaction mixture was allowed to warm to room temperature and was stirred for 40 min, when satd aqueous $NaHCO_3$ solution was added. The separated aqueous layer was extracted with Et_2O (2 x 10 mL) and the combined organic extract was dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was purified by silica gel chromatography (12:88 hexanes/ethyl acetate) to afford **296** (16 mg, 51%) as a colorless oil: R_f 0.56 (7:3 hexanes-ethyl acetate); $[\alpha]^{20}_{D}$ – 23.7 (*c* 0.75, $CHCl_3$); IR (neat) 3431, 2871, 1458 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (q, *J* = 7.9 Hz, 6H), 0.98 (t, *J* = 8.0 Hz, 9H), 1.08 (m, 21H), 1.64-1.71 (m, 1H), 1.95-2.04 (m, 1H), 2.24-2.30 (m, 1H), 2.68 (dt, *J* = 3.7, 8.4 Hz, 1H), 3.59 (dt, *J* = 3.4, 9.7 Hz, 1H), 3.75 (t, *J* =

5.2 Hz, 1H), 3.78 (d, *J* = 4.4 Hz, 1H), 4.18 (ddd, *J* = 4.0, 5.0, 7.8 Hz, 1H), 4.24 (dd, *J* = 5.3, 8.1 Hz, 1H), 5.02 (dd, *J* = 2.1, 12.3 Hz, 2H), 6.02 (ddd, *J* = 8.8, 10.3, 17.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.1 (3C), 6.6 (3C), 12.0 (3C), 17.9 (6C), 32.0, 40.0, 45.7, 62.2, 74.7, 75.5, 114.9, 138.3; CI-HRMS calcd for $C_{23}H_{49}O_3Si_2$ $[M + H]^+$ (*m/z*) 429.3220, found 429.3203.

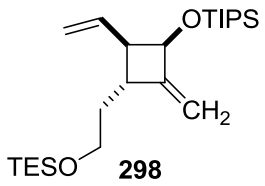


297

(2*R*,3*R*,4*R*)-2-(2-(Triethylsilyloxy)ethyl)-4-(triisopropylsilyloxy)-3-vinylcyclobutanone (297)

To a solution of **296** (16.0 mg, 0.037 mmol) in CH_2Cl_2 (0.4 mL) under argon atmosphere were added activated 4Å molecular sieves, TPAP (1.0 mg, 0.003 mmol) and NMO (8.66 mg, 0.074 mmol). The reaction mixture was stirred at room temperature for 20 min. The suspension was filtered through a short pad of silica gel which was washed with CH_2Cl_2 (5.0 mL). Evaporation of the filtrate and purification of the crude residue by chromatography on silica gel (1:9 ethyl acetate:hexanes) afforded **297** (12.0 mg, 75%) as a colorless oil: R_f 0.56 (7:3 hexanes-ethyl acetate); $[\alpha]^{20}_{D}$ + 38.7 (*c* 0.40, $CHCl_3$); IR (neat) 2955, 2863, 1790, 1465 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.61 (q, *J* = 7.6 Hz, 6H), 0.97 (t, *J* = 7.8 Hz, 9H), 1.08 (m, 21H), 1.84-1.95 (m, 2H), 2.94-3.03 (m, 2H), 3.69 (t, *J* = 6.2 Hz, 2H), 5.07-5.20 (m, 3H), 5.92 (ddd, *J* = 8.6, 10.5, 17.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.3 (3C), 6.7 (3C),

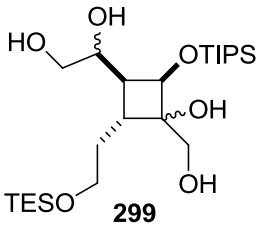
11.9 (3C), 17.6 (6C), 33.8, 43.1, 57.4, 60.4, 82.6, 116.7, 135.6, 209.8; CI-HRMS calcd for $C_{23}H_{47}O_3Si_2$ $[M + H]^+$ (*m/z*) 427.3064, found 427.3050.



298

Triethyl-(2-((1*R*,3*R*,4*R*)-2-methylene-3-(triisopropylsilyloxy)-4-vinylcyclobutyl)ethoxy)silane (298)

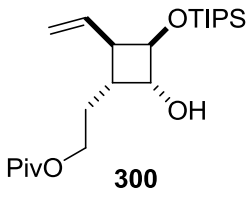
To a solution of **297** (21.0 mg, 0.049 mmol) in dry THF (0.2 mL) at 0 ^oC was added $Ph_3P{=}CH_2$ (2.72 mL, 0.197 mmol, 0.076 M in THF, freshly prepared from Ph_3PCH_3Br (100.0 mg, 0.28 mmol) in and *n*-BuLi (95.6 μL, 0.23 mmol, 2.5 M solution in hexane) THF (3.0 mL) at 0 ^oC) and the mixture was stirred at 0 ^oC for 1 h. The reaction was quenched with satd NH_4Cl solution and the separated aqueous layer was extracted with Et_2O (2 x 5 mL). The combined organic extract was dried (Na_2SO_4), filtered and concentrated, and the crude oil was purified by silica gel chromatography (3:97 ethyl acetate:pentane) to afford **298** (12.0 mg, 60%) as a colorless oil: R_f 0.74 (95:5 hexanes/Et_2O); $[\alpha]^{20}{}_D$ – 13.0 (*c* 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.61 (q, *J* = 7.4 Hz, 6H), 0.97 (t, *J* = 7.8 Hz, 9H), 1.07 (m, 2H), 1.78 (dd, *J* = 5.8, 7.0 Hz, 2H), 2.62 (m, 1H), 2.75 (dd, *J* = 3.9, 4.0 Hz, 1H), 3.64 (t, *J* = 6.9 Hz, 2H), 4.87-5.13 (m, 5H), 6.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.4, 6.7, 12.0, 17.8, 37.5, 42.3, 49.5, 61.1, 72.2, 105.9, 115.2, 137.5, 155.6; CI-HRMS calcd for $C_{24}H_{49}O_2Si_2$ $[M + H]^+$ *m/z* 425.3271, found *m/z* 425.3282.



299

1-((1*S*,2*R*,4*R*)-3-Hydroxy-3-(hydroxymethyl)-2-(2-(triethylsilyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)ethane-1,2-diol (299)

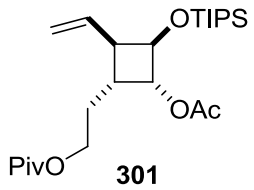
To a solution of **298** (4.0 mg, 0.0094 mmol) in a mixture of THF-H_2O (0.13 mL, 1:1, v/v) were added NMO (3.3 mg, 0.028 mmol) and OsO_4 (4.71 μL, 0.1M in 2-methyl-2-propanol, 0.0004 mmol). The mixture was stirred at room temperature for 24 h and water (5 mL) was added. The separated aqueous layer was extracted with EtOAc (3 x 10 mL) and the combined organic extract was washed with satd $NaHCO_3$ solution. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo and the crude residue was purified by silica gel chromatography (35:65 ethyl acetate:hexanes) to afford **299** (4.0 mg, 87%) as a colorless oil: R_f 0.35 (6:4 hexanes/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (q, *J* = 7.8 Hz, 6H), 0.98 (t, *J* = 7.9 Hz, 10H), 1.09-1.11 (m, 21H), 1.60-1.63 (m, 1H), 1.94-2.05 (m, 1H), 2.08-2.14 (m, 1H), 2.24 (ddd, *J* = 2.9, 7.5, 9.4 Hz, 1H), 2.60-2.65 (m, 1H), 3.50-3.54 (m, 2H), 3.60 (dt, *J* = 2.6, 10.0 Hz, 1H), 3.74-3.81 (m, 3H), 4.13-4.17 (m, 1H), 4.18 (bs, OH), 4.55 (dd, *J* = 0.7, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.0, 6.6, 12.0, 17.8, 17.9, 29.7, 30.3, 36.6, 41.7, 62.5, 64.8, 65.4, 70.4, 74.8, 76.6; CI-HRMS calcd for $C_{24}H_{53}O_6Si_2$ $[M + H]^+$ *m/z* 493.3381, found *m/z* 493.3362.



300

2-((1*R*,2*R*,3*R*,4*R*)-2-Hydroxy-3-(triisopropylsilyloxy)-4-vinylcyclobutyl)ethyl Pivalate (300)

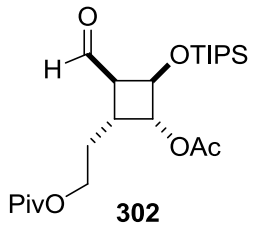
To a CH_2Cl_2 solution (0.8 mL) of **289** (27 mg, 0.085 mmol) at 0 ^oC were added pyridine (13.8 µL, 0.171 mmol), trimethylacetyl chloride (13.6 µL, 0.11 mmol) and DMAP (1.04 mg, 0.085 mmol). The mixture was allowed to warm to room temperature and was stirred for 18 h, after which the reaction was quenched by addition of a satd aqueous $NaHCO_3$ solution (10 mL). The separated aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organic extract was washed with saturated $CuSO_4$ solution, dried (Na_2SO_4), filtered, and concentrated. The crude residue was purified by silica gel chromatography (7:93 ethyl acetate/hexanes) to give **300** (22 mg, 64%) as a colorless oil: R_f 0.66 (8:2 hexanes/ethyl acetate); $[\alpha]^{25}{}_D$ – 86.3 (*c* 1.0, $CHCl_3$); IR (neat) 3470, 2941, 2859, 1731 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.07 (s, 21H), 1.21 (s, 9H), 1.63-1.73 (m, 1H), 1.96-2.06 (m, 1H), 2.08 (d, *J* = 2.0 Hz, OH), 2.16-2.23 (m, 1H), 2.67-2.72 (m, 1H), 4.06-4.20 (m, 2H), 4.23-4.31 (m, 2H), 5.00-5.08 (m, 2H), 5.98 (ddd, *J* = 8.3, 10.1, 17.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.9 (3C), 17.8 (6C), 27.2 (3C), 28.1, 36.8, 38.7, 44.9, 63.2, 75.1, 75.3, 115.5, 137.4, 178.7; CI-HRMS calcd for $C_{22}H_{42}O_4Si$ $[M + H]^+$ *m/z* 399.2930, found *m/z* 399.2943.



301

2-((1*R*,2*R*,3*R*,4*R*)-2-Acetoxy-3-(triisopropylsilyloxy)-4-vinylcyclobutyl)ethyl Pivalate (301)

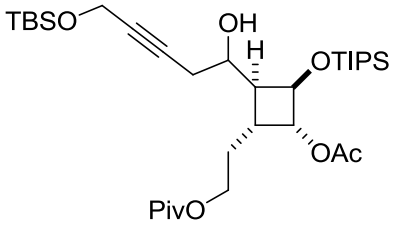
To a CH_2Cl_2 solution (0.5 mL) of **300** (22 mg, 0.055 mmol) at 0 ^oC was slowly added pyridine (13.4 µL, 0.165 mmol), acetic anhydride (15.6 µL, 0.165 mmol) and DMAP (0.65 mg, 0.085 mmol). The mixture was allowed to warm to room temperature and stirred for 1 h. The reaction was quenched by addition of satd aqueous $NaHCO_3$ solution (5 mL), the separated aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organic extract was washed with satd $CuSO_4$ solution, dried (Na_2SO_4), filtered, and concentrated. The crude mixture was purified by silica gel chromatography (5:95 ethyl acetate/hexanes) to afford **301** (21 mg, 87%) as a colorless oil: R_f 0.51 (9:1 hexanes/ethyl acetate); $[\alpha]^{25}{}_D$ – 77.5 (*c* 1.0, $CHCl_3$), IR (neat) 2945, 2870, 1751, 1729, 1462 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 21H), 1.19 (s, 9H), 1.58-1.62 (m, 1H), 1.73-1.83 (m, 1H), 2.08 (s, 3H), 2.38 (m, 1H), 2.81 (t, *J* = 8.5 Hz, 1H), 4.05 (t, *J* = 6.6 Hz, 2H), 4.48 (dd, *J* = 6.8, 8.5 Hz, 1H), 5.04-5.14 (m, 3H), 6.01 (ddd, *J* = 8.4, 10.6, 17.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.8 (3C), 17.6 (6C), 20.6, 27.1 (3C), 28.2, 35.7, 38.7, 45.3, 62.4, 71.7, 76.1, 116.2, 136.5, 170.2, 178.5; CI-HRMS calcd for $C_{24}H_{44}O_5NaSi$ $[M + Na]^+$ *m/z* 463.2856, found *m/z* 463.2842.



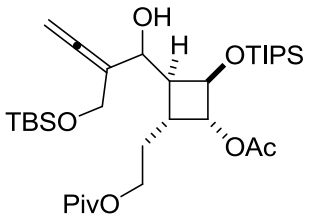
302

2-((1*R*,2*R*,3*R*,4*R*)-2-Acetoxy-4-formyl-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (302)

To a solution of **301** (22 mg, 0.049 mmol) in dioxane-water (3:1, 0.5 mL) were added 2,6-lutidine (11.35 µL, 0.248 mmol), OsO_4 (0.05M in 2-methyl-2-propanol, 50.0 µL , 0.0024 mmol), and $NaIO_4$ (42.0 mg, 0.196 mmol). The reaction mixture was stirred at room temperature for 2 h and was diluted with water (10 mL) and CH_2Cl_2 (10 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extract was washed with aqueous $CuSO_4$ solution, brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude residue was purified by silica gel chromatography (1:9 ethyl acetate:hexanes) to afford **302** (15.0 mg, 68%) as a pale brown oil: R_f 0.41 (15:85 hexanes-ethyl acetate); $[\alpha]^{26}{}_D$ – 53.8 (*c* 1.0, $CHCl_3$); IR (neat) 2944, 2861, 1754, 1724(2) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 21H), 1.19 (s, 9H), 1.54-1.61 (m, 1H), 1.78-1.86 (m, 1H), 2.09 (s, 3H), 2.90-2.97 (m, 1H), 3.13 (d, *J* = 9.3 Hz, 1H), 3.97-4.07 (m, 2H), 4.72 (dd, *J* = 6.8, 9.2 Hz, 1H), 5.24 (dd, *J* = 6.4, 7.9 Hz, 1H), 9.88 (d, *J* = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7 (3C), 17.5 (6C), 20.5, 27.1 (3C), 27.2, 30.1, 38.7, 52.5, 62.1, 72.7, 75.7, 169.8, 178.4, 200.7; EI-HRMS calcd for $C_{23}H_{42}O_6NaSi$ $[M + Na]^+$ (*m/z*) 465.2648, found 465.2659.



303
(single isomer by NMR)



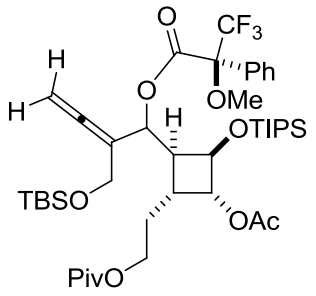
304
(single isomer by NMR)

2-((1*R*,2*R*,3*R*,4*S*)-2-Acetoxy-4-((*S*)-5-(*tert*-butyldimethylsilyloxy)-1-hydroxypent-3-ynyl)-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (303) and 2-((1*R*,2*R*,3*R*,4*S*)-2-Acetoxy-4-((*R*)-2-((*tert*-butyldimethylsilyloxy)methyl)-1-hydroxybuta-2,3-dienyl)-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (304)

To a solution of **264** (149.0 mg, 0.568 mmol) in 3.0 mL of DMF at room temperature under argon were added $SnCl_2$ (129.0 mg, 0.68 mmol) and NaI (102.0 mg, 0.68 mmol) and the resulting mixture was stirred for 3 h while protected from light in a flask wrapped with aluminum foil. After the foil was removed, the bright yellow solution was cooled to 0 °C and a solution of **302** (84.0 mg, 0.189 mmol) in 2.0 mL of DMF was added over a 10 min period. After stirring for 30 h at 0 ^{o}C in the absence of light, the reaction mixture was diluted with Et_2O (20 mL) and satd aqueous solution of NH_4Cl (20 mL) while being vigorously stirred. The separated aqueous layer was extracted with Et_2O (3 x 20 mL) and the combined organic extract was washed with satd aqueous $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure and flash chromatographic purification of the residual oil on silica gel (6:94 ethyl acetate:hexanes) afforded **303** (21.0 mg, 17%) and **304** (61.0 mg, 53%) as colorless oils.

303: R_f 0.42 (85:15 hexanes-ethyl acetate); $[\alpha]^{20}{}_D$ – 49.0 (*c* 1.60, $CHCl_3$); IR (neat) 3544, 2964, 2929, 2867,1746, 1731, 1458, 1376, 1232, 1143 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 6H), 0.91 (s, 9H), 1.07 (s, 21H), 1.20 (s, 9H), 1.47-1.57 (m, 1H), 1.75-1.84 (m, 1H), 2.08 (s, 3H), 2.33 (tdd, *J* = 1.8, 10.3, 15.9 Hz, 1H), 2.46-2.54 (m, 2H), 2.63-2.70 (m, 1H), 2.87 (d, *J* = 2.3 Hz, OH), 3.94-4.00 (m, 1H), 4.14-4.19 (m, 2H), 4.30 (t, *J* = 1.8 Hz, 2H), 4.63 (dd, *J* = 6.3, 9.7 Hz, 1H), 5.18 (dd, *J* = 6.3, 9.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.1 (2C), 11.7 (3C), 17.6 (6C), 20.6, 23.5, 25.8 (3C), 27.2 (3C), 28.2, 29.5, 38.7, 44.4, 51.9, 61.8, 67.8, 71.9, 76.6, 17.8, 80.7, 81.2, 169.8, 178.3 ; CI-HRMS calcd for $C_{33}H_{63}O_7Si_2$ $[M]^+$ (*m/z*) 627.4112, found 627.4120.

304: R_f 0.50 (85:15 hexanes-ethyl acetate); $[\alpha]^{20}{}_D$ – 53.1 (*c* 1.20, $CHCl_3$); IR (neat) 3540, 2953, 2867, 1960, 1742, 1731, 1458, 1369, 1236, 1151 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 3H), 0.07 (s, 3H), 0.89 (s, 9H), 1.06 (s, 21H), 1.19 (s, 9H), 1.58-1.67 (m, 1H), 1.76-1.85 (m, 1H), 2.07 (s, 3H), 2.48 (td, *J* = 2.7, 9.2 Hz, 1H), 2.68 (dd, *J* = 3.0, 8.5 Hz, 1H), 3.01 (d, *J* = 3.1 Hz, OH), 3.96 (t, *J* = 7.3 Hz, 2H), 4.18 (td, J = 2.0, 11.6 Hz, 1H), 4.31 (td, *J* = 2.0, 11.6 Hz, 1H), 4.62 (dd, *J* = 6.2, 9.4 Hz, 1H), 4.69 (pentet, *J* = 2.9 Hz, 1H), 4.91 (qq, *J* = 2.2, 10.5 Hz, 2H), 5.27 (dd, *J* = 5.9, 9.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.4, -5.3, 11.8 (3C), 17.6 (3C), 17.8 (3C), 20.7, 25.8 (3C), 27.1 (3C), 28.9, 29.7, 30.2, 38.6, 44.9, 62.6, 63.1, 66.2, 72.1, 76.5, 78.1, 104.2, 169.8, 178.4, 205.5 ; CI-HRMS calcd for $C_{33}H_{63}O_7Si_2$ $[M]^+$ (*m/z*) 627.4112, found 627.4088.

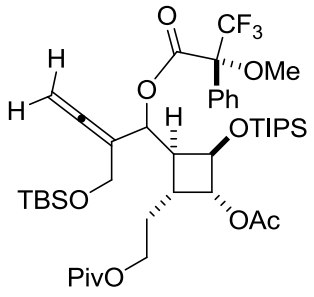


306 (*S*-Mosher ester)

2-((1*R*,2*R*,3*R*,4*S*)-2-Acetoxy-4-((*R*)-2-((*tert*-butyldimethylsilyloxy)methyl)-1-((*S*)-1'-methoxy-1'-phenyl-1'-triflouromethyl-acetoxy)buta-2,3-dienyl)-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (304)

To a solution of **304** (7.0 mg, 0.011 mmol) in CH_2Cl_2 (0.2 mL) were sequentially added DMAP (13.4 mg, 0.11 mmol) and (*R*)-(-)-α-methoxy-α-trifluoromethylphenylacetyl chloride (14.1 mg, 10.4 μL, 0.055 mmol). After stirring for 2 h at room temperature, the solvent was evaporated and the residual oil was loaded directly on to a silica gel column and was purified by chromatography (5:95 ethyl acetate /hexanes) to provide (*S*)-MTPA ester **306** (9.0 mg, 95%) as a colorless oil: R_f 0.66 (85:15 hexanes/ethyl acetate); $[\alpha]^{21}{}_D$ – 87.8 (*c* 0.5, $CHCl_3$); IR (neat) 2952, 2870, 1752, 1729, 1471 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 3H), 0.06 (s, 3H), 0.89 (s, 9H), 1.02 (s, 21H), 1.19 (s, 9H), 1.50–1.57 (m, 1H), 1.68-1.76 (m, 1H), 2.05 (s, 3H), 2.59-2.69 (m, 2H), 3.62 (s, 3H), 3.84-3.97 (m, 2H), 4.24 (td, *J* = 2.1, 11.9 Hz, 1H), 4.33 (td, *J* = 2.9, 12.3 Hz, 1H), 4.50 (dd, *J* = 6.9, 8.9 Hz, 1H), 4.86 (td, *J* = 3.0, 10.9 Hz, 1H), 4.95 (td, *J* = 2.6, 11.0 Hz, 1H), 5.14 (dd, *J* = 7.2, 8.4 Hz, 1H), 5.52 (s, 1H), 7.37-7.39 (m, 3H), 7.62-7.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.4 (2C),

11.9 (3C), 17.6 (3C), 17.8 (3C), 20.6, 25.8 (3C), 27.1 (3C), 28.7, 31.0, 38.6, 44.8, 55.3, 62.5, 63.5, 70.6, 71.3, 80.1, 104.5, 127.7 (2C), 128.2 (3C), 129.3 (2C), 132.1, 165.5, 169.7, 206.3; CI-HRMS calcd for $C_{43}H_{69}O_9F_3NaSi_2$ [M + Na] $^+$ *m/z* 865.4330, found *m/z* 865.4362.

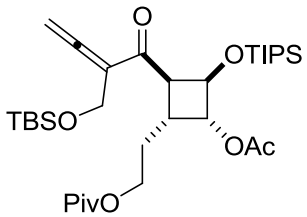


308 (*R*-Mosher ester)

2-((1*R*,2*R*,3*R*,4*S*)-2-Acetoxy-4-((*R*)-2-((*tert*-butyldimethylsilyloxy)methyl)-1-((*R*)-1'-methoxy-1'-phenyl-1'-triflouromethyl-acetoxy)buta-2,3-dienyl)-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (304)

To a solution of **304** (20.0 mg, 0.031 mmol) in CH_2Cl_2 (0.6 mL) were sequentially added DMAP (38.9 mg, 0.11 mmol) and (*S*)-(+)-α-methoxy-α-trifluoromethylphenylacetyl chloride (40.1 mg, 30.0 μL, 0.159 mmol). After stirring for 1 h at room temperature, the solvent was evaporated and the crude residue was loaded directly on to silica gel and was purified by chromatography (5:95 ethyl acetate/hexanes) to give (*R*)-MTPA ester **308** (23.0 mg, 86%) as a colorless oil: R_f 0.66 (85:15 hexanes/ethyl acetate); $[\alpha]^{21}{}_D$ – 83.8 (*c* 0.9, $CHCl_3$); IR (neat) 2952, 2870, 1752, 1729, 1471 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 3H), 0.08 (s, 3H), 0.90 (s, 9H), 1.06 (s, 21H), 1.17 (s, 9H), 1.52-1.61 (m, 1H), 1.73-1.81 (m, 1H), 2.06 (s, 3H), 2.60-2.68 (m, 2H), 3.66 (s, 3H), 3.85-3.99 (m, 2H), 4.21 (dt, *J* = 1.6, 11.5 Hz,

1H), 4.33 (dt, *J* = 2.5, 11.7 Hz, 1H), 4.88 (d, *J* = 11.2 Hz, 1H), 4.55 (dd, *J* = 6.7, 8.2 Hz, 1H), 4.72 (d, *J* = 11.2 Hz, 1H), 5.34 (t, *J* = 7.5 Hz, 1H), 5.53 (s, 1H), 7.39-7.40 (m, 3H), 7.61-7.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.3 (2C), 11.9 (3C), 17.6 (3C), 17.8 (3C), 20.6, 25.9 (3C), 27.1 (3C), 28.8, 30.4, 38.6, 45.0, 55.8, 62.5, 63.9, 70.3, 71.1, 75.4, 79.7, 103.9, 127.6 (2C), 128.3 (3C), 129.3 (2C), 132.0, 165.6, 169.8, 178.3, 205.9; CI-HRMS calcd for $C_{43}H_{69}O_9F_3NaSi_2$ $[M + Na]^+$ *m/z* 865.4330, found *m/z* 865.4362.

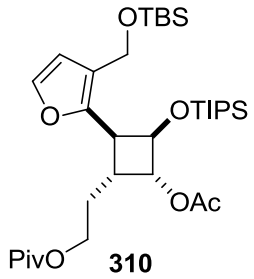


309

2-((1*R*,2*R*,3*R*,4*R*)-2-Acetoxy-4-(2-((*tert*-butyldimethylsilyloxy)methyl)buta-2,3-dienoyl)-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (309)

To a solution of **304** (61.0 mg, 0.097 mmol) in 1.0 mL of CH_2Cl_2 at 0 ^oC was added $NaHCO_3$ (32.5 mg, 0.38 mmol) followed by Dess-Martin periodinane (82.5 mg, 0.194 mmol). The slurry was stirred at 0 ^oC for 1 h and was diluted with CH_2Cl_2 (5.0 mL). The reaction was quenched with satd $Na_2S_2O_3$ solution (15 mL) by stirring the biphasic mixture vigorously for 20 min. The layers were separated, the aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL), and the combined organic extract was washed with satd $NaHCO_3$ solution, water and brine and dried over Na_2SO_4. The drying agent was removed by filtration and the filtrate was concentrated in vacuo. Purification of the crude residue by silica gel chromatography (94:6 hexanes/ethyl acetate) provided

309 (59 mg, 97%) as a yellow oil: R_f 0.50 (85:15 hexanes/ethyl acetate); $[\alpha]^{18}{}_D$ – 14.6 (*c* 0.98, $CHCl_3$); IR (neat) 2953, 2863, 1933, 1750, 1731, 1664, 1466, 1369, 1228 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.08 (s, 9H), 1.01 (s, 21H), 1.17 (s, 9H), 1.50-1.60 (m, 1H), 1.72-1.81 (m, 1H), 2.06 (s, 3H), 2.78-2.85 (m, 1H), 3.90 (dd, *J* = 3.2, 9.8 Hz, 1H), 3.97 (t, *J* = 6.5 Hz, 2H), 4.28 (td, *J* = 3.6, 13.3 Hz, 1H), 4.44 (td, *J* = 3.4, 13.3 Hz, 1H), 4.60 (dd, *J* = 6.5, 9.5 Hz, 1H), 5.24-5.29 (m, 2H), 5.36 (td, *J* = 3.4, 13.9 Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.4, -5.3, 12.1 (3C), 17.6 (3C), 17.7 (3C), 18.2, 20.5, 25.8 (3C), 27.1 (3C), 27.5, 31.9, 38.6, 48.8, 58.4, 62.2, 72.2, 75.9, 82.1, 112.0, 169.6, 178.3, 197.3, 216.3; CI-HRMS calcd for $C_{33}H_{61}O_7Si_2$ $[M]^+$ *m/z* 625.3956, found *m/z* 625.3955.

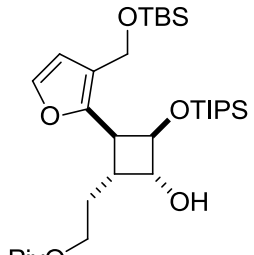


310

2-((1*R*,2*R*,3*R*,4*R*)-2-Acetoxy-4-(3-((*tert*-butyldimethylsilyloxy)methyl)furan-2-yl)-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (310)

To a solution of **309** (54.0 mg, 0.086 mmol) in 3.58 mL of hexane and 0.70 mL of CH_2Cl_2 at room temperature was added 73.3 mg of $AgNO_3$ on SiO_2 (10 wt.%, 0.043 mmol) in a single portion. The suspension was stirred at room temperature for 2 h in the absence of light, then it was diluted with Et_2O and filtered through a short pad of Celite which was washed with Et_2O (20 mL). The filtrate was concentrated in vacuo,

and the crude mixture was purified by silica gel chromatography (96/4, hexanes/ethyl acetate) to furnish **310 (**43.0 mg, 79%) as a pale yellow oil: R_f 0.57 (85:15 hexanes/ethyl acetate); $[\alpha]^{18}{}_D$ – 27.3 (*c* 1.00, $CHCl_3$); IR (neat) 2953, 2863, 1746, 1731, 1462, 1365 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 6H), 0.92 (s, 30H), 1.17 (s, 9H), 1.67-1.73 (m, 1H), 1.84-1.92 (m, 1H), 2.10 (s, 3H), 2.78-2.85 (m, 1H), 3.46 (dd, *J* = 3.2, 9.1 Hz, 1H), 3.97-4.08 (m, 2H), 4.50 (d, *J* = 2.9 Hz, 2H), 4.63 (dd, *J* = 6.6, 8.3 Hz, 1H), 5.52 (dd, *J* = 6.6, 8.8 Hz, 1H), 6.31 (d, *J* = 1.7 Hz, 1H), 7.31 (d, *J* = 1.6 Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.2 (2C), 11.8 (3C), 17.5 (3C), 17.6 (3C), 18.3, 20.6, 25.9 (3C), 27.1 (3C), 28.7, 35.0, 38.6, 39.0, 57.2, 62.2, 72.5, 76.2, 110.6, 121.6, 140.9, 147.8, 170.0, 178.3; CI-HRMS calcd for $C_{33}H_{61}O_7Si_2$ $[M]^+$ *m/z* 625.3955, found *m/z* 625.3938.

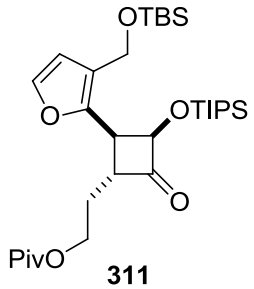


287

2-((1*R*,2*R*,3*R*,4*R*)-2-(3-((*tert*-Butyldimethylsilyloxy)methyl)furan-2-yl)-4-hydroxy-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (287)

To a stirred solution of **310** (38.0 mg, 0.06 mmol) in dry MeOH (0.6 mL) at 0 ^oC was added K_2CO_3 (21.0 mg, 0.152 mmol). The mixture was stirred at 0 ^oC for 3 h and water (10 mL) was added to the reaction mixture. The separated aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic extract was dried over

anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified by silica gel chromatography (92:8 hexane: ethyl acetate) to afford **287** (29.0 mg, 82%) as a colorless oil: R_f 0.68 (8:2 hexanes/ethyl acetate); $[\alpha]^{20}{}_D$ – 6.0 (*c* 1.45, $CHCl_3$); IR (neat) 3466, 2933, 2871, 1734, 1711, 1454 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 3H), 0.09 (s, 3H), 0.95 (s, 30H), 1.20 (s, 9H), 1.72-1.81 (m, 1H), 2.06-2.14 (m, 1H), 2.16 (d, *J* = 4.7 Hz, 1H), 2.64 (dd, *J* = 3.6, 8.0 Hz, 1H), 3.34 (dd, *J* = 6.2, 8.4 Hz, 1H), 4.06-4.22 (m, 2H), 4.44 (dd, *J* = 6.2, 8.4 Hz, 1H), 4.49 (d, *J* = 2.0 Hz, 2H), 4.66 (dd, *J* = 5.7, 9.4 Hz, 1H), 6.32 (d, *J* = 1.5 Hz, 1H), 7.29 (d, *J* = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.2 (2C), 11.9 (3C), 17.6 (6C), 25.9 (3C), 27.1 (3C), 28.8, 29.7, 38.6, 57.2, 63.1, 75.3, 76.0, 110.7, 121.3, 121.3, 140.6, 148.7, 178.6; CI-HRMS calcd for $C_{33}H_{57}O_6NaSi_2$ $[M + Na]^+$ *m/z* 605.3670, found *m/z* 605.3654.

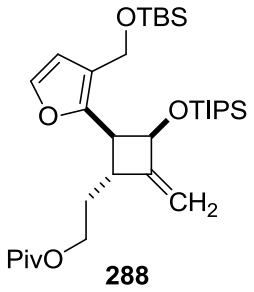


311

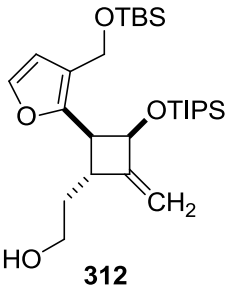
2-((1*R*,2*R*,3*R*)-2-(3-((*tert*-Butyldimethylsilyloxy)methyl)furan-2-yl)-4-oxo-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (311)

To a CH_2Cl_2 (0.5 mL) solution of **287** (31.0 mg, 0.053 mmol) were added 4Å MS, TPAP (1.86 mg, 0.0052 mmol) and NMO (18.69 mg, 0.159 mmol). The reaction mixture was stirred at room temperature for 30 min after which the suspension was loaded directly on a silica gel column. The crude mixture was purified by

chromatography (93/7 hexanes/ethyl acetate) to yield **311** (29.0 mg, 94%) as a colorless oil: R_f 0.75 (2:8 hexanes-ethyl acetate); $[\alpha]^{21}{}_D$ + 38.7 (*c* 1.45, $CHCl_3$); IR (neat) 2957, 2868, 1792, 1733, 1470, 1158 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 6H), 0.93-0.96 (m, 30H), 1.17 (s, 9H), 1.95-2.14 (m, 2H), 3.53-3.59 (m, 1H), 3.69 (dd, *J* = 5.9, 9.1 Hz, 1H), 4.13 (t, *J* = 6.1 Hz, 2H), 4.56 (d, *J* = 7.0 Hz, 2H), 5.18 (dd, *J* = 2.9, 9.3 Hz, 1H), 6.32 (d, *J* = 1.3 Hz, 1H), 7.29 (d, *J* = 1.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.2 (2C), 11.8 (3C), 17.4 (3C), 17.5 (3C), 18.3, 25.9 (3C), 27.1 (3C), 29.9, 36.8, 38.7, 56.2, 57.2, 61.8, 83.2, 110.7, 122.1, 141.3, 147.2, 178.3, 208.4; CI-HRMS calcd for $C_{13}H_{56}O_6Si_2$ $[M]^+$ *m/z* 580.3615, found *m/z* 580.3616.



288



312

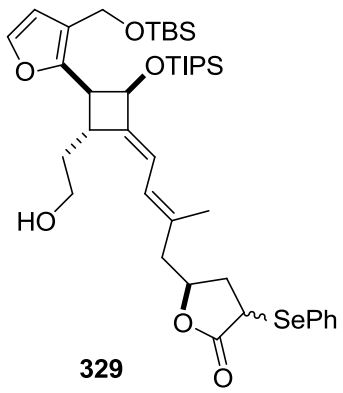
2-((1*R*,2*R*,3*R*)-2-(3-((*tert*-Butyldimethylsilyloxy)methyl)furan-2-yl)-4-methylene-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (288) and 2-((1*R*,2*R*,3*R*)-2-(3-((*tert*-Butyldimethylsilyloxy)methyl)furan-2-yl)-4-methylene-3-(triisopropylsilyloxy)cyclobutyl)ethanol (312)

To a solution of **311** (26.0 mg, 0.044 mmol) in dry THF (1.0 mL) at 0 ^oC was added $Ph_3P{=}CH_2$ (1.50 mL, 0.179 mmol, 0.119 M in THF, freshly prepared from Ph_3PCH_3Br (200.0 mg, 0.56 mmol) and *n*-BuLi (0.17 mL, 0.47 mmol, 2.7 M solution in hexane in THF (4.0 mL) at 0 ^oC) and the mixture was stirred at 0 ^oC for 10 min and at room temperature for 45 min. The reaction was quenched with satd aqueous NH_4Cl solution

(10 mL) and the separated aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic extract was dried (Na_2SO_4), filtered and concentrated, and the crude residue was purified by silica gel chromatography (3:97 ethyl acetate:hexanes) to give **288** (12.0 mg, 48%) and **312** (3.0 mg, 15%) as colorless oils.

288: R_f 0.8 (9:1 hexanes/ethyl acetate); $[\alpha]^{19}{}_D$ – 4.1 (*c* 0.6, $CHCl_3$); IR (neat) 2953, 2959, 1725, 1466 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 3H), 0.09 (s, 3H), 0.95 (m, 30H), 1.18 (s, 9H), 1.94 (dd, *J* = 6.9, 7.5 Hz, 2H), 3.53 (m, 1H), 3.46 (dd, *J* = 5.9, 7.8 Hz, 1H), 4.10 (t, *J* = 6.7 Hz, 2H), 4.54 (d, *J* = 2.6 Hz, 2H), 5.03 (s, 1H), 5.08 (m, 1H), 5.22 (s, 1H), 6.33 (d, *J* = 1.5 Hz, 1H), 7.30 (d, *J* = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.2 (2C), 12.0 (3C), 17.7 (6C), 25.9 (3C), 27.1 (3C), 29.6, 33.4, 38.6, 41.6, 43.1, 57.3, 62.3, 72.7, 77.1, 107.3, 110.8, 121.4, 148.8, 154.9, 178.4; CI-HRMS calcd for $C_{32}H_{58}O_5Si_2$ $[M]^+$ *m/z* 578.3822, found *m/z* 578.3814.

312: R_f 0.46 (8:2 hexanes/ethyl acetate); $[\alpha]^{23}{}_D$ – 18.0 (*c* 0.4, $CHCl_3$); IR (neat) 3400, 2941, 2863, 1462, 1246 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 3H), 0.11 (s, 3H), 0.95 (s, 30H), 1.72 (t, *J* = 4.3 Hz, OH), 1.76-1.85 (m, 1H), 1.90-1.98 (m, 1H), 3.39-3.49 (m, 2H), 3.67 (d, *J* = 4.3 Hz, 2H), 4.55 (q, *J* = 1.4, 7.1 Hz, 2H), 5.03 (s, 1H), 5.07 (dd, *J* = 1.4, 7.1 Hz, 1H), 5.20 (s, 1H), 6.32 (d, *J* = 1.4 Hz, 1H), 7.30 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.1 (2C), 11.7 (3C), 17.7 (6C), 25.9 (3C), 37.3, 42.6, 43.2, 57.2, 58.8, 61.0, 72.9, 106.8, 111.1, 121.2, 140.8, 149.4, 155.4; EI-HRMS calcd for $C_{27}H_{50}O_4Si_2$ $[M]^+$ *m/z* 494.3247, found *m/z* 494.3229.

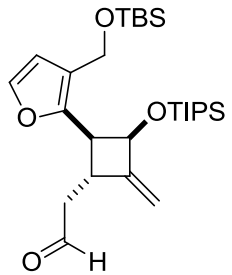


329

(*S*)-5-((2*E*,4*E*)-4-((2*R*,3*R*,4*R*)-3-(3-((*tert*-Butyldimethylsilyloxy)methyl)furan-2-yl)-2-(2-hydroxyethyl)-4-(triisopropylsilyloxy)cyclobutylidene)-2-methylbut-2-enyl)-3-(phenylselanyl)dihydrofuran-2(3H)-one (329)

To a mixture of vinyl iodide **228** (6.14 mg, 0.014 mmol) and furan **312** (6.0 mg, 0.012 mmol) in 0.2 mL of DMF were added KOAc (2.35 mg, 0.024 mmol) and $Pd(OAc)_2$ (0.26 mg, 0.00012 mmol). The reaction mixture was heated in a sealed vessel at 100 ^oC for 6 h and, after cooling, was diluted with water (10 mL). The mixture was extracted with Et_2O (2 x 10 mL) and the combined organic extract was dried (Na_2SO_4), filtered, and concentrated. Purification of the crude residue by silica gel chromatography (3/7 ethyl acetate/hexanes) afforded **329** (2.0 mg, 34%) as a colorless oil: R_f 0.16 (3:7 hexanes-ethyl acetate); IR (neat) 2925, 2855, 1769 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 0.09–0.10 (m, 14H), 0.93–0.94 (m, 20H), 0.96-0.97 (m, 37H), 1.75 (s, 3H), 1.76 (s, 3H), 1.92-1.96 (m, 4H), 1.9–2.03 (m, 1H), 2.15–2.17 (m, 1H), 2.26–2.29 (m, 1H), 2.38 (dd, *J* = 5.5, 7.5 Hz, 4H), 2.47–2.50 (m, 1H), 2.76–2.81 (m, 1H), 3.34–3.37 (m, 1H), 3.57–3.60 (m, 1H), 3.66–3.70 (m, 2H), 3.73–3.77 (m, 1H), 3.98 (t, *J* = 5.9 Hz, 1H), 4.04 (t, *J* = 8.9 Hz, 1H), 4.42–4.46 (m, 1H), 4.48–4.51 (m,

1H), 4.53 (dd, *J* = 2.2, 4.0 Hz, 2H), 5.21 (d, *J* = 7.2 Hz, 1H), 5.88 (d, *J* = 11.3 Hz, 1H), 5.96 (d, *J* = 11.5 Hz, 1H), 6.33 (d, *J* = 1.8 Hz, 1H), 6.34 (d, *J* = 1.8 Hz, 1H), 6.36 (t, *J* = 1.6 Hz, 1H), 6.38 (t, *J* = 2.2 Hz, 1H), 7.31 (d, *J* = 1.8 Hz, 1H), 7.32 (d, *J* = 1.8 Hz, 1H), 7.34–7.42 (m, 8H), 7.68–7.71 (m, 5H); ^{13}C NMR (700 MHz, $CDCl_3$) δ -5.1, 11.9, 12.0, 14.1, 16.8, 17.5, 17.7, 17.8, 18.4, 25.9, 29.7, 30.3, 31.9, 35.5, 36.4, 36.9, 37.2, 37.5, 40.3, 43.6, 45.6, 45.9, 57.3, 61.1, 71.9, 77.3, 110.8, 117.8, 121.3, 124.4, 126.7, 129.2, 129.4, 131.2, 135.8, 135.9, 140.9, 149.3, 149.5, 176.0, 176.1; EI-HRMS calcd for $C_{40}H_{65}O_6SeSi_2Na$ $[M + Na]^+$ (*m/z*) 811.3476, found 811.3398.

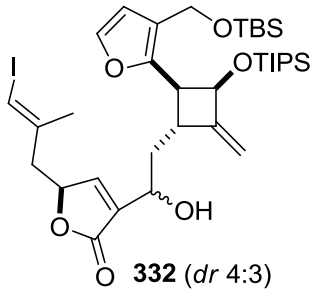


330

2-((1*R*,2*R*,3*R*)-2-(3-((*tert*-Butyldimethylsilyloxy)methyl)furan-2-yl)-4-methylene-3-(triisopropylsilyloxy)cyclobutyl)acetaldehyde (330)

To a CH_2Cl_2 solution (0.5 mL) of alcohol **312** (15.0 mg, 0.03 mmol) were added 4Å MS, TPAP (1.06 mg, 0.003 mmol) and NMO (10.54 mg, 0.09 mmol). The reaction mixture was stirred at room temperature for 1 h, after which the suspension was loaded on a silica gel column and eluted (95/5 hexanes/ethyl acetate) to give aldehyde **330** (9.0 mg, 60%) as a colorless oil: R_f 0.66 (15:85 hexanes-ethyl acetate); $[\alpha]^{20}{}_D$ − 10.2 (*c* 0.4, $CHCl_3$); IR (neat) 2947, 2866, 1721, 1462 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 3H), 0.09 (s, 3H), 0.92 (s, 9H), 0.95 (s, 21H), 2.72 (dd, *J* = 1.8, 7.3

Hz, 2H), 3.50 (t, *J* = 7.0 Hz, 1H), 3.78–3.85 (m, 1H), 4.53 (d, *J* = 8.2 Hz, 2H), 5.06 (t, *J* = 2.0 Hz, 1H), 5.09 (dd, *J* = 2.4, 7.5 Hz, 1H), 5.23 (t, *J* = 2.0 Hz, 1H), 6.33 (d, *J* = 1.7 Hz, 1H), 7.32 (d, *J* = 1.7 Hz, 1H), 9.75 (t, *J* = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.2, -5.1, 11.9 (3C), 17.7 (6C), 18.3, 25.9 (3C), 39.1, 42.7, 48.1, 57.2, 72.9, 108.3, 110.9, 121.7, 141.1, 148.0, 153.9, 200.7; CI-HRMS calcd for $C_{27}H_{48}O_4NaSi_2$ $[M + Na]^+$ *m/z* 515.2989, found *m/z* 515.2938.



332 (*dr* 4:3)

(*S*)-3-(2-((1*R*,2*R*,3*R*)-2-(3-((*tert*-Butyldimethylsilyloxy)methyl)furan-2-yl)-4-methylene-3-(triisopropylsilyloxy)cyclobutyl)-1-hydroxyethyl)-5-((*E*)-3-iodo-2-methylallyl)furan-2(5H)-one (332)

To a solution of **228** (13.0 mg, 0.03 mmol) in dry THF (0.2 mL) at -78 ^{o}C was added dropwise LiHMDS (46.1 μL, 0.046 mmol, 1.0 M solution in THF). The mixture was stirred at -78 ^{o}C for 40 min and a solution of **330** (9.0 mg, 0.018 mmol) in dry THF (0.2 mL) was added dropwise over 10 min. The mixture was stirred at -78 ^{o}C for 1.5 h and then at 0 ^{o}C for 15 min. The reaction was quenched with satd aqueous NH_4Cl solution (10 mL) and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 10 mL) and the combined organic extract was dried over Na_2SO_4, filtered,

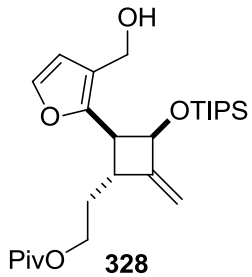
and concentrated to leave a crude oil (20.0 mg) which was immediately used for the next reaction.

To a solution of the crude residue (20.0 mg) obtained above in THF (0.3 mL) at 0 ^{o}C was added dropwise H_2O_2 (0.10 mL, 30% w/w in water) and the mixture was warmed to room temperature. After stirring at room temperature for 20 min, the reaction was quenched with satd aqueous $NaHCO_3$ solution (5.0 mL). The separated aqueous layer was extracted with Et_2O (2 x 5 mL) and the combined organic extract was dried (Na_2SO_4), filtered, and concentrated. The crude mixture was purified by silica gel chromatography (14%-16% ethyl acetate in hexanes) to afford separable diastereomers of **332** (less polar 4.0 mg, more polar 3.0 mg, total 51% based on **330**) as colorless oils:

Less polar: R_f 0.46 (75:25 hexanes-ethyl acetate); $[\alpha]^{23}_{D}$ +6.9 (*c* 0.26, $CHCl_3$); IR (neat) 3464, 2922, 2855, 1752, 1468, 1258 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 0.13 (s, 3H), 0.14 (s, 3H), 0.93-0.94 (m, 30H), 1.92 (d, *J* = 1.0 Hz, 3H), 1.94 (ddd, *J* = 7.5, 10.1, 14.0 Hz, 1H), 2.27 (td, *J* = 5.0, 14.0 Hz, 1H), 2.50 (dd, *J* = 7.4, 14.9 Hz, 2H), 3.07 (d, *J* = 5.8 Hz, OH), 3.46-3.50 (m, 1H), 3.53 (dd, *J* = 7.1, 7.5 Hz, 1H), 4.50 (d, *J* = 12.2 Hz, 1H), 4.52 (dd, *J* = 4.8, 11.9 Hz, 1H), 4.60 (d, *J* = 11.9 Hz, 1H), 4.94 (ddd, *J* = 1.3, 6.1, 7.6 Hz, 1H), 5.06 (dd, *J* = 2.0, 4.0 Hz, 1H), 5.08 (t, *J* = 1.9 Hz, 1H), 5.22 (t, *J* = 1.9 Hz, 1H), 6.11 (q, *J* = 1.0 Hz, 1H), 6.33 (d, *J* = 1.8 Hz, 1H), 6.95 (t, *J* = 1.4 Hz, 1H), 7.32 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (700 MHz, $CDCl_3$) δ -5.1, 11.9, 17.7, 18.5, 24.5, 26.0, 29.7, 30.3, 39.4, 42.7, 42.8, 43.1, 57.1, 66.4, 73.2, 79.3, 79.4, 107.8, 111.4,

121.1, 125.5, 131.7, 136.4, 140.8, 141.8, 149.9, 154.3, 171.7; EI-HRMS calcd for $C_{35}H_{57}O_6IO_6Si_2Na$ [M + Na] $^+$ (*m/z*) 779.2636, found 779.2601.

More polar: R_f 0.42 (75:25 hexanes-ethyl acetate); $[\alpha]^{23}{}_D$ -2.0 (*c* 0.3, $CHCl_3$); IR (neat) 3457, 2930, 2862, 1752, 1456 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 0.12 (s, 3H), 0.14 (s, 3H), 0.94-0.93 (m, 30H), 1.93 (d, *J* = 1.0 Hz, 3H), 1.99-2.03 (m, 1H), 2.10 (ddd, *J* = 3.8, 10.4, 14.0 Hz, 1H), 2.54 (dd, *J* = 5.9, 10.4 Hz, 2H), 3.52 (dd, *J* = 7.0, 7.4 Hz, 1H), 3.59-3.63 (m, 1H), 4.47-4.48 (m, 1H), 4.50 (d, *J* = 12.1 Hz, 1H), 4.67 (d, *J* = 12.1 Hz, 1H), 4.99 (tt, *J* = 1.8, 5.7 Hz, 1H), 5.04-5.05 (m, 2H), 5.20 (s, 1H), 6.12 (q, *J* = 1.0 Hz, 1H), 6.33 (d, *J* = 1.8 Hz, 1H), 7.09 (t, *J* = 1.5 Hz, 1H), 7.32 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.1, 12.0, 17.7, 18.5, 24.6, 25.9, 29.7, 30.3, 39.8, 42.6, 42.7, 43.0, 57.2, 65.6, 73.3, 79.3, 79.4, 107.5, 111.5, 121.1, 125.5, 135.7, 136.8, 140.8, 141.8, 147.9, 149.6, 154.2, 171.6; EI-HRMS calcd for $C_{35}H_{57}O_6IO_6Si_2Na$ [M + Na] $^+$ (*m/z*) 779.2636, found 779.2601.

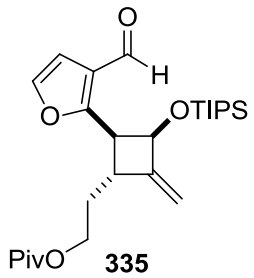


328

2-((1*R*,2*R*,3*R*)-2-(3-(Hydroxymethyl)furan-2-yl)-4-methylene-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (328)

To a solution of **288** (18.0 mg, 0.031 mmol) in EtOH (0.3 mL) was added $TsOH.H_2O$ (0.59 mg, 0.0031 mmol) and the mixture was stirred for 1.5 h at room temperature.

The reaction was quenched with satd aqueous $NaHCO_3$ solution, the separated aqueous layer was extracted with Et_2O (2 x 10 mL) and the combined organic extract was dried (Na_2SO_4), filtered, and concentrated. The crude residue was purified by silica gel chromatography (1:9 ethyl acetate/hexanes) to afford **328** (13.0 mg, 90%) as a pale yellow oil: R_f 0.41 (15:85 hexanes-ethyl acetate); $[\alpha]^{20}{}_D$ – 2.5 (*c* 0.2, $CHCl_3$); IR (neat) 3459, 2921, 2871, 1723, 1458 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91–1.02 (m, 21H), 1.14 (s, 9H), 1.90–1.95 (s, 1H), 2.00–2.05 (m, 1H), 2.64 (s, broad, OH), 3.23–3.27 (m, 1H), 3.58 (dd, *J* = 5.4, 8.4 Hz, 1H), 4.03–4.06 (m, 1H), 4.25–4.28 (m, 1H), 4.39 (dd, *J* = 7.7, 12.2 Hz, 1H), 4.60–4.62 (m, 1H), 5.10 (t, *J* = 2.0 Hz, 1H), 5.13–5.15 (m, 1H), 5.31 (t, *J* = 2.0 Hz, 1H), 6.40 (d, *J* = 1.8 Hz, 1H), 7.30 (d, *J* = 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.9 (3C), 17.5 (3C), 17.6 (3C), 27.1 (3C), 34.2, 38.7, 41.7, 43.4, 56.2, 61.9, 71.9, 108.3, 112.0, 121.5, 140.7, 150.2, 154.5, 178.6; EI-HRMS calcd for $C_{26}H_{44}O_5NaSi$ $[M + Na]^+$ (*m/z*) 487.2856, found 487.2844.

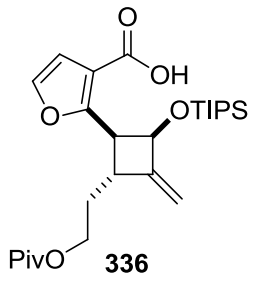


335

2-((1*R*,2*R*,3*R*)-2-(3-Formylfuran-2-yl)-4-methylene-3-(triisopropylsilyloxy)cyclobutyl)ethyl Pivalate (335)

To a solution of **328** (18.0 mg, 0.038 mmol) in CH_2Cl_2 (0.5 mL) were added 4Å MS, TPAP (1.36 mg, 0.0038 mmol) and NMO (13.35 mg, 0.114 mmol). The reaction mixture was stirred at room temperature for 1 h and the suspension was loaded on a

silica gel column and eluted (92/8 hexanes/ethyl acetate) to give **335** (12.0 mg, 67%) as a colorless oil: R_f 0.56 (15:85 hexanes-ethyl acetate); $[\alpha]^{23}{}_D$ +36.7 (*c* 0.7, $CHCl_3$); IR (neat) 2938, 2864, 1736, 1678, 1465 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 0.93–0.99 (m, 21H), 1.17 (s, 9H), 1.96–2.05 (m, 2H), 3.40–3.44 (m, 1H), 3.94 (dd, *J* = 5.7, 7.9 Hz, 1H), 4.12 (dt, *J* = 2.6, 5.6 Hz, 2H), 5.11 (t, *J* = 1.9 Hz, 1H), 5.23 (qd, *J* = 2.1, 7.8 Hz, 1H), 5.29 (t, *J* = 1.9 Hz, 1H), 6.74 (d, *J* = 1.9 Hz, 1H), 7.38 (d, *J* = 1.9 Hz, 1H), 10.0 (s, 1H); ^{13}C NMR (700 MHz, $CDCl_3$) δ 11.9 (3C), 17.6 (3C), 17.7 (3C), 27.1 (3C), 33.2, 38.7, 41.9, 43.7, 62.1, 72.6, 108.3, 108.6, 124.2, 142.5, 153.6, 162.7, 178.4, 185.3; EI-HRMS calcd for $C_{26}H_{43}O_5Si$ $[M + H]^+$ *m/z* 463.2880, found *m/z* 463.2888.

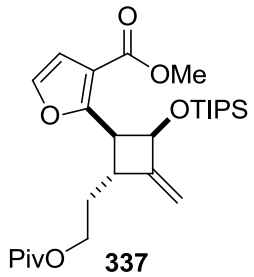


336

2-((1*R*,2*R*,4*R*)-3-Methylene-2-(2-(pivaloyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)furan-3-carboxylic Acid (336)

To a cold (0 ºC) solution of **335** (14.0 mg, 0.03 mmol) in a mixture of *t*BuOH (0.3 mL) and 2-methyl-2-butene (0.3 mL) was added dropwise a solution of $NaClO_2$ (80%, 10.1 mg, 0.09 mmol) and NaH_2PO_4 (16.5 mg, 0.12 mmol) in water (0.2 mL). The reaction mixture was stirred for 16 h at room temperature and was diluted with H_2O (10 mL) and Et_2O (10 mL). The layers were separated and the aqueous layer was

extracted with Et_2O (2 x 10 mL). The combined organic extract was washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (hexanes:ethyl acetate 22:78) to give **336** (13.0 mg, 91%) as a pale yellow oil: R_f 0.31 (25:75 hexanes-ethyl acetate); $[\alpha]^{24}{}_D$ +52.7 (*c* 0.65, $CHCl_3$); IR (neat) 2945, 2863, 1727, 1684, 1587 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 0.94 - 0.98 (m, 21H), 1.17 (s, 9H), 1.89–1.95 (m, 1H), 2.01–2.06 (m, 1H), 3.55–3.59 (m, 1H), 4.11 (t, *J* = 6.5 Hz, 2H), 4.26 (dd, *J* = 6.8, 7.4 Hz, 1H), 5.07 (t, *J* = 2.1 Hz, 1H), 5.19 (ddd, *J* = 1.7, 4.3, 6.2 Hz, 1H), 5.22 (t, *J* = 1.7 Hz, 1H), 6.72 (d, *J* = 1.9 Hz, 1H), 7.37 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (700 MHz, $CDCl_3$) δ 12.0 (3C), 17.7 (6C), 27.1 (3C), 32.8, 38.7, 41.0, 43.4, 62.4, 73.3, 107.7, 110.8, 114.2, 141.4, 154.0, 161.4, 169.4, 178.5; EI-HRMS calcd for $C_{26}H_{43}O_6Si$ $[M + H]^+$ *m/z* 479.2829, found *m/z* 479.2845.

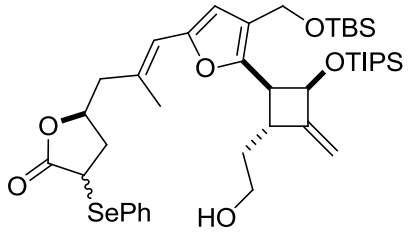


337

Methyl 2-((1*R*,2*R*,4*R*)-3-Methylene-2-(2-(pivaloyloxy)ethyl)-4-(triisopropylsilyloxy)cyclobutyl)furan-3-carboxylate (337)

To a solution of **336** (5.0 mg, 0.01 mmol) in a mixture of toluene (0.1 mL) and MeOH (0.1 mL) at room temperature was added dropwise trimethylsilyldiazomethane (16.0 μL, 0.03 mmol, 2.0 M in hexane). The mixture was stirred for 30 min at room

temperature and the solvents were removed under reduced pressure. The residual oil was purified by silica gel chromatography (7/93 ethyl acetate/hexane) to yield **337** (5.0 mg, 98%) as a colorless oil: R_f 0.69 (25:75 hexanes-ethyl acetate); $[\alpha]^{25}_D$ +59.2 (*c* 0.25, $CHCl_3$); IR (neat) 2941, 2871, 1727 (2), 1594, 1462 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 0.92-0.96 (m, 21H), 1.16 (s, 9H), 1.88–1.94 (m, 1H), 2.00–2.05 (m, 1H), 3.51–3.56 (m, 1H), 3.82 (s, 3H), 4.08 (t, *J* = 6.7 Hz, 2H), 4.23 (dd, *J* = 6.6, 7.5 Hz, 1H), 5.06 (t, *J* = 1.9 Hz, 1H), 5.17 (ddd, *J* = 1.9, 4.4, 6.3 Hz, 1H), 5.21 (dd, *J* = 1.9 Hz, 1H), 6.66 (d, *J* = 1.9 Hz, 1H), 7.33 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (700 MHz, $CDCl_3$) δ 12.0 (3C), 17.6 (3C), 17.7 (3C), 27.1 (3C), 32.9, 38.6, 41.0, 43.2, 51.3, 62.3, 73.2, 107.6, 110.5, 114.7, 141.2, 154.2, 159.9, 164.4, 178.5; EI-HRMS calcd for $C_{27}H_{45}O_6Si$ $[M + H]^+$ *m/z* 493.2985, found *m/z* 493.2995.



320

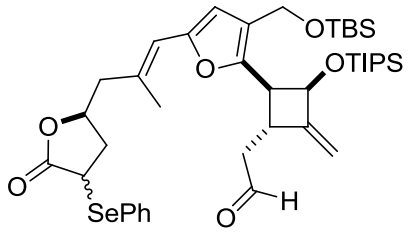
(*S*)-5-((*E*)-3-(4-((*tert*-Butyldimethylsilyloxy)methyl)-5-((1*R*,2*R*,4*R*)-2-(2-hydroxyethyl)-3-methylene-4-(triisopropylsilyloxy)cyclobutyl)furan-2-yl)-2-methylallyl)-3-(phenylselanyl)dihydrofuran-2(3H)-one (320)

To a solution of **312** (9.0 mg, 0.018 mmol) in dry THF (0.2 mL) at –78 °C were added dropwise freshly distilled TMEDA (16.0 μL, 0.108 mmol) and *s*-BuLi (50.0 μL, 0.054 mmol, 1.08 M solution in cyclohexane). The mixture was stirred at –78 °C for 15 min

and then at 0 ^{o}C for 30 min. The solution was cooled to -78 ^{o}C and Me_3SnCl (90.0 μL, 0.09 mmol, 1.0 M solution in hexane) was added. The reaction mixture was stirred at -78 ^{o}C for 1 h and then warmed to room temperature. After stirring at room temperature for 1 h, the reaction was quenched with water (10 mL) and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 10 mL) and the combined organic extract was dried over Na_2SO_4, filtered, and concentrated to leave a crude oil which was immediately used for the next reaction.

To a solution of the crude oil (13.0 mg, 0.019 mmol) obtained above and **228** (9.0 mg, 0.021 mmol) in degassed DMF (0.3 mL) under an argon atmosphere were added $Pd(PPh_3)_4$ (1.09 mg, 0.00095 mmol) and CuI (0.36 mg, 0.0019 mg). After stirring at room temperature for 4 h, the mixture was diluted with water (10 mL) and Et_2O (10 mL). The separated aqueous layer was extracted with Et_2O (3 x 10 mL) and the combined organic extract was dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by silica gel chromatography (3:22:75 NEt_3:ethyl acetate:hexanes) under argon to afford **320** (8.0 mg, 54% based on **312**) as a colorless oil: R_f 0.28 (7:3 hexanes-ethyl acetate); $[\alpha]^{22}_{D}$ -10.2 (*c* 0.46, $CHCl_3$); IR (neat) 3478, 2929, 2855, 1769, 1462, 1170 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 0.10-0.12 (m, 19H), 0.92-0.95 (m, 76H), 1.80-1.85 (m, 3H), 1.92-1.94 (m, 2H), 1.96 (s, 6H), 2.00-2.04 (m, 2H), 2.14-2.18 (dd, *J* = 7.1, 13.6 Hz, 1H), 2.31-2.35 (m, 2H), 2.38-2.42 (m, 1H), 2.54 (dd, *J* = 5.9, 13.9 Hz, 1H), 2.60 (dd, *J* = 6.4, 14.4 Hz, 1H), 2.72 (ddd, *J* = 6.6, 9.3, 13.5 Hz, 1H), 3.37-3.41 (m, 2H), 3.45 (dd, *J* = 5.9, 7.1 Hz, 2H), 3.66-3.72 (m, 4H), 3.96 (dd, *J* = 2.5, 8.3 Hz, 1H), 4.04 (t, *J* = 9.5 Hz, 1H), 4.42-4.46 (m, 1H), 4.49

(d, *J* = 12.0 Hz, 2H), 4.59 (d, *J* = 12.0 Hz, 2H), 4.60 (dd, *J* = 6.5, 7.3 Hz, 1H), 5.00 (s, 2H), 5.08 (d, *J* = 7.4 Hz, 2H), 5.17 (s, 2H), 5.92 (s, 1H), 5.98 (s, 1H), 6.13-6.15 (m, 2H), 7.34-7.37 (m, 4H), 7.38-7.42 (m, 2H), 7.62-7.64 (m, 2H), 7.68-7.71 (m, 4H) ; ^{13}C NMR (700 MHz, $CDCl_3$) δ -5.1, 11.9, 17.7, 18.4, 26.0, 26.4, 29.7, 30.3, 35.2, 36.2, 36.9, 37.3, 42.5, 43.2, 45.9, 46.4, 57.2, 61.1, 73.1, 77.6, 77.9, 106.6, 110.4, 117.4, 117.5, 122.6, 126.7, 127.0, 127.7, 128.9, 129.2, 129.4, 130.1, 131.4, 135.7, 135.9, 148.5, 151.0, 155.2, 175.7, 175.8; EI-HRMS calcd for $C_{41}H_{64}O_6SeSi_2Na$ $[M + Na]^+$ (*m/z*) 811.3304, found 811.3210.

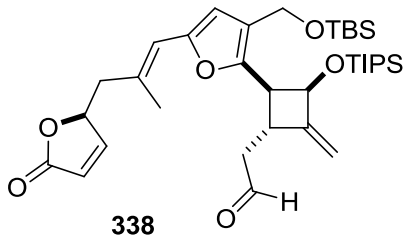


321

2-((1*R*,2*R*,3*R*)-2-(3-((*tert*-butyldimethylsilyloxy)methyl)-5-((*E*)-2-methyl-3-((*S*)-5-oxo-4-(phenylselanyl)tetrahydrofuran-2-yl)prop-1-enyl)furan-2-yl)-4-methylene-3-(triisopropylsilyloxy)cyclobutyl)acetaldehyde (321)

To a solution of **320** (7.0 mg, 0.0076 mmol) in 0.15 mL of CH_2Cl_2 at 0 ^oC was added $NaHCO_3$ (2.0 mg, 0.024 mmol) followed by Dess-Martin periodinane (4.1 mg, 0.0097 mmol). The slurry was stirred at 0 ^oC for 1.5 h and was diluted with CH_2Cl_2 (5.0 mL). The reaction was quenched with satd $Na_2S_2O_3$ solution (5.0 mL) by stirring the biphasic mixture vigorously for 20 min. The layers were separated, the aqueous phase was extracted with CH_2Cl_2 (2 x 5.0 mL), and the combined organic extract was

washed with satd $NaHCO_3$ solution, water and brine and was dried over Na_2SO_4. The drying agent was removed by filtration and the filtrate was concentrated in vacuo. Purification of the crude residue by silica gel chromatography (15:85 hexanes/ethyl acetate) provided **321** (2.5 mg, 42%) as a colorless oil: R_f 0.58 (75:25 hexanes/ethyl acetate); ^{1}H NMR (700 MHz, $CDCl_3$) δ 0.93 (s, 3H), 0.95 (s, 3H), 0.10 (s, 6H), 1.90-1.95 (m, 54H), 1.97 (s, 4H), 2.02-2.05 (m, 2H), 2.16-2.20 (m, 0.5H), 2.30-2.35 (m, 2H), 2.37-2.43 (m, 1.5H), 2.54 (dd, *J* = 6.1, 14.0 Hz, 0.5H), 2.72 (dd, *J* = 6.4, 13.8Hz, 1H), 2.75 (dd, *J* = 1.8, 7.3 Hz, 2H), 3.48 (dd, *J* = 6.2, 7.3 Hz, 1H), 3.78-3.81 (m, 1H), 3.96 (dd, *J* = 2.5, 8.3 Hz, 1H), 4.04 (t, *J* = 9.4Hz, 0.5H), 4.44 (dd, *J* = 6.5, 8.7 Hz, 1H), 4.48-4.53 (m, 3H), 4.58-4.62 (m, 0.5H), 5.04 (s, 1H), 5.09-5.10 (m, 1H), 5.18-5.19 (m, 0.5H), 5.21 (s, 1H), 5.90 (s, 0.3H), 5.99 (s, 0.7H), 6.15 (s, 1H), 7.34-7.43 (m, 5H), 7.69-7.71 (m, 3H), 9.77 (t, *J* = 1.6, 3.2 Hz, 1H); ^{13}C NMR (700 MHz, $CDCl_3$) δ -5.1, 11.9, 17.7, 18.4, 25.9, 29.7, 30.3, 31.9, 36.2, 36.9, 37.3, 42.6, 45.9, 46.3, 48.1, 57.2, 73.1, 77.6, 77.9, 108.1, 110.2, 117.4, 117.5, 123.2, 125.5, 126.6, 127.0, 128.9, 129.2, 129.4, 130.3, 135.7, 135.9, 147.0, 151.7, 175.7, 200.8.



338

2-((1*R*,2*R*,3*R*)-2-(3-((*tert*-Butyldimethylsilyloxy)methyl)-5-((*E*)-2-methyl-3-((S)-5-oxo-2,5-dihydrofuran-2-yl)prop-1-enyl)furan-2-yl)-4-methylene-3-(triisopropylsilyloxy)cyclobutyl)acetaldehyde (338)

To a solution of **320** (6.0 mg, 0.0076 mmol) in 0.15 mL of CH_2Cl_2 at 0 ^oC was added $NaHCO_3$ (2.0 mg, 0.0152 mmol) followed by Dess-Martin periodinane (4.6 mg, 0.01 mmol). The slurry was stirred at 0 ^oC for 1.5 h and was diluted with CH_2Cl_2 (5.0 mL). The reaction was quenched with satd $Na_2S_2O_3$ solution (5.0 mL) by stirring the biphasic mixture vigorously for 20 min. The layers were separated, the aqueous phase was extracted with CH_2Cl_2 (2 x 5.0 mL), and the combined organic extract was washed with satd $NaHCO_3$ solution, water and brine and was dried over Na_2SO_4. The drying agent was removed by filtration and the filtrate was concentrated in vacuo. Purification of the crude residue by silica gel chromatography (72:25:3 hexanes/ethyl acetate/NEt_3) provided **338** (2.0 mg, 43%) as a colorless oil: R_f 0.27 (7:3 hexanes/ethyl acetate); $[\alpha]^{25}_{D}$ – 4.6 (*c* 0.35, $CHCl_3$); IR (neat) 3478, 2929, 2855, 1746, 1721, 1271 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 0.90 (s, 3H), 0.10 (s, 3H), 0.93-0.95 (m, 30H), 2.09 (d, *J* = 0.7 Hz, 3H), 2.45 (dd, *J* = 7.3, 13.7 Hz, 1H), 2.70 (dd, *J* = 6.6, 13.8 Hz, 1H), 2.75 (dd, *J* = 1.5, 7.0 Hz, 2H), 3.49 (dd, *J* = 3.4, 7.6 Hz, 1H), 3.78-3.82 (m, 1H), 4.51 (d, *J* = 9.6 Hz, 2H), 5.04 (t, *J* = 2.0 Hz, 1H), 5.10 (qd, *J* = 2.0, 7.6 Hz, 1H), 5.19-5.22 (m, 2H), 6.07 (q, *J* = 0.7 Hz, 1H), 6.16 (dd, *J* = 1.9, 5.7 Hz, 1H), 6.18 (s, 1H), 7.18 (s, 1H), 7.50 (dd, *J* = 1.4, 5.7 Hz, 1H), 9.77 (t, *J* =1.8 Hz, 1H); ^{13}C NMR (700 MHz, $CDCl_3$) δ -5.1, 11.9, 14.1, 17.7, 18.4, 19.1, 22.7, 25.9, 29.4, 39.0, 42.6, 44.5, 48.1, 57.2, 73.1, 82.2, 108.1, 110.5, 117.9, 121.7, 123.2, 129.5, 147.3, 151.1, 156.1, 172.9, 200.8; CI-HRMS calcd for $C_{35}H_{56}O_6Si_2Na$ $[M + Na]^+$ *m/z* 651.3513, found *m/z* 651.3529.

CHAPTER 6

Conclusion

The study described in this dissertation outlines a conceptually novel approach to (+)-providencin. The key features the approach are (1) extension of Taguchi's zirconium-mediated ring contraction of a furanose to yield an enantiopure cyclobutane, (2) stereoselective allenol formation by reaction of an aldehyde with a propargyllic bromide using an extension of Harada's tin(II) chloride-mediated allenol construction, and (3) application of Marshall's allenone-to-furan isomerization to complete the cyclobutylfuran subunit **288** of providencin. Synthesis of the iodolactone subunit **228** employed Negishi carbometallation-iodination of an alkyne and nucleophilic substitution of a tosylate with the dianion of phenylselenyl acetic acid followed by acid-catalyzed lactone formation as key steps. Although attempts to couple our two advanced fragments using palladium-catalyzed C-H activation of a furan were unsuccessful, we were able to link two major subunits of **1** at C12-C13 using an aldol reaction to give **332** and at C6-C7 using a Stille cross-coupling to afford **320**.

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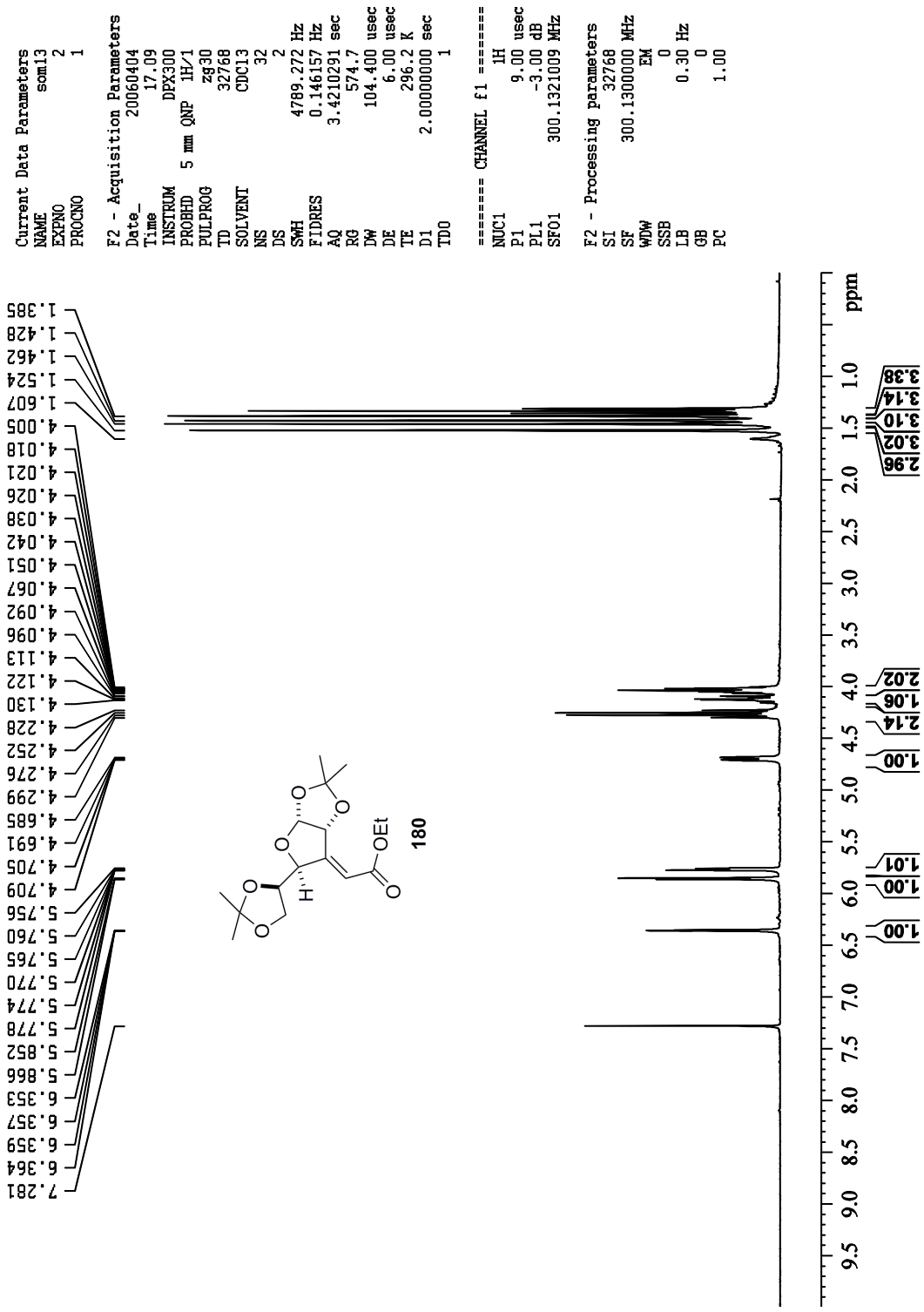
APPENDICES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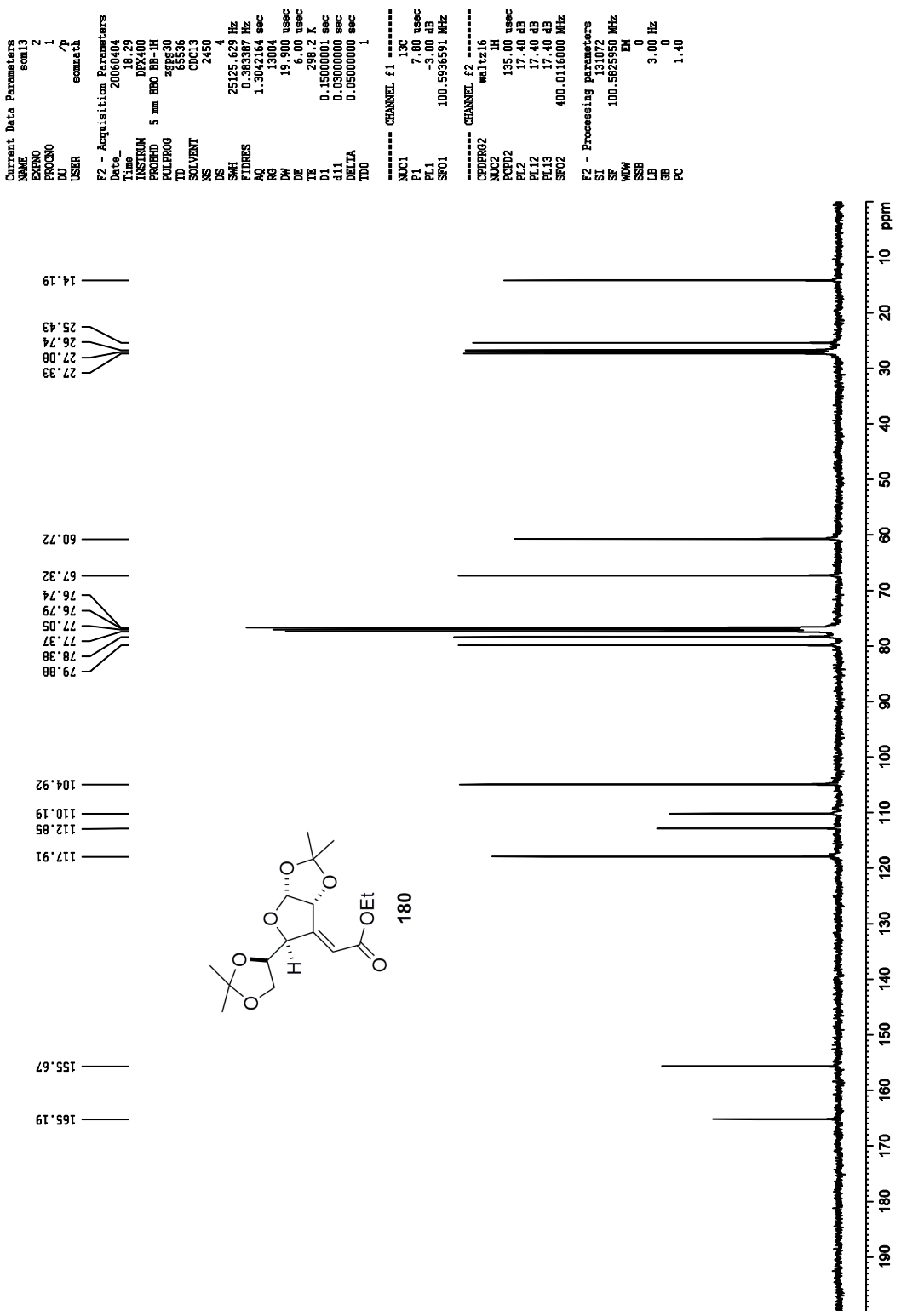
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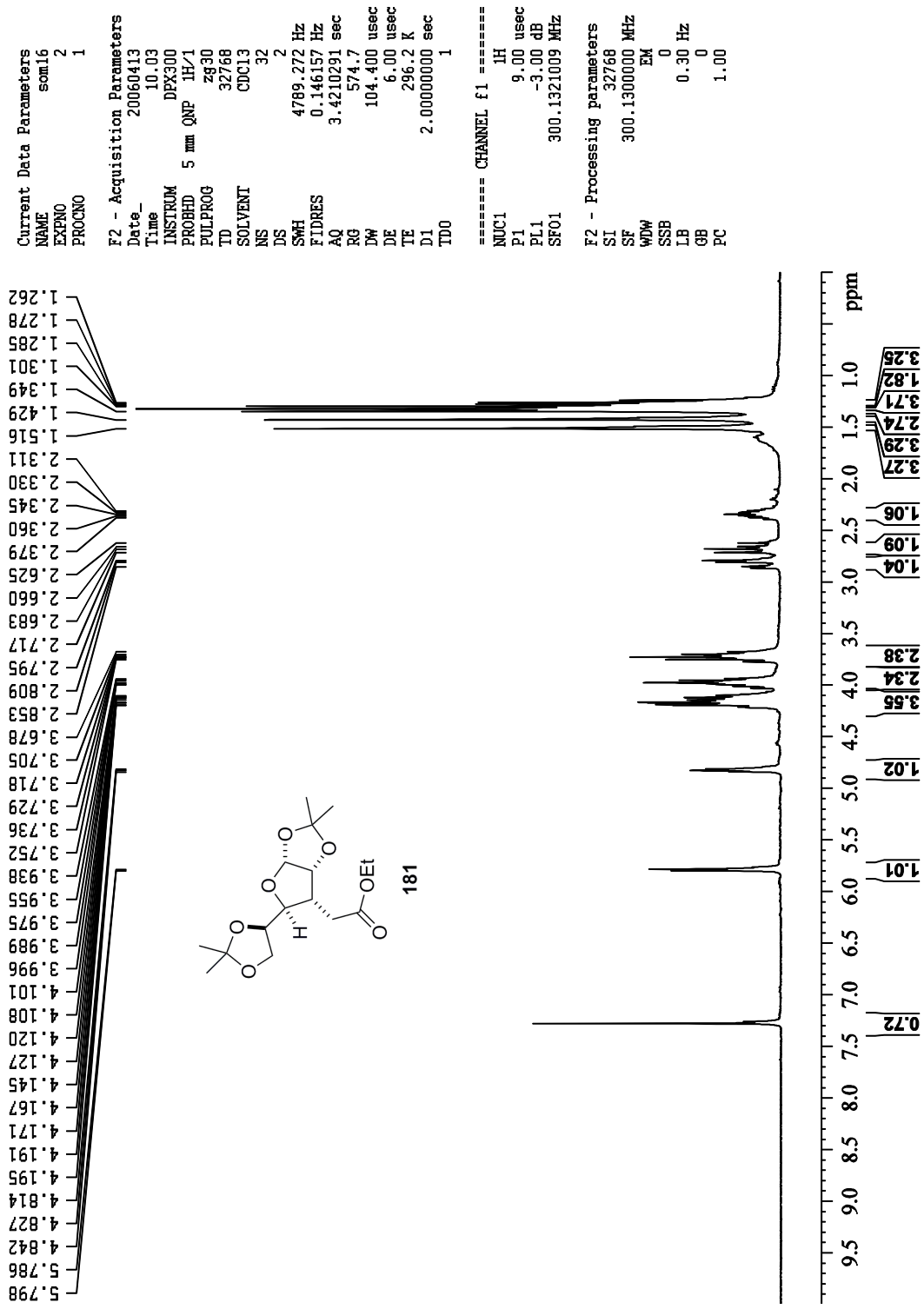
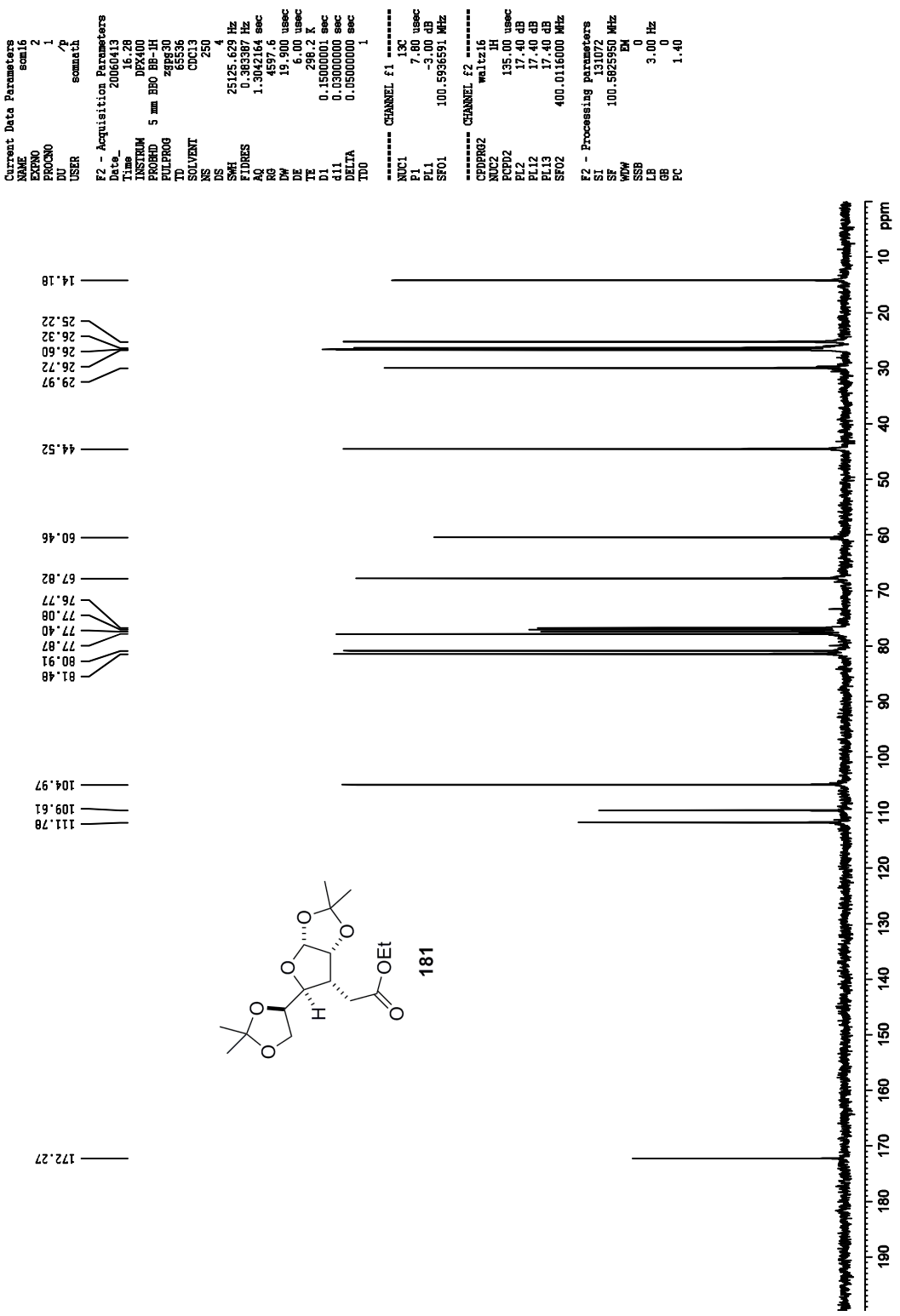
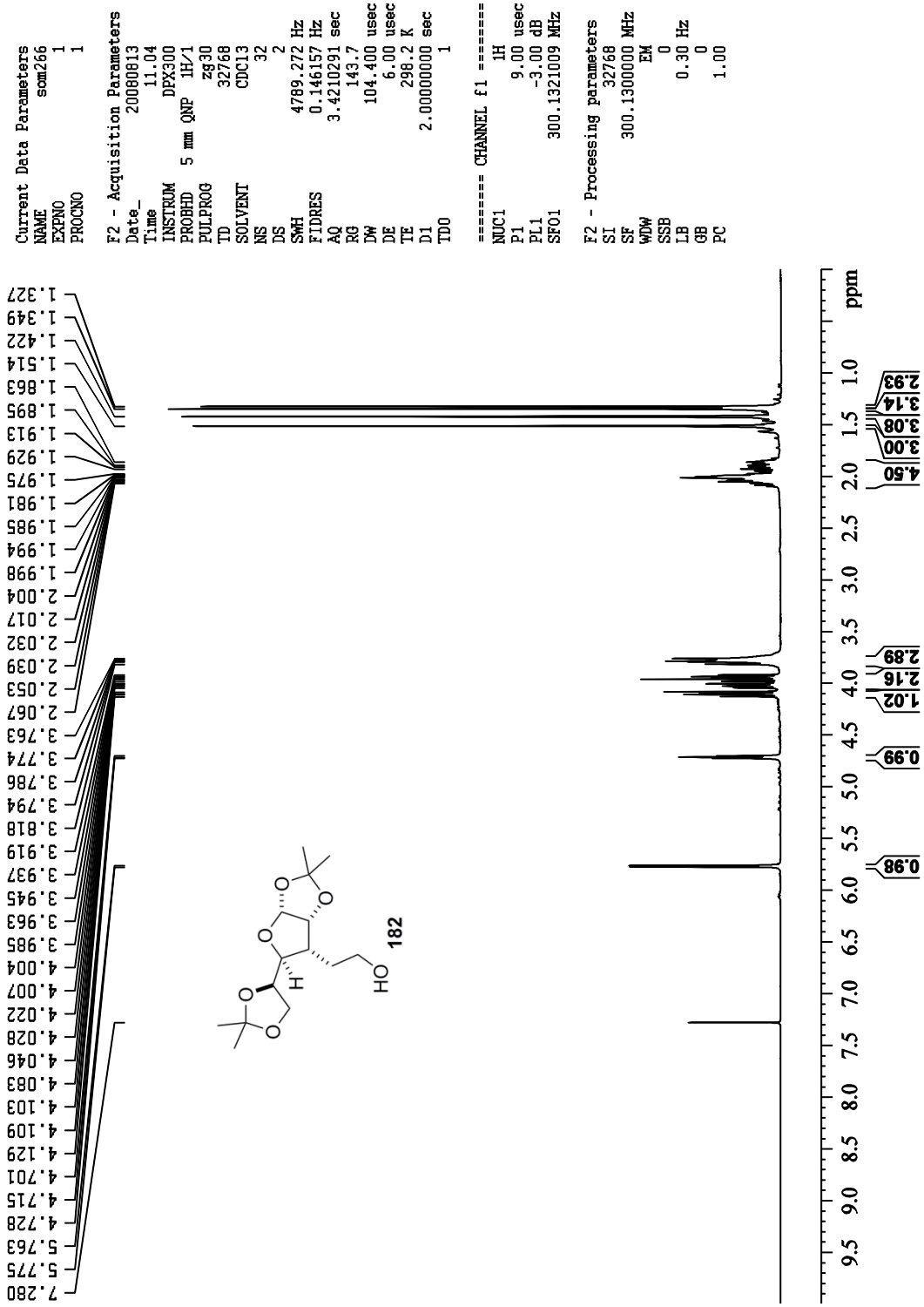
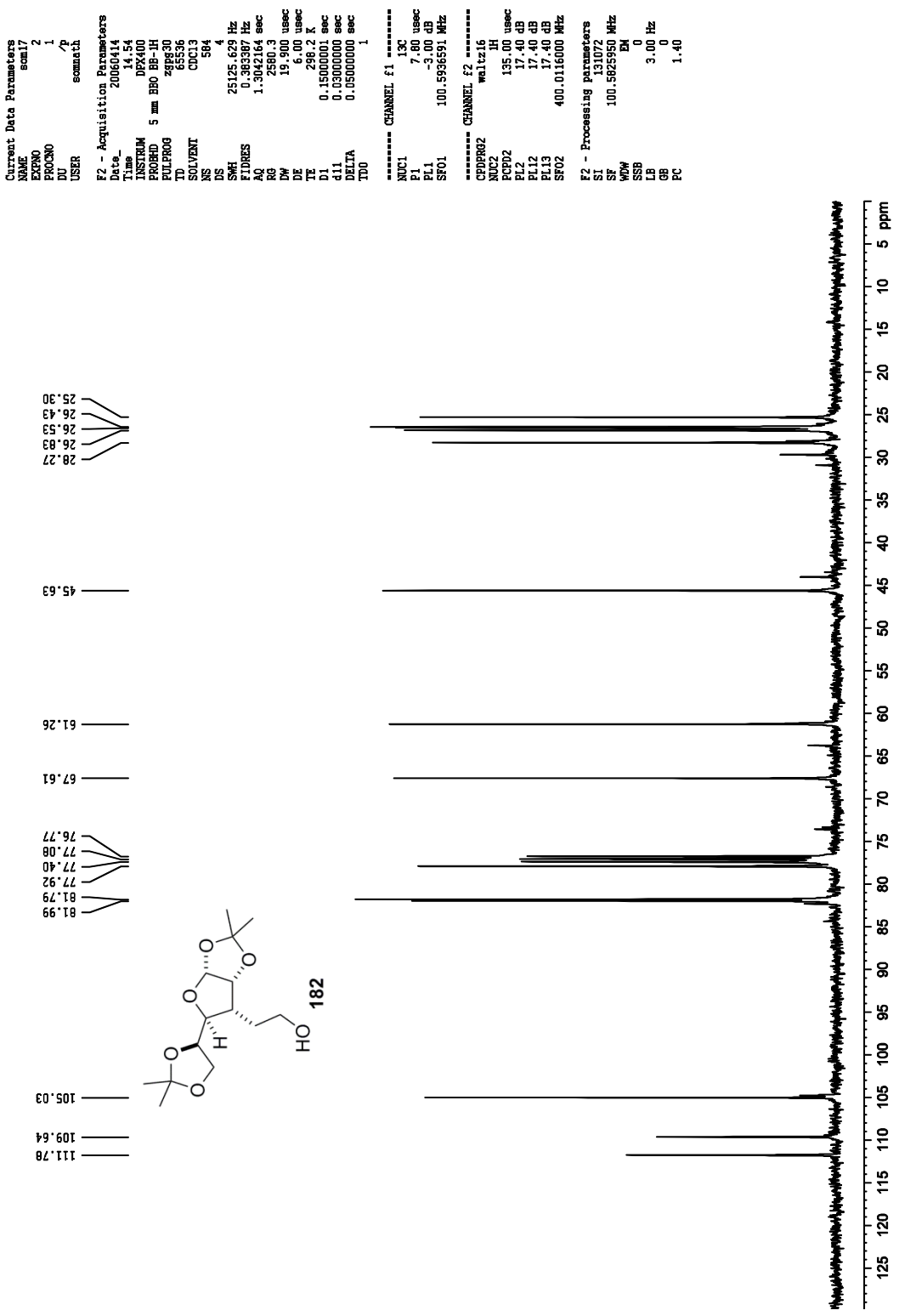
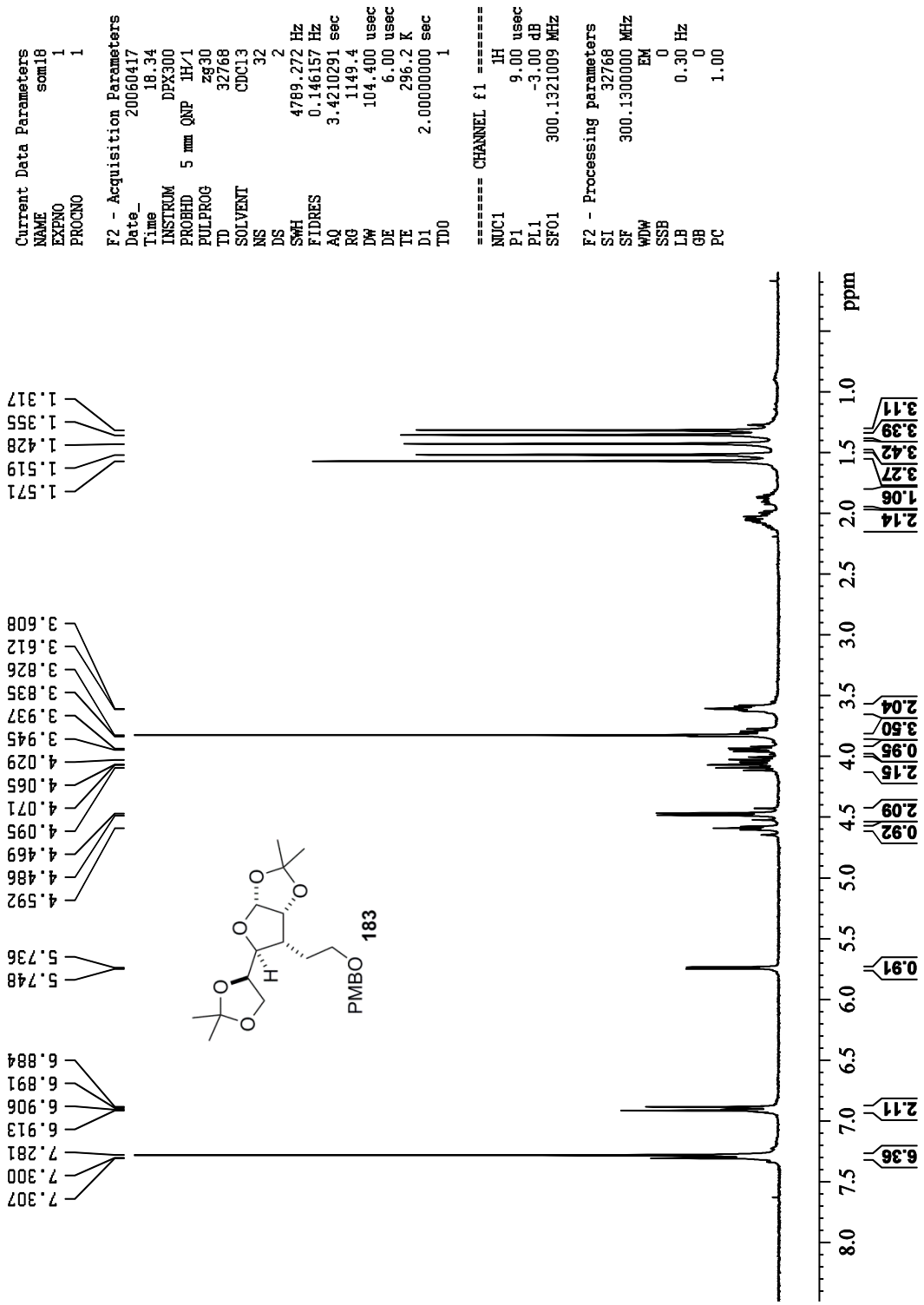
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 13004
DW 19.900 usec
DE 6.00 usec
TE 296.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
14.19
25.43
26.74
27.08
27.33
60.72
67.32
76.74
76.79
77.05
77.37
78.38
79.88
104.92
110.19
112.85
117.91
155.67
165.19
180
ppm

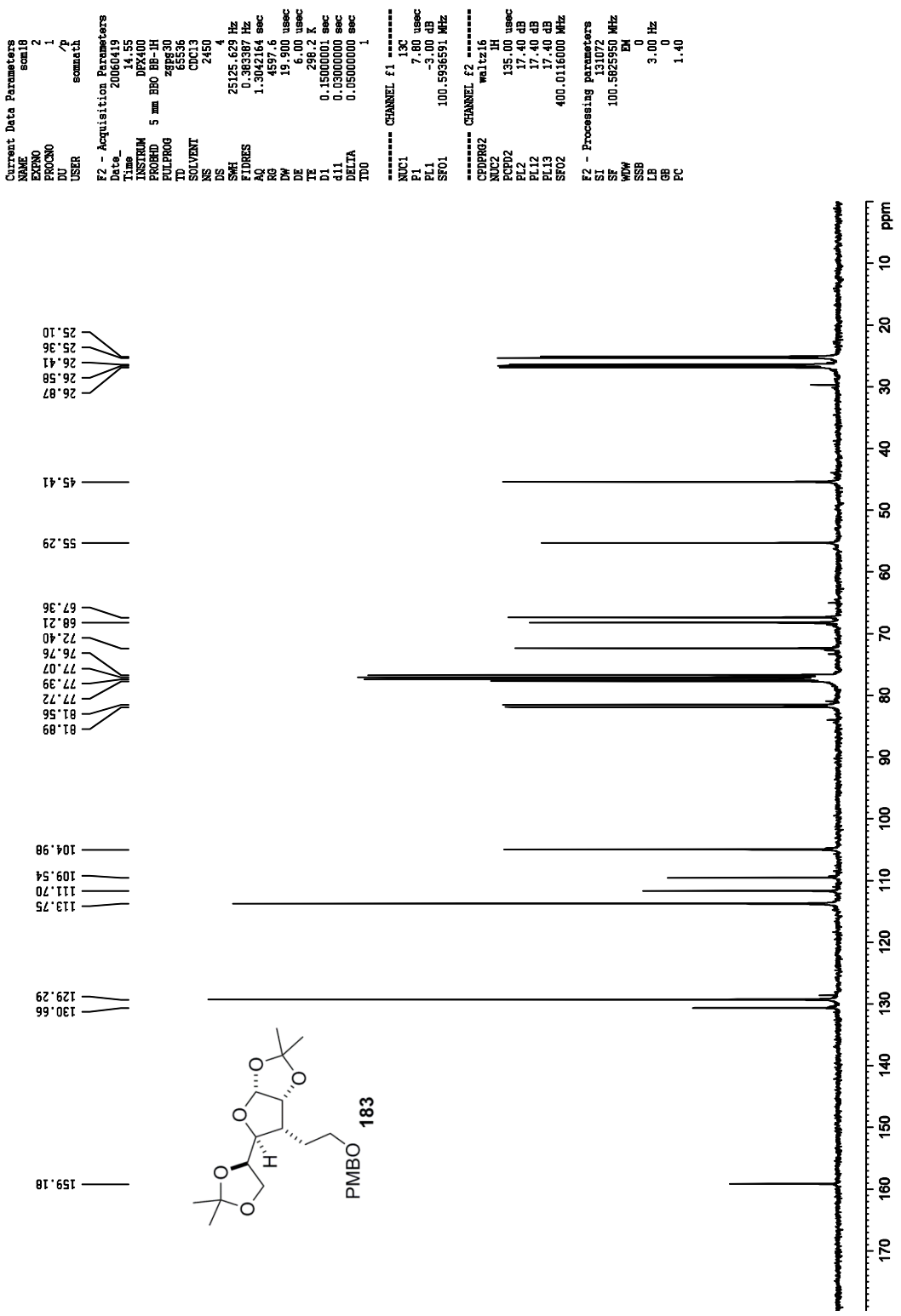

Current Data Parameters
NAME som16
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060413
Time 10.03
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 574.7
DW 104.400 usec
DE 6.00 usec
TE 296.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OEt
H
181
ppm

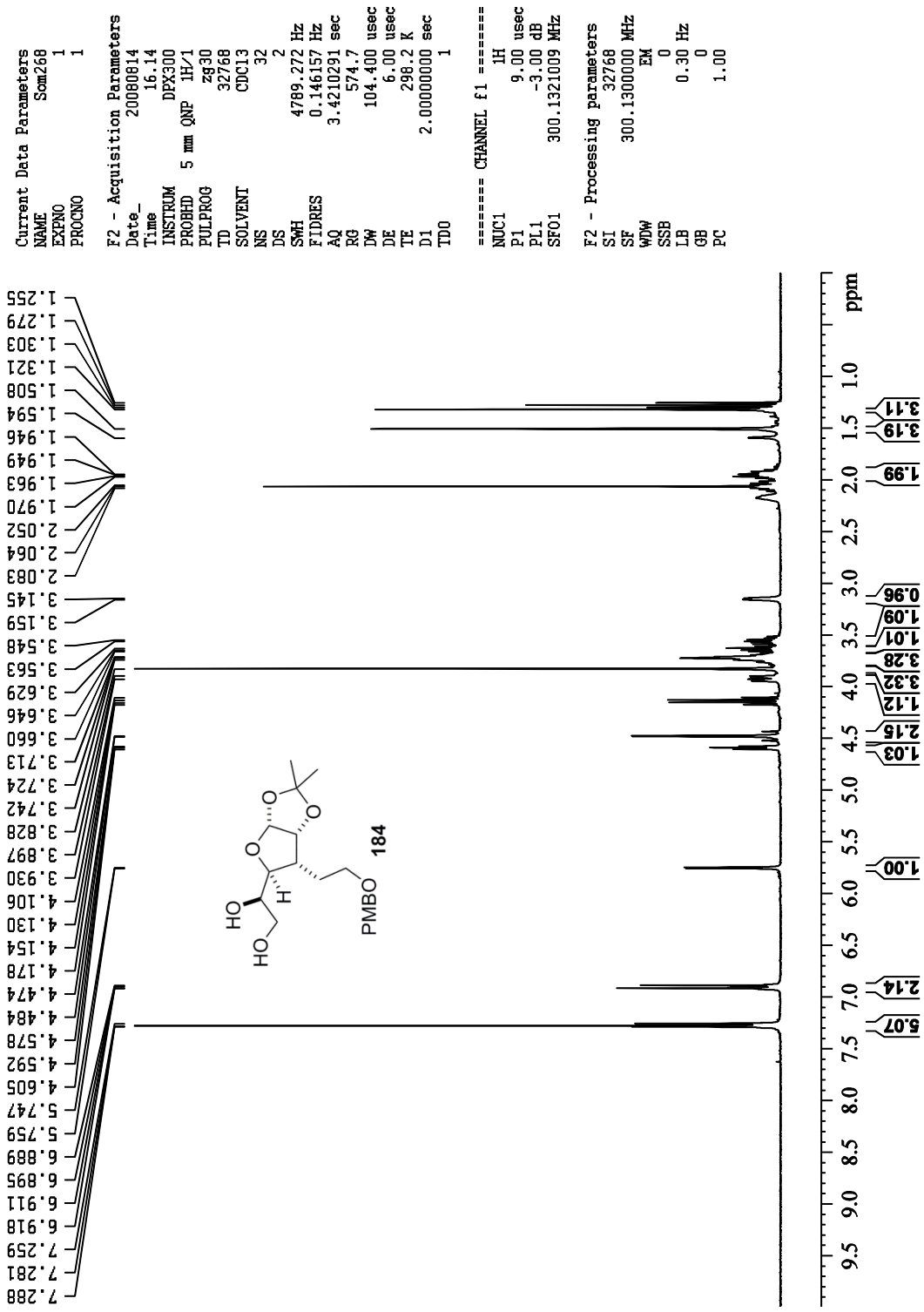

Current Data Parameters
NAME scm16
EXPNO 2
PROCNO 1
DU /p
USER scmath
F2 - Acquisition Parameters
Date_ 20060413
Time 16.28
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 250
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4597.6
DW 19.900 usec
DE 6.00 usec
TE 296.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
14.18
25.22
26.32
26.60
26.72
29.97
44.52
60.46
67.82
76.77
77.08
77.40
77.87
80.91
81.48
104.97
109.61
111.78
172.27
OEt
181
ppm

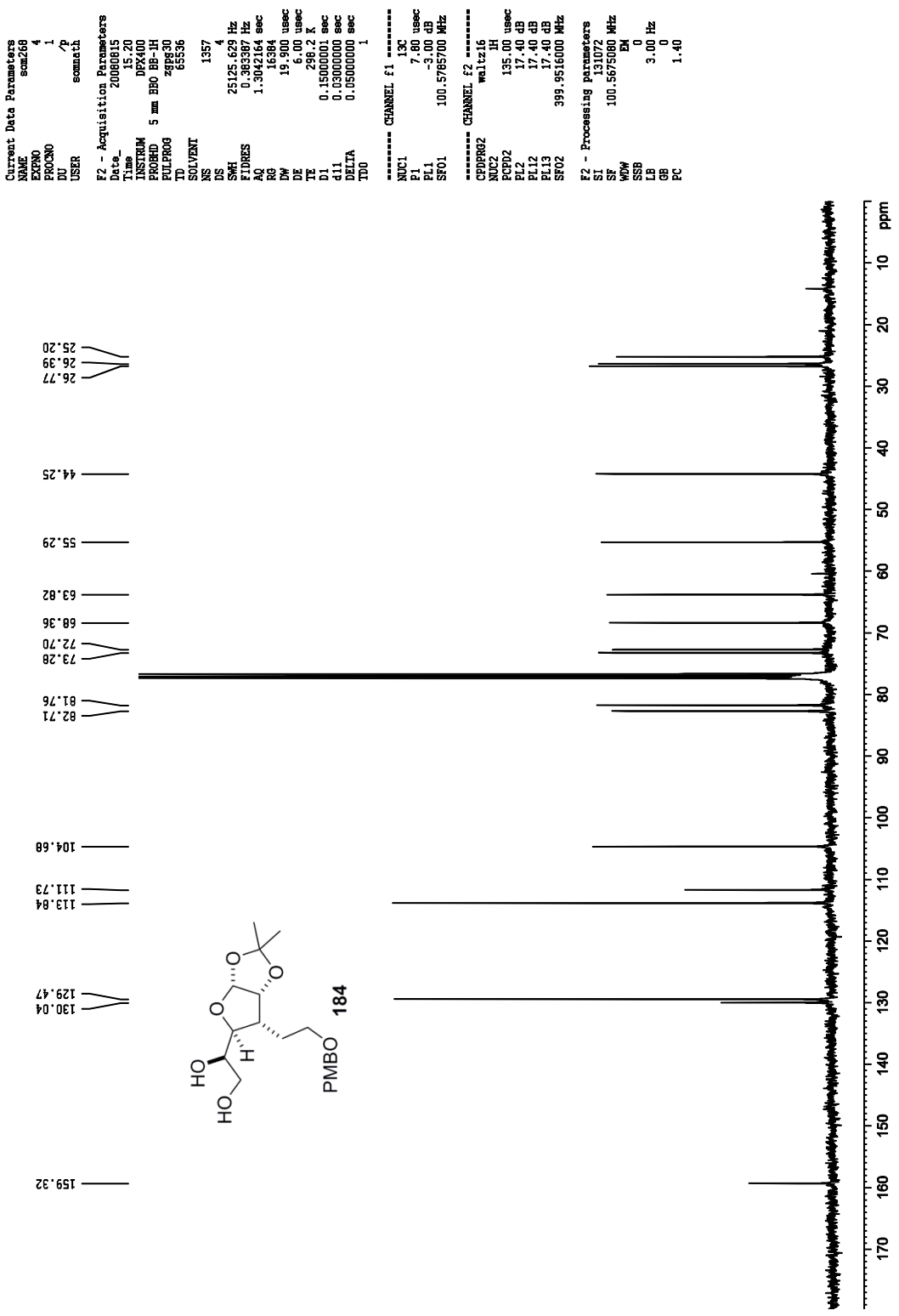

Current Data Parameters
NAME scm266
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080813
Time 11.04
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 143.7
DW 104.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
182
OH
H
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.98
0.99
1.02
2.16
2.89
4.50
3.00
3.08
3.14
2.93
7.280
5.775
5.763
4.728
4.715
4.701
4.129
4.109
4.103
4.083
4.046
4.028
4.022
4.007
4.004
3.985
3.963
3.945
3.937
3.919
3.818
3.794
3.786
3.774
3.763
2.067
2.053
2.039
2.032
2.017
2.004
1.998
1.994
1.985
1.981
1.975
1.929
1.913
1.895
1.863
1.514
1.422
1.349
1.327

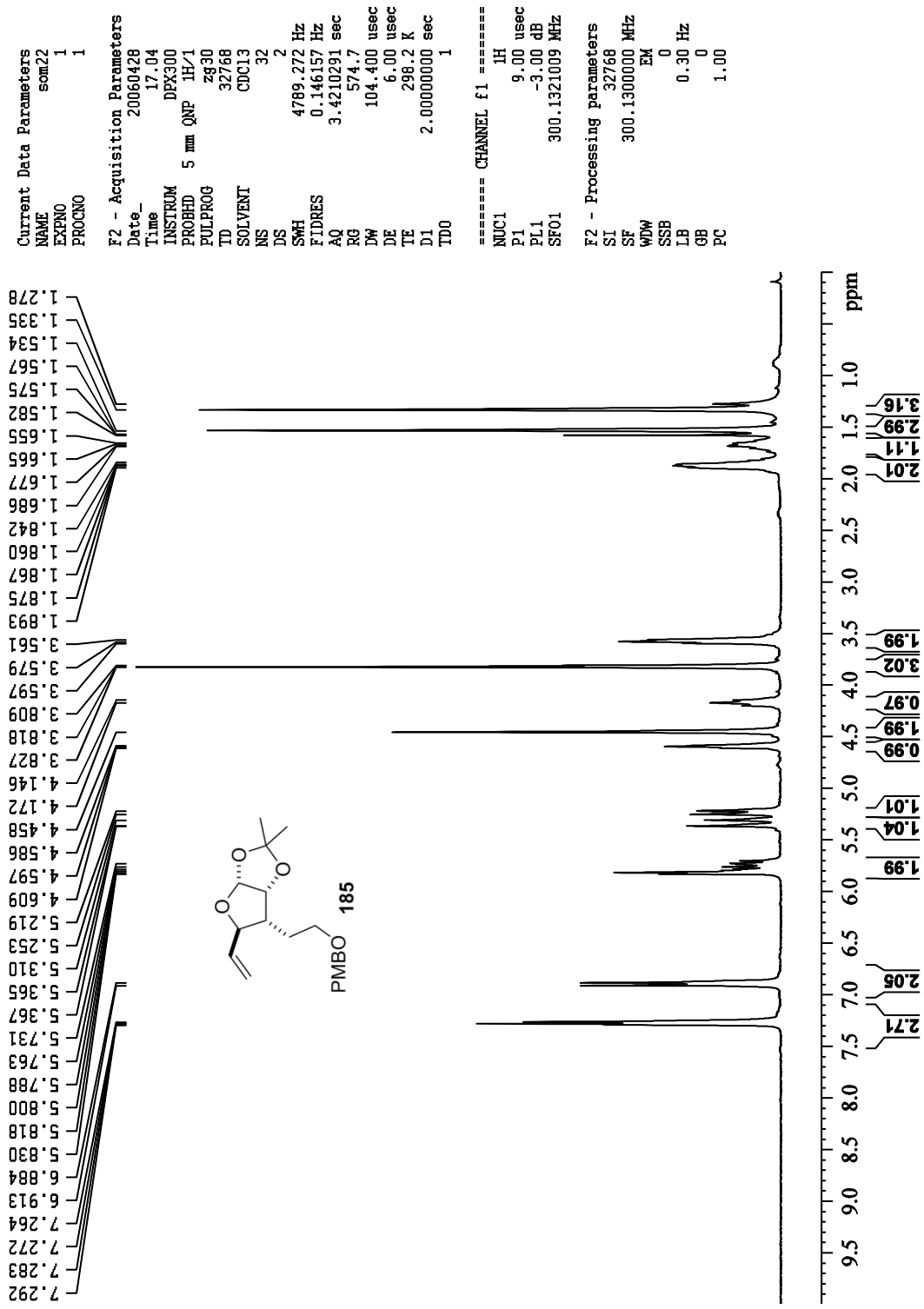

Current Data Parameters
NAME scm17
EXPNO 2
PROCNO 1
DU /p
USER scmath
F2 - Acquisition Parameters
Date_ 20060414
Time 14.54
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 584
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 2580.3
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
25.30
26.43
26.53
26.83
28.27
45.63
61.26
67.61
76.77
77.08
77.40
77.92
81.79
81.99
105.03
109.64
111.78
182
OH
H
O
O
O
O
O
O
5 ppm

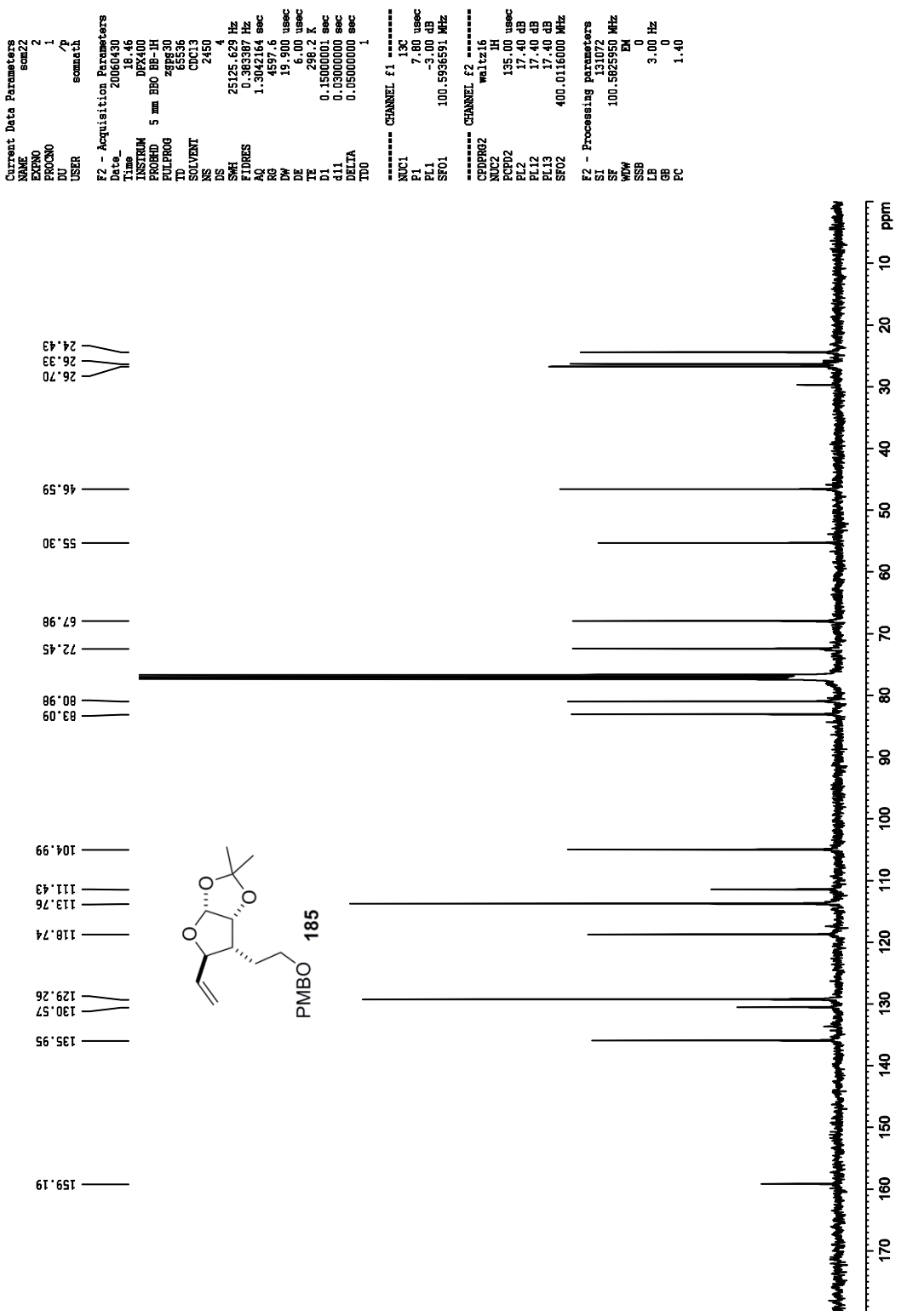

Current Data Parameters
NAME som18
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060417
Time 18.34
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 1149.4
DW 104.400 usec
DE 6.00 usec
TE 296.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
PMBO
183
ppm

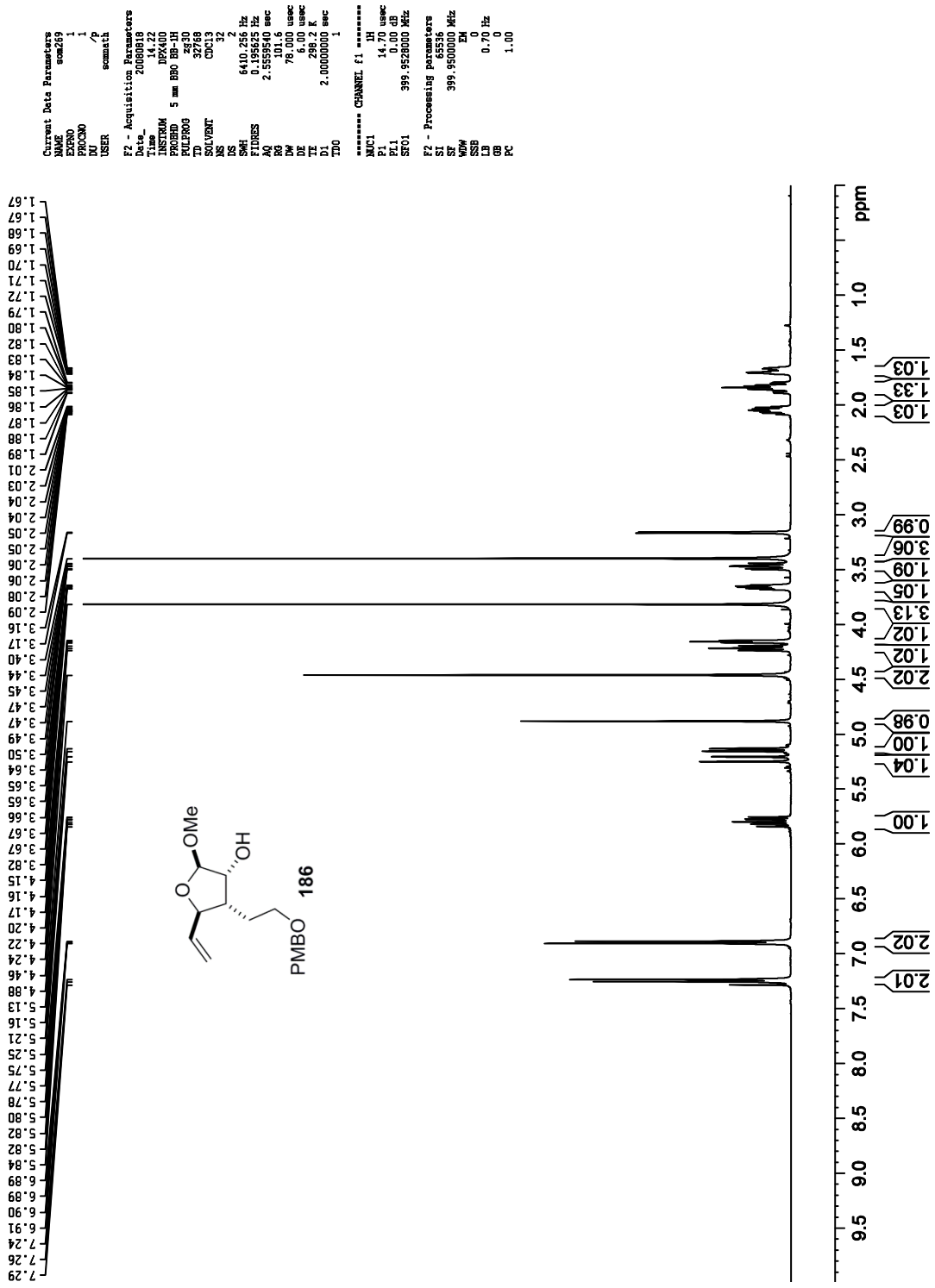

Current Data Parameters
NAME scm18
EXPNO 2
PROCNO 1
DU /p
USER scmath
F2 - Acquisition Parameters
Date_ 20060419
Time 14.55
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2450
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4597.6
DW 19.900 usec
DE 6.00 usec
TE 296.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
25.10
25.36
26.41
26.58
26.87
45.41
55.29
67.36
68.21
72.40
76.76
77.07
77.39
77.72
81.56
81.89
104.98
109.54
111.70
113.75
129.29
130.66
159.18
PMBO
183
ppm

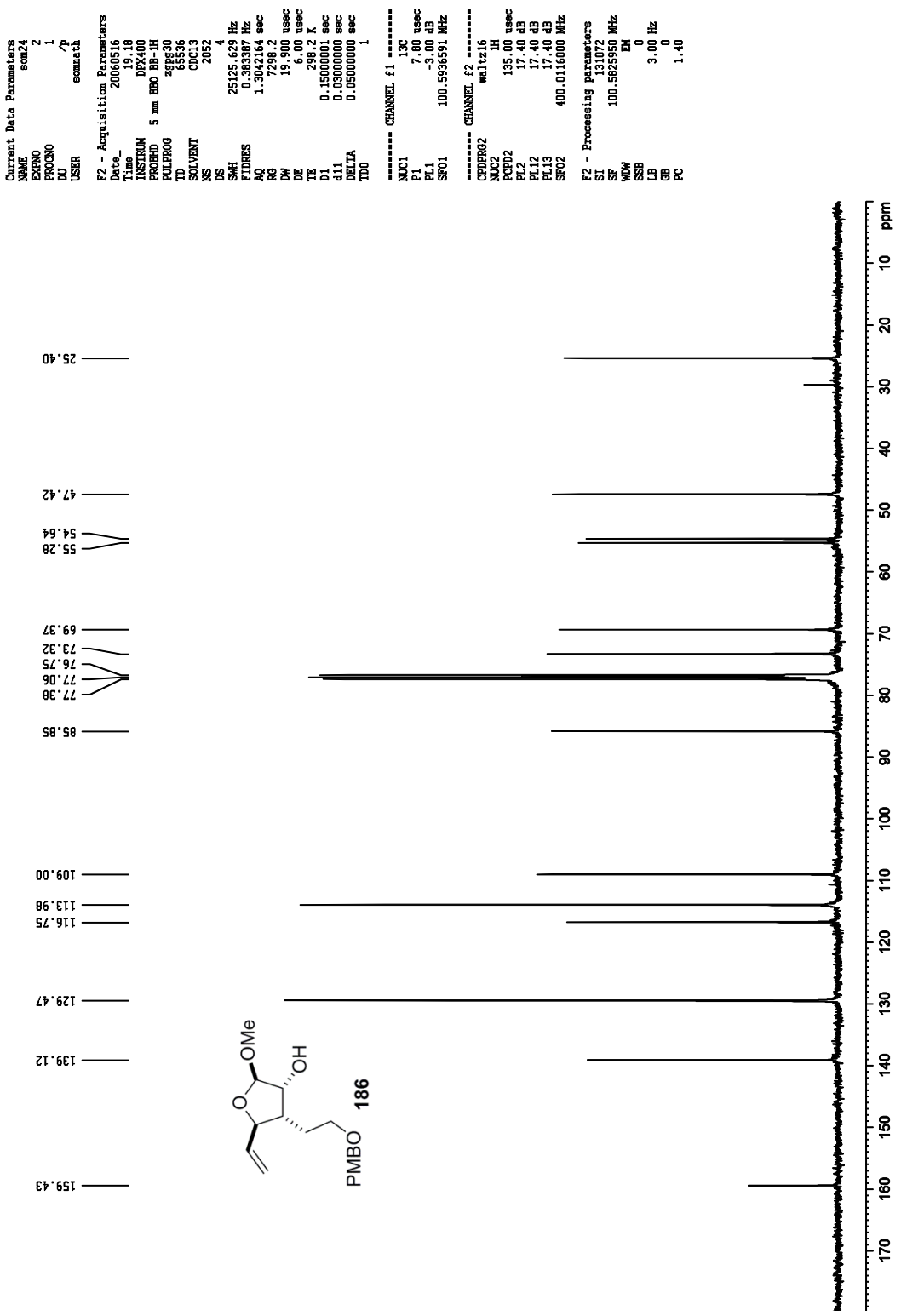

Current Data Parameters
NAME Som268
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080814
Time 16.14
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 574.7
DW 104.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
HO
HO
H
O
O
O
PMBO
184
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
5.07
2.14
1.00
1.03
2.15
1.12
3.32
3.28
1.01
1.09
0.96
1.99
3.19
3.11
7.288
7.281
7.259
6.918
6.911
6.895
6.889
5.759
5.747
4.605
4.592
4.578
4.484
4.474
4.178
4.154
4.130
4.106
3.930
3.897
3.828
3.742
3.724
3.713
3.660
3.646
3.629
3.563
3.548
3.159
3.145
2.083
2.064
2.052
1.970
1.963
1.949
1.946
1.594
1.508
1.321
1.303
1.279
1.255

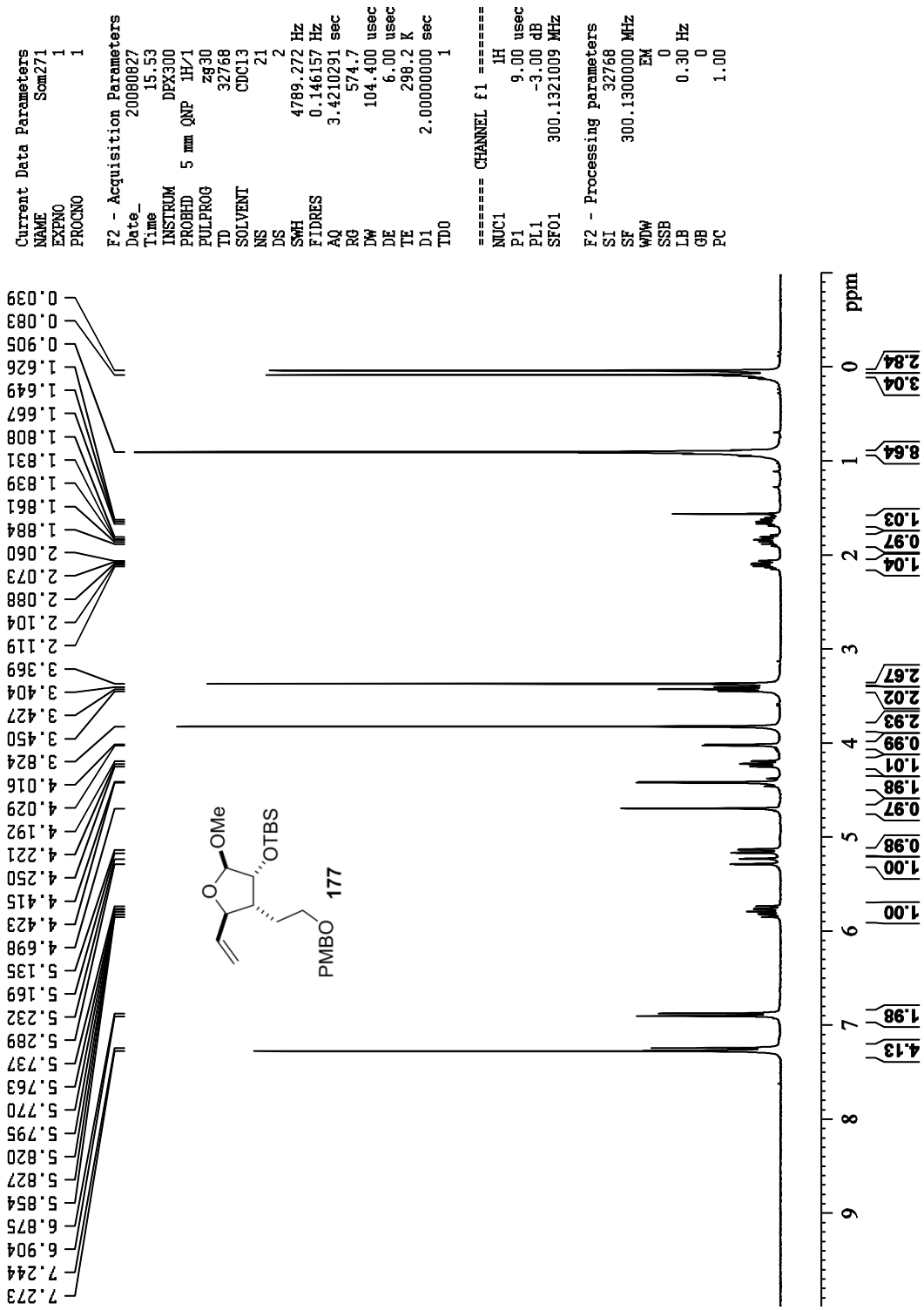

Current Data Parameters
NAME som268
EXPNO 4
PROCNO 1
DU /p
USER somnath
F2 - Acquisition Parameters
Date_ 20060815
Time 15.20
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 1357
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 296.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5765700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675060 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
25.20
26.39
26.77
44.25
55.29
63.82
68.36
72.70
73.28
81.76
82.71
104.68
111.73
113.84
129.47
130.04
159.32
HO
HO
H
O
O
O
PMBO
184
ppm

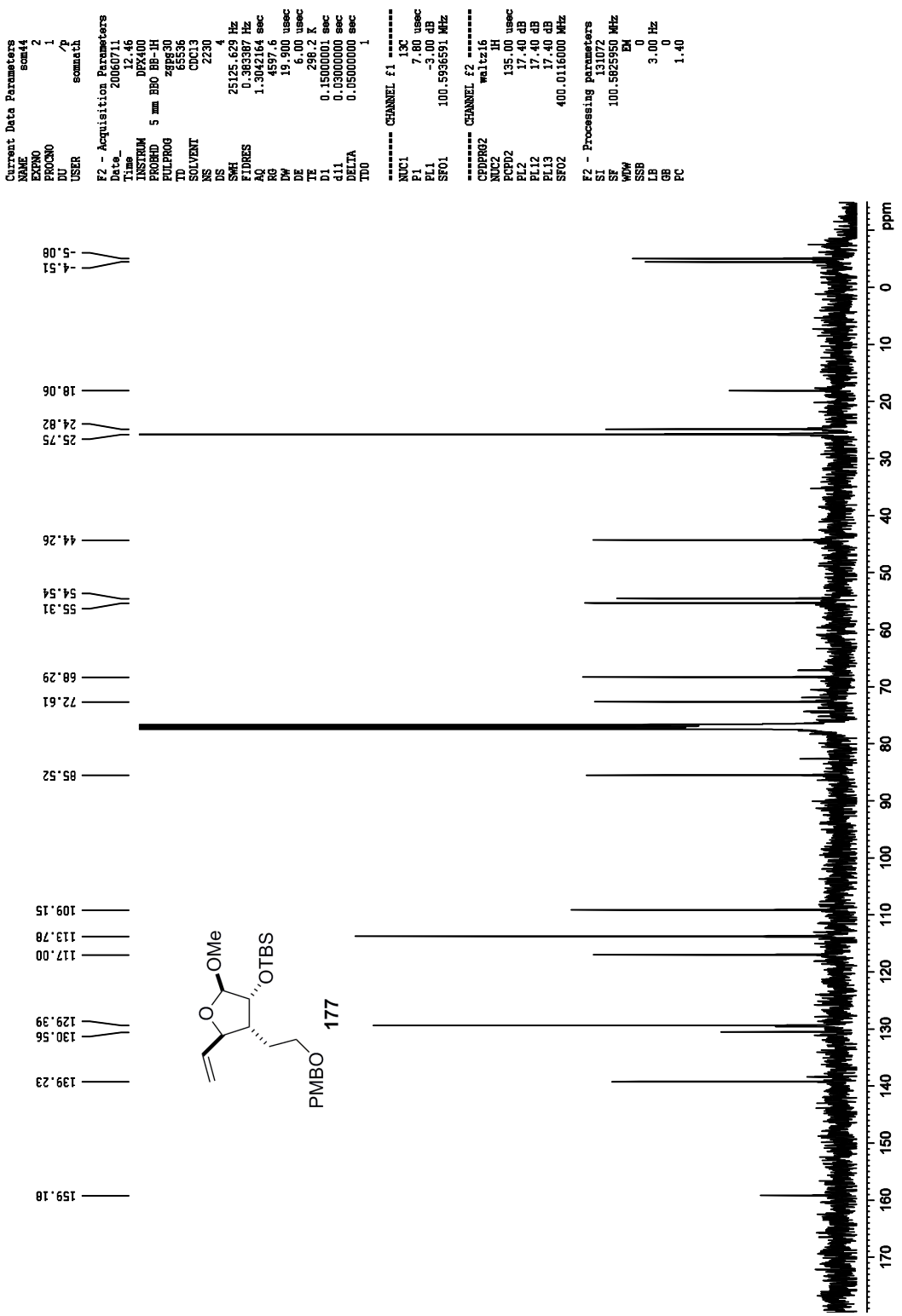

Current Data Parameters
NAME som22
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060428
Time 17.04
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 574.7
DW 104.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
PMBO
185
ppm

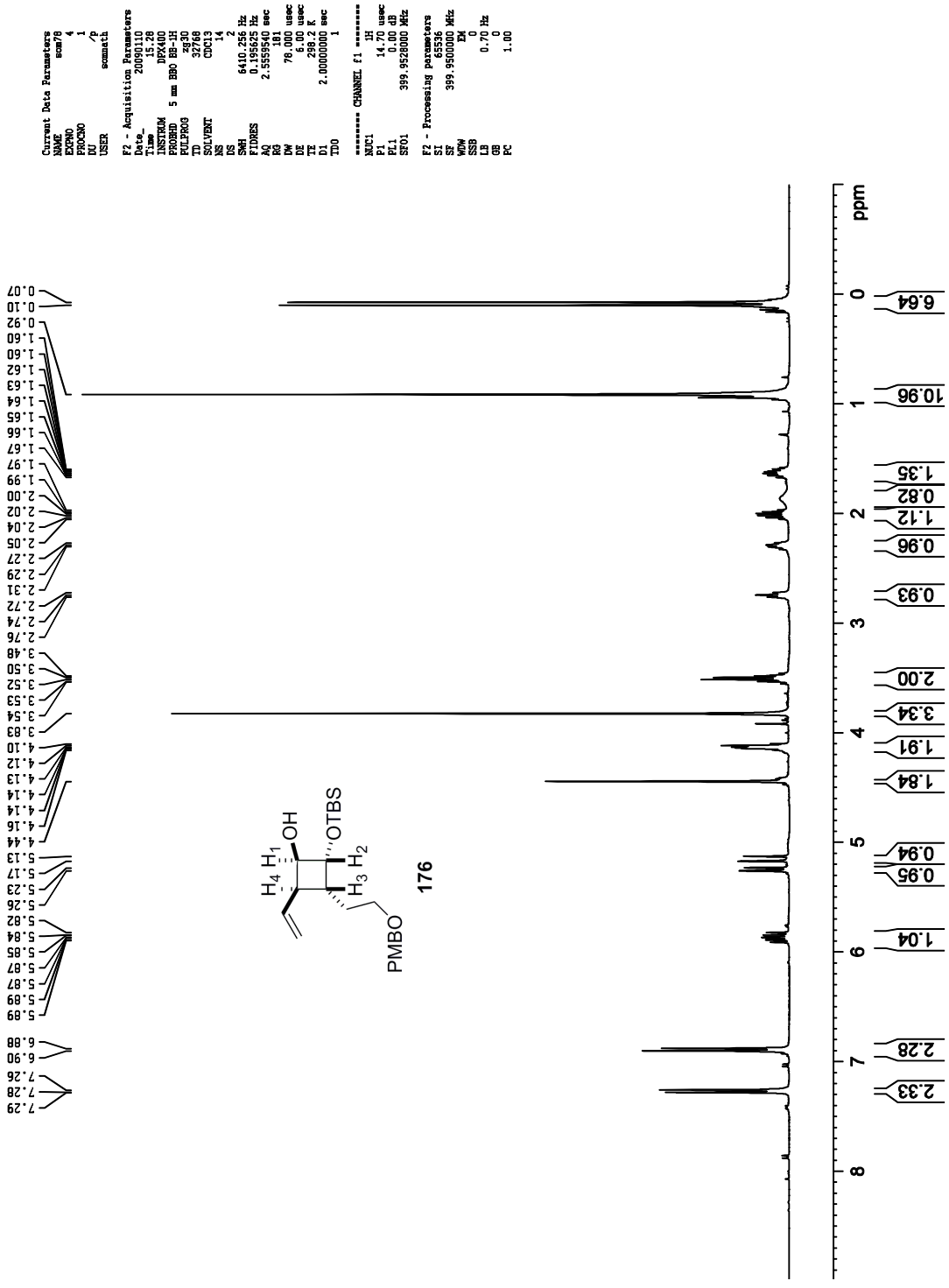

Current Data Parameters
NAME scm22
EXPNO 2
PROCNO 1
DU /p
USER scmath
F2 - Acquisition Parameters
Date_ 20060430
Time 18.46
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2450
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4597.6
DW 19.900 usec
DE 6.00 usec
TE 296.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
24.43
26.33
26.70
46.59
55.30
67.98
72.45
80.98
83.09
104.99
111.43
113.76
118.74
129.26
130.57
135.95
159.19
PMBO
185
ppm

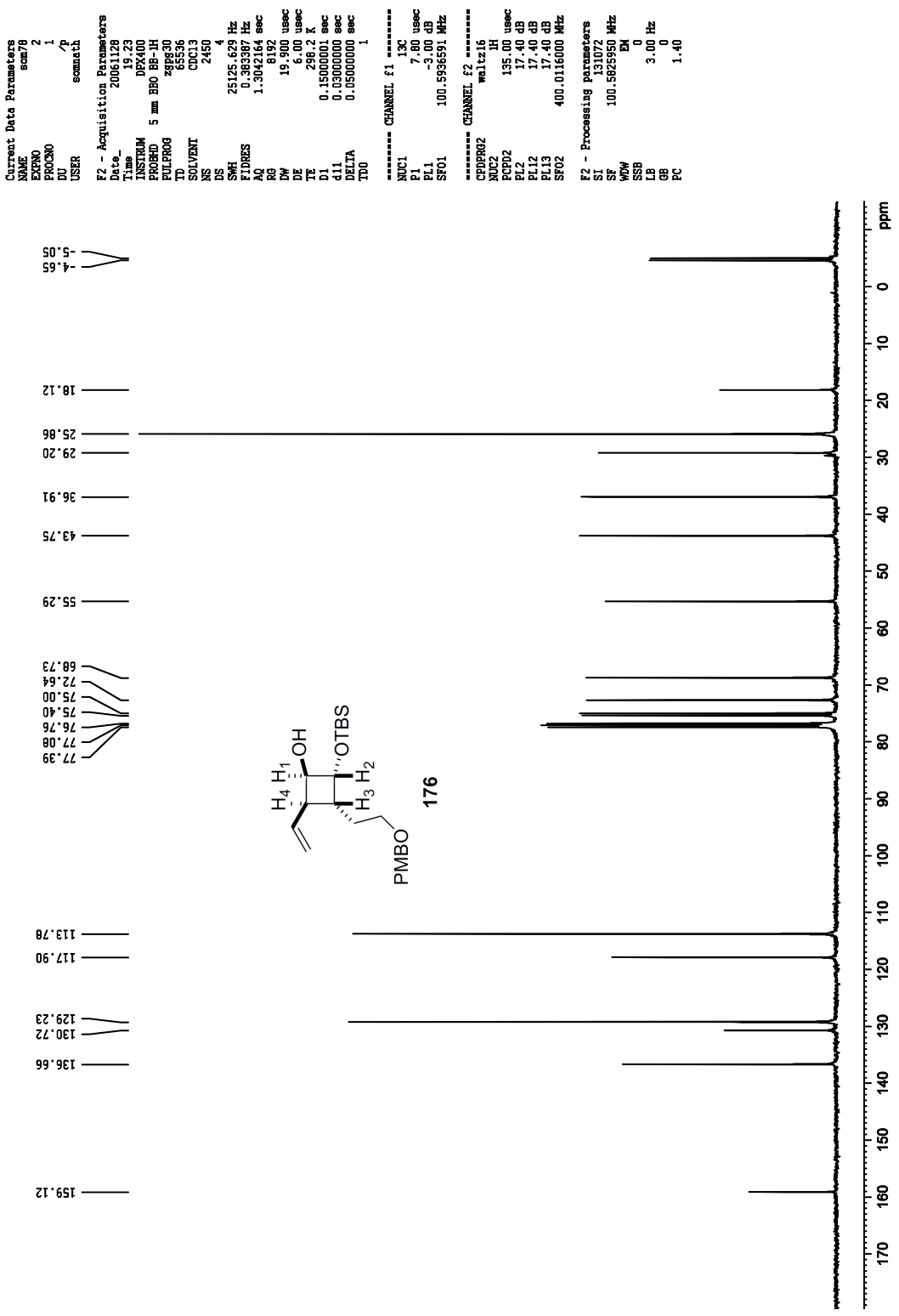

Current Data Parameters
NAME som269
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080818
Time 14.22
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 101.6
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9528000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
OMe
OH
O
PMBO
186
1.03
1.33
1.03
0.99
3.06
1.09
1.05
3.13
1.02
1.02
2.02
0.98
1.00
1.04
1.00
2.02
2.01
ppm

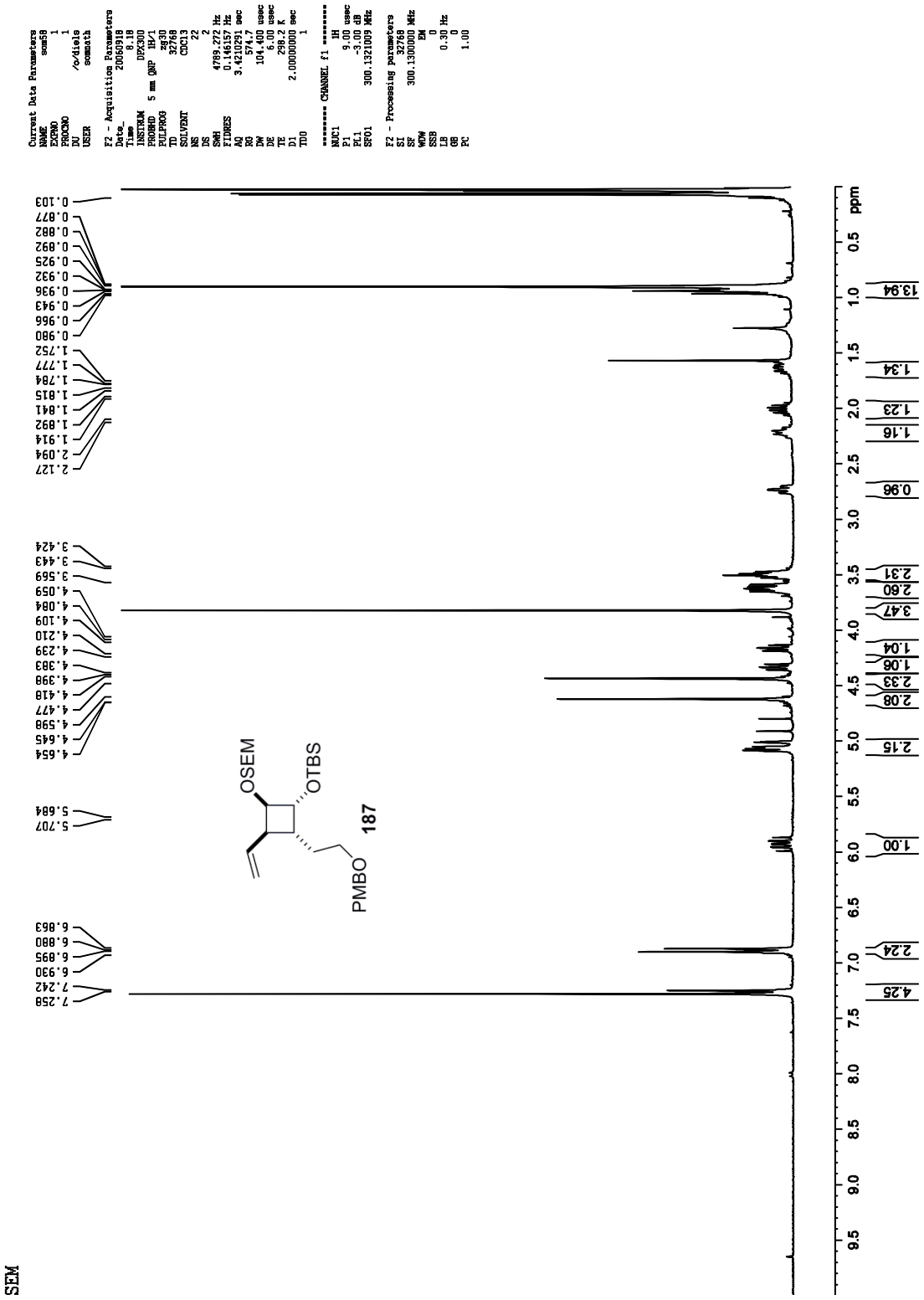

Current Data Parameters
NAME scm24
EXPNO 2
PROCNO 1
DU /p
USER scmath
F2 - Acquisition Parameters
Date_ 20060516
Time 19.18
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2052
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 7298.2
DW 19.900 usec
DE 6.00 usec
TE 296.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
25.40
47.42
54.64
55.28
69.37
73.32
76.75
77.06
77.38
85.85
109.00
113.98
116.75
129.47
139.12
159.43
OMe
OH
O
PMBO
186
ppm

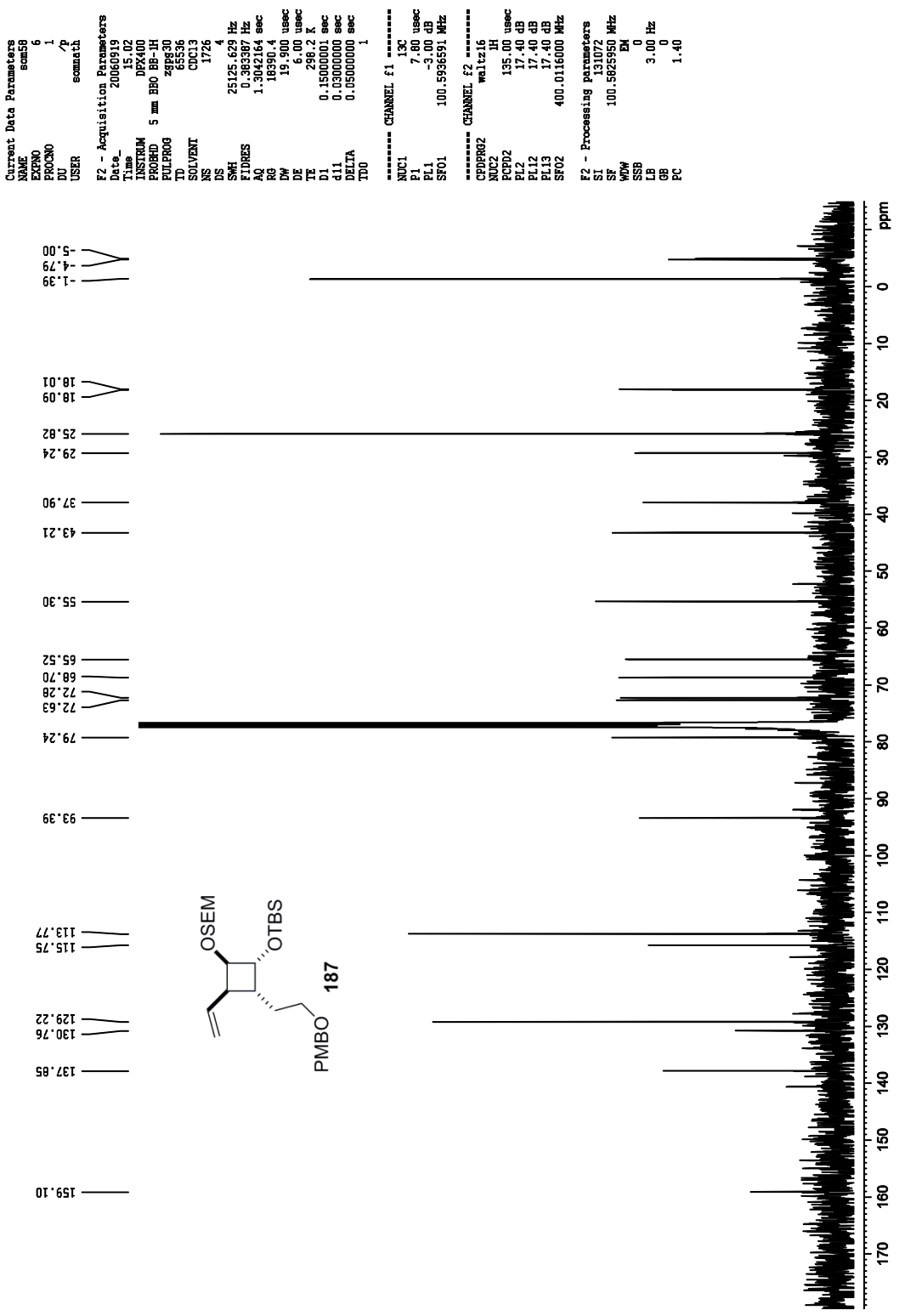

Current Data Parameters
NAME Som271
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080827
Time 15.53
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 21
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 574.7
DW 104.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OMe
OTBS
PMBO
177
ppm

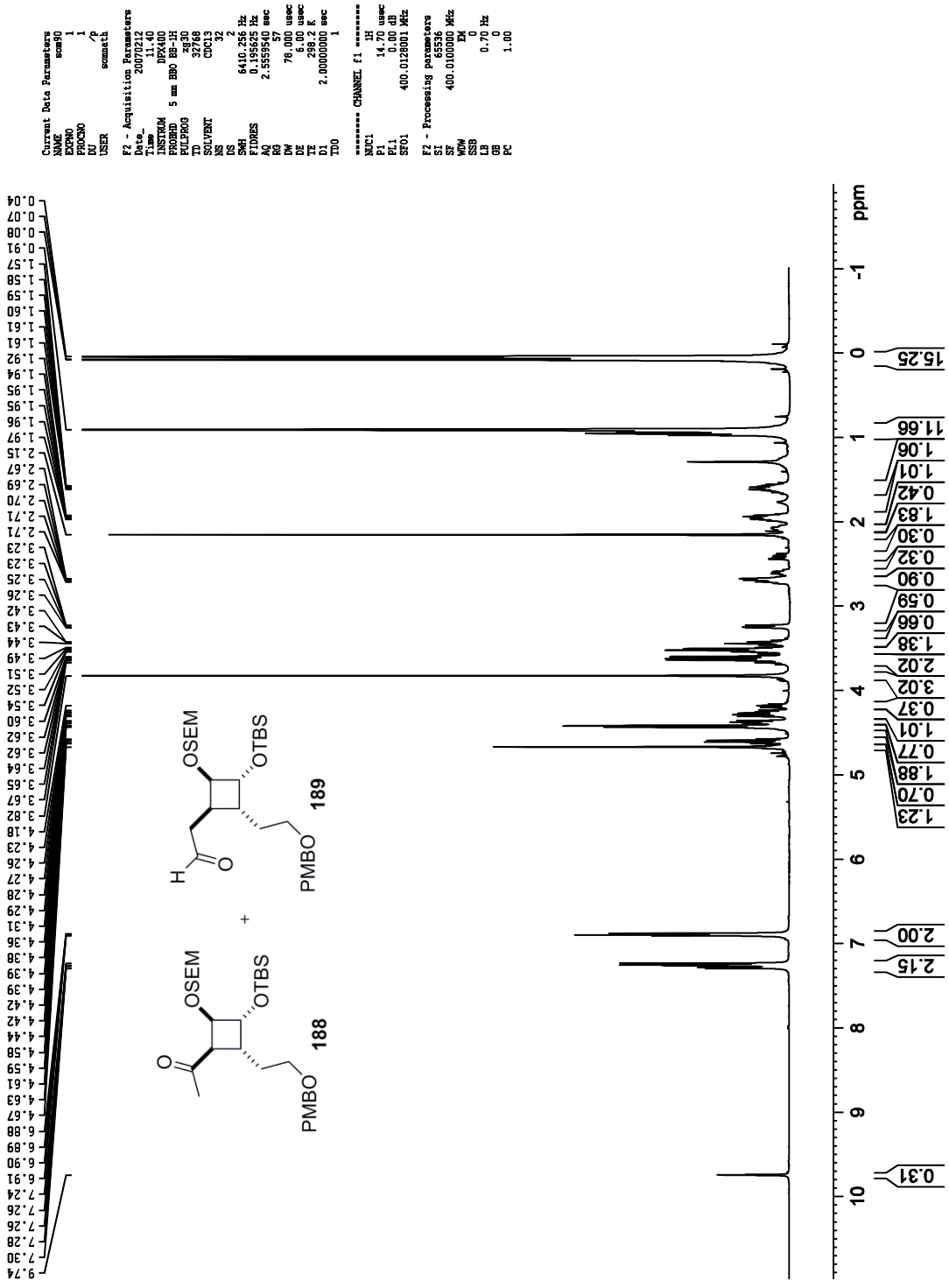

Current Data Parameters
NAME scm44
EXPNO 2
PROCNO 1
DU /p
USER scmath
F2 - Acquisition Parameters
Date_ 20060711
Time 12.46
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2230
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4597.6
DW 19.900 usec
DE 6.00 usec
TE 296.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.08
-4.51
18.06
24.82
25.75
44.26
54.54
55.31
68.29
72.61
85.52
109.15
113.78
117.00
129.39
130.56
139.23
159.18
OMe
OTBS
O
PMBO
177
ppm

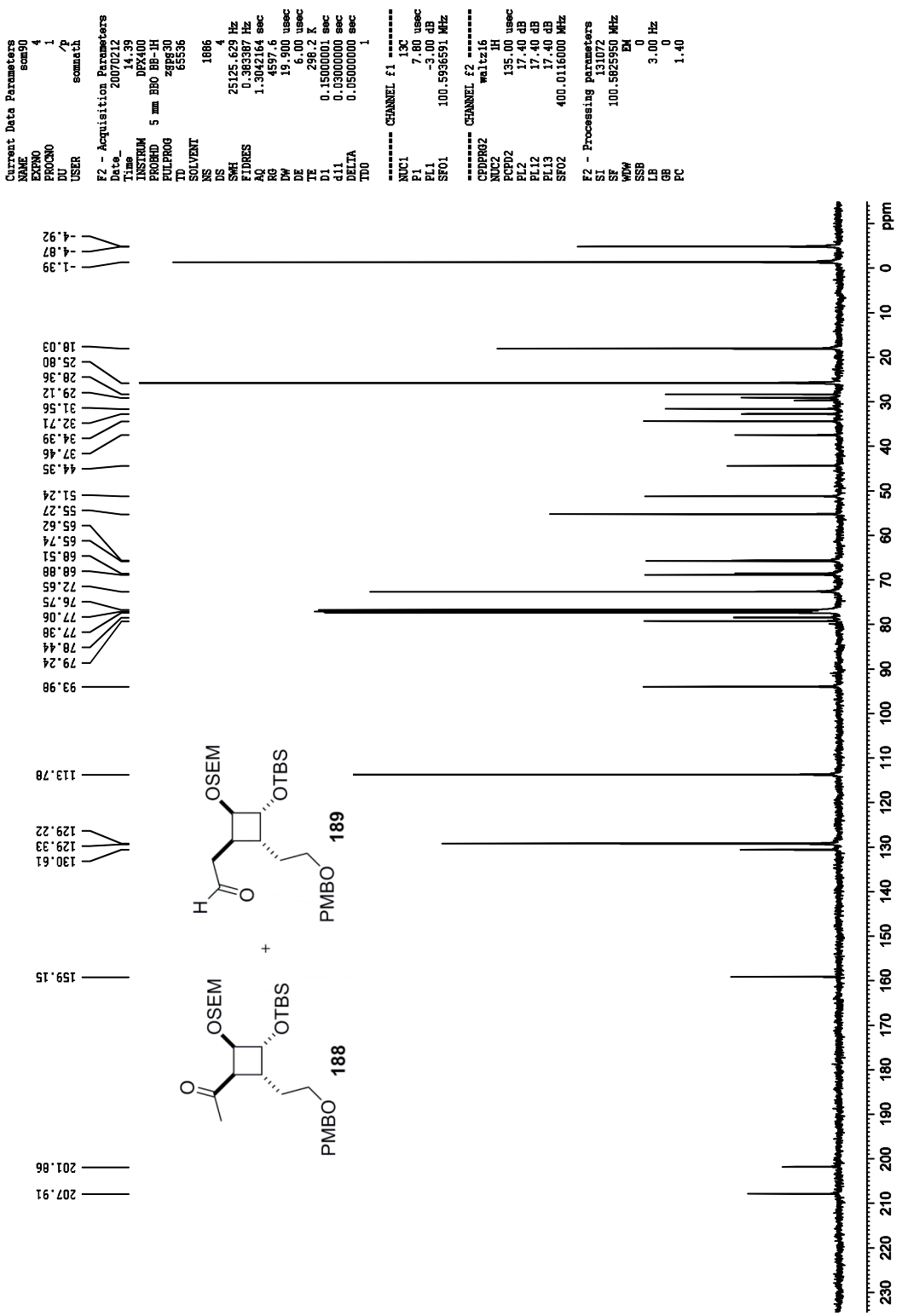

Current Data Parameters
NAME scm76
EXPNO 4
PROCNO 1
DU /0
USER scmath
F2 - Acquisition Parameters
Date_ 20090110
Time 15.28
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 14
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 181
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9528000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
OH
OTBS
PMBO
176
ppm
6.64
10.96
1.35
0.82
1.12
0.96
0.93
2.00
3.34
1.91
1.84
0.94
0.95
1.04
2.28
2.33

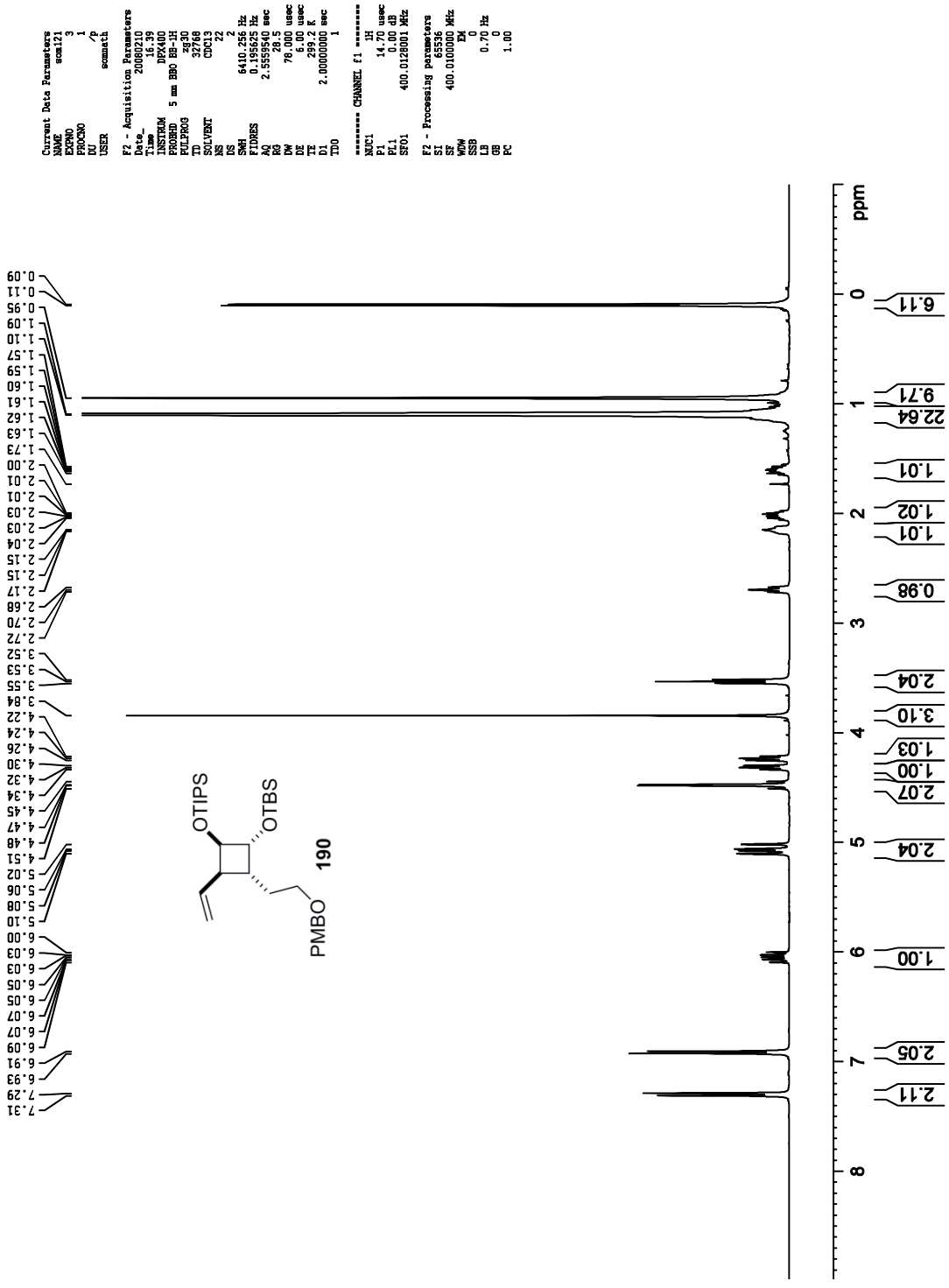

Current Data Parameters
NAME scm78
EXPNO 2
PROCNO 1
DU /p
USER scmmath
F2 - Acquisition Parameters
Date_ 20061128
Time 19.23
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2450
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 8192
DW 19.900 usec
DE 6.00 usec
TE 296.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.05
-4.65
18.12
25.86
29.20
36.91
43.75
55.29
68.73
72.64
75.00
75.40
76.76
77.08
77.39
113.78
117.90
129.23
130.72
136.66
159.12
OTBS
OH
PMBO
H1
H2
H3
H4
176
ppm

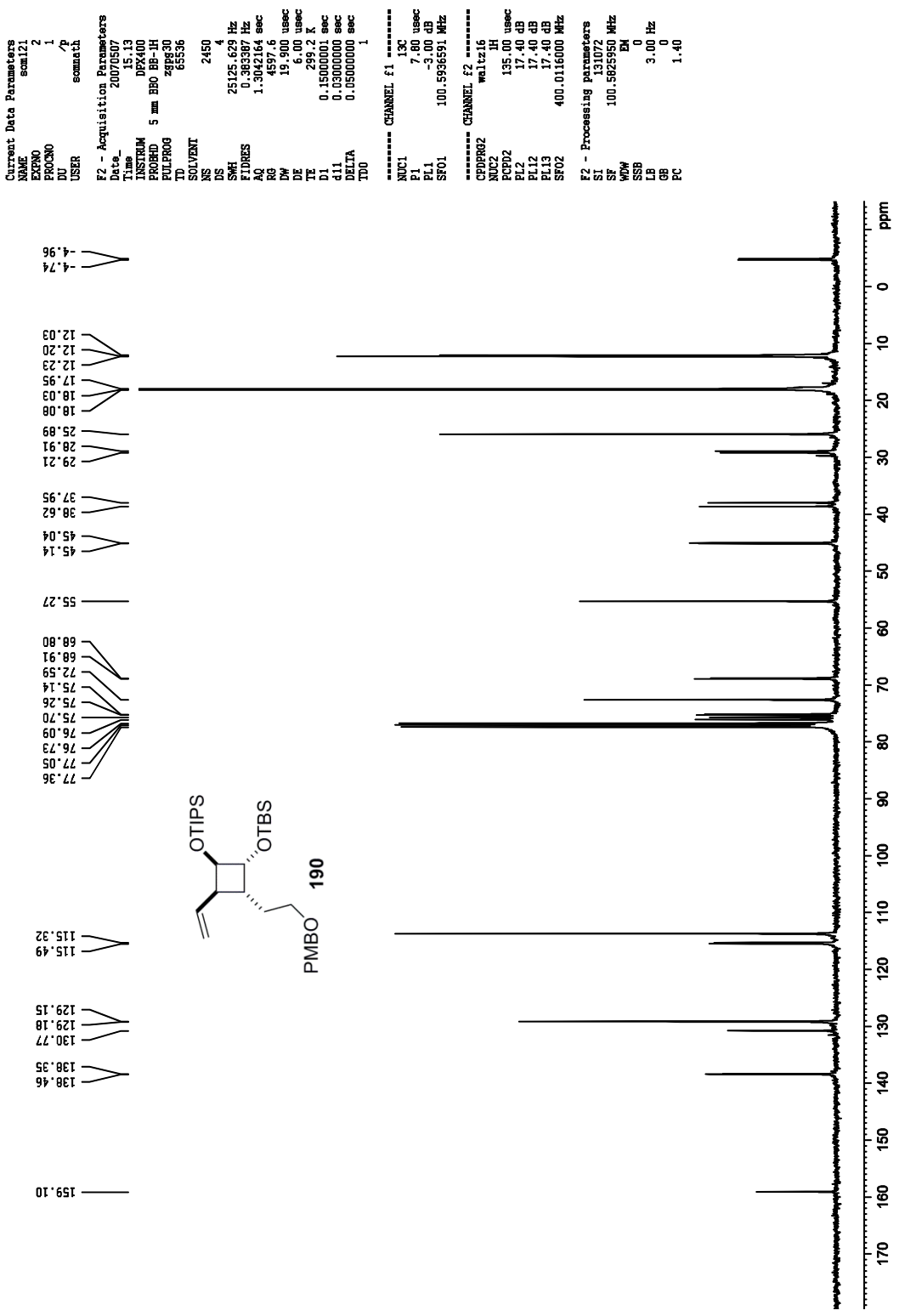

Current Data Parameters
NAME sem58
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060918
Time 8.18
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 22
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 574.7
DW 104.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OSEM
OTBS
PMBO
187
SEM
ppm

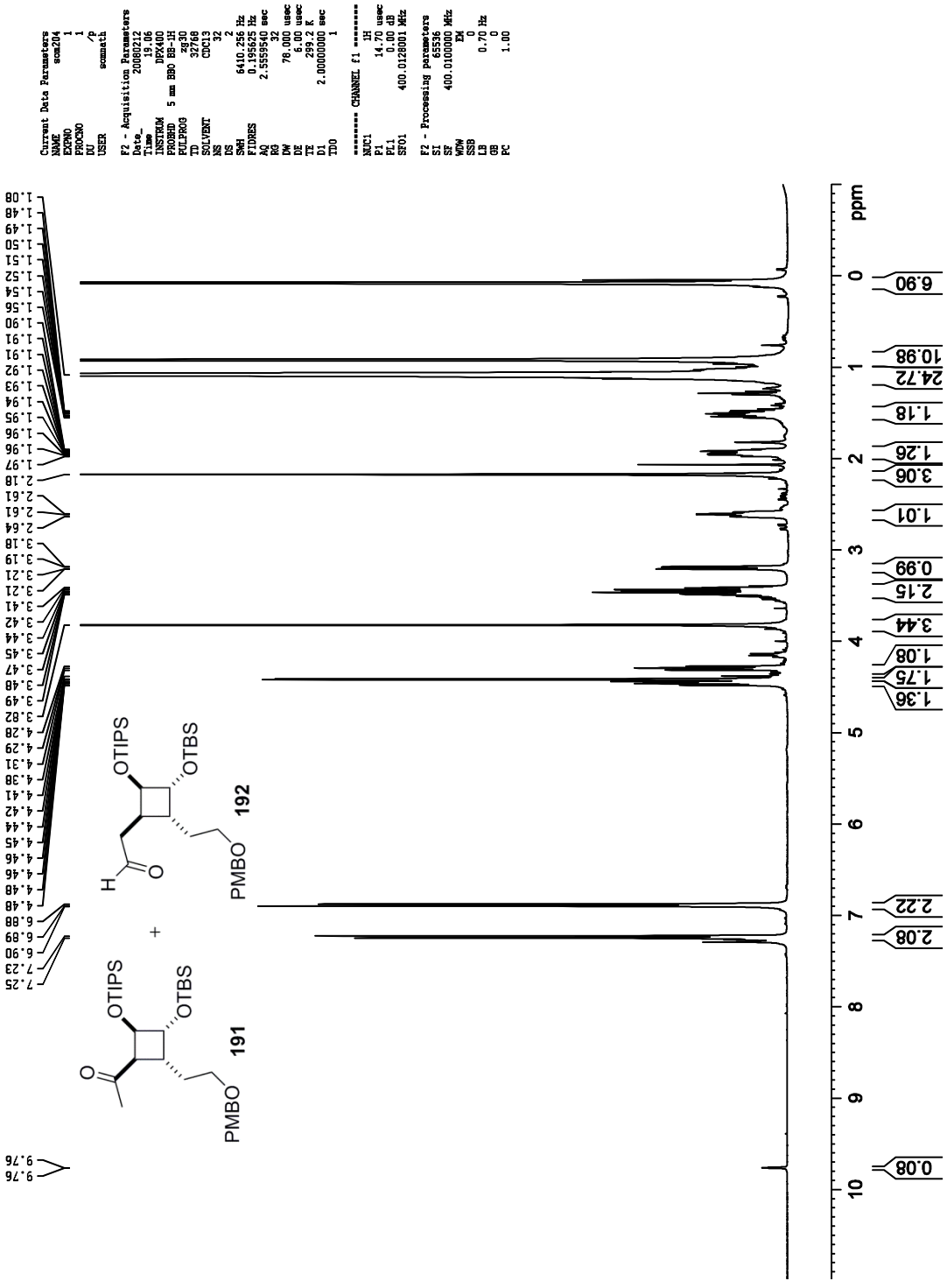

Current Data Parameters
NAME scm58
EXPNO 6
PROCNO 1
DU /p
USER scmath
F2 - Acquisition Parameters
Date_ 20060919
Time 15.02
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1726
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 18390.4
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-1.39
-4.79
-5.00
18.01
18.09
25.82
29.24
37.90
43.21
55.30
65.52
68.70
72.28
72.63
79.24
93.39
113.77
115.75
129.22
130.76
137.85
159.10
OSEM
OTBS
PMBO
187
ppm

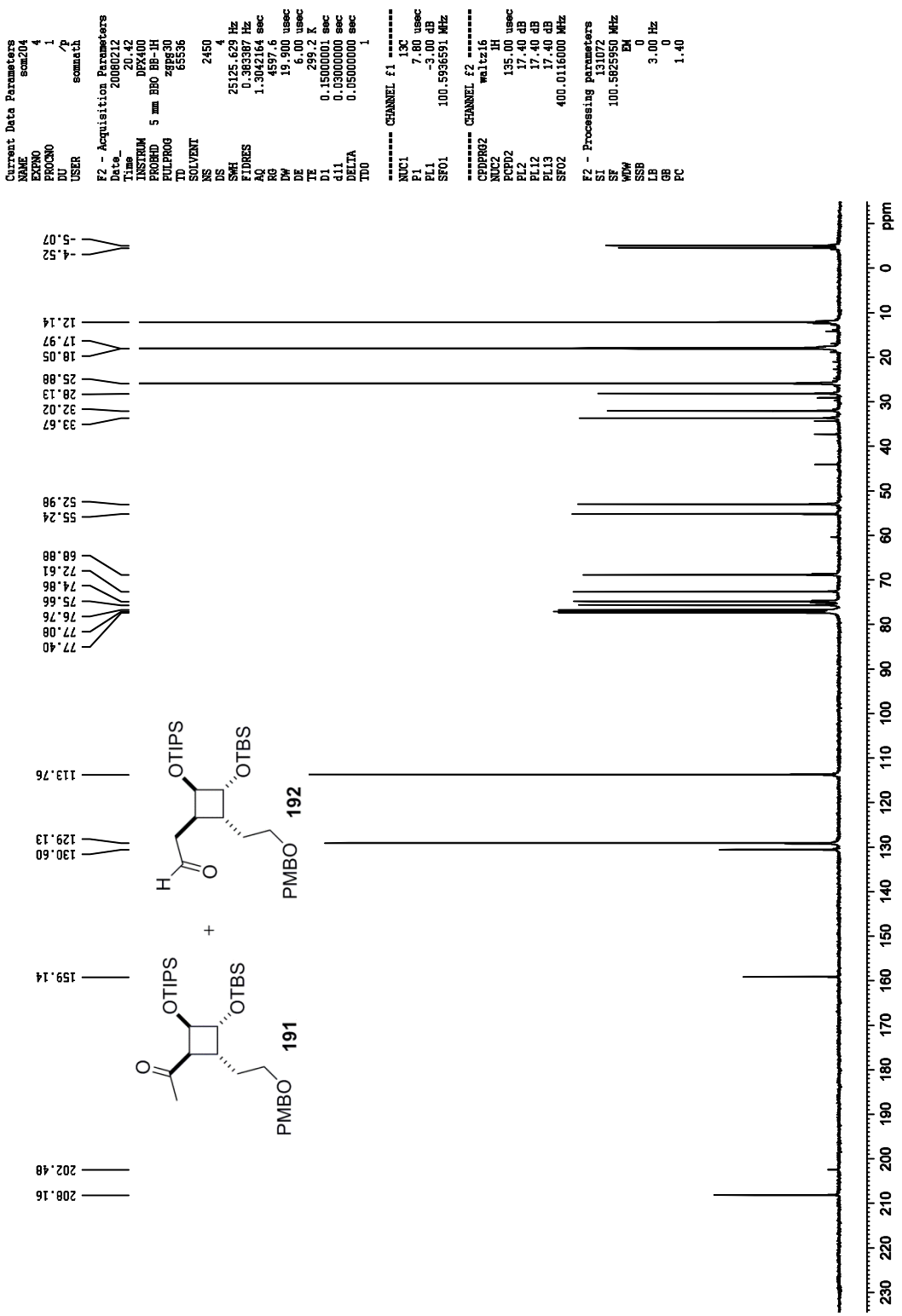

OSEM
OTBS
PMBO
189
OSEM
OTBS
PMBO
188
ppm

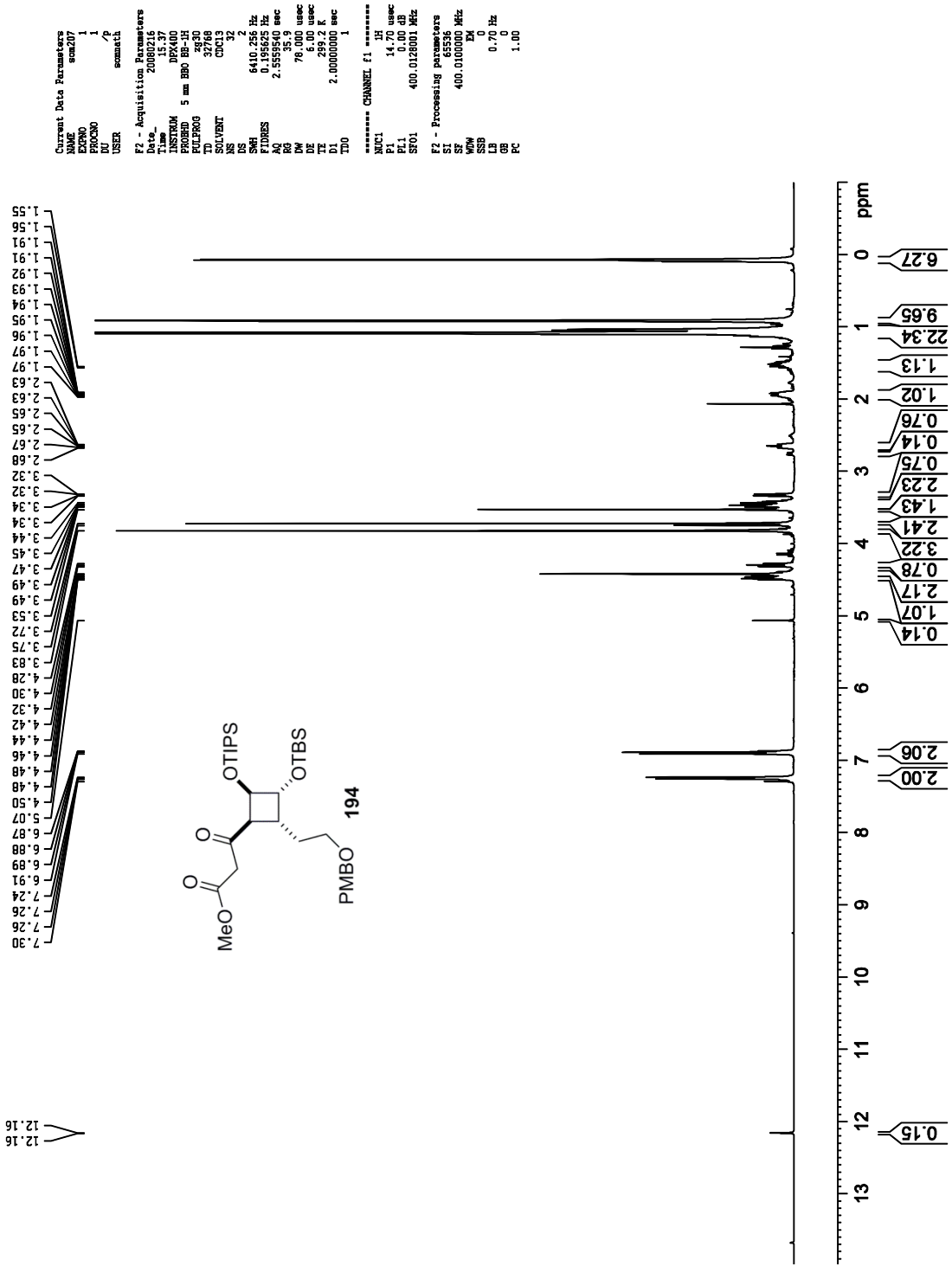

Current Data Parameters
NAME scm90
EXPNO 4
PROCNO 1
DU /p
USER scmath
F2 - Acquisition Parameters
Date_ 20070212
Time 14.39
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 1886
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4597.6
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-4.92
-4.87
-1.39
18.03
25.80
26.36
29.12
31.56
32.71
34.39
37.46
44.35
51.24
55.27
65.62
65.74
68.51
68.88
72.65
76.75
77.06
77.38
78.44
79.24
93.98
113.78
129.22
129.33
130.61
159.15
201.86
207.91
OSEM
OTBS
PMBO
189
188
ppm


OTIPS
OTBS
PMBO
190
ppm


Current Data Parameters
NAME som121
EXPNO 2
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20070507
Time 15.13
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 2450
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4597.6
DW 19.900 usec
DE 6.00 usec
TE 299.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-4.96
-4.74
12.03
12.20
12.23
17.95
18.03
18.08
25.89
28.91
29.21
37.95
38.62
45.04
45.14
55.27
68.80
68.91
72.59
75.14
75.26
75.70
76.09
76.73
77.05
77.36
115.32
115.49
129.15
129.18
130.77
138.35
138.46
159.10
OTIPS
OTBS
PMBO
190
ppm


OTIPS
OTBS
PMBO
191
OTIPS
OTBS
PMBO
192
ppm


Current Data Parameters
NAME som204
EXPNO 4
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20080212
Time 20.42
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 2450
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4597.6
DW 19.900 usec
DE 6.00 usec
TE 299.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.07
-4.52
12.14
17.97
18.05
25.88
28.13
32.02
33.67
52.98
55.24
68.88
72.61
74.86
75.66
76.76
77.08
77.40
113.76
129.13
130.60
159.14
202.48
208.16
OTIPS
OTBS
PMBO
192
191
ppm


OTIPS
OTBS
PMBO
MeO
194
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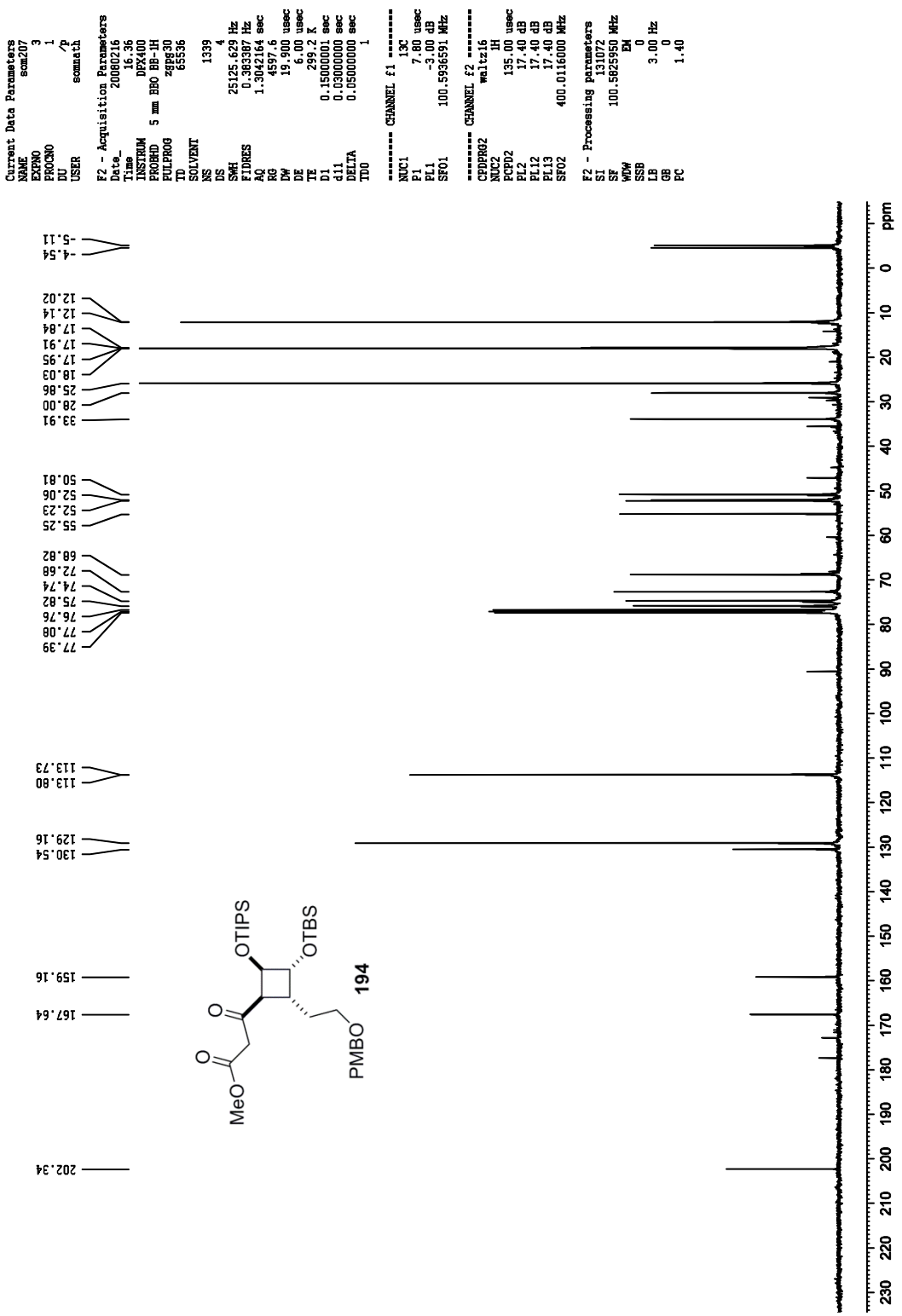
Current Data Parameters
NAME som207
EXPNO 3
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20080216
Time 16.36
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 1339
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4597.6
DW 19.900 usec
DE 6.00 usec
TE 299.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.11
-4.54
12.02
12.14
17.84
17.91
17.95
18.03
25.86
28.00
33.91
50.81
52.06
52.23
55.25
68.82
72.68
74.74
75.82
76.76
77.08
77.39
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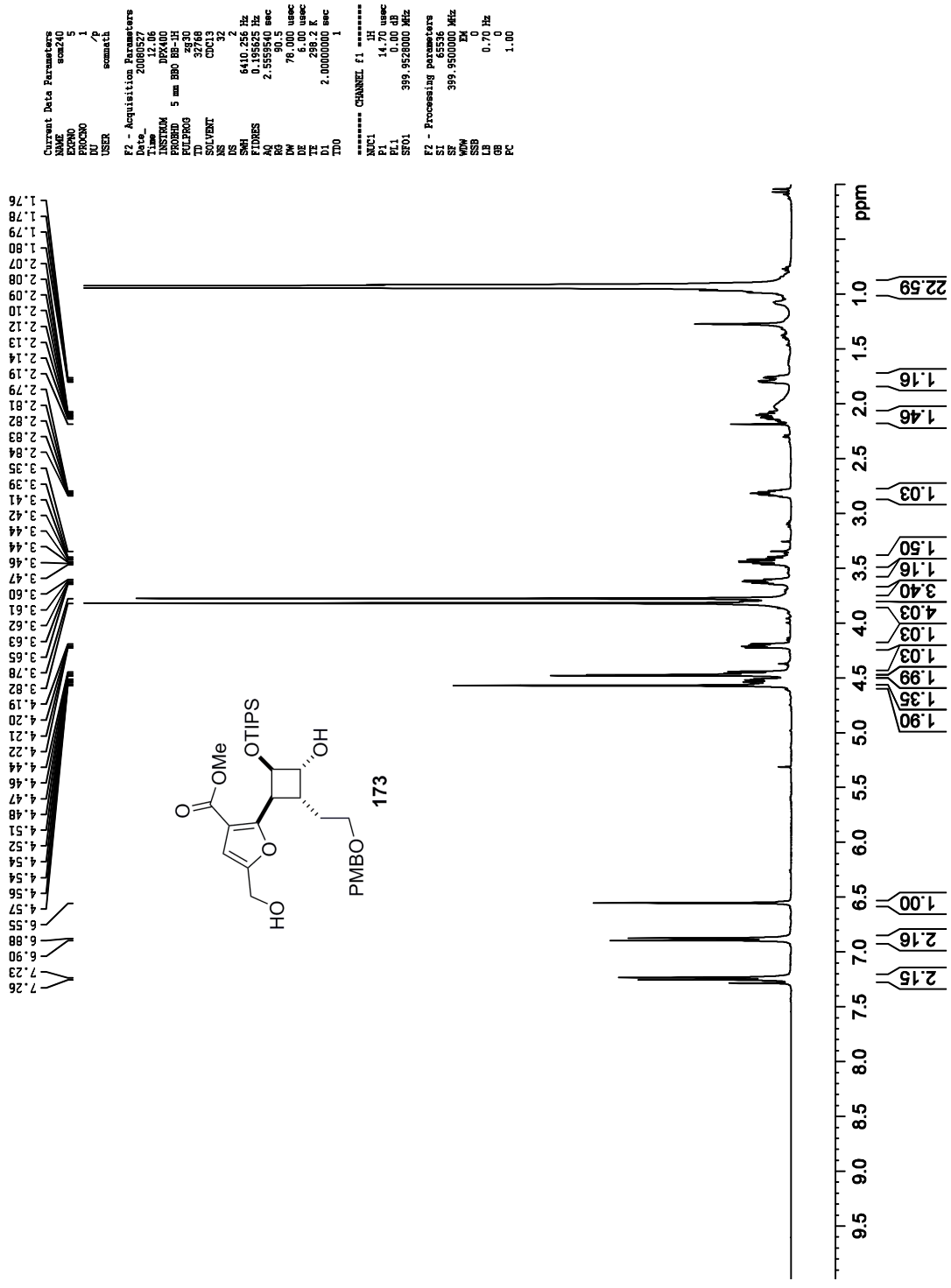
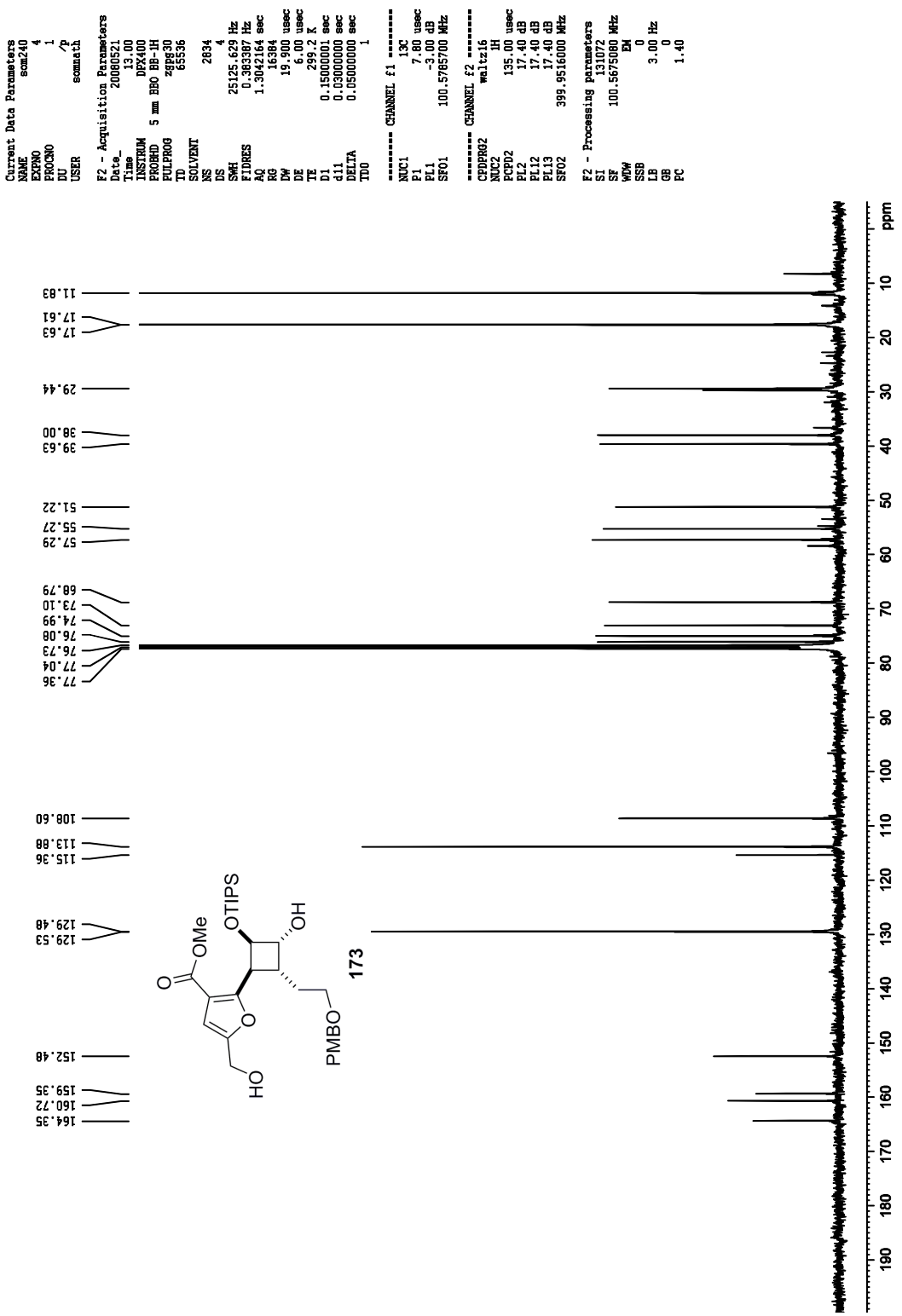
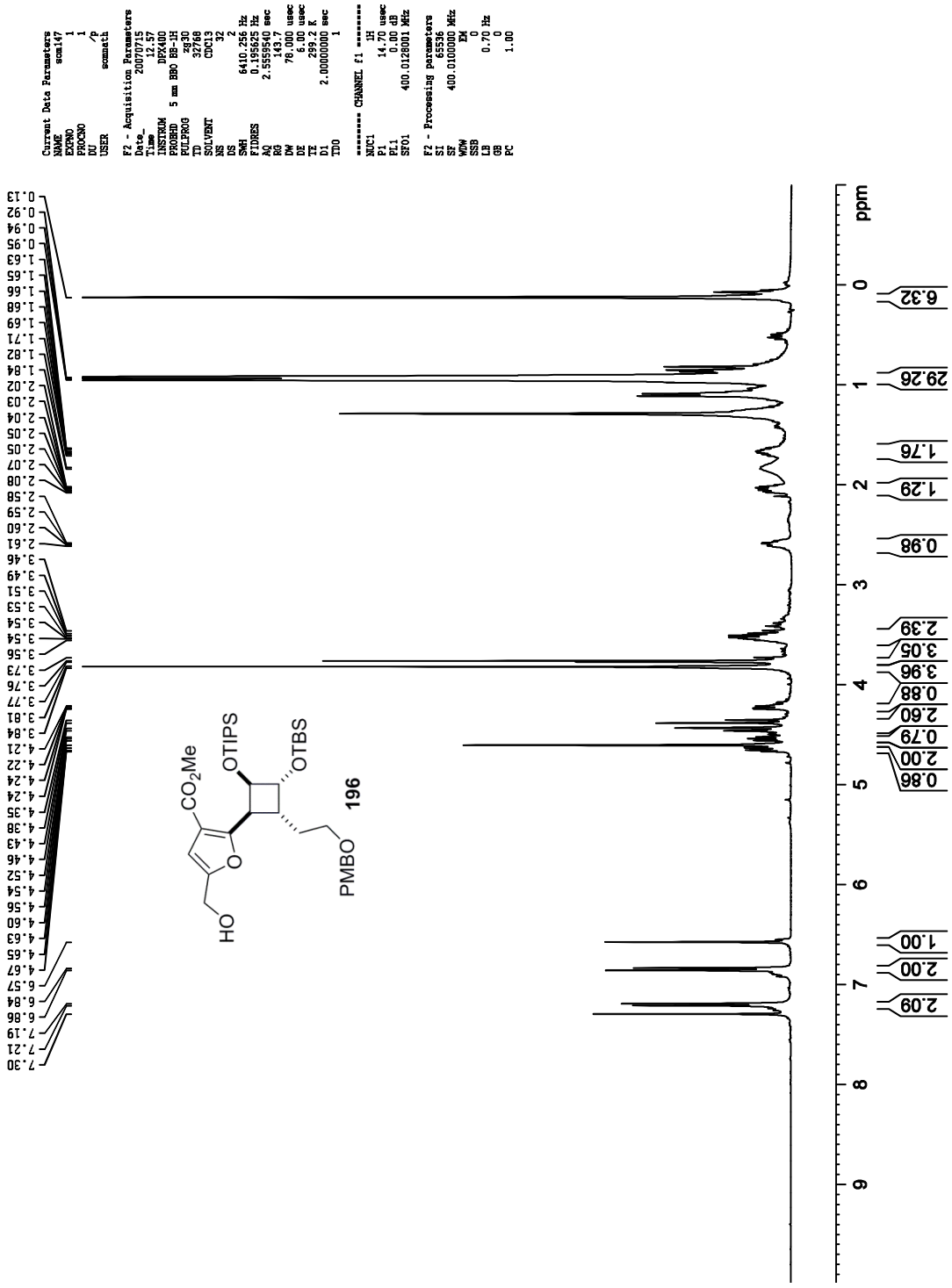
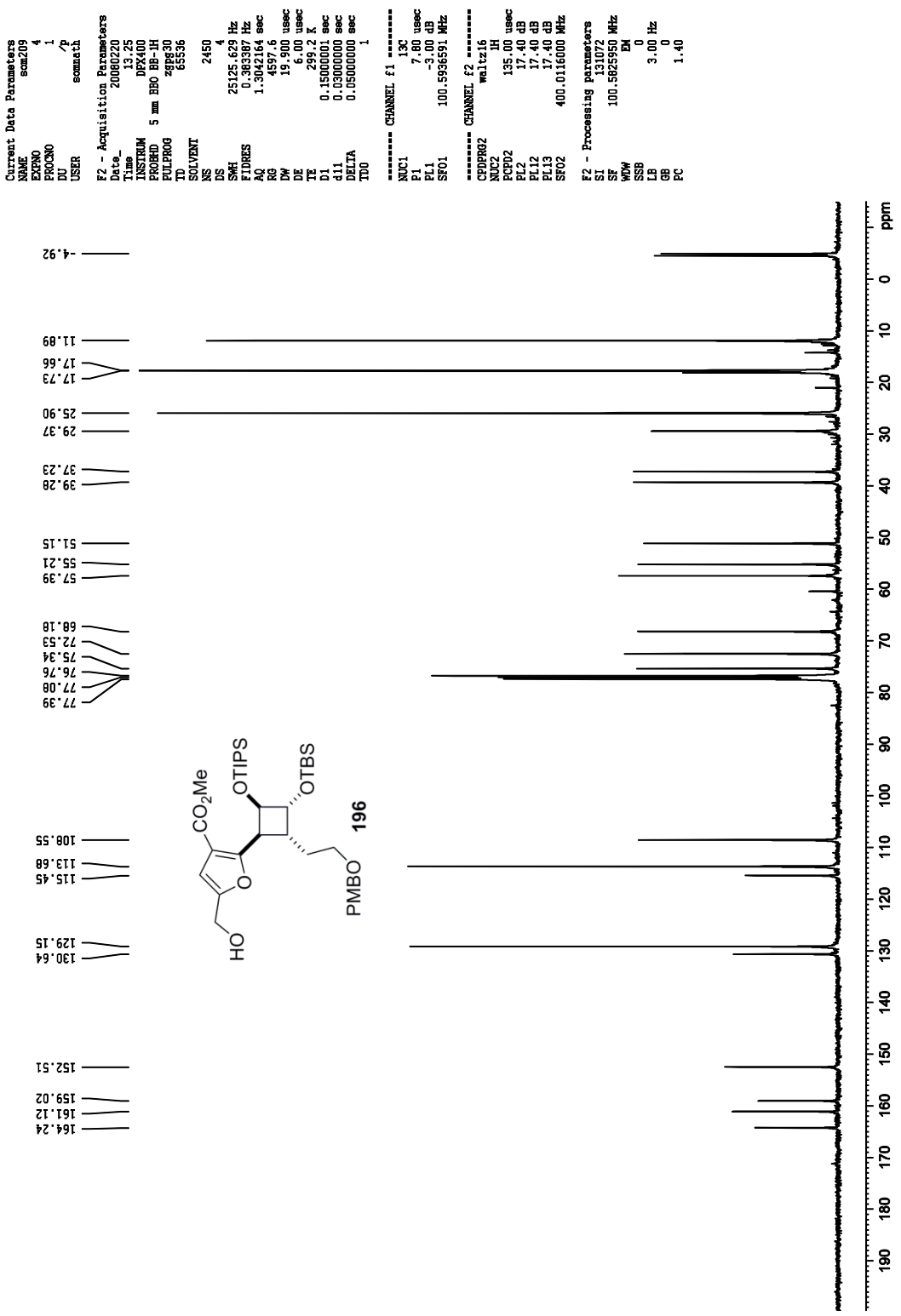
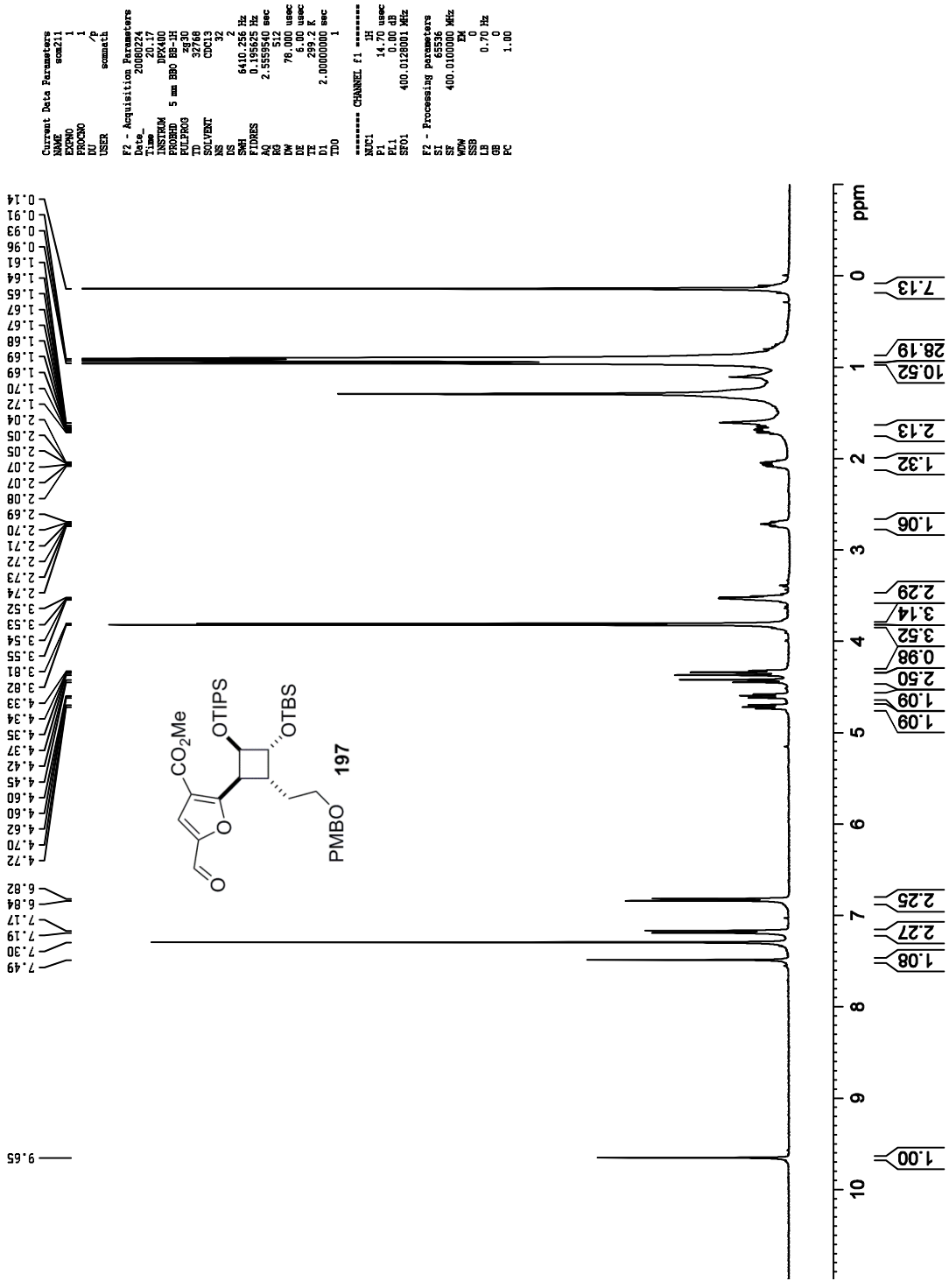
167.64
202.34
OTIPS
OTBS
PMBO
MeO
O
O
194
ppm

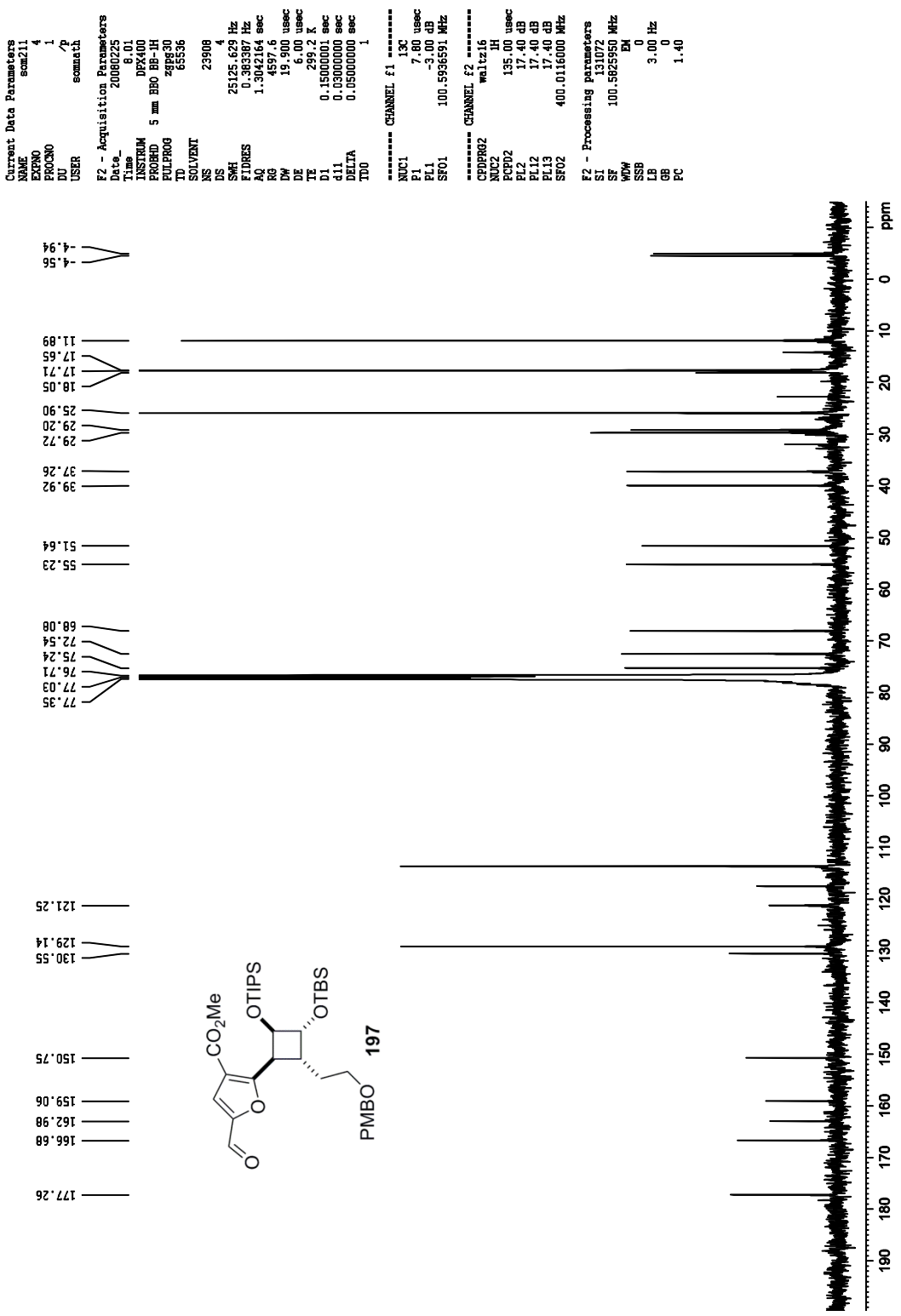

Current Data Parameters
NAME sem240
EXPNO 5
PROCNO 1
DU /0
USER somath
F2 - Acquisition Parameters
Date_ 20080527
Time 12.06
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 90.5
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9528000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
OMe
OTIPS
OH
O
HO
PMBO
173
ppm
22.59
1.16
1.46
1.03
1.50
1.16
3.40
4.03
1.03
1.03
1.99
1.35
1.90
1.00
2.16
2.15

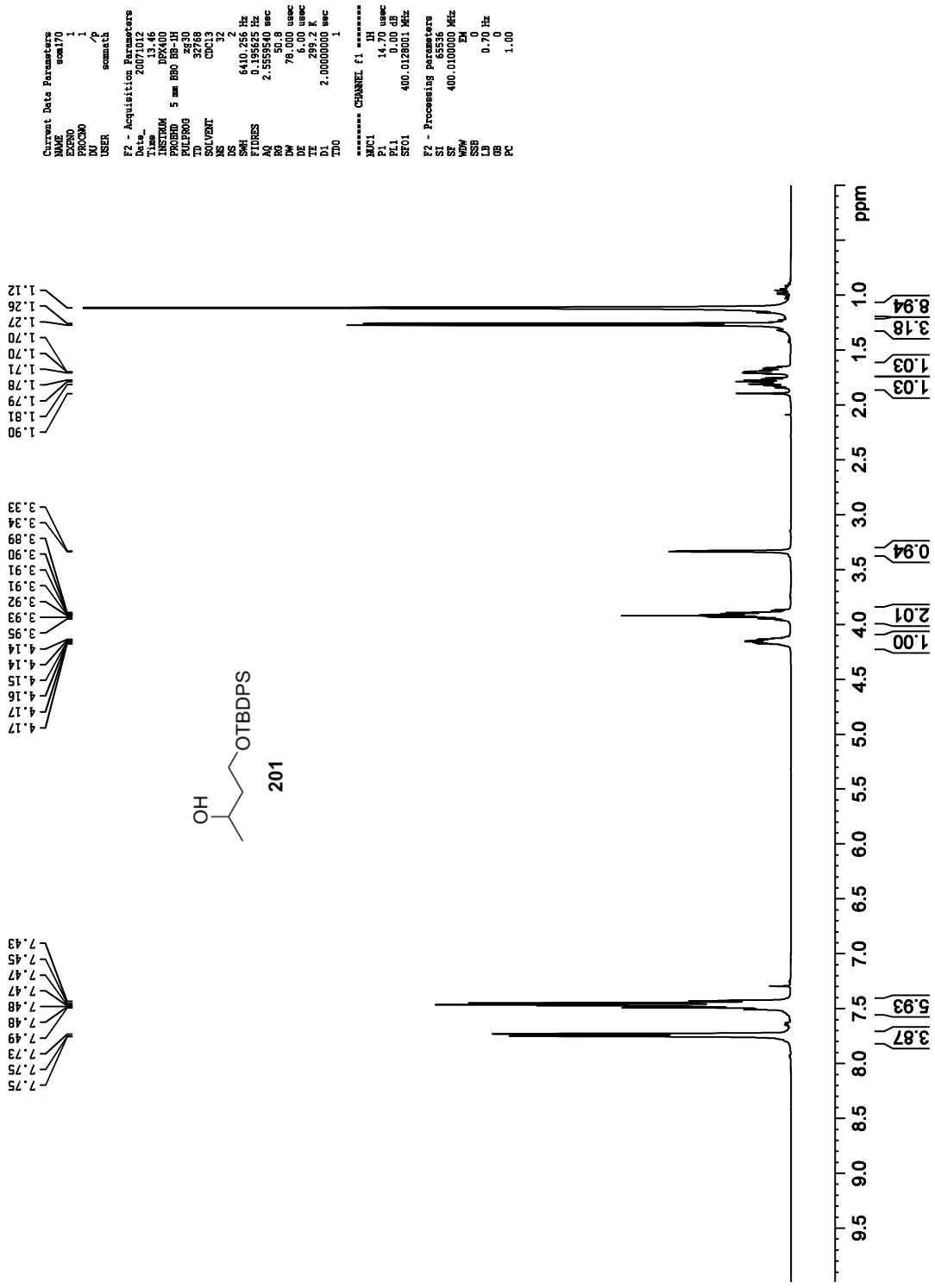

Current Data Parameters
NAME som240
EXPNO 4
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20080521
Time 13.00
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 2634
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 299.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5765700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675060 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
11.83
17.61
17.63
29.44
38.00
39.63
51.22
55.27
57.29
68.79
73.10
74.99
76.08
76.73
77.04
77.36
108.60
113.88
115.36
129.48
129.53
152.48
159.35
160.72
164.35
OTIPS
OMe
O
OH
HO
PMBO
173
ppm

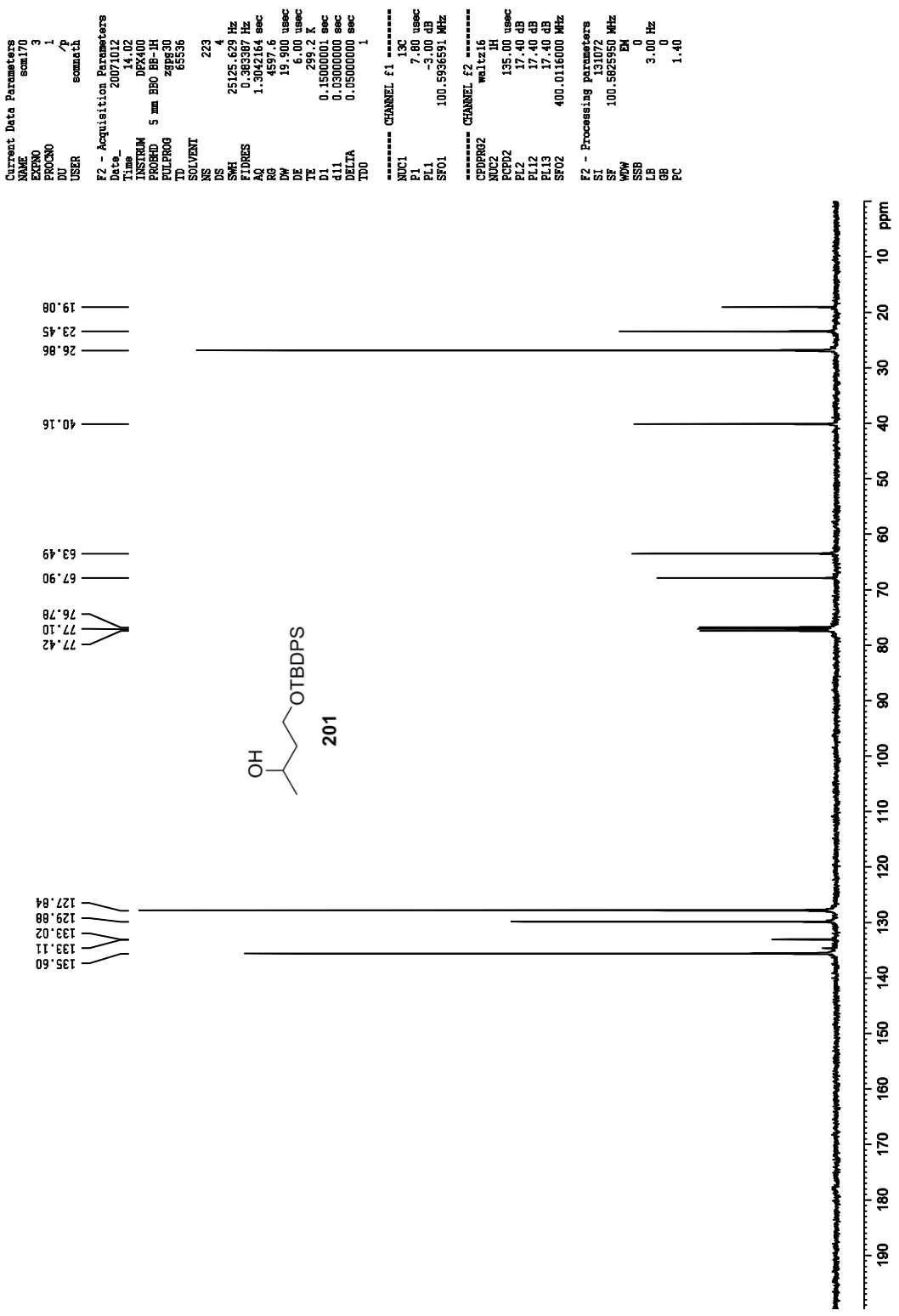

Current Data Parameters
NAME scm147
EXPNO 1
PROCNO 1
DU /0
USER scmath
F2 - Acquisition Parameters
Date_ 20070715
Time 12.57
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 143.7
DW 78.000 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 400.0128001 MHz
F2 - Processing parameters
SI 65536
SF 400.0100000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
CO2Me
OTIPS
OTBS
PMBO
HO
196
ppm
6.32
29.26
1.76
1.29
0.98
2.39
3.05
3.96
0.88
2.60
0.79
2.00
0.86
1.00
2.00
2.09

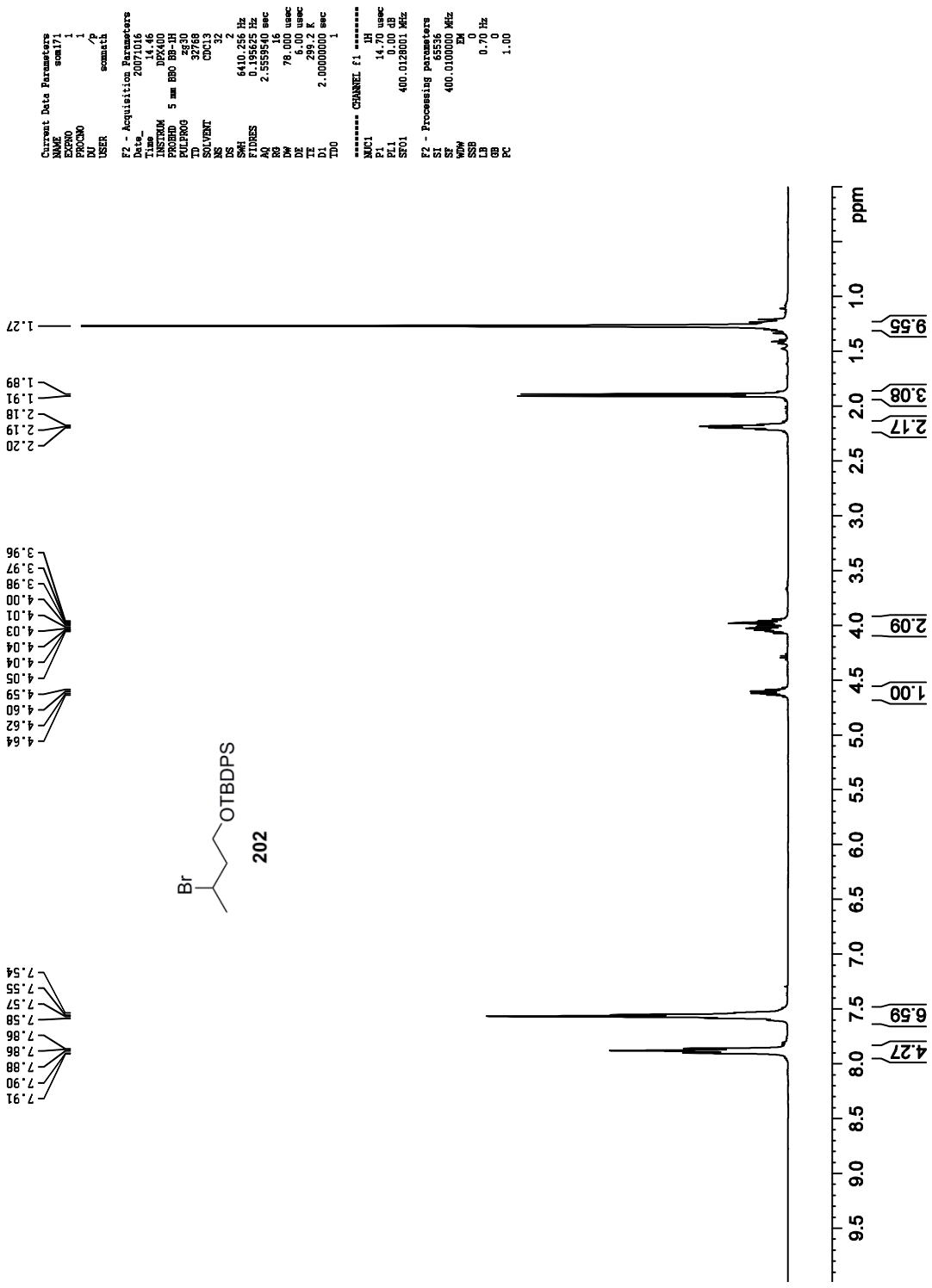

Current Data Parameters
NAME som209
EXPNO 4
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20080220
Time 13.25
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 2450
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4597.6
DW 19.900 usec
DE 6.00 usec
TE 299.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-4.92
11.89
17.66
17.73
25.90
29.37
37.23
39.28
51.15
55.21
57.39
68.18
72.53
75.34
76.76
77.08
77.39
108.55
113.68
115.45
129.15
130.64
152.51
159.02
161.12
164.24
CO2Me
OTIPS
OTBS
PMBO
HO
O
196
ppm

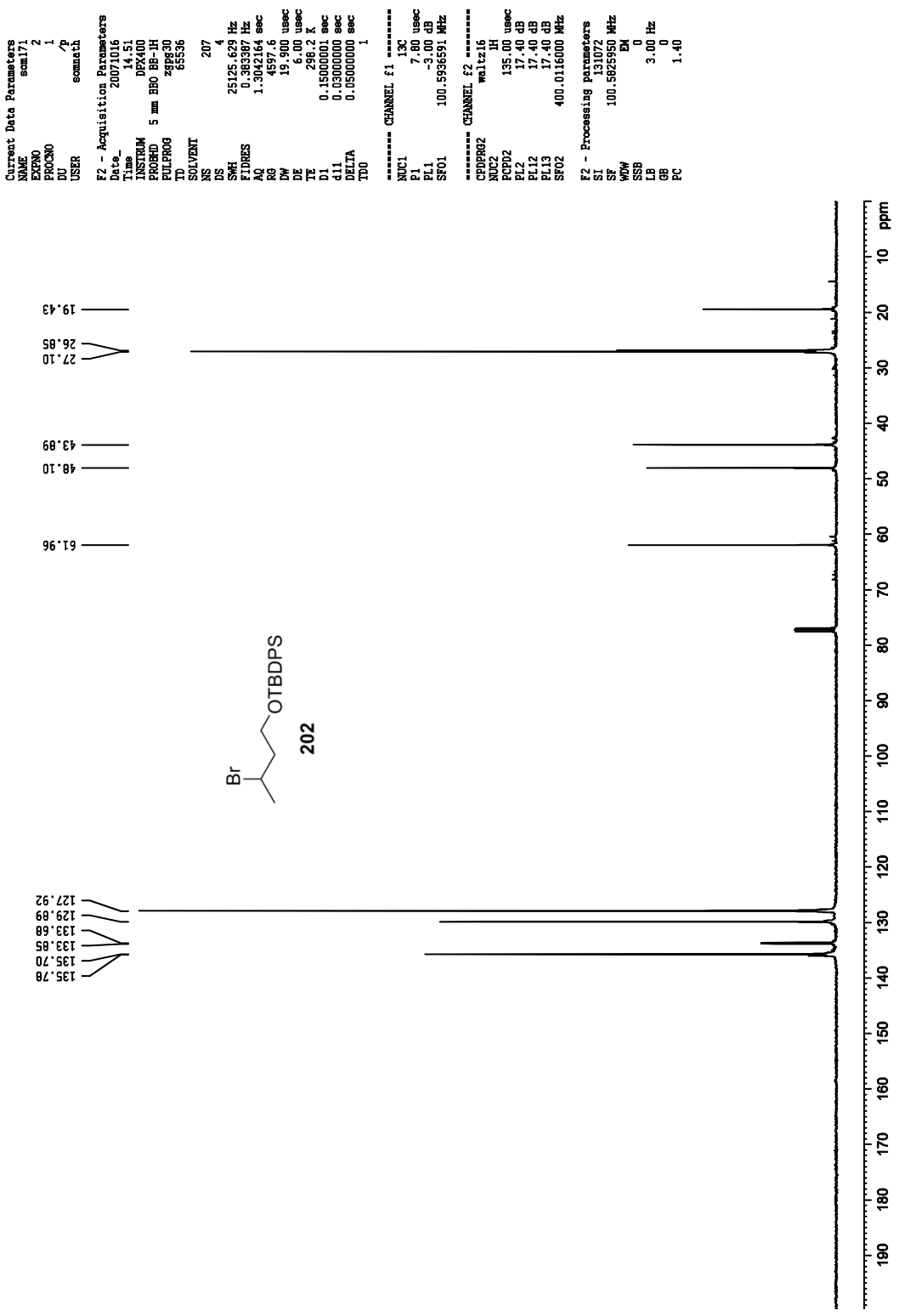

Current Data Parameters
NAME scm211
EXPNO 1
PROCNO 1
DU /0
USER scmath
F2 - Acquisition Parameters
Date_ 20080224
Time 20.17
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 512
DW 78.000 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 400.0128001 MHz
F2 - Processing parameters
SI 65536
SF 400.0100000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
CO2Me
OTIPS
OTBS
PMBO
197
ppm
0
1
2
3
4
5
6
7
8
9
10
7.13
28.19
10.52
2.13
1.32
1.06
2.29
3.14
3.52
0.98
2.50
1.09
1.09
2.25
2.27
1.08
1.00
9.65
7.49
7.30
7.19
7.17
6.84
6.82
4.72
4.70
4.62
4.60
4.60
4.45
4.42
4.37
4.35
4.34
4.33
3.82
3.81
3.55
3.54
3.59
3.52
2.74
2.73
2.72
2.71
2.70
2.69
2.08
2.07
2.07
2.05
2.05
2.04
1.72
1.70
1.69
1.69
1.68
1.67
1.67
1.65
1.64
1.61
0.96
0.93
0.91
0.14

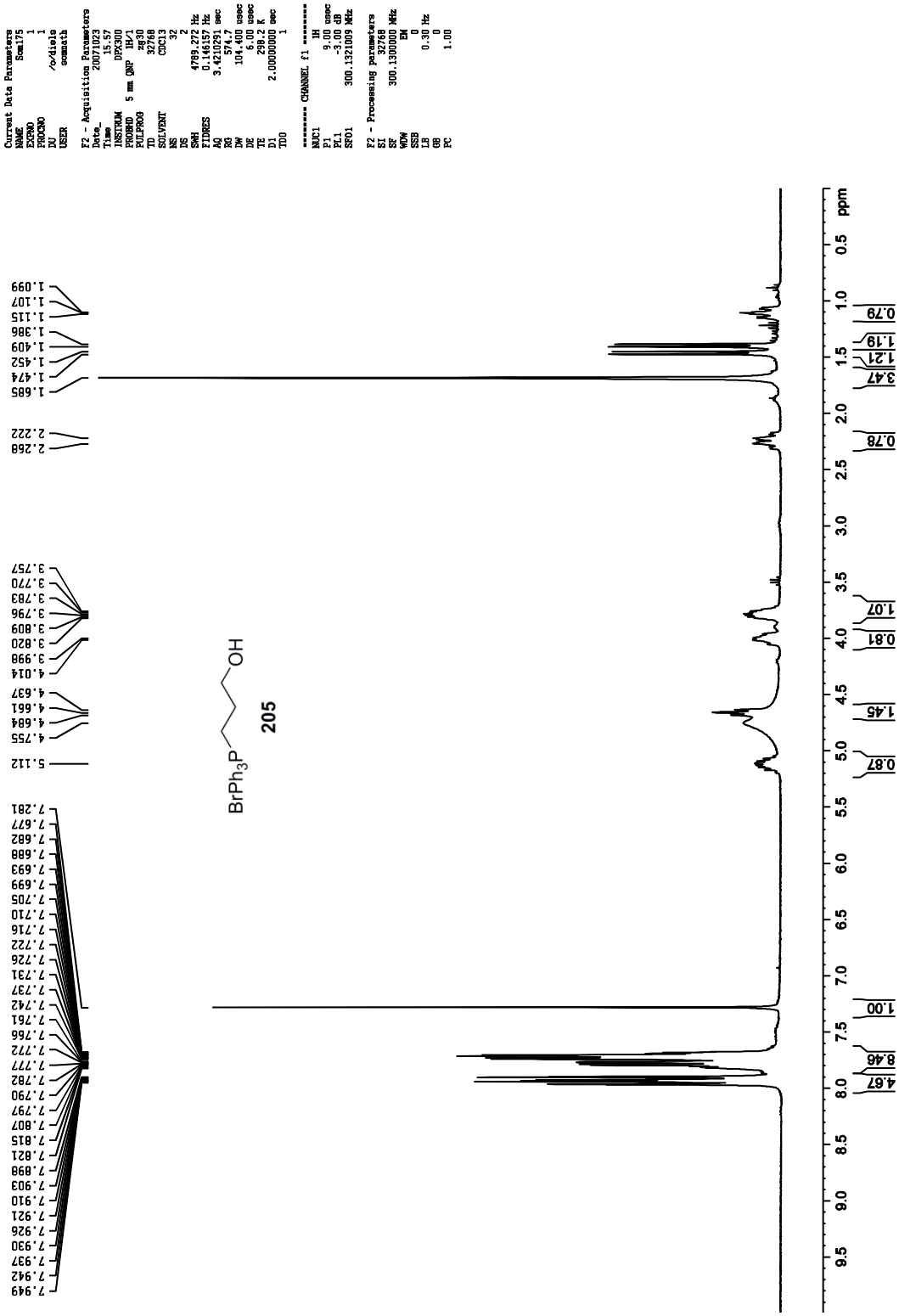

Current Data Parameters
NAME som211
EXPNO 4
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20060225
Time 8.01
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 23908
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4597.6
DW 19.900 usec
DE 6.00 usec
TE 299.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-4.94
-4.56
11.89
17.65
17.71
18.05
25.90
29.20
29.72
37.26
39.92
51.64
55.23
68.08
72.54
75.24
76.71
77.03
77.35
121.25
129.14
130.55
150.75
159.06
162.98
166.68
177.26
CO2Me
OTIPS
OTBS
PMBO
197
ppm

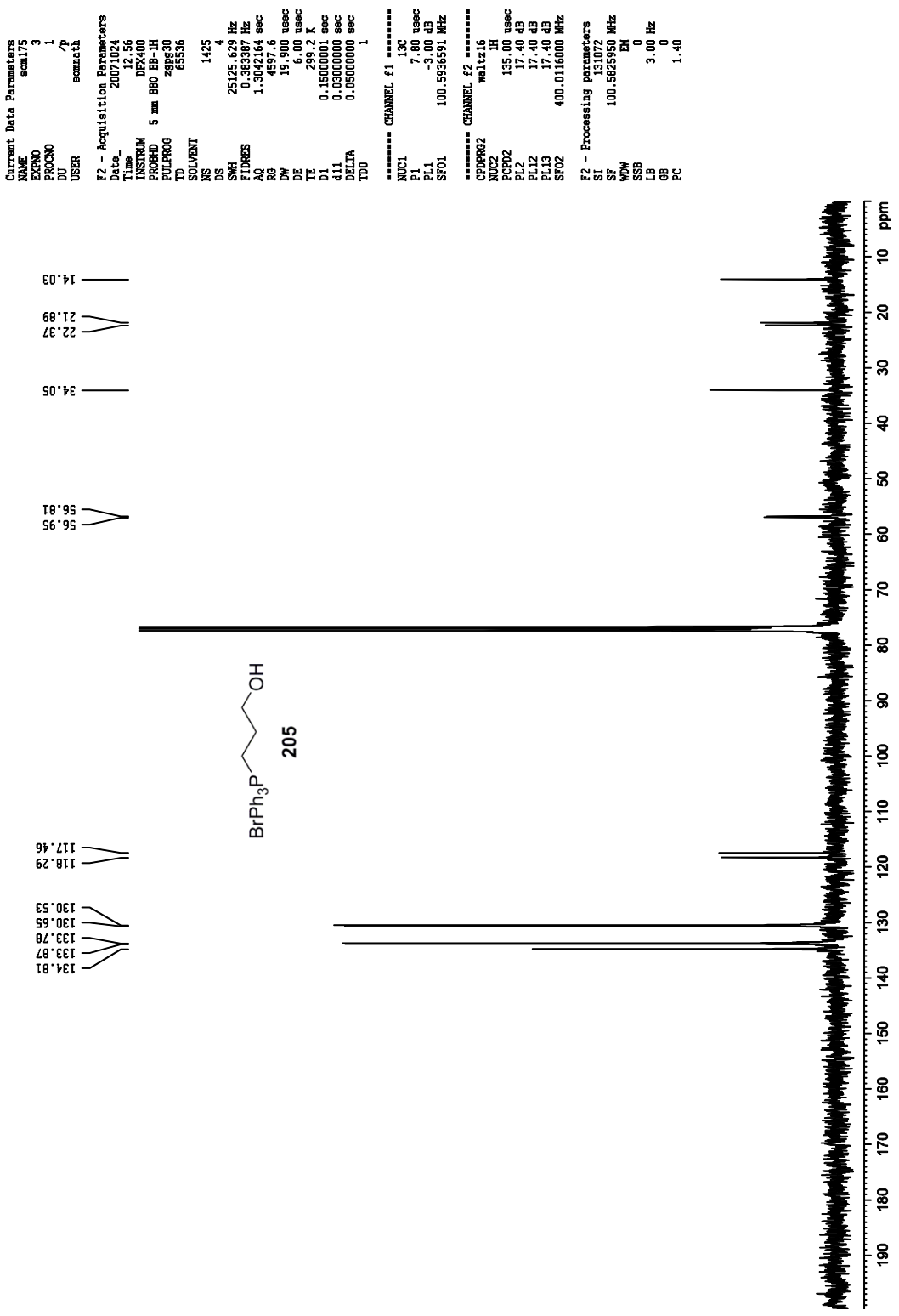

Current Data Parameters
NAME som170
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071012
Time 13.46
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 50.8
DW 78.000 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 400.0128001 MHz
F2 - Processing parameters
SI 65536
SF 400.0100000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
OH
OTBDPS
201
ppm
1.12
1.26
1.27
1.70
1.70
1.71
1.78
1.79
1.81
1.90
3.33
3.34
3.89
3.90
3.91
3.91
3.92
3.93
3.95
4.14
4.14
4.15
4.16
4.17
4.17
7.43
7.45
7.47
7.47
7.48
7.48
7.49
7.73
7.75
7.75
8.94
3.18
1.03
1.03
0.94
2.01
1.00
5.93
3.87

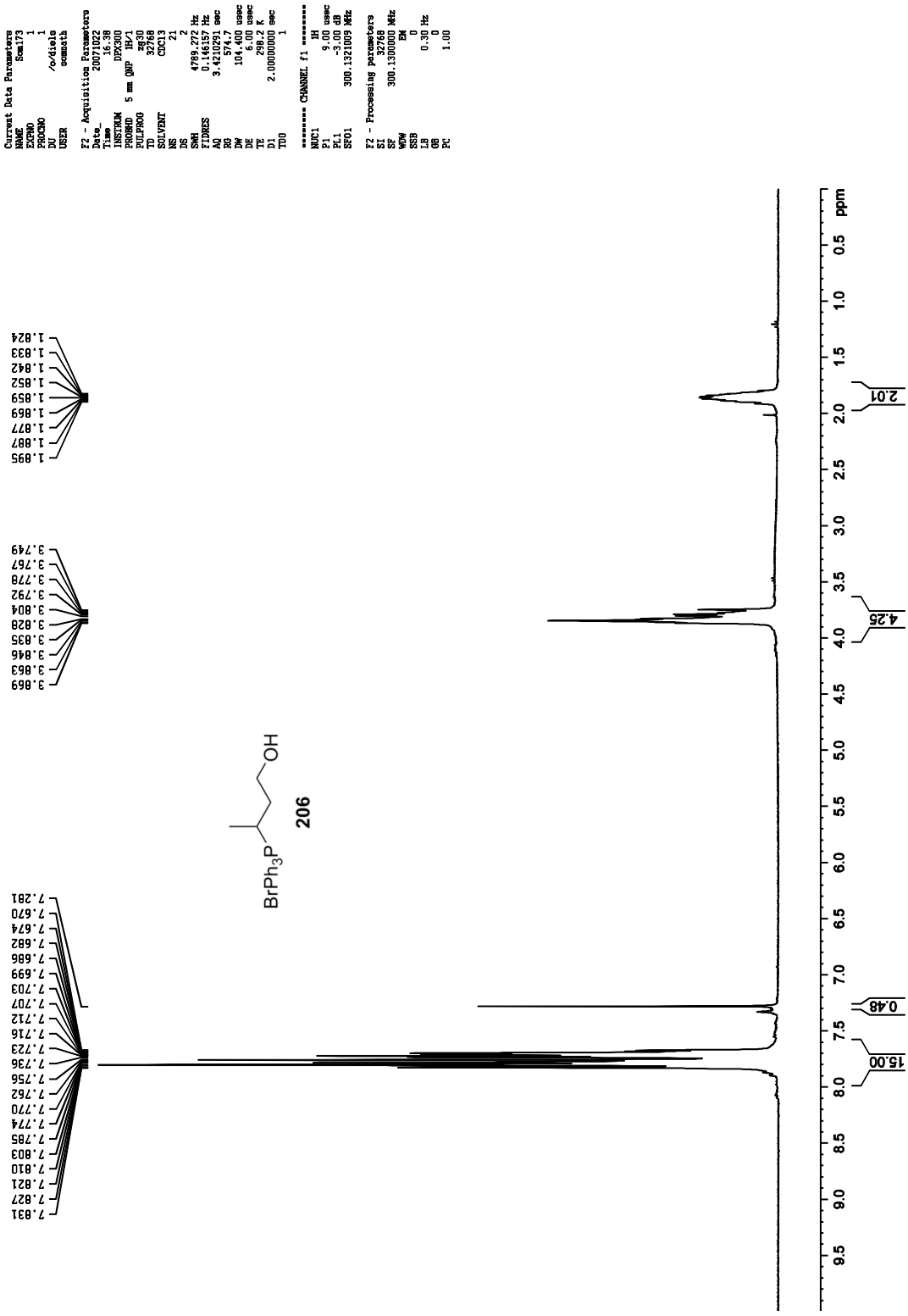

Current Data Parameters
NAME som170
EXPNO 3
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20071012
Time 14.02
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 223
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4597.6
DW 19.900 usec
DE 6.00 usec
TE 299.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
19.08
23.45
26.86
40.16
63.49
67.90
76.78
77.10
77.42
127.84
129.88
133.02
133.11
135.60
OH
OTBDPS
201
ppm

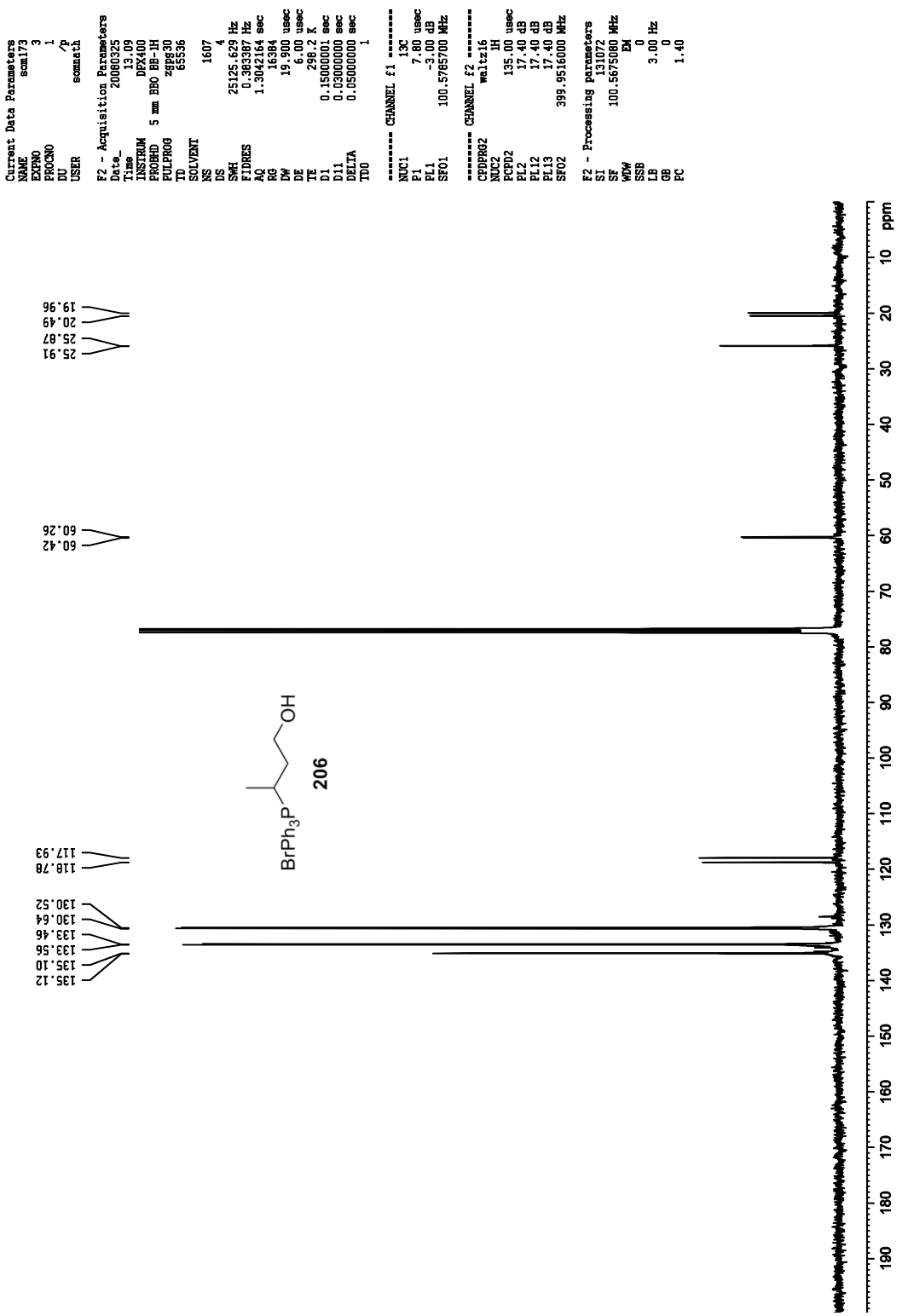

Br
OTBDPS
202
ppm
9.55
3.08
2.17
2.09
1.00
6.59
4.27

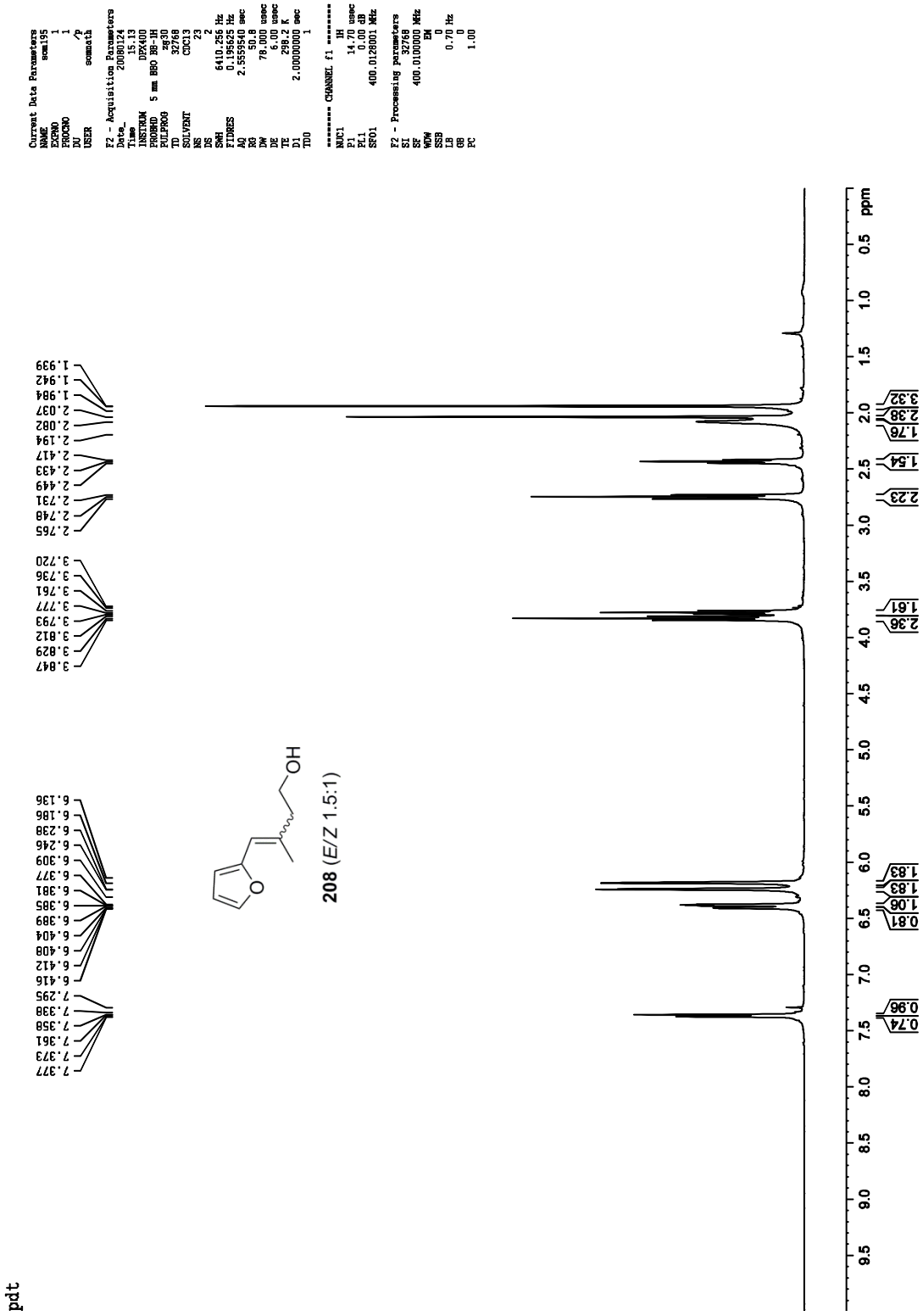

Current Data Parameters
NAME som171
EXPNO 2
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20071016
Time 14.51
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 207
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4597.6
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
19.43
26.85
27.10
43.89
48.10
61.96
127.92
129.89
133.68
133.85
135.70
135.78
Br
OTBDPS
202
ppm

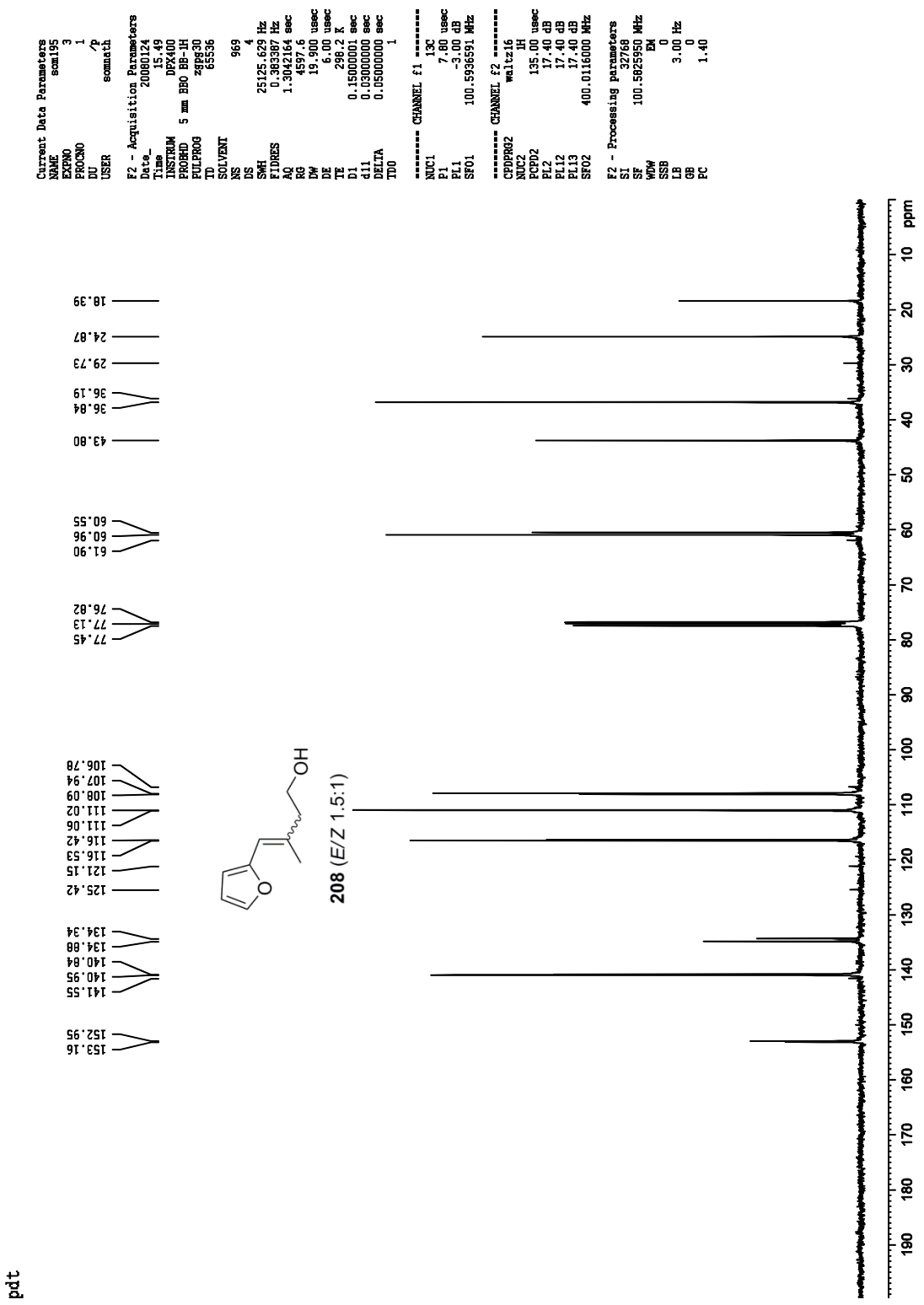

Current Data Parameters
NAME Sm175
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071023
Time 15.57
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 574.7
DW 104.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
BrPh3P
OH
205
ppm

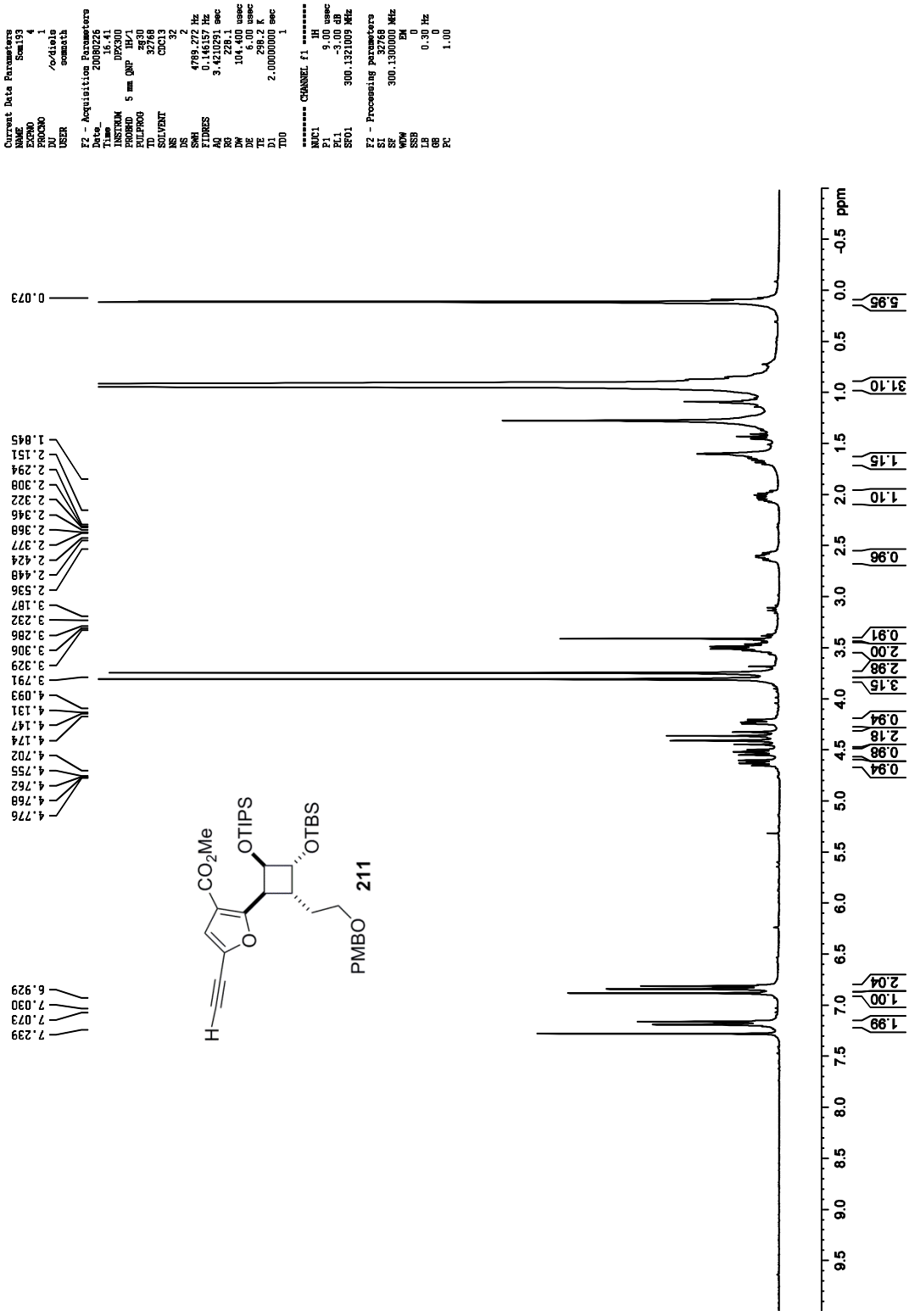

Current Data Parameters
NAME som175
EXPNO 3
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20071024
Time 12.56
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 1425
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4597.6
DW 19.900 usec
DE 6.00 usec
TE 299.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 131072
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
14.03
21.89
22.37
34.05
56.81
56.95
117.46
118.29
130.53
130.65
133.78
133.87
134.81
BrPh3P
OH
205
ppm

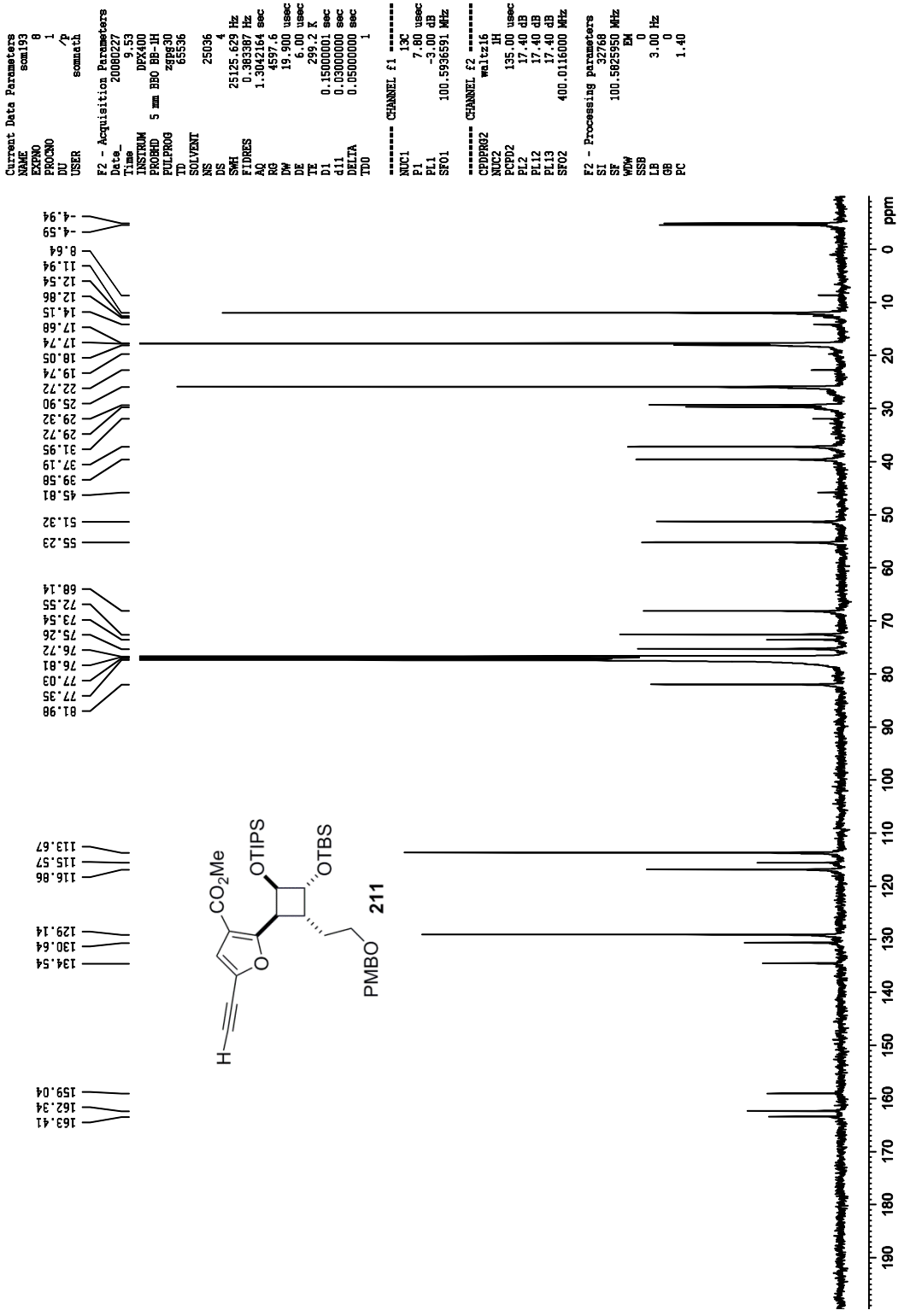

Current Data Parameters
NAME Sm173
EXPNO 1
PROCNO 1
DU /o/diels
USER somath
F2 - Acquisition Parameters
Date_ 20071022
Time 16.38
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 21
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 574.7
DW 104.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.824
1.833
1.842
1.852
1.859
1.869
1.877
1.887
1.895
3.749
3.767
3.778
3.792
3.804
3.828
3.835
3.846
3.863
3.869
7.281
7.670
7.674
7.682
7.686
7.699
7.703
7.707
7.712
7.716
7.723
7.736
7.756
7.762
7.770
7.774
7.785
7.803
7.810
7.821
7.827
7.831
OH
BrPh3P
206
2.01
4.25
0.48
15.00
ppm

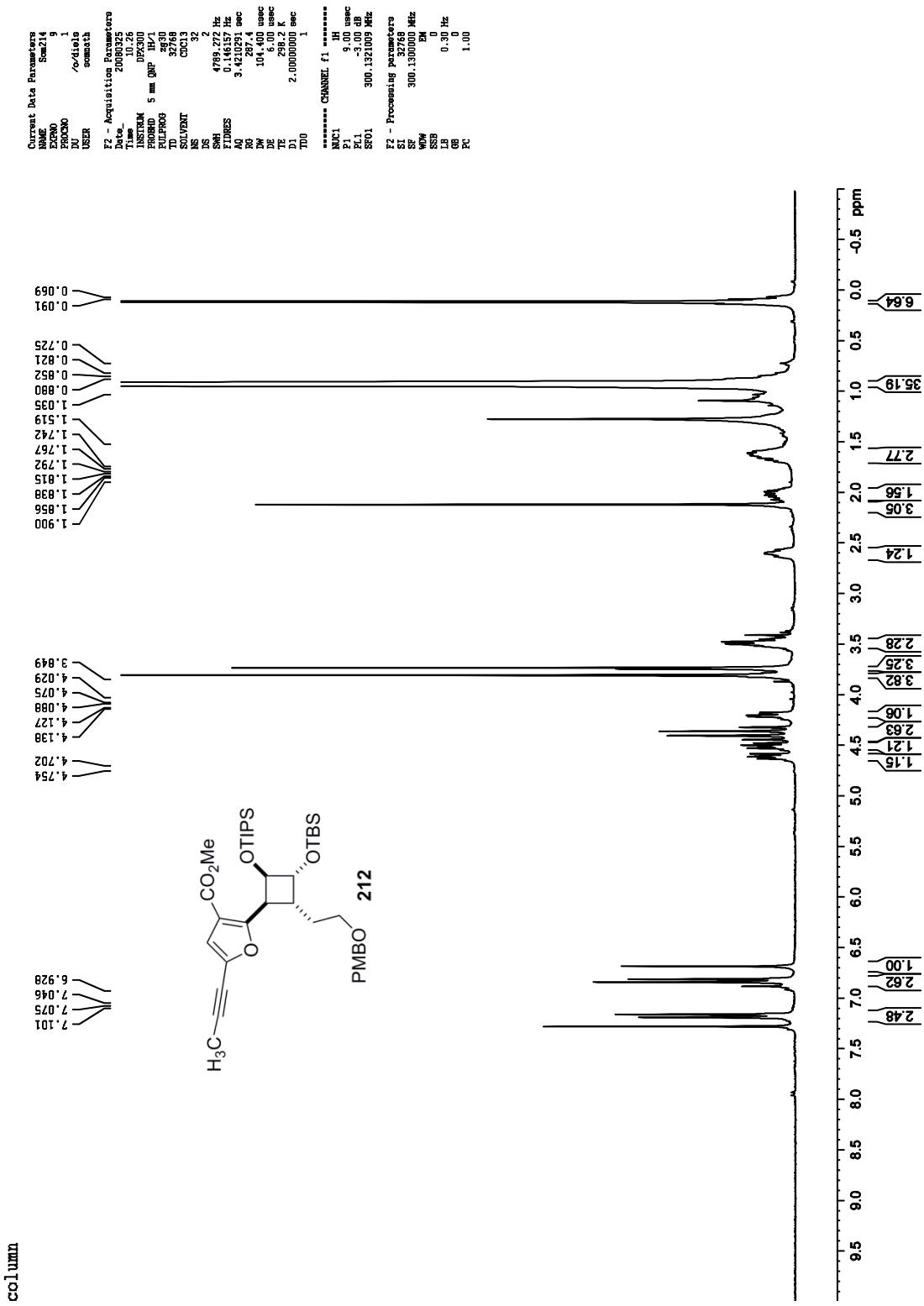

Current Data Parameters
NAME som173
EXPNO 3
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20080325
Time 13.09
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 1607
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
D11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5765700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675060 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
19.96
20.49
25.87
25.91
60.26
60.42
117.93
118.78
130.52
130.64
133.46
133.56
135.10
135.12
BrPh3P
OH
206
ppm

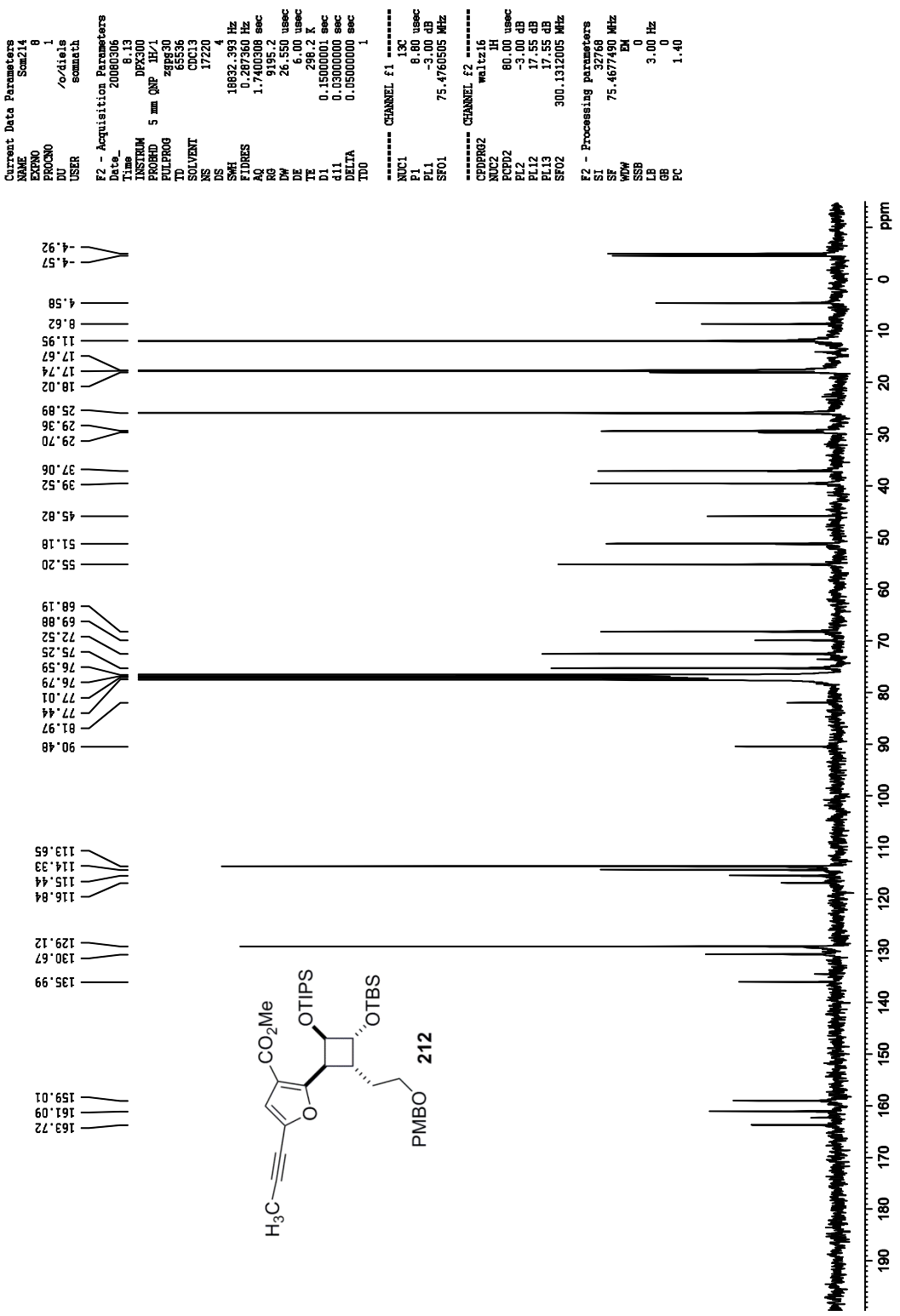

Current Data Parameters
NAME scm195
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080124
Time 15.13
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 2
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 50.8
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 400.0128001 MHz
F2 - Processing parameters
SI 32768
SF 400.0100000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
OH
O
208 (E/Z 1.5:1)
pdt
ppm
0.74
0.96
0.81
1.06
1.83
1.83
2.36
1.61
2.23
1.54
1.76
2.38
3.32

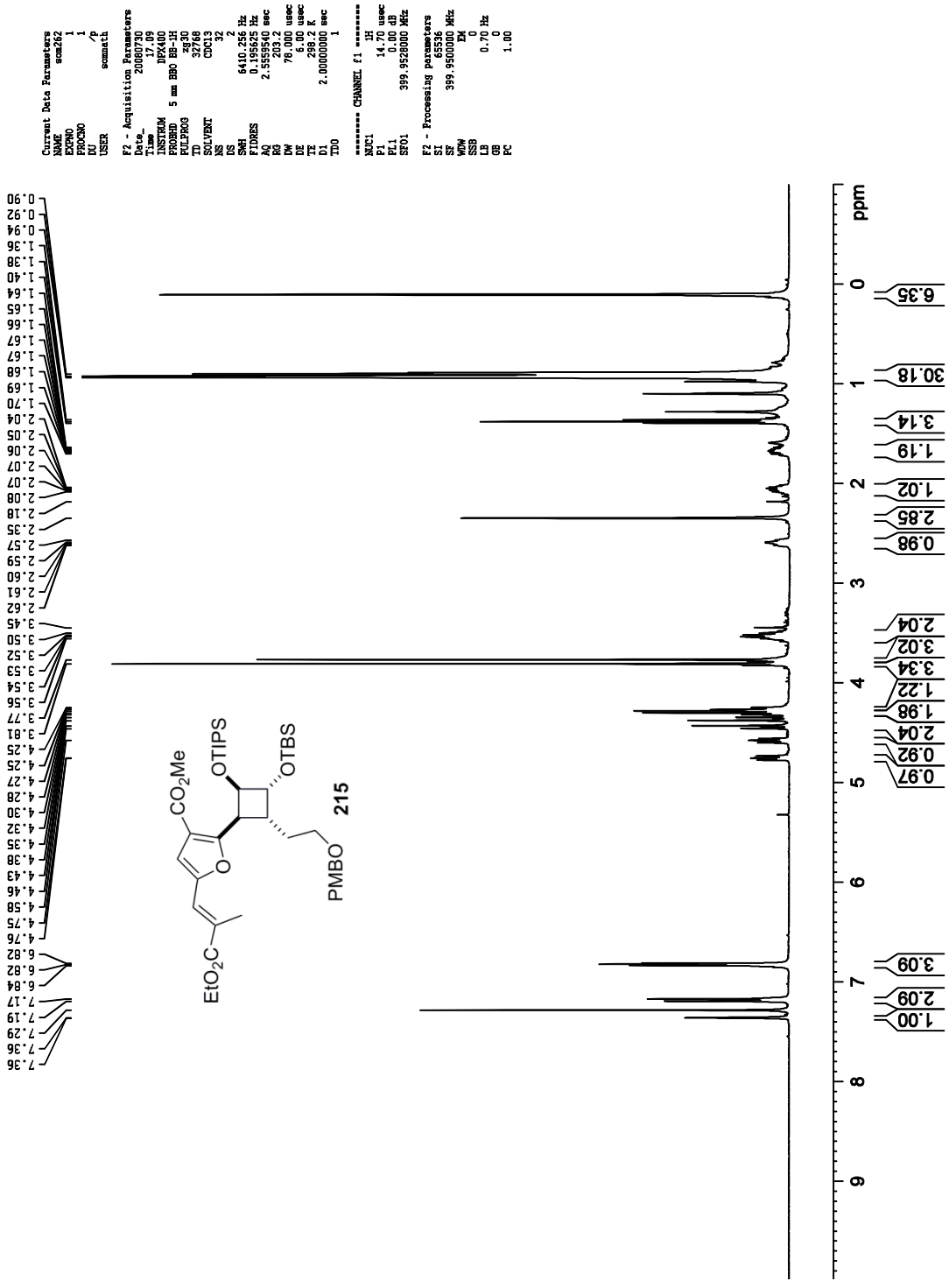

Current Data Parameters
NAME scm195
EXPNO 3
PROCNO 1
DU /p
USER scommath
F2 - Acquisition Parameters
Date_ 20060124
Time 15.49
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 969
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4597.6
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.60 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 32768
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
18.39
24.87
29.73
36.19
36.84
43.80
60.55
60.96
61.90
76.82
77.13
77.45
106.78
107.94
108.09
111.02
111.06
116.42
116.53
121.15
125.42
134.34
134.88
140.84
140.95
141.55
152.95
153.16
OH
O
208 (E/Z 1.5:1)
pdt
ppm

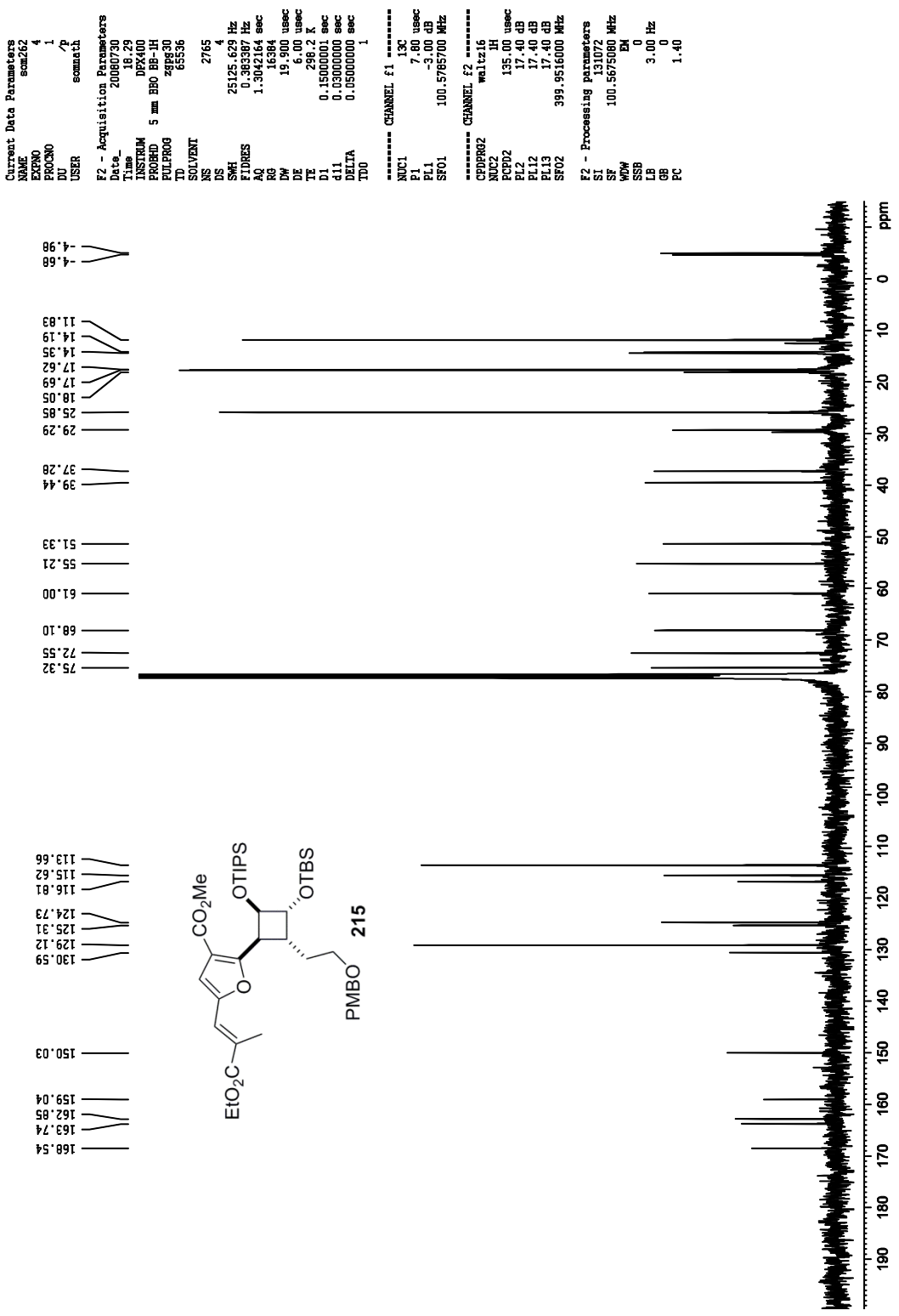

Current Data Parameters
NAME Sm153
EXPNO 4
PROCNO 1
DU /o/diels
USER scomath
F2 - Acquisition Parameters
Date_ 20080226
Time 16.41
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 228.1
DW 104.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TDO 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.073
1.845
2.151
2.294
2.308
2.322
2.346
2.368
2.377
2.424
2.448
2.536
3.187
3.232
3.286
3.306
3.329
3.791
4.093
4.131
4.147
4.174
4.702
4.755
4.762
4.768
4.776
6.929
7.030
7.073
7.239
CO2Me
OTIPS
OTBS
PMBO
211
H
O
ppm
5.95
31.10
1.15
1.10
0.96
0.91
2.00
2.98
3.15
0.94
2.18
0.98
0.94
2.04
1.00
1.99

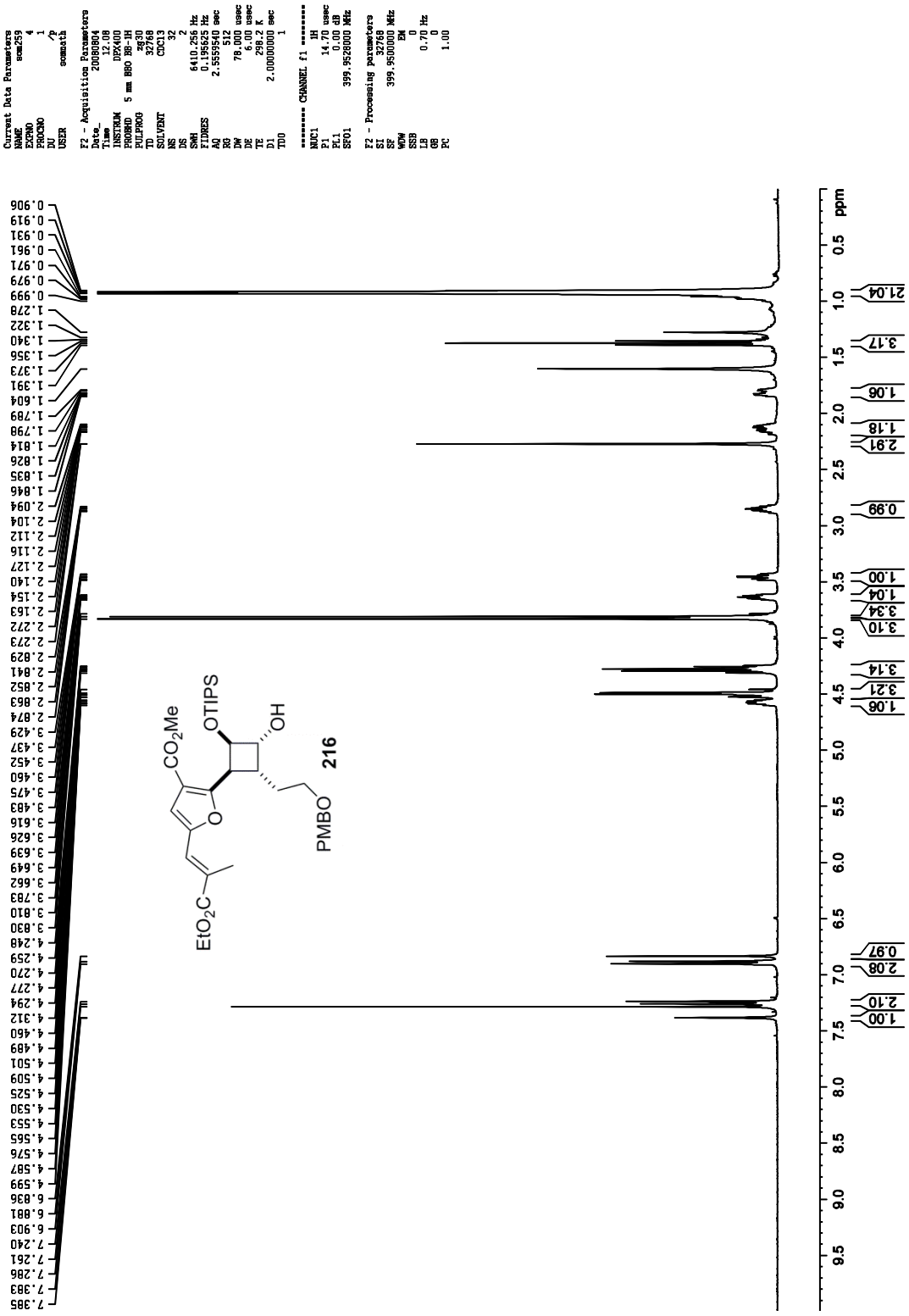

Current Data Parameters
NAME som193
EXPNO 8
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20080227
Time 9.53
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 25036
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 4597.6
DW 19.900 usec
DE 6.00 usec
TE 299.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5936591 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 400.0116000 MHz
F2 - Processing parameters
SI 32768
SF 100.5825950 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-4.94
-4.59
8.64
11.94
12.54
12.86
14.15
17.68
17.74
18.05
19.74
22.72
25.90
29.32
29.72
31.95
37.19
39.58
45.81
51.32
55.23
68.14
72.55
73.54
75.26
76.72
76.81
77.03
77.35
81.98
113.67
115.57
116.86
129.14
130.64
134.54
159.04
162.34
163.41
CO2Me
OTIPS
OTBS
PMBO
211
H
O
ppm

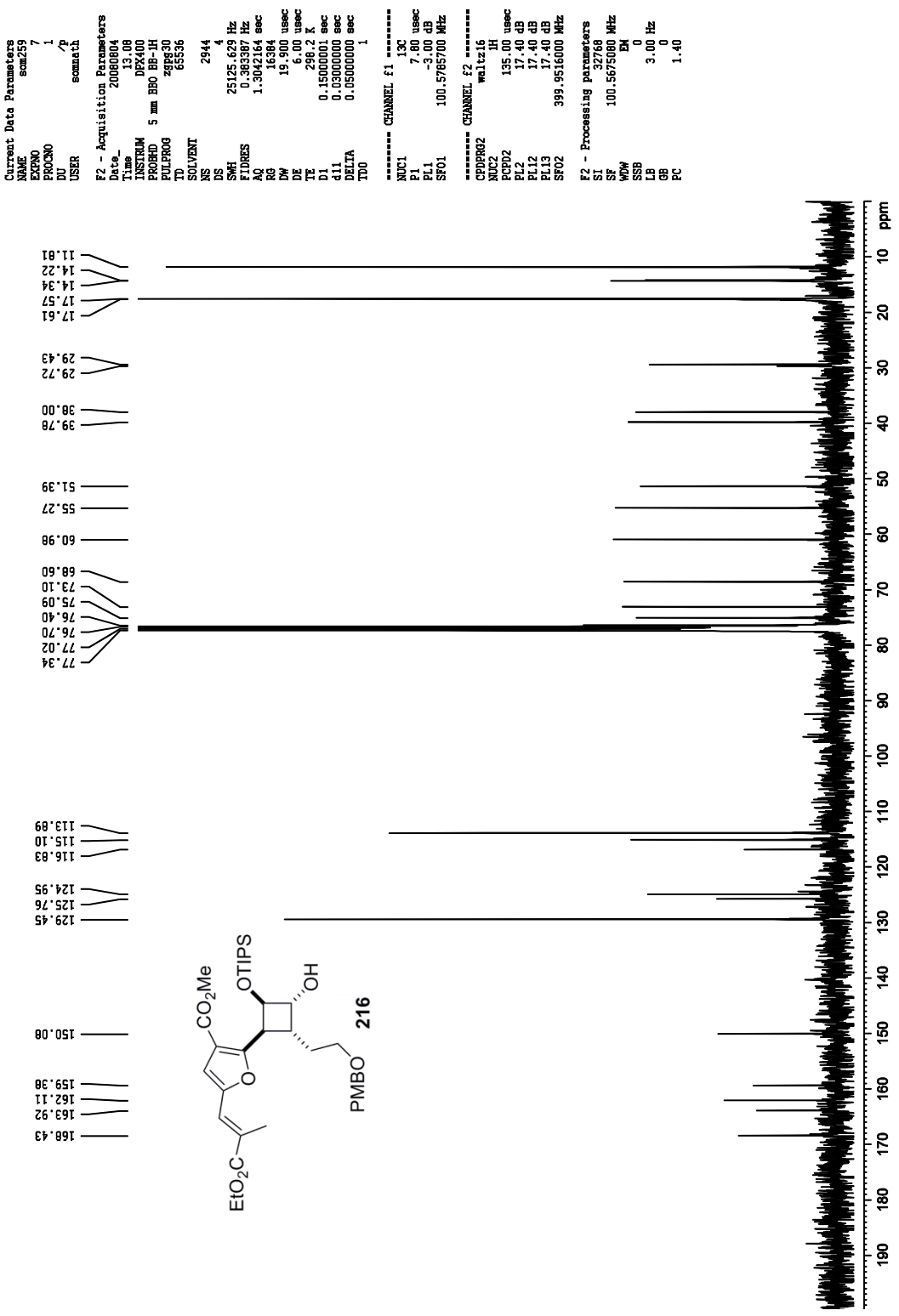

Current Data Parameters
NAME Sam214
EXPNO 9
PROCNO 1
DU /o/diels
USER somath
F2 - Acquisition Parameters
Date_ 20080325
Time 10.26
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 287.4
DW 104.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
column
0.069
0.091
0.725
0.821
0.852
0.880
1.035
1.519
1.742
1.767
1.792
1.815
1.838
1.856
1.900
3.849
4.029
4.075
4.088
4.127
4.138
4.702
4.754
6.928
7.046
7.075
7.101
CO2Me
OTIPS
OTBS
PMBO
212
H3C
ppm
6.84
35.19
2.77
1.56
3.05
1.24
2.28
3.25
3.82
1.06
2.63
1.21
1.15
1.00
2.62
2.48

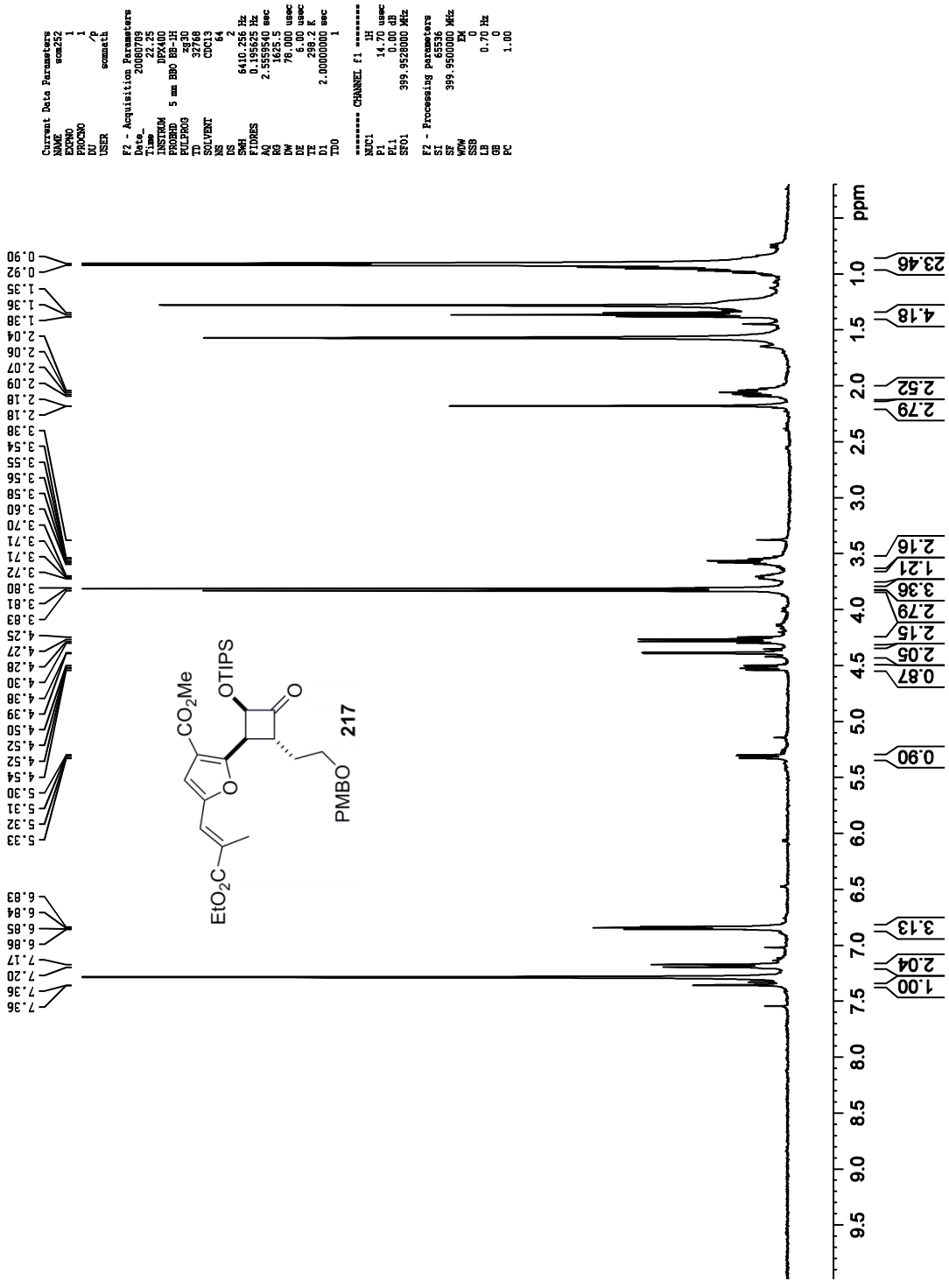

Current Data Parameters
NAME Som214
EXPNO 8
PROCNO 1
DU /c/diels
USER somnath
F2 - Acquisition Parameters
Date_ 20080306
Time 8.13
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 17220
DS 4
SWH 16832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 9195.2
DW 26.550 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.80 usec
PL1 -3.00 dB
SFO1 75.4760505 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 17.55 dB
PL13 17.55 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-4.92
-4.57
4.58
8.62
11.95
17.67
17.74
18.02
25.89
29.36
29.70
37.06
39.52
45.82
51.18
55.20
68.19
69.88
72.52
75.25
76.59
76.79
77.01
77.44
81.97
90.48
113.65
114.33
115.44
116.84
129.12
130.67
135.99
159.01
161.09
163.72
CO2Me
OTIPS
OTBS
PMBO
212
H3C
O
ppm

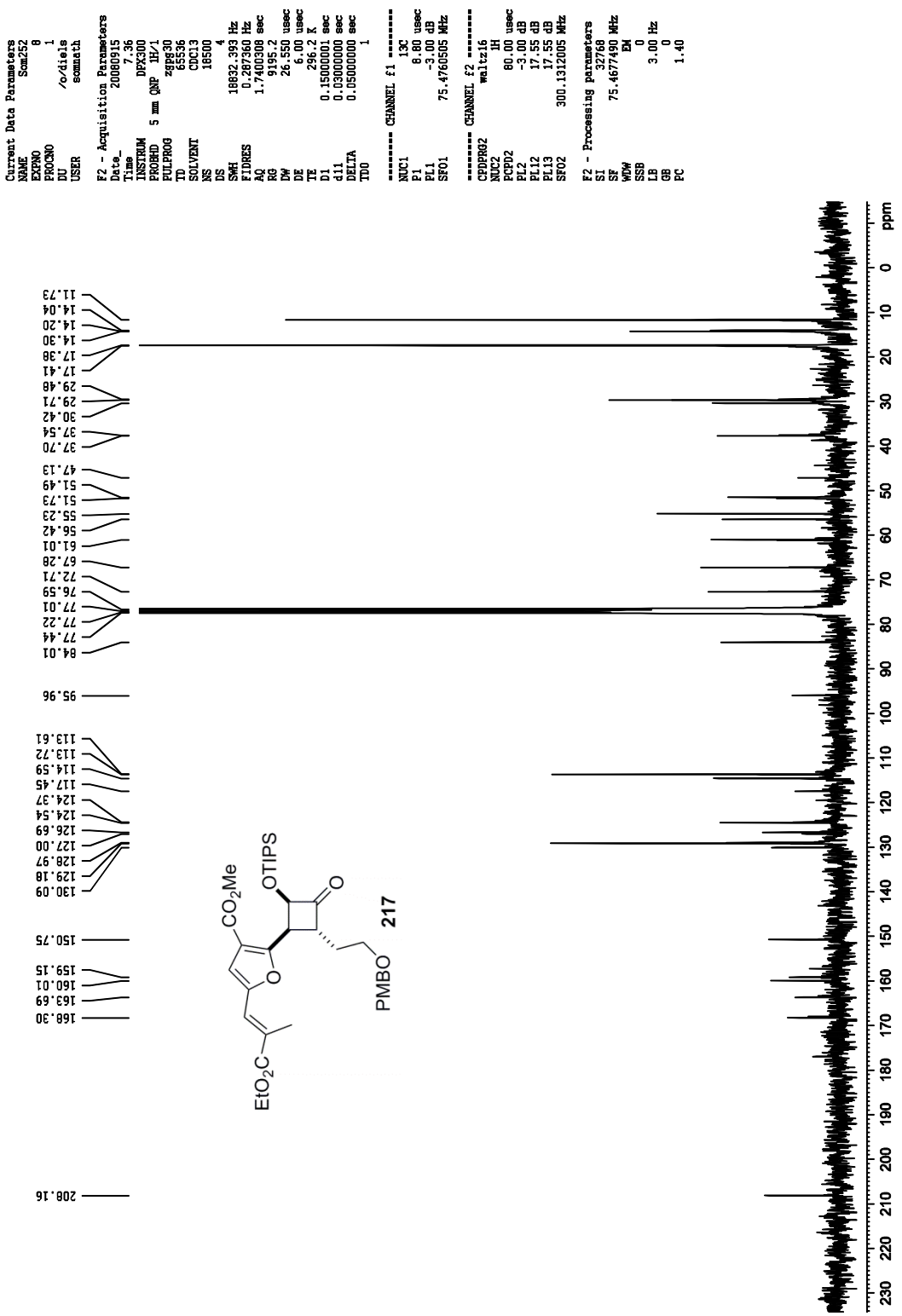

Current Data Parameters
NAME scm262
EXPNO 1
PROCNO 1
DU /0
USER scmath
F2 - Acquisition Parameters
Date_ 20080730
Time 17.09
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 203.2
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9528000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
CO2Me
OTIPS
OTBS
PMBO
EtO2C
215
ppm
6.35
30.18
3.14
1.19
1.02
2.85
0.98
2.04
3.02
3.34
1.22
1.98
2.04
0.92
0.97
3.09
2.09
1.00

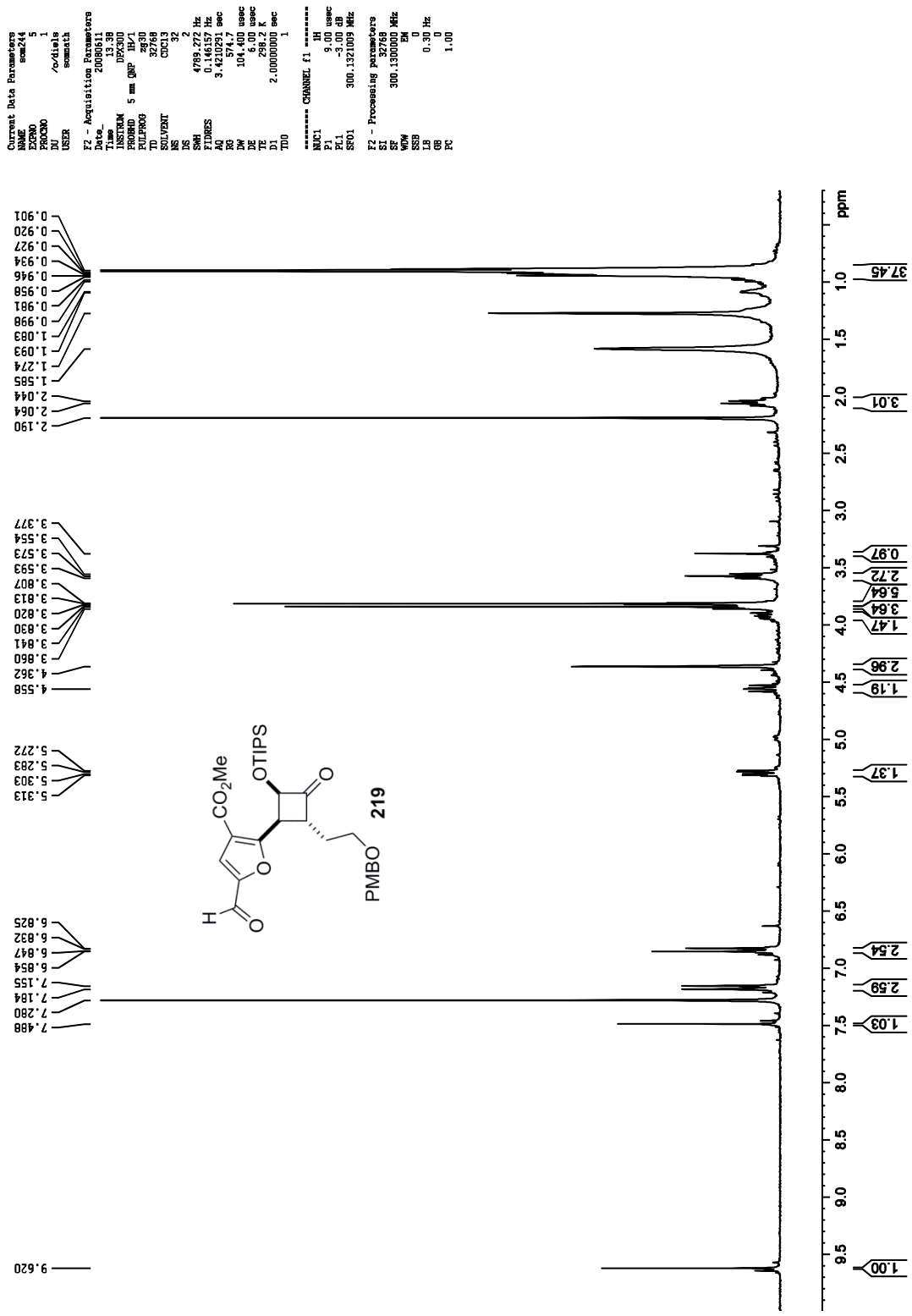

Current Data Parameters
NAME som262
EXPNO 4
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20060730
Time 18.29
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 2765
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 296.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5765700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675060 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-4.98
-4.68
11.83
14.19
14.35
17.62
17.69
18.05
25.85
29.29
37.28
39.44
51.33
55.21
61.00
68.10
72.55
75.32
113.66
115.62
116.81
124.73
125.31
129.12
130.59
150.03
159.04
162.85
163.74
168.54
ppm
OTIPS
OTBS
CO2Me
EtO2C
PMBO
215

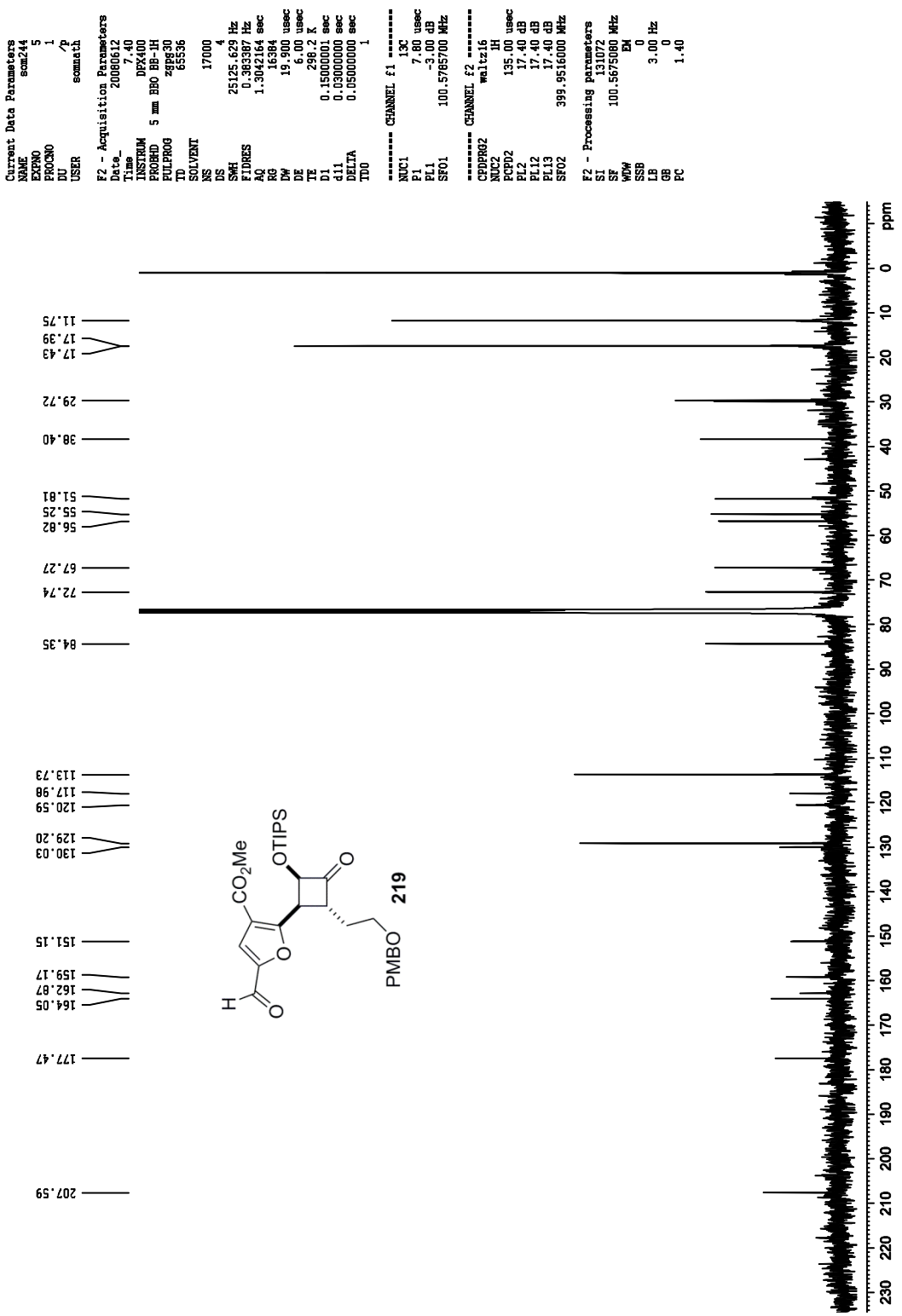

Current Data Parameters
NAME sam253
EXPNO 4
PROCNO 1
DU /p
USER somsath
F2 - Acquisition Parameters
Date_ 20080804
Time 12.08
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 512
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9528000 MHz
F2 - Processing parameters
SI 32768
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
CO2Me
OTIPS
OH
O
PMBO
EtO2C
216
ppm
21.04
3.17
1.06
1.18
2.91
0.99
1.00
1.04
3.34
3.10
3.14
3.21
1.06
0.97
2.08
2.10
1.00

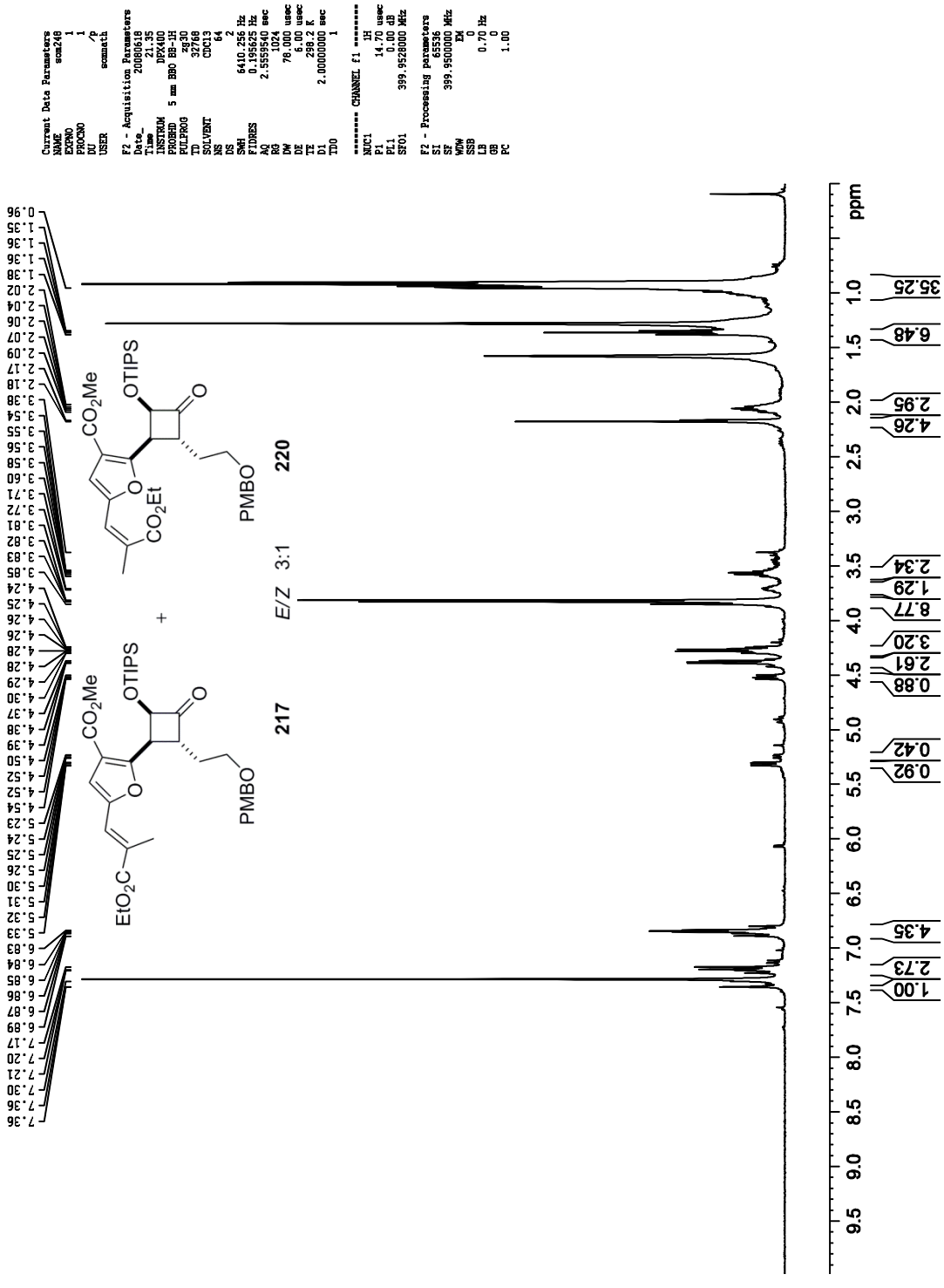

Current Data Parameters
NAME som259
EXPNO 7
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20060804
Time 13.08
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 2944
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 296.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5765700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 32768
SF 100.5675060 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
11.81
14.22
14.34
17.57
17.61
29.43
29.72
38.00
39.78
51.39
55.27
60.98
68.60
73.10
75.09
76.40
76.70
77.02
77.34
113.89
115.10
116.83
124.95
125.76
129.45
150.08
159.38
162.11
163.92
168.43
CO2Me
OTIPS
OH
O
PMBO
EtO2C
216
ppm

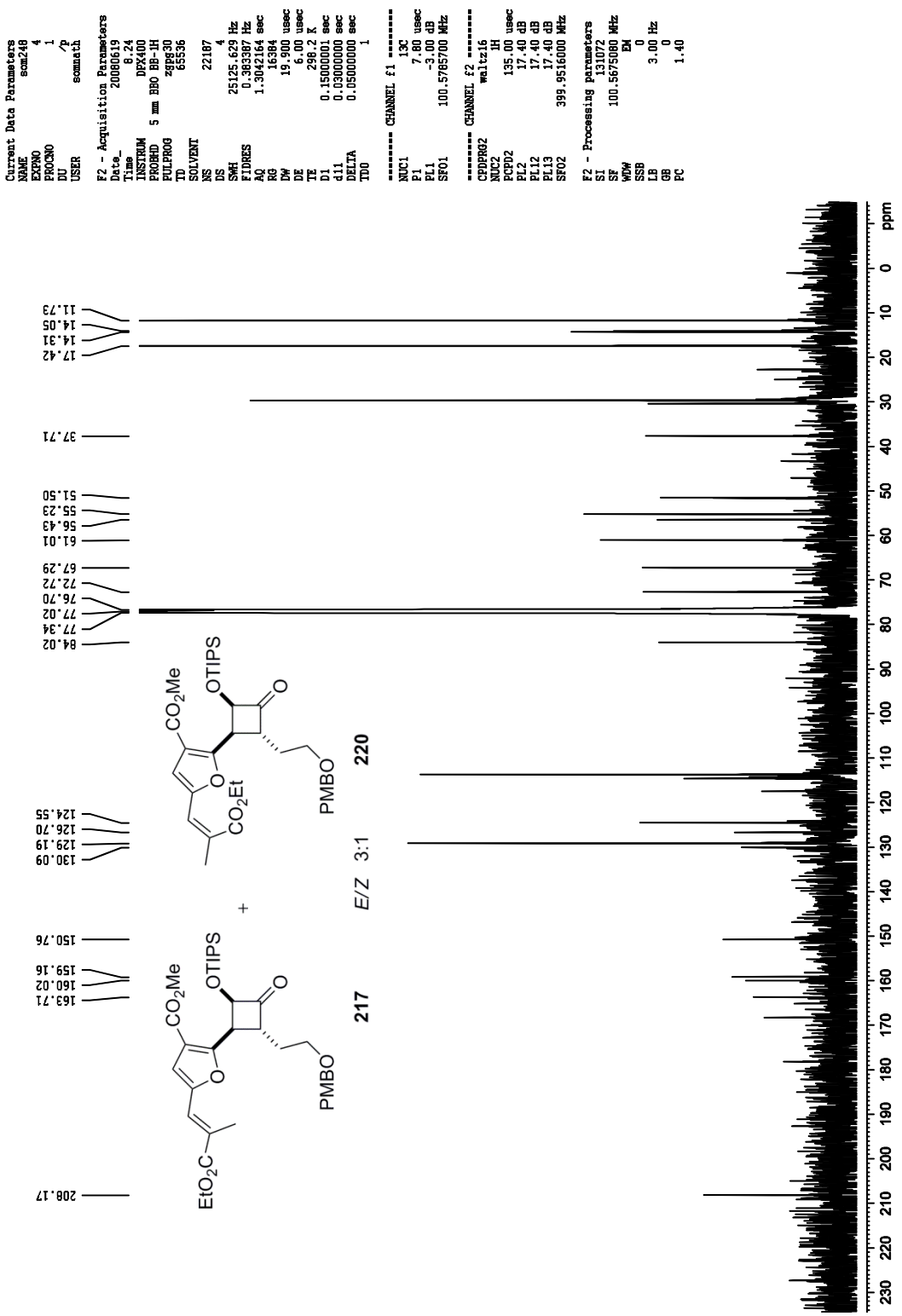

Current Data Parameters
NAME sem252
EXPNO 1
PROCNO 1
DU /9
USER acmath
F2 - Acquisition Parameters
Date_ 20080709
Time 22.25
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 1625.5
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9528000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
CO2Me
OTIPS
O
O
PMBO
217
EtO2C
ppm
23.46
4.18
2.52
2.79
2.16
1.21
3.36
2.79
2.15
2.05
0.87
0.90
3.13
2.04
1.00

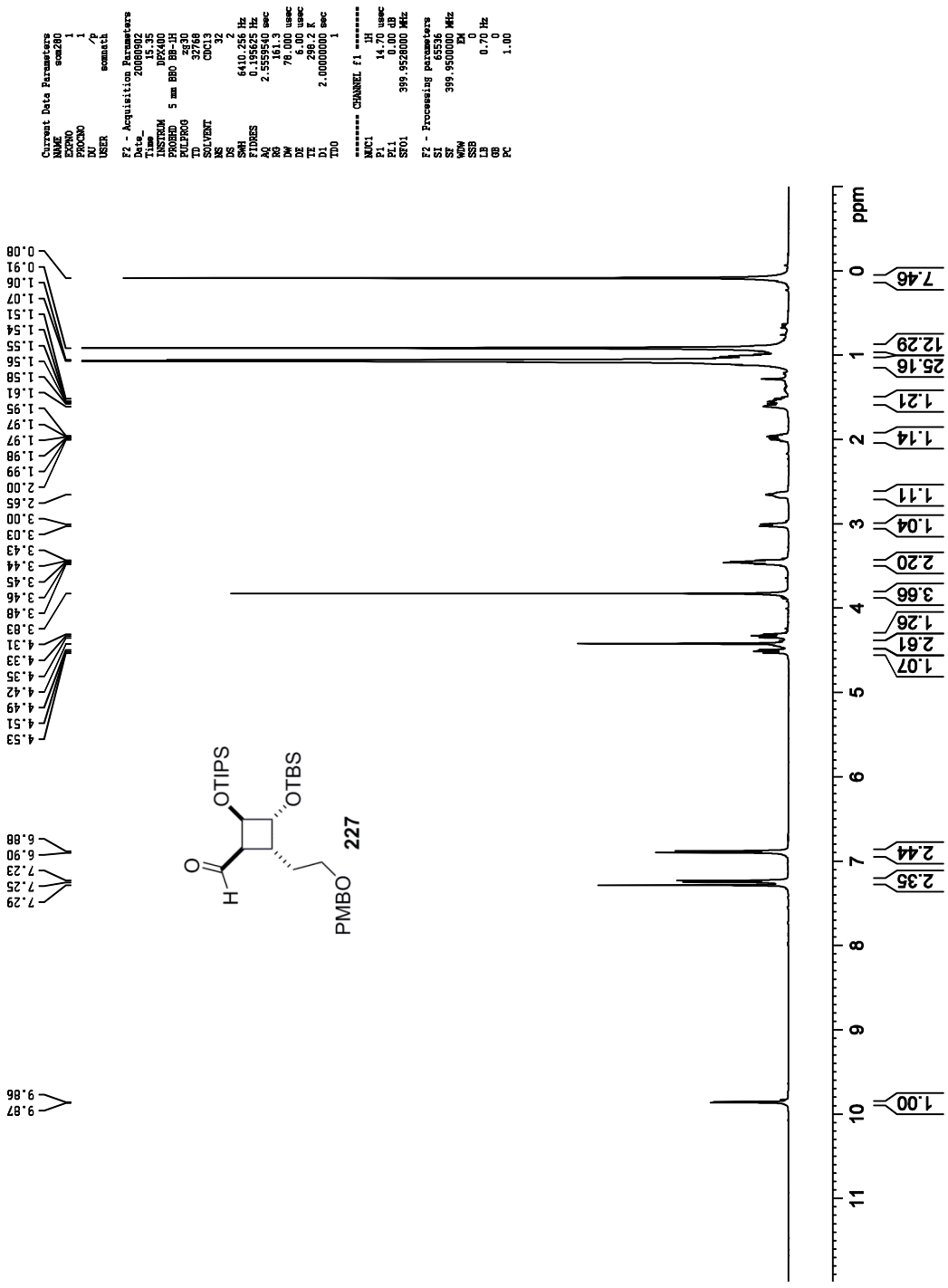

Current Data Parameters
NAME Som252
EXPNO 8
PROCNO 1
DU /c/diels
USER somath
F2 - Acquisition Parameters
Date_ 20080915
Time 7.36
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16500
DS 4
SWH 16832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 9195.2
DW 26.550 usec
DE 6.00 usec
TE 296.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.80 usec
PL1 -3.00 dB
SFO1 75.4760505 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 17.55 dB
PL13 17.55 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
208.16
168.30
163.69
160.01
159.15
150.75
130.09
129.18
128.97
127.00
126.69
124.54
124.37
117.45
114.59
113.72
113.61
95.96
84.01
77.44
77.22
77.01
76.59
72.71
67.28
61.01
56.42
55.23
51.73
51.49
47.13
37.70
37.54
30.42
29.71
29.48
17.41
17.38
14.30
14.20
14.04
11.73
CO2Me
OTIPS
O
O
PMBO
EtO2C
217
ppm

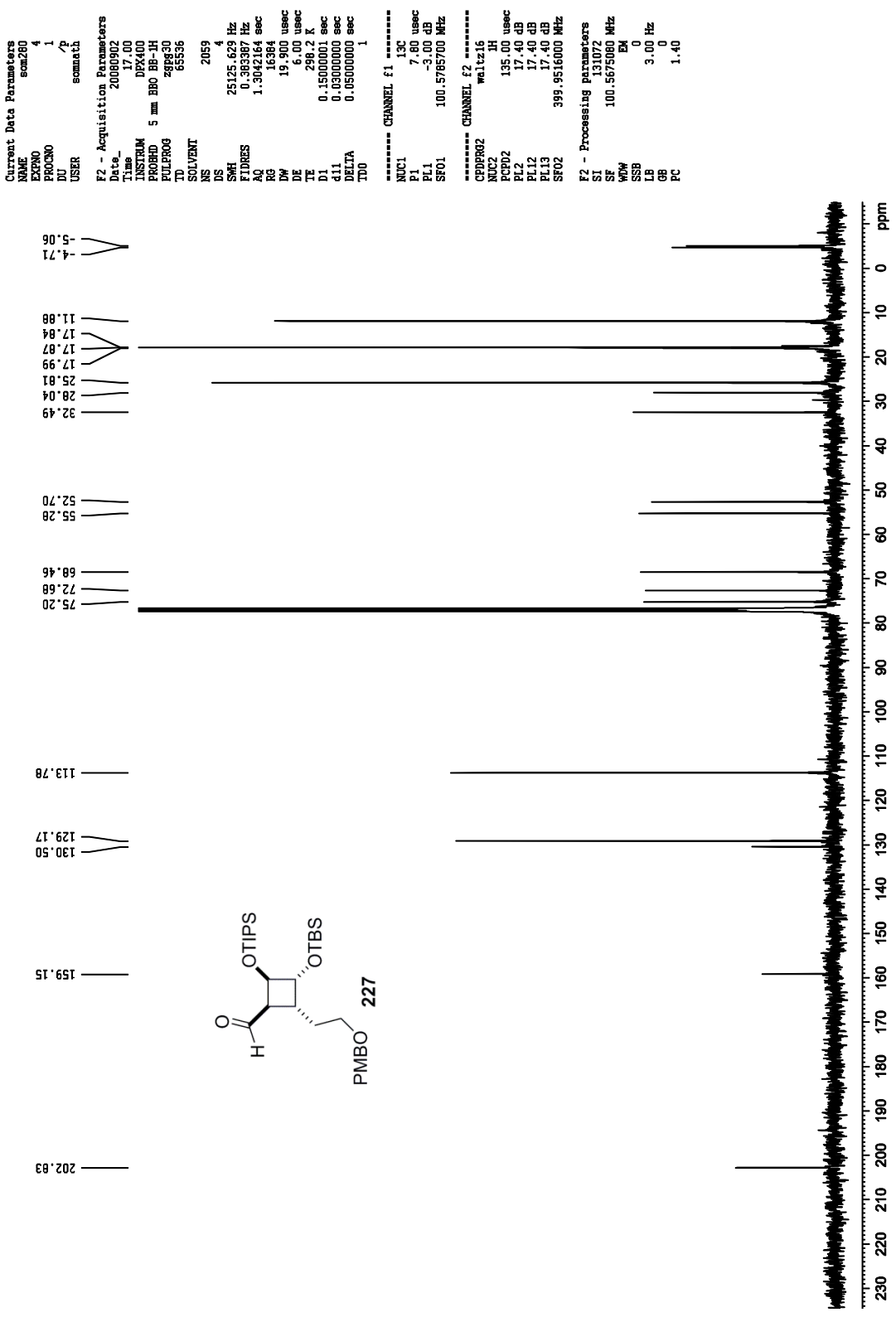

Current Data Parameters
NAME sca244
EXPNO 5
PROCNO 1
DU /o/diels
USER scamath
F2 - Acquisition Parameters
Date_ 20080611
Time 13.38
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 574.7
DW 104.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.620
7.488
7.280
7.184
7.155
6.854
6.847
6.832
6.825
5.313
5.303
5.283
5.272
4.558
4.362
3.860
3.841
3.830
3.820
3.813
3.807
3.593
3.573
3.554
3.377
2.190
2.064
2.044
1.585
1.274
1.093
1.083
0.998
0.981
0.958
0.946
0.934
0.927
0.920
0.901
CO2Me
OTIPS
O
O
H
O
PMBO
219
ppm
1.00
1.03
2.59
2.54
1.37
1.19
2.96
1.47
3.64
5.64
2.72
0.97
3.01
37.45

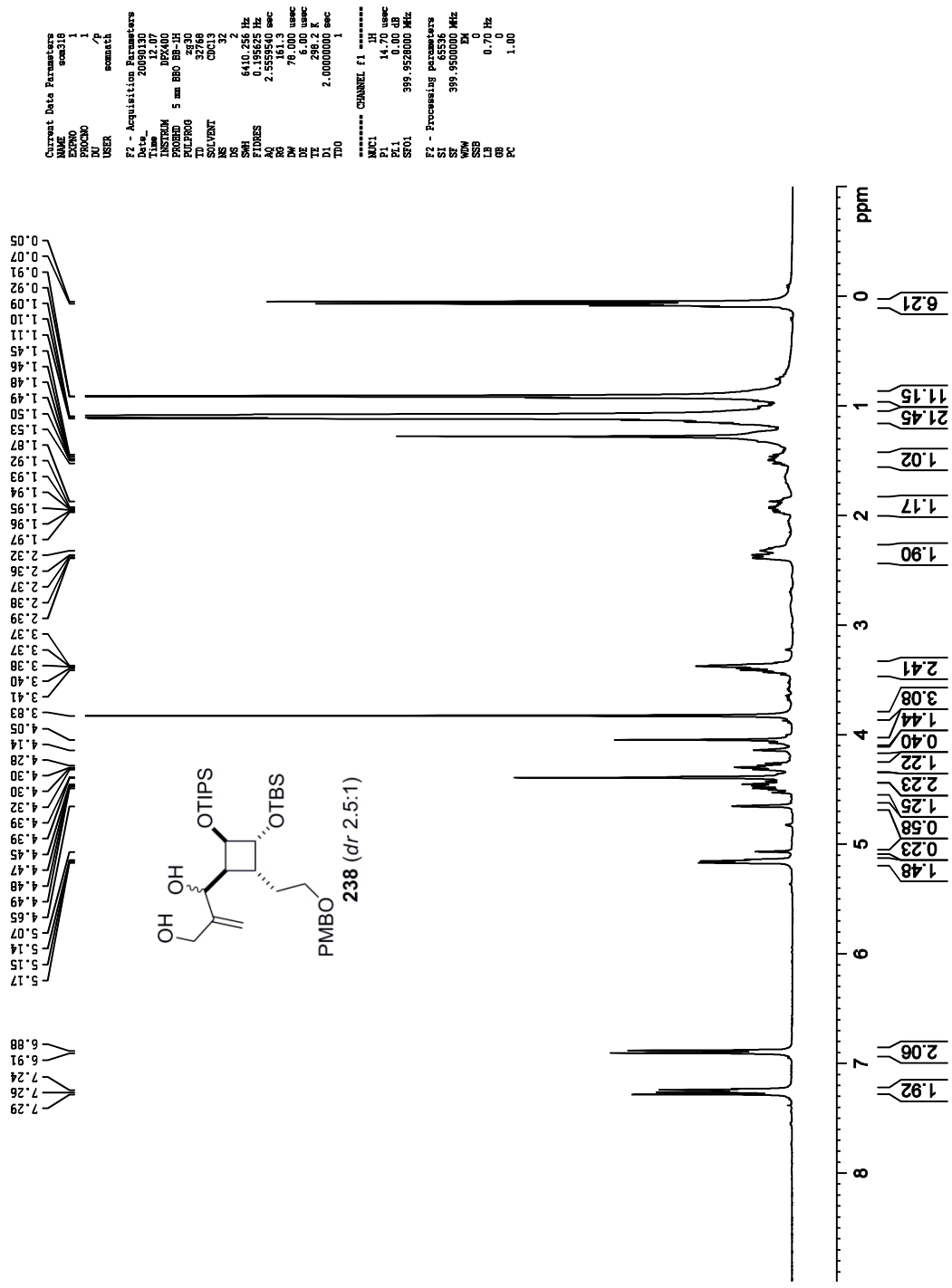

Current Data Parameters
NAME som244
EXPNO 5
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20080612
Time 7.40
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 17000
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5765700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675060 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
11.75
17.39
17.43
29.72
38.40
51.81
55.25
56.82
67.27
72.74
84.35
113.73
117.98
120.59
129.20
130.03
151.15
159.17
162.87
164.05
177.47
207.59
CO2Me
OTIPS
O
O
H
O
PMBO
219
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230

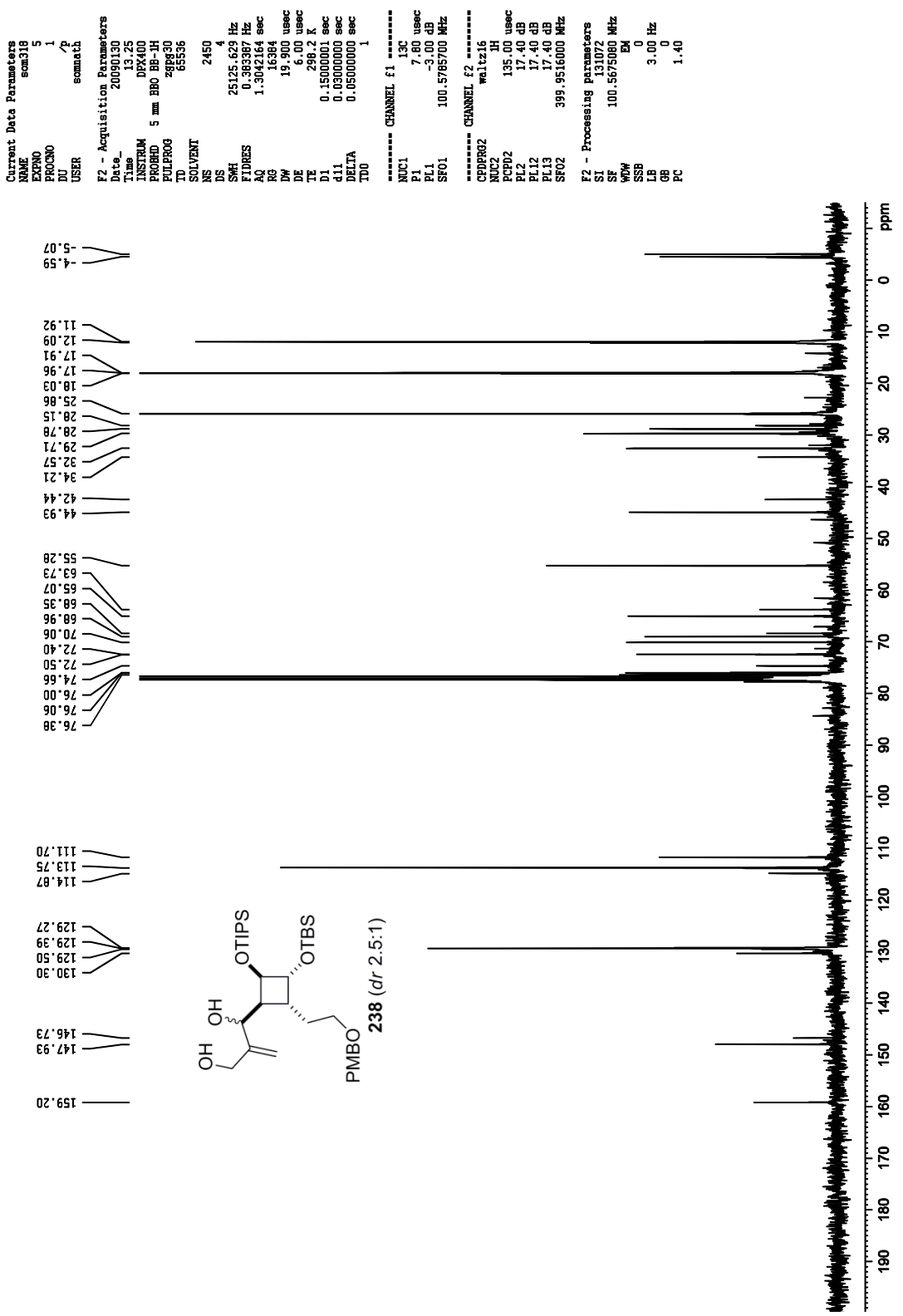

Current Data Parameters
NAME scm246
EXPNO 1
PROCNO 1
DU /9
USER scmath
F2 - Acquisition Parameters
Date_ 20080618
Time 21.35
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 1024
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9528000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
CO2Me
OTIPS
CO2Et
PMBO
+
E/Z 3:1
217
220
EtO2C
CO2Me
OTIPS
PMBO
ppm
35.25
6.48
4.26
2.95
2.34
1.29
8.77
3.20
2.61
0.88
0.92
0.42
4.35
2.73
1.00

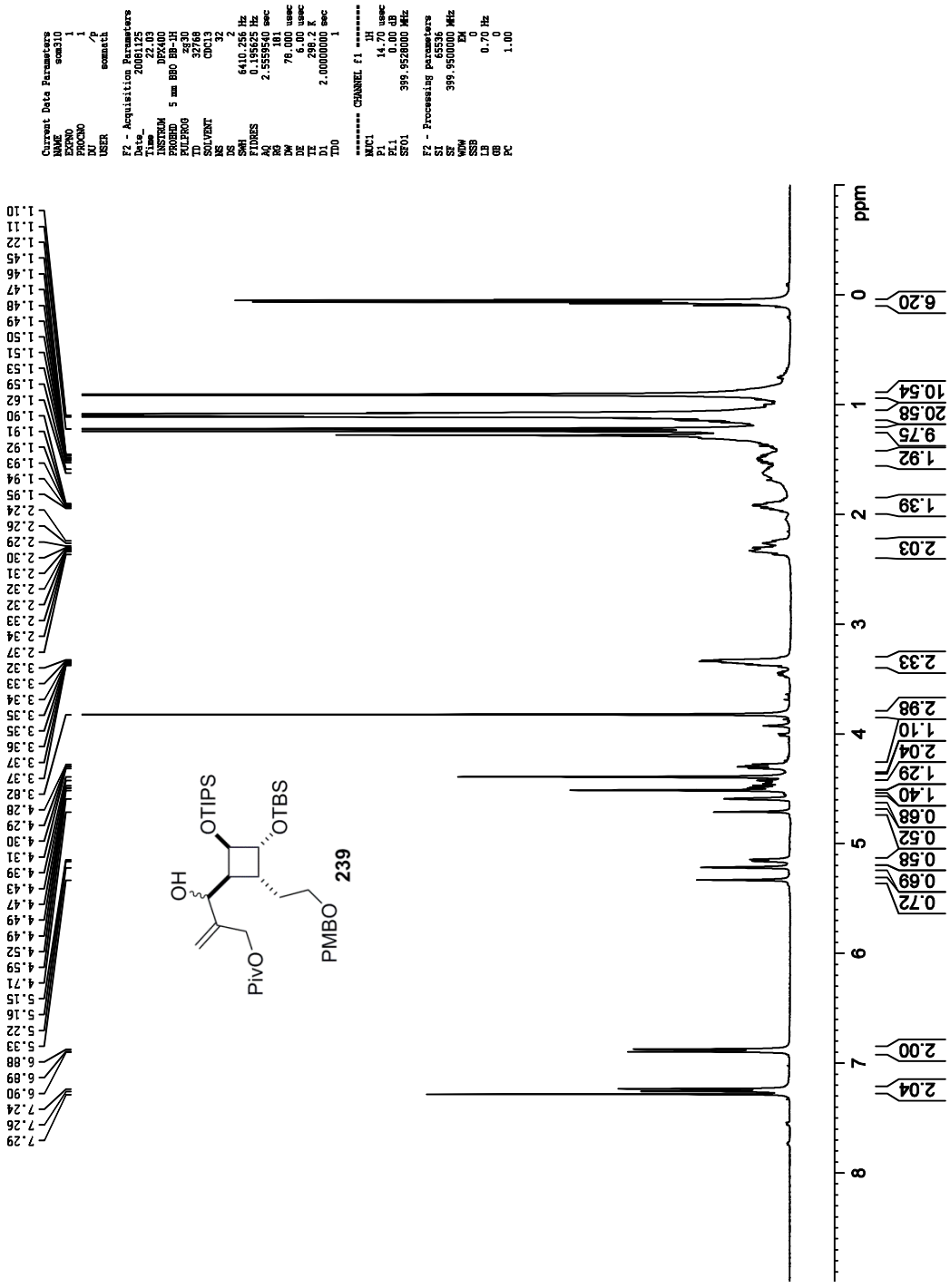

Current Data Parameters
NAME som248
EXPNO 4
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20080619
Time 8.24
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 22187
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 296.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5765700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675060 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
208.17
163.71
160.02
159.16
150.76
130.09
129.19
126.70
124.55
84.02
77.34
77.02
76.70
72.72
67.29
61.01
56.43
55.23
51.50
37.71
17.42
14.31
14.05
11.73
CO2Me
OTIPS
O
O
CO2Et
PMBO
EtO2C
CO2Me
OTIPS
O
O
PMBO
217
E/Z 3:1
220
ppm

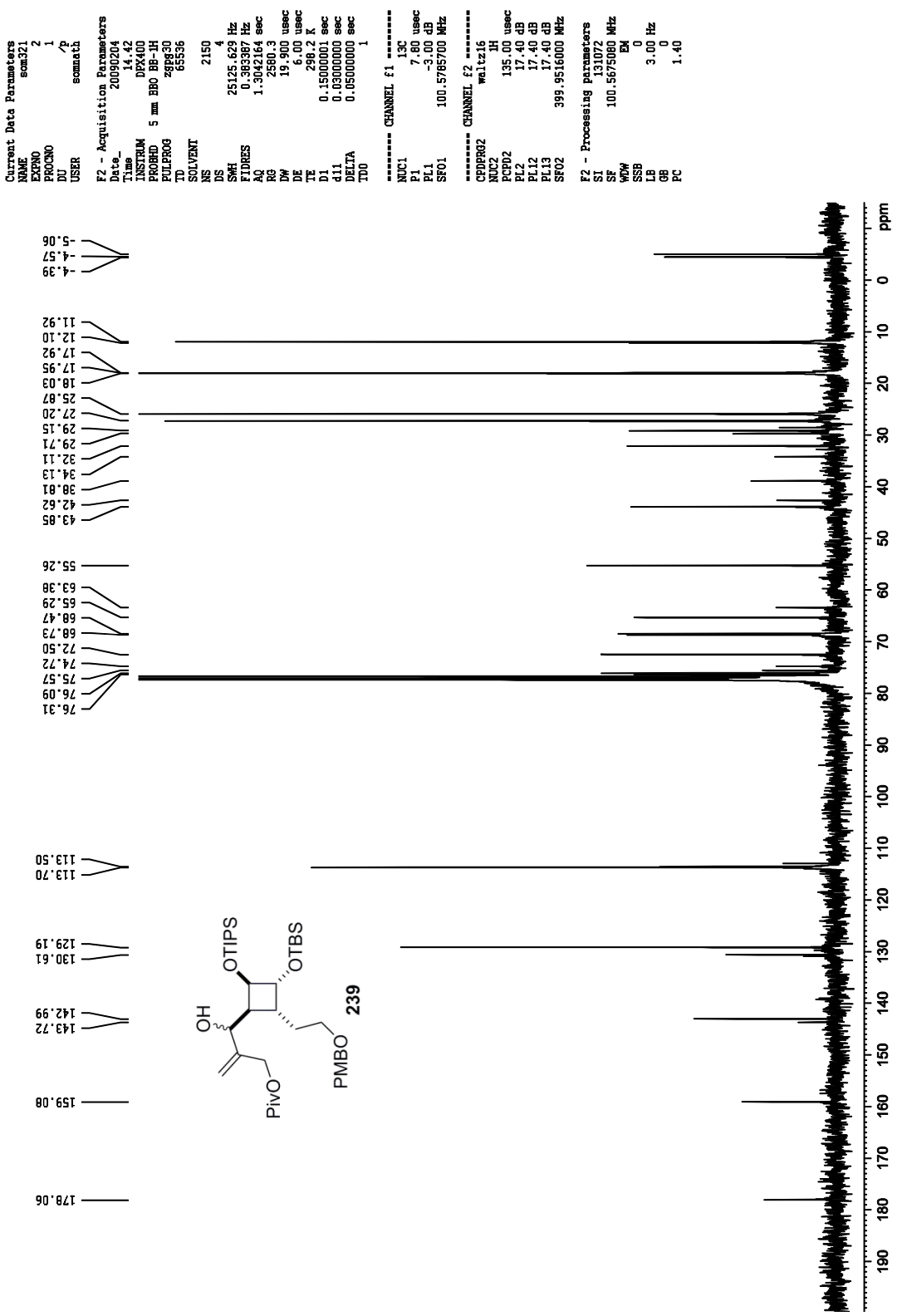

Current Data Parameters
NAME exam280
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080902
Time 15:35
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 161.3
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9520000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
OTIPS
OTBS
PMBO
227
ppm

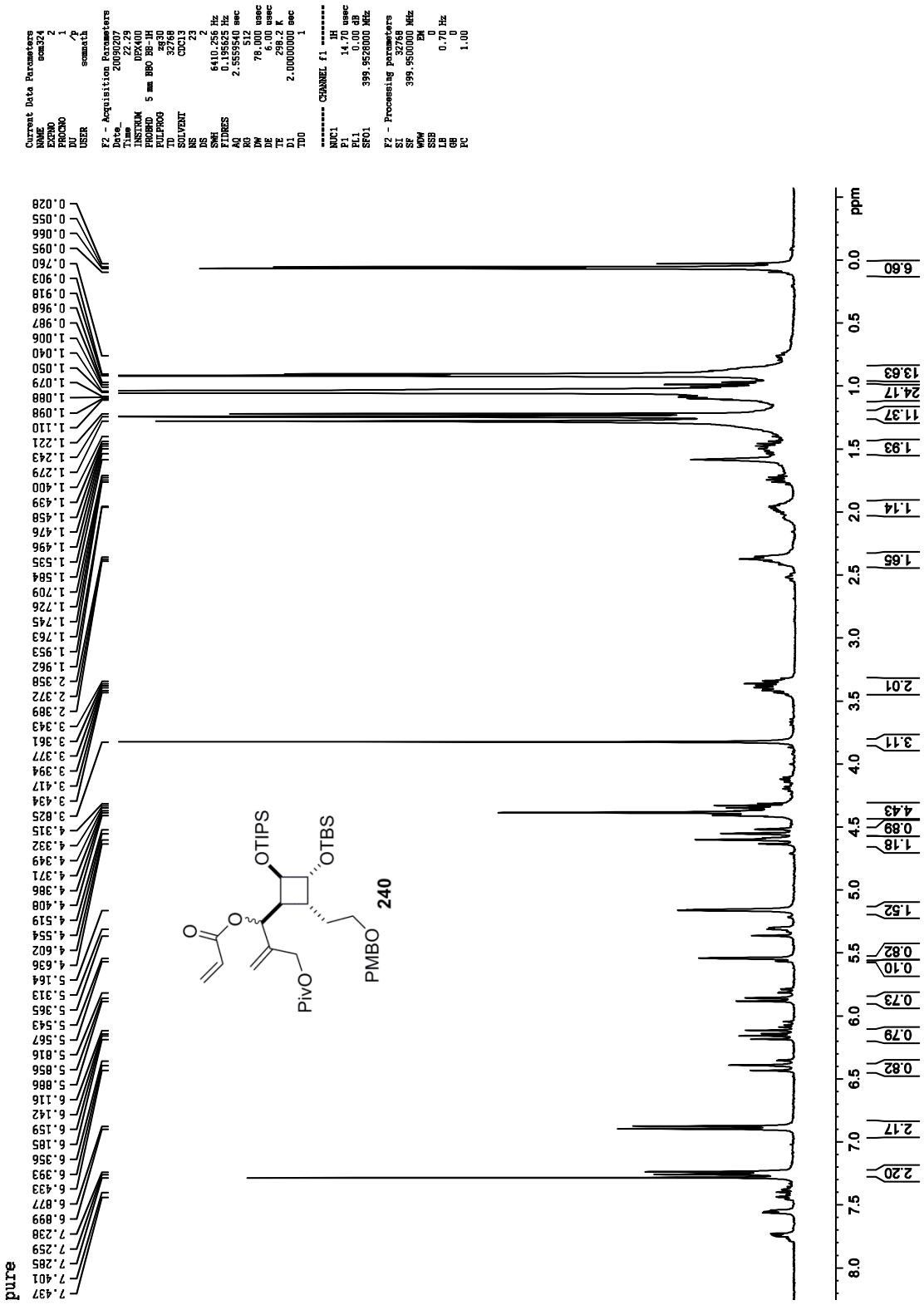

Current Data Parameters
NAME scm280
EXPNO 4
PROCNO 1
DU /p
USER somnath
F2 - Acquisition Parameters
Data_ 20080902
Time_ 17.00
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 2059
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.06
-4.71
11.88
17.84
17.87
17.99
25.81
28.04
32.49
52.70
55.28
68.46
72.68
75.20
113.78
129.17
130.50
159.15
202.83
OTIPS
OTBS
O
H
PMBO
227
ppm

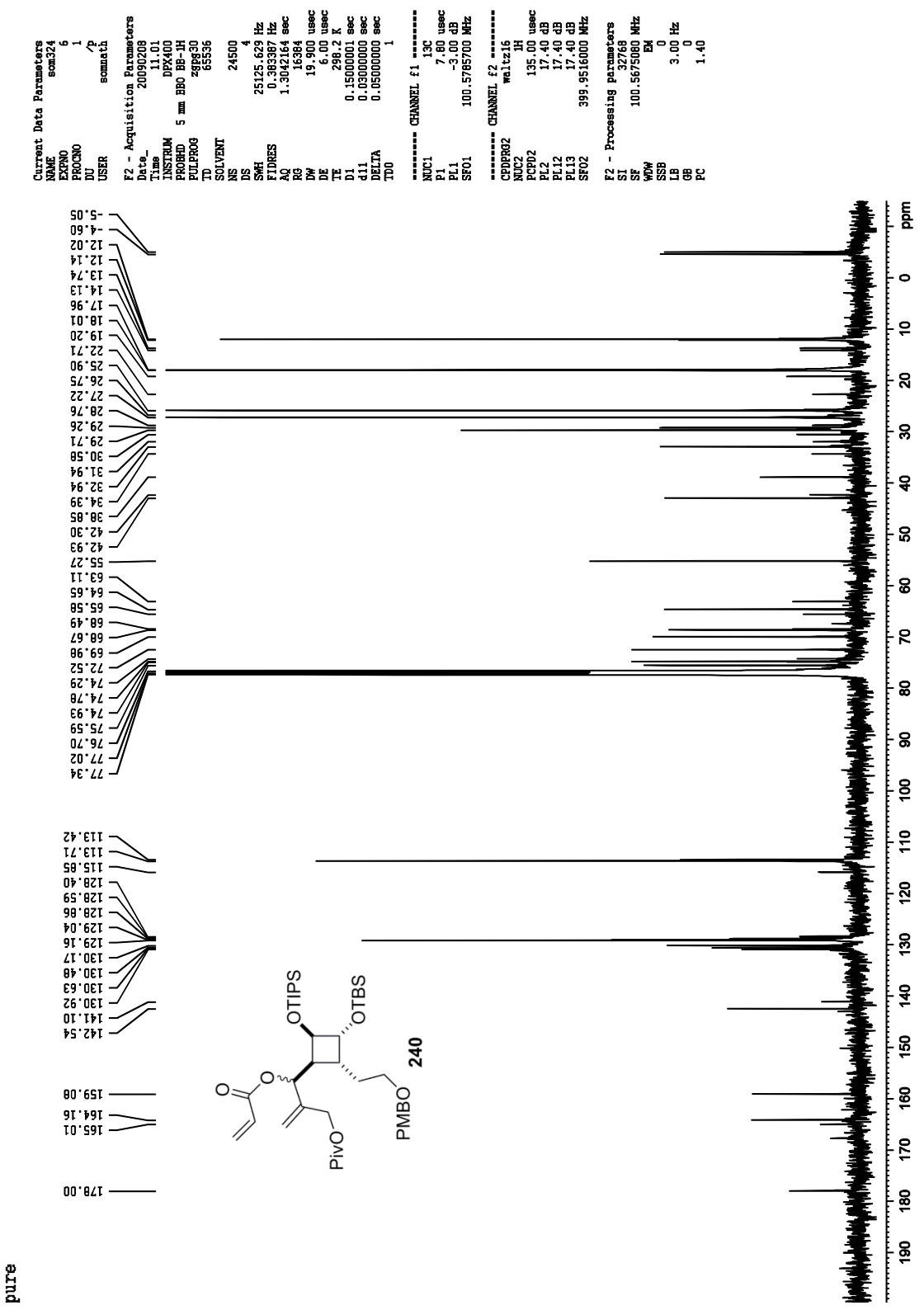

Current Data Parameters
NAME scm318
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091130
Time 17.27
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 161.3
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9520000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
OTIPS
OTBS
OH
OH
PMBO
238 (dr 2.5:1)
ppm
6.21
11.15
21.45
1.02
1.17
1.90
2.41
3.08
1.44
0.40
1.22
2.23
1.25
0.58
0.23
1.48
2.06
1.92

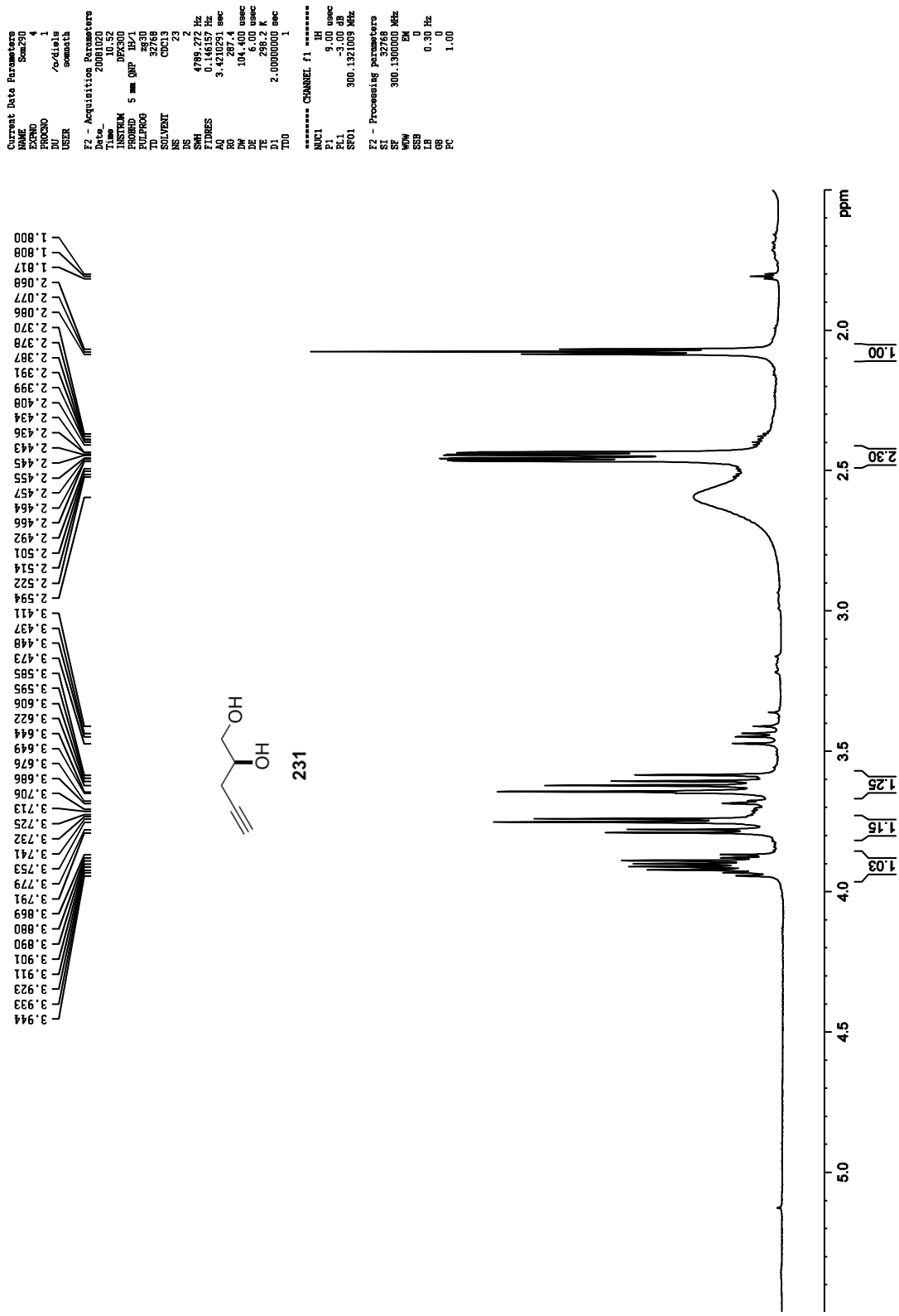

Current Data Parameters
NAME scm318
EXPNO 5
PROCNO 1
DU /p
USER sonnath
F2 - Acquisition Parameters
Date_ 20090130
Time 13.25
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 2450
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.07
-4.59
11.92
12.09
17.91
17.96
18.03
25.86
28.15
28.78
29.71
32.57
34.21
42.44
44.93
55.28
63.73
65.07
68.35
68.96
70.06
72.40
72.50
74.66
76.00
76.06
76.38
111.70
113.75
114.87
129.27
129.39
129.50
130.30
146.73
147.93
159.20
OH
OH
OTIPS
OTBS
PMBO
238 (dr 2.5:1)
ppm

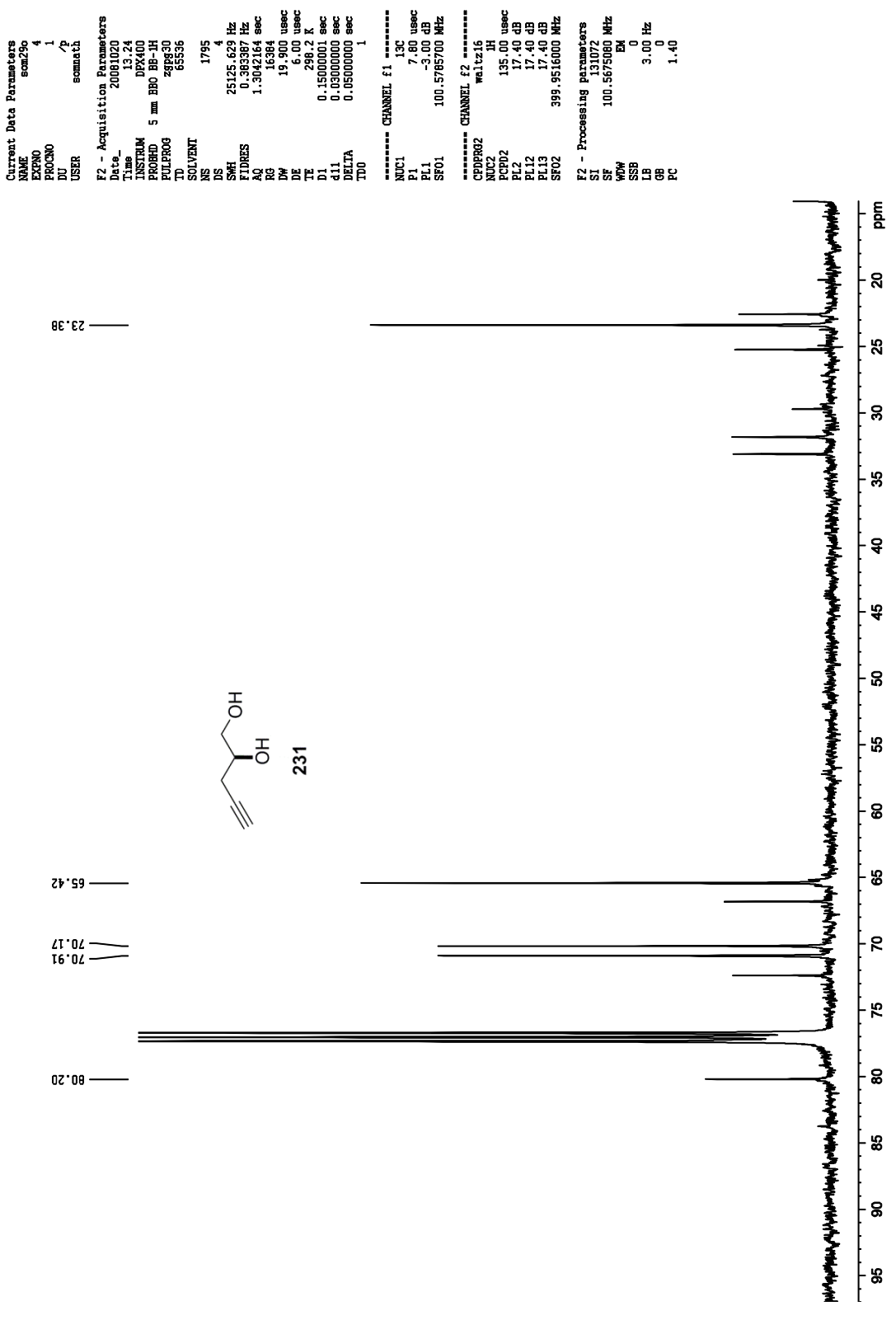

Current Data Parameters
NAME sem310
EXPNO 1
PROCNO 1
DU /p
USER nomatch
F2 - Acquisition Parameters
Date_ 20051125
Time 22.03
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 181
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9520000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
OH
OTIPS
OTBS
PivO
PMBO
239
ppm
6.20
10.54
20.58
9.75
1.92
1.39
2.03
2.33
2.98
1.10
2.04
1.29
1.40
0.68
0.52
0.58
0.69
0.72
2.00
2.04

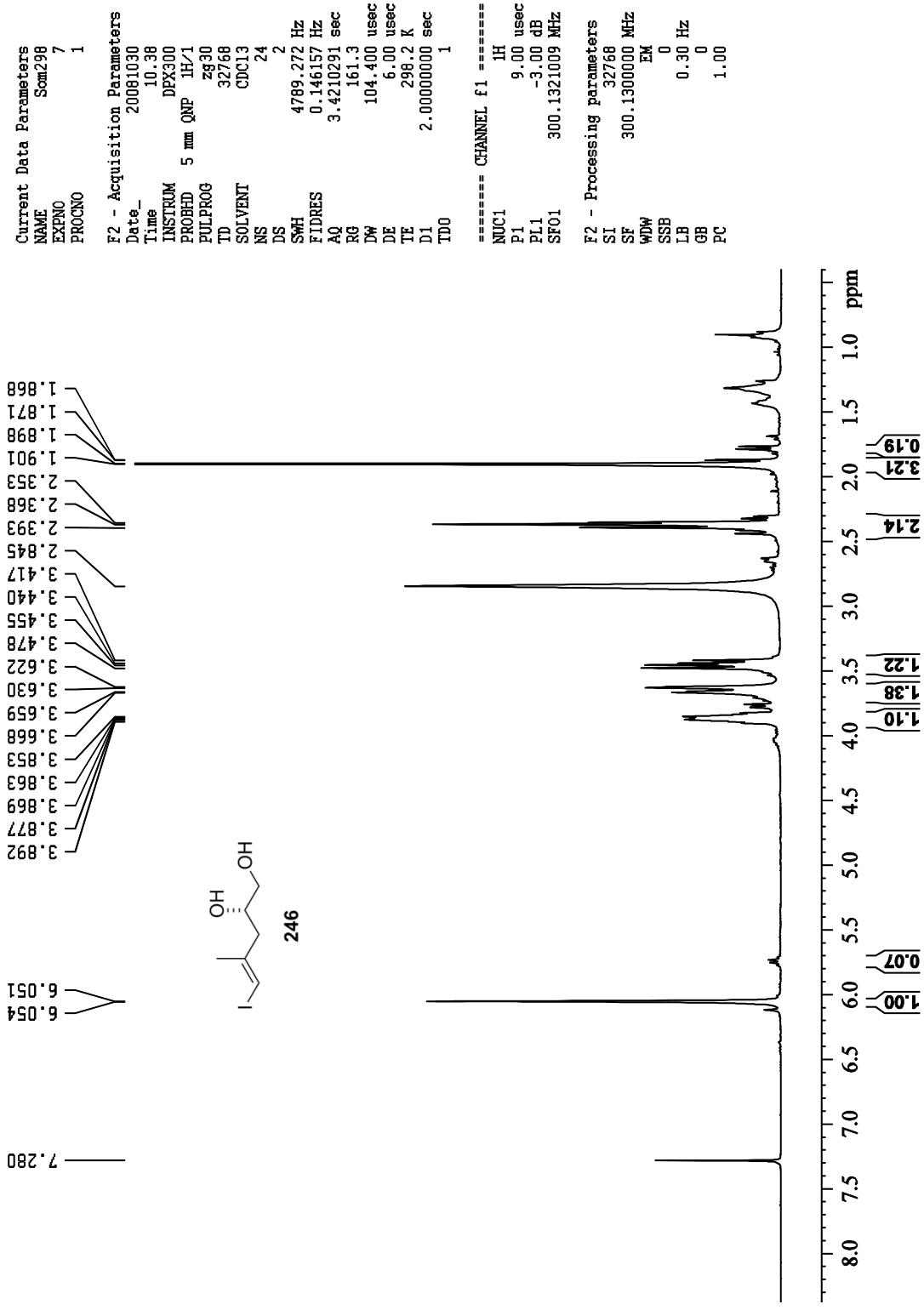

Current Data Parameters
NAME scm321
EXPNO 2
PROCNO 1
DU /p
USER scmnath
F2 - Acquisition Parameters
Date_ 20090204
Time 14.42
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 2150
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 2580.3
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.06
-4.57
-4.39
11.92
12.10
17.92
17.95
18.03
25.87
27.20
29.15
29.71
32.11
34.13
38.81
42.62
43.85
55.26
63.38
65.29
68.47
68.73
72.50
74.72
75.57
76.09
76.31
113.70
113.50
129.19
130.61
142.99
143.72
159.08
178.06
OTIPS
OTBS
OH
PivO
PMBO
239
ppm

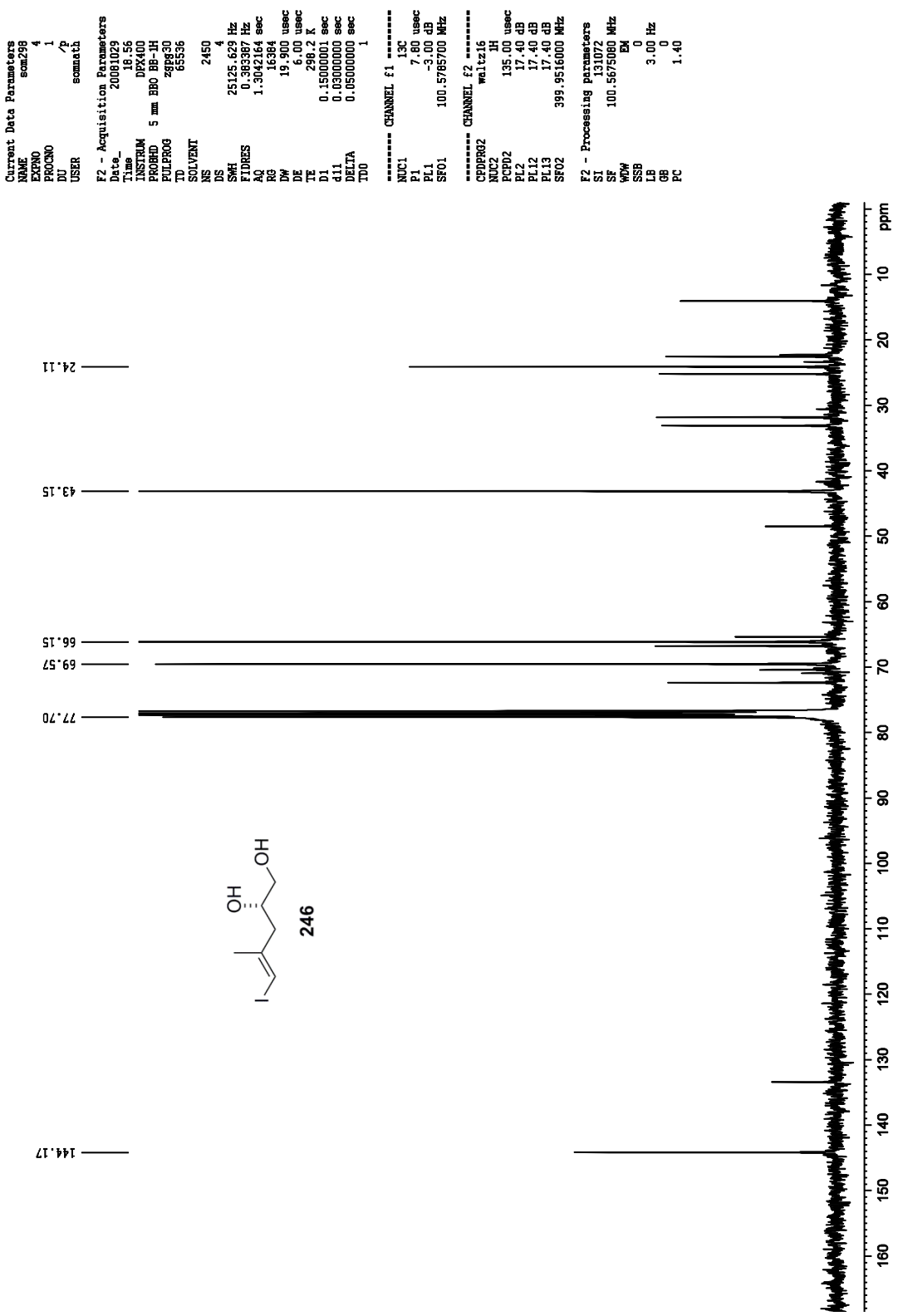

pure
OTIPS
OTBS
PivO
PMBO
240
ppm

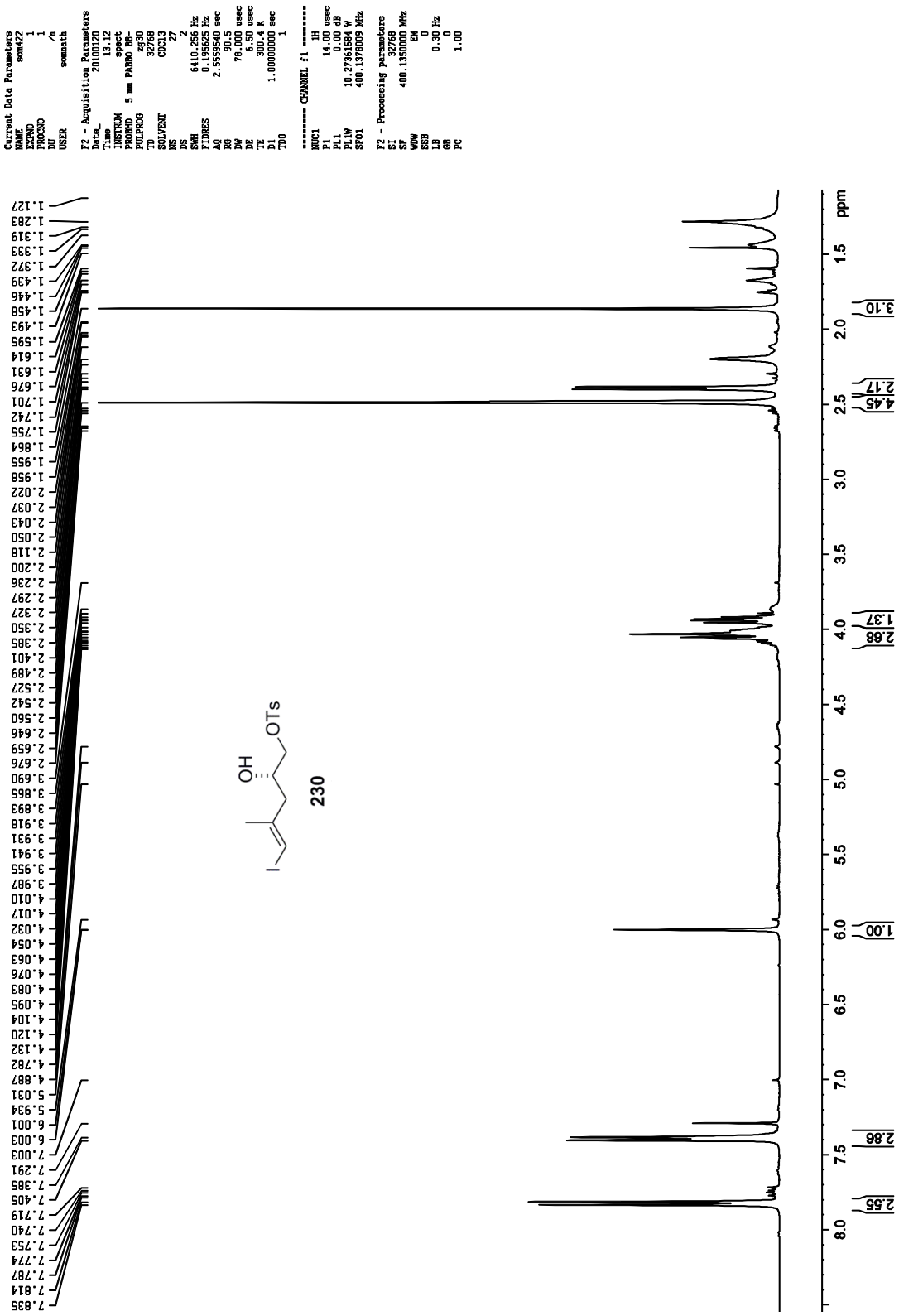

pure
Current Data Parameters
NAME scm324
EXPNO 6
PROCNO 1
DU /p
USER scmnath
F2 - Acquisition Parameters
Data_ 20090208
Time 11.01
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 24500
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 32768
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
178.00
165.01
164.16
159.08
142.54
141.10
130.92
130.63
130.48
130.17
129.16
129.04
128.86
128.59
128.40
115.85
113.71
113.42
77.34
77.02
76.70
75.59
74.93
74.78
74.29
72.52
69.98
68.67
68.49
65.58
64.65
63.11
55.27
42.93
42.30
38.85
34.39
32.94
31.94
30.58
29.71
29.26
28.76
27.22
26.75
25.90
22.71
19.20
18.01
17.96
14.13
13.74
12.14
12.02
-4.60
-5.05
OTIPS
OTBS
PivO
PMBO
240
ppm

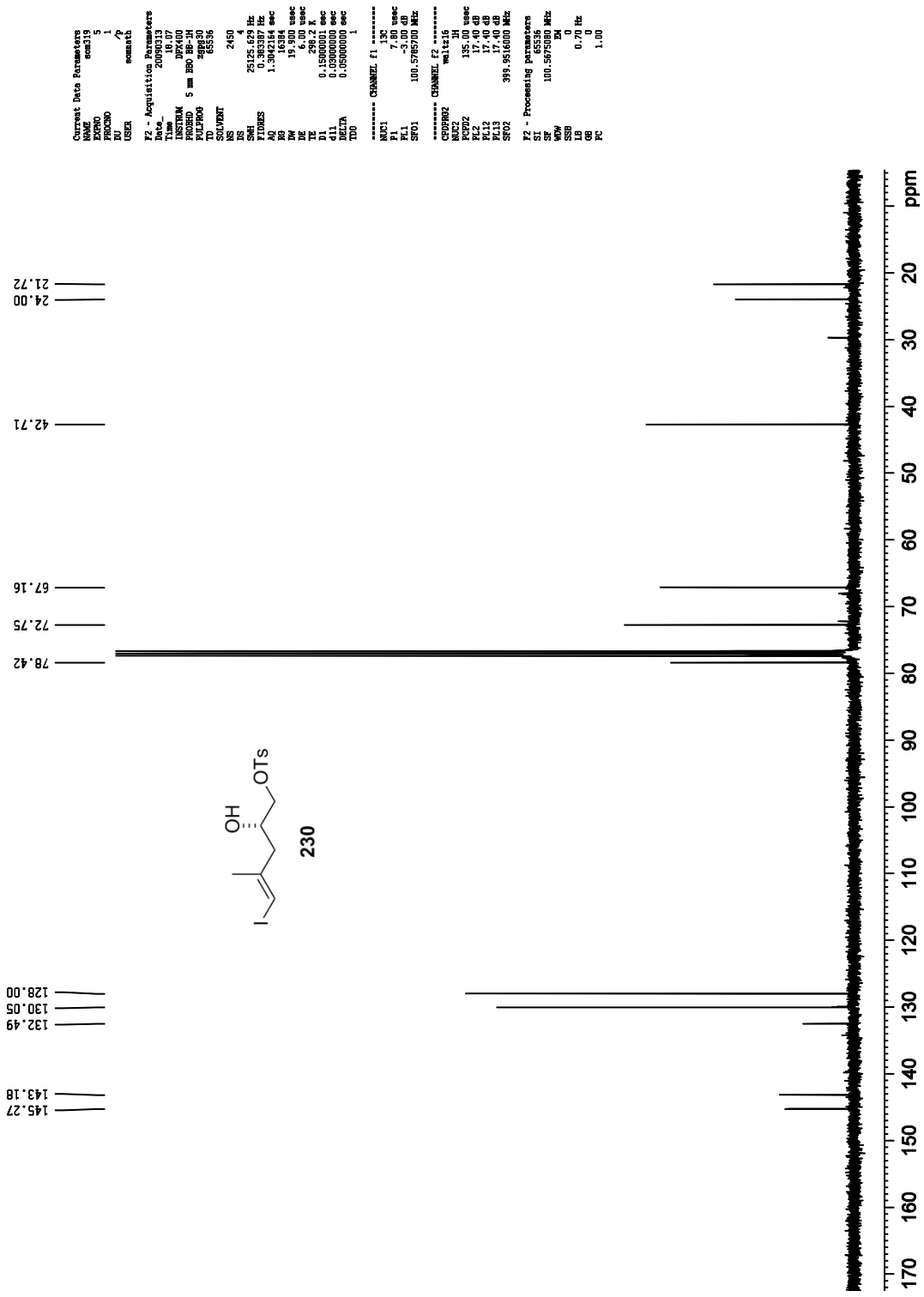

Current Data Parameters
NAME Sam290
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Data_ 20081020
Time 10.52
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDC13
NS 23
DS 2
SWH 4799.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 287.4
DW 104.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.800
1.808
1.817
2.068
2.077
2.086
2.370
2.378
2.387
2.391
2.399
2.408
2.434
2.436
2.443
2.445
2.455
2.457
2.464
2.466
2.492
2.501
2.514
2.522
2.594
3.411
3.437
3.448
3.473
3.585
3.595
3.606
3.622
3.644
3.649
3.676
3.686
3.706
3.713
3.725
3.732
3.741
3.753
3.779
3.791
3.869
3.880
3.890
3.901
3.911
3.923
3.933
3.944
OH
OH
231
ppm
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.00
2.30
1.25
1.15
1.03

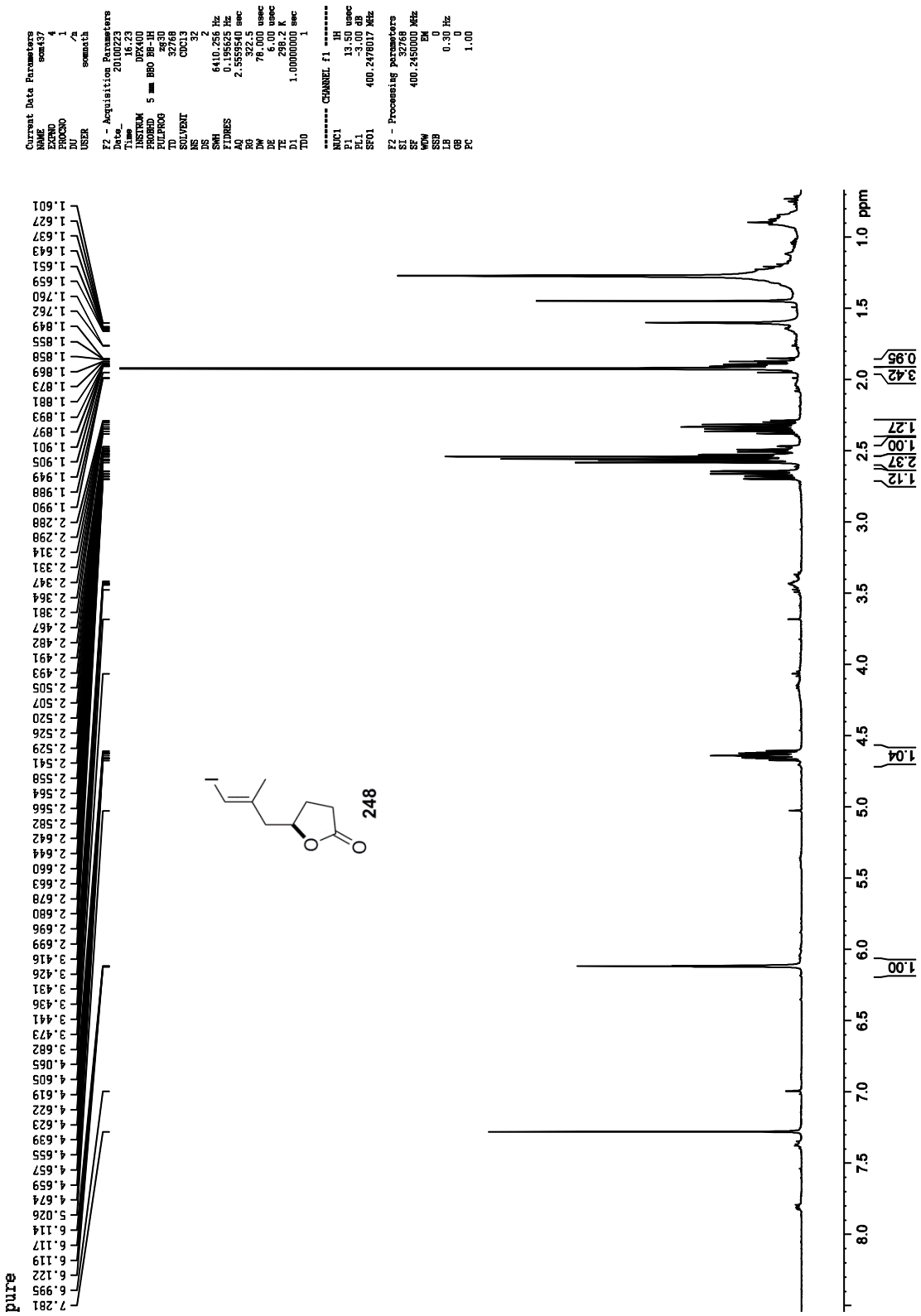

Current Data Parameters
NAME scm29o
EXPNO 4
PROCNO 1
DU /p
USER sommath
F2 - Acquisition Parameters
Date_ 20061020
Time 13.24
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 1795
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
OH
OH
231
23.38
65.42
70.17
70.91
80.20
ppm

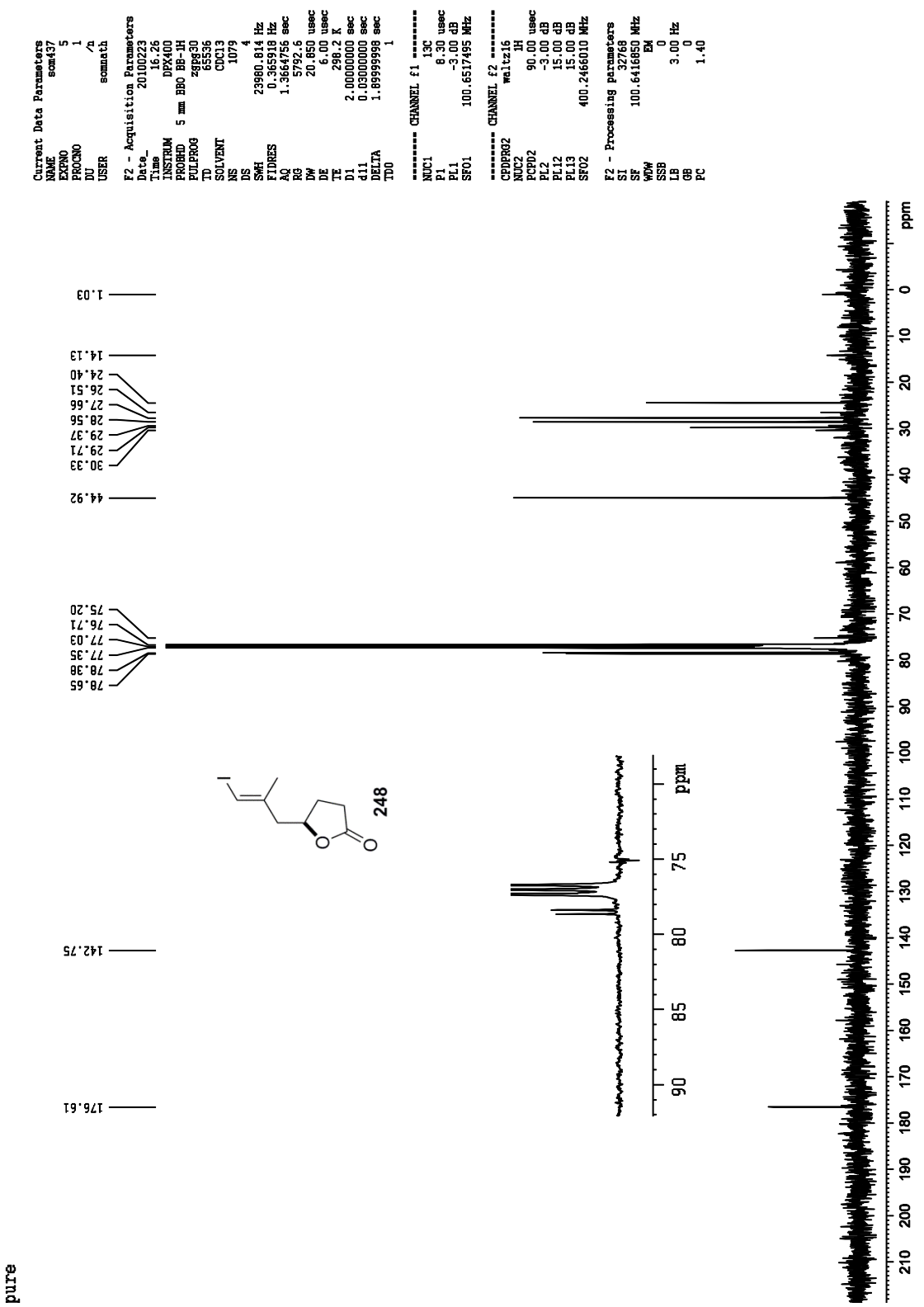

Current Data Parameters
NAME Som298
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20081030
Time 10.38
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 24
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 161.3
DW 104.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.280
6.054
6.051
3.892
3.877
3.869
3.863
3.853
3.668
3.659
3.630
3.622
3.478
3.455
3.440
3.417
2.845
2.393
2.368
2.353
1.901
1.898
1.871
1.868
OH
OH
I
246
1.00
0.07
1.10
1.38
1.22
2.14
3.21
0.19
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

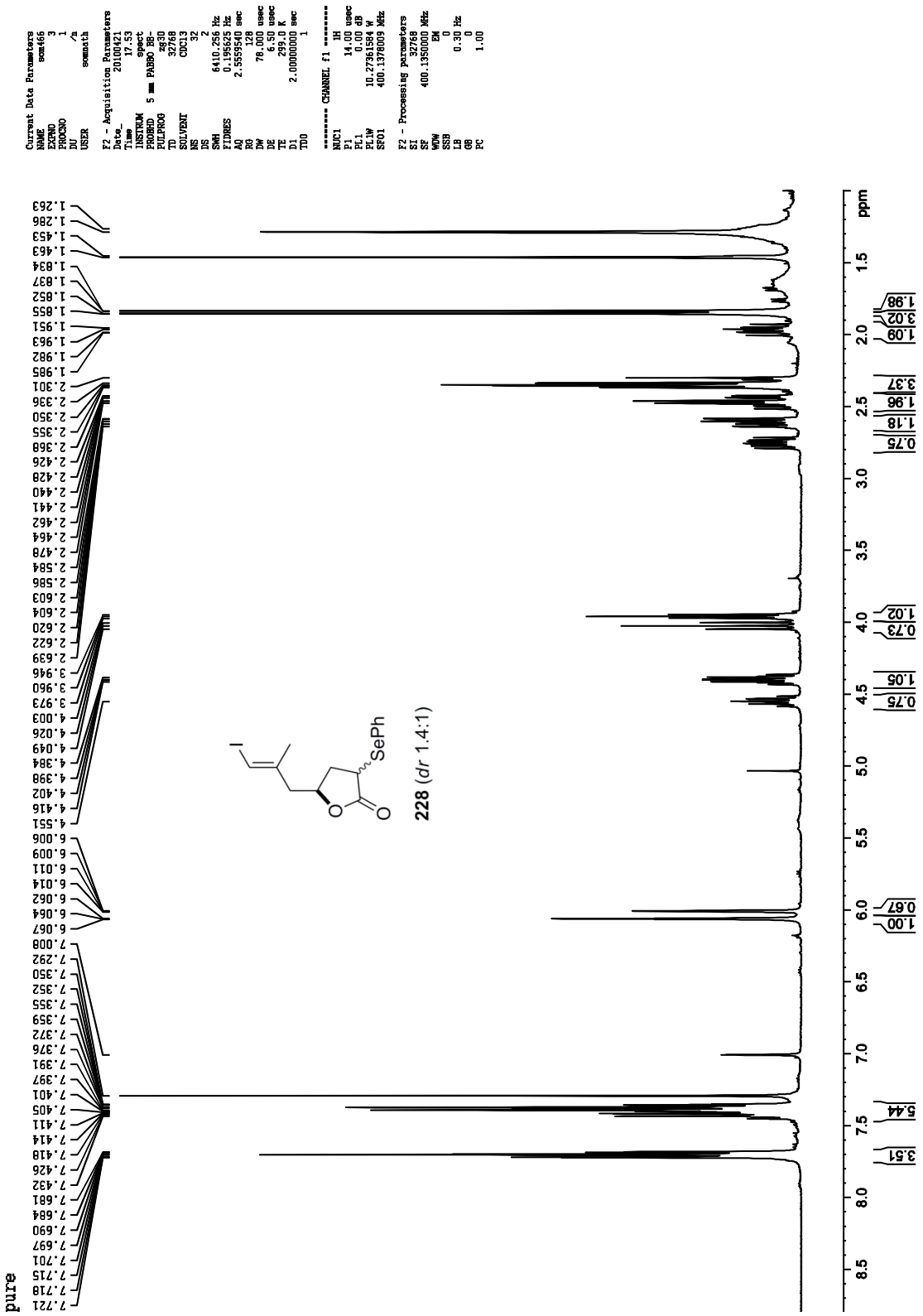

Current Data Parameters
NAME som298
EXPNO 4
PROCNO 1
DU /p
USER somnath
F2 - Acquisition Parameters
Date_ 20081029
Time_ 18.56
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 2450
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
24.11
43.15
66.15
69.57
77.70
144.17
OH
OH
I
246
ppm

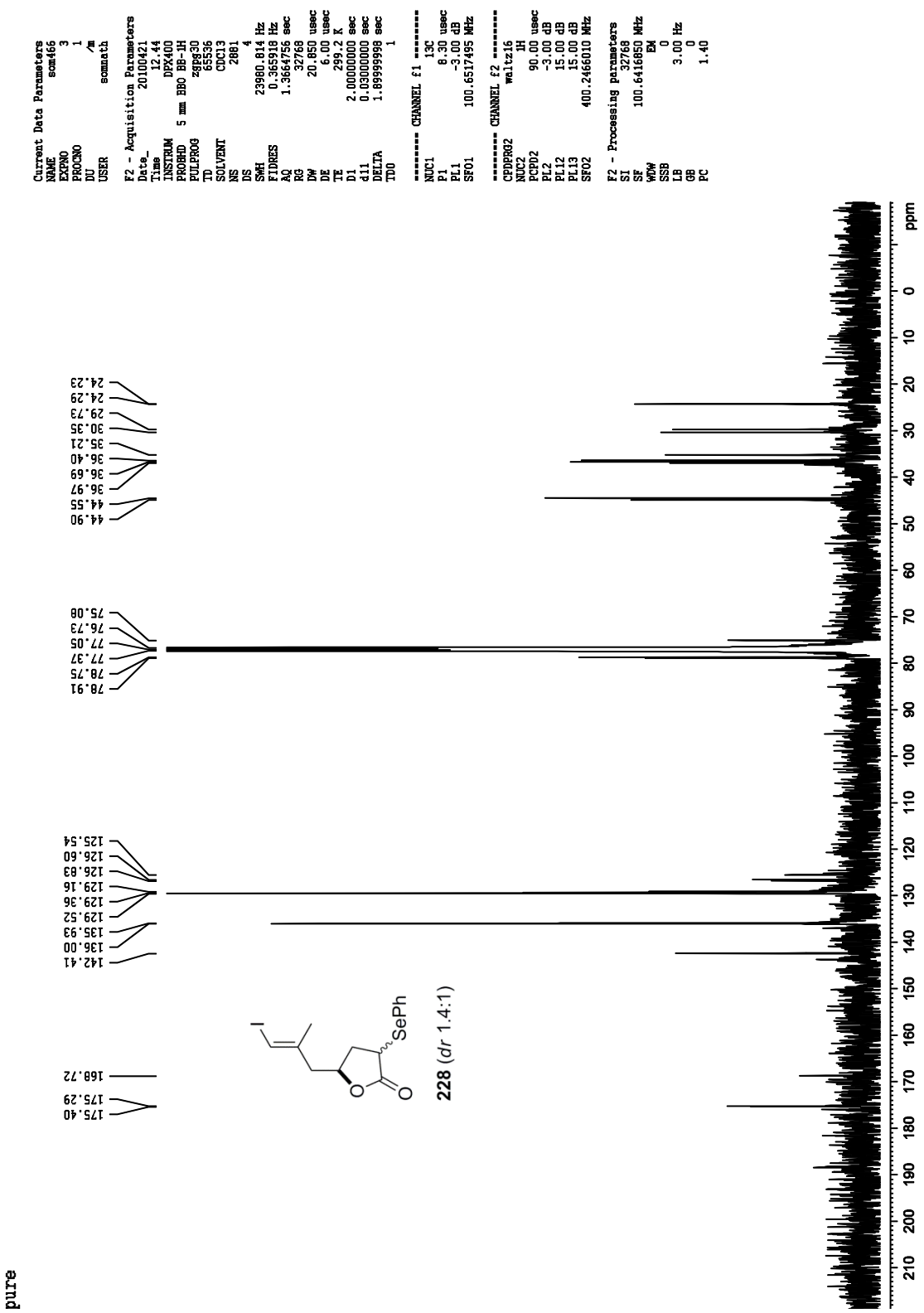

Current Data Parameters
NAME somf22
EXPNO 1
PROCNO 1
DU /n
USER somnath
F2 - Acquisition Parameters
Date_ 20100120
Time 13.12
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 27
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 203.5
DW 78.000 usec
DE 6.50 usec
TE 300.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
PL1W 10.27361584 W
SFO1 400.1378009 MHz
F2 - Processing parameters
SI 32768
SF 400.1350000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
OTs
I
230
ppm
1.00
2.86
2.55
3.10
2.17
4.45
1.37
2.68

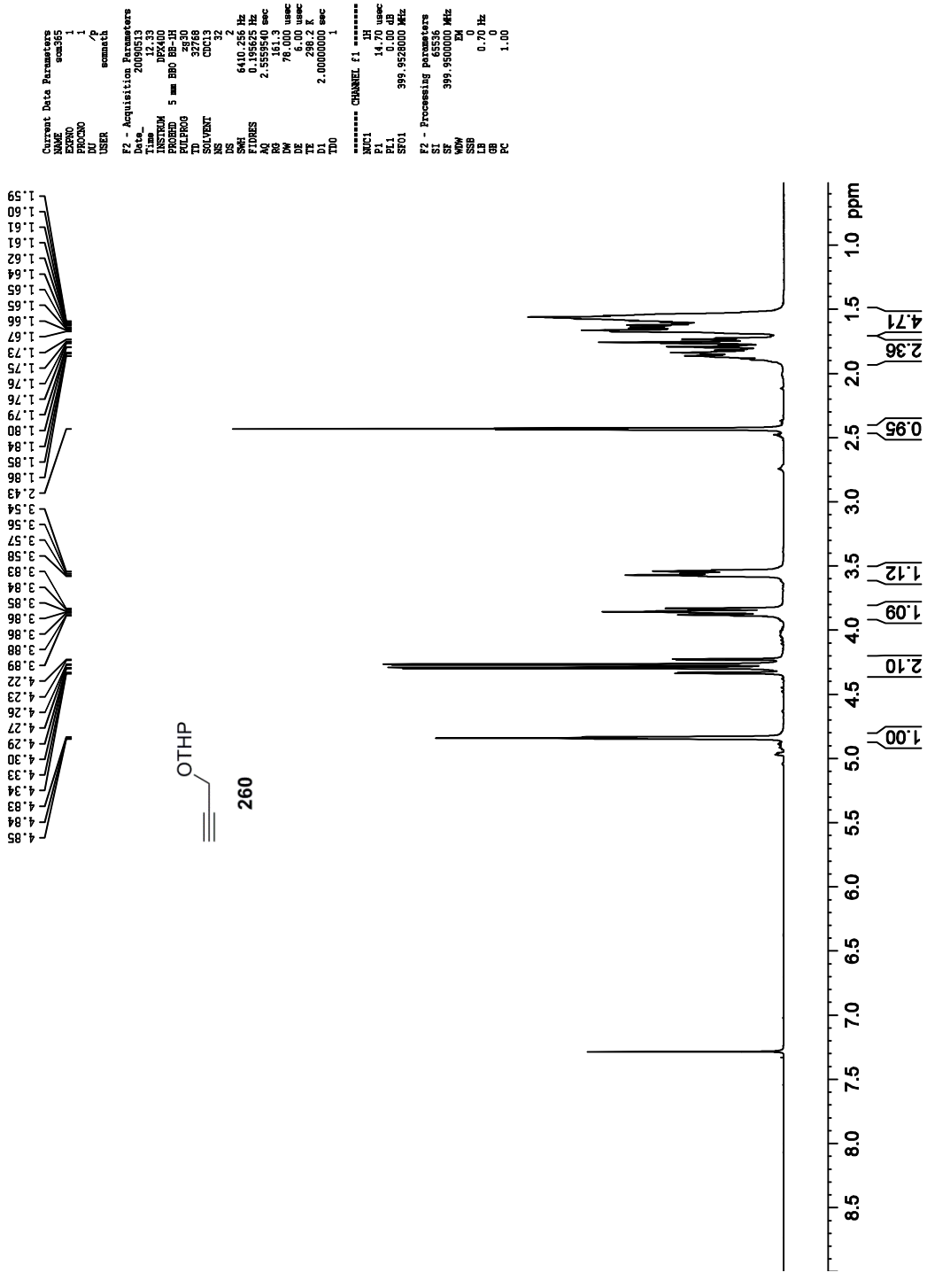

Current Data Parameters
NAME eom319
EXPNO 5
PROCNO 1
IU /e
USER eomanch
F2 - Acquisition Parameters
Date_ 20050313
Time 18.07
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 2450
DS 4
SWH 25125.629 Hz
FIDRES 0.383397 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 65536
SF 100.5675080 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
21.72
24.00
42.71
67.16
72.75
78.42
128.00
130.05
132.49
143.18
145.27
OH
OTs
I
230
ppm

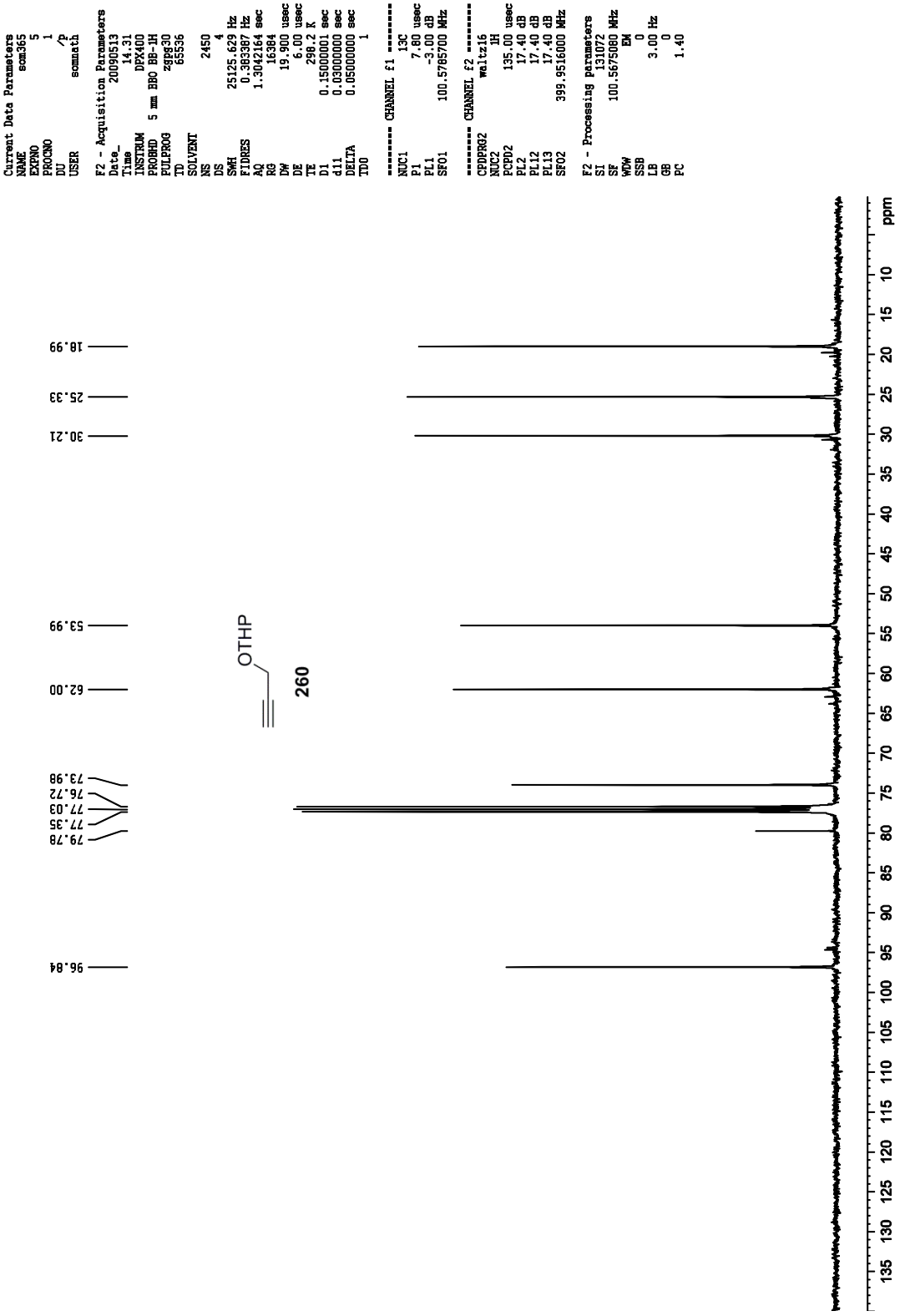

Current Data Parameters
NAME soni37
EXPNO 4
PROCNO 1
DU /n
USER somnath
F2 - Acquisition Parameters
Date_ 20100223
Time 16.23
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 722.5
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
248
pure
ppm
1.00
1.04
1.12
2.37
1.00
1.27
3.42
0.95

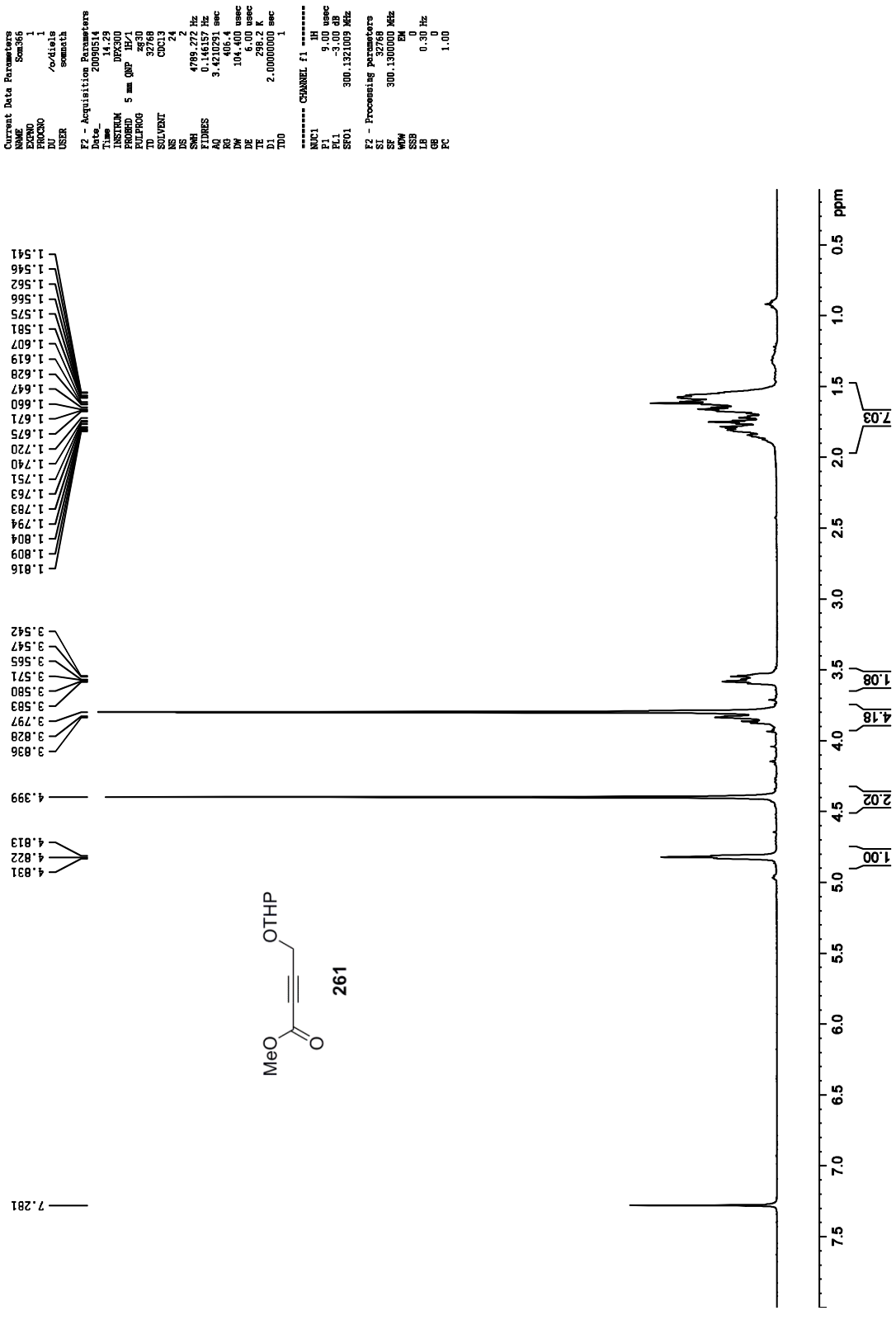

pure
Current Data Parameters
NAME scm437
EXPNO 5
PROCNO 1
DU /n
USER scmnath
F2 - Acquisition Parameters
Date_ 20100223
Time 16.26
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1079
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 5792.6
DW 20.850 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
1.03
14.13
24.40
26.51
27.66
28.56
29.37
29.71
30.33
44.92
75.20
76.71
77.03
77.35
78.38
78.65
142.75
176.61
248
ppm
ppm

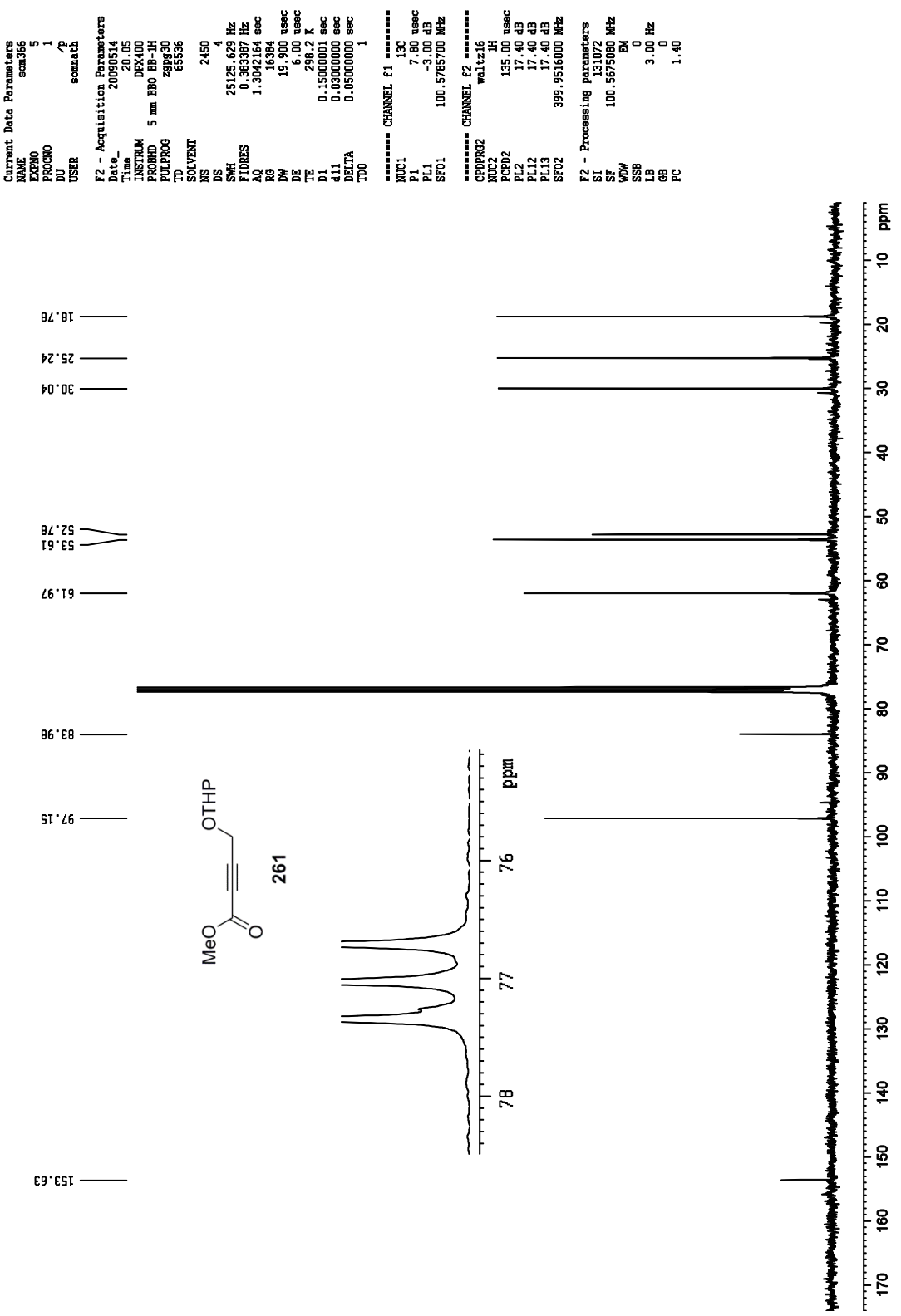

Current Data Parameters
NAME scan66
EXPNO 3
PROCNO 1
DU /n
USER sumnath
F2 - Acquisition Parameters
Date_ 20100421
Time 17.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDC13
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 228
DW 78.000 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
PL1W 10.27361584 W
SFO1 400.1378009 MHz
F2 - Processing parameters
SI 32768
SF 400.1350000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
SePh
O
O
228 (dr 1.4:1)
ppm
1.263
1.286
1.453
1.463
1.834
1.837
1.852
1.855
1.951
1.963
1.982
1.985
2.301
2.336
2.350
2.355
2.368
2.426
2.428
2.440
2.441
2.462
2.464
2.478
2.584
2.586
2.603
2.604
2.620
2.622
2.639
3.946
3.960
3.973
4.003
4.026
4.049
4.384
4.398
4.402
4.416
4.551
6.006
6.009
6.011
6.014
6.062
6.064
6.067
7.008
7.292
7.350
7.352
7.355
7.359
7.372
7.376
7.391
7.397
7.401
7.405
7.411
7.414
7.418
7.426
7.432
7.681
7.684
7.690
7.697
7.701
7.715
7.718
7.721
0.75
1.18
1.96
3.37
0.73
1.02
0.75
1.05
1.00
0.67
5.44
3.51
1.09
3.02
1.98

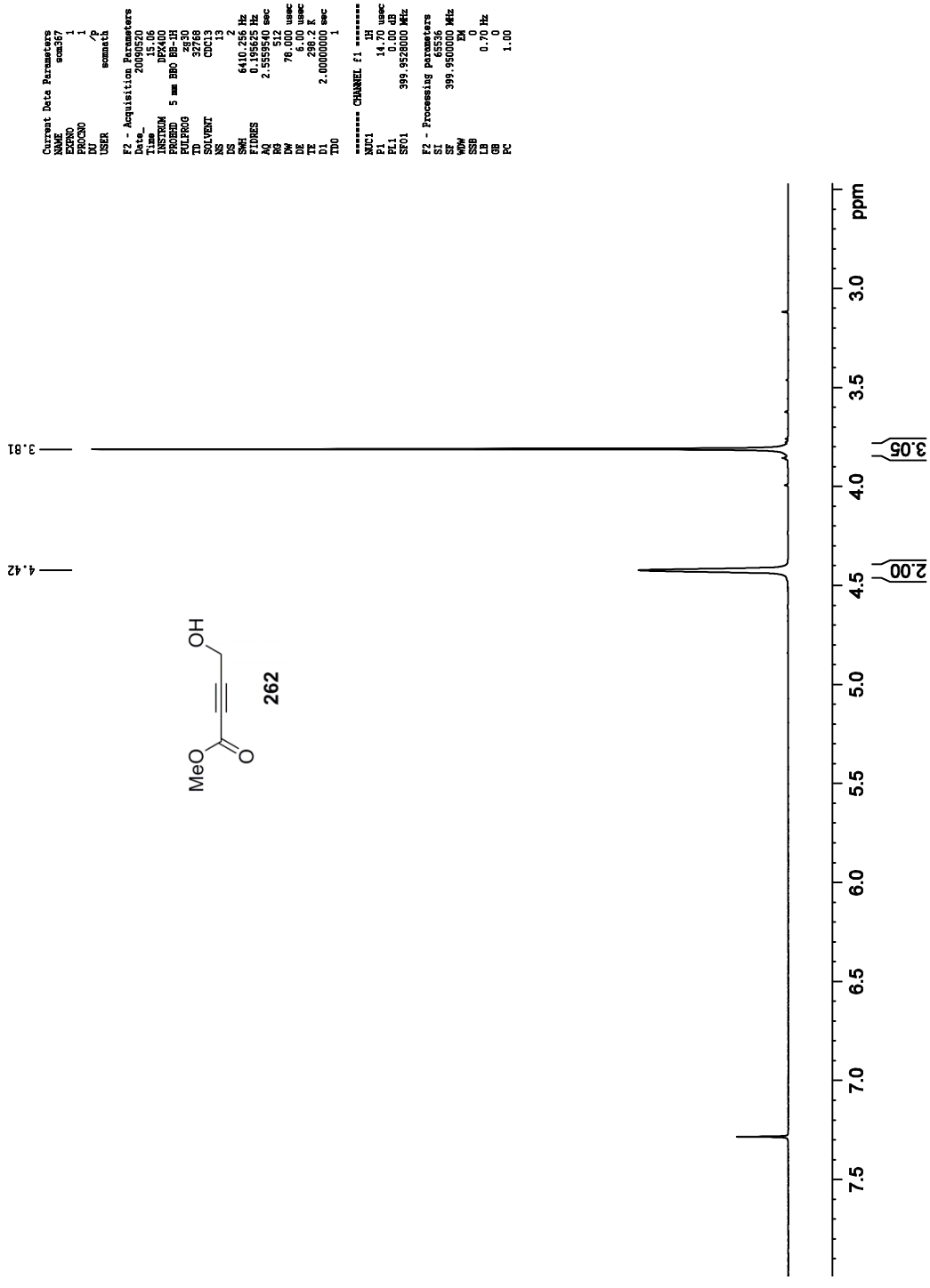

pure
Current Data Parameters
NAME scm466
EXPNO 3
PROCNO 1
DU /m
USER sommath
F2 - Acquisition Parameters
Data_ 20100421
Time_ 12.44
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2081
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 32768
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
175.40
175.29
168.72
142.41
136.00
135.93
129.52
129.36
129.16
126.83
126.60
125.54
78.91
78.75
77.37
77.05
76.73
75.08
44.90
44.55
36.97
36.69
36.40
35.21
30.35
29.73
24.29
24.23
I
SePh
O
O
228 (dr 1.4:1)
ppm

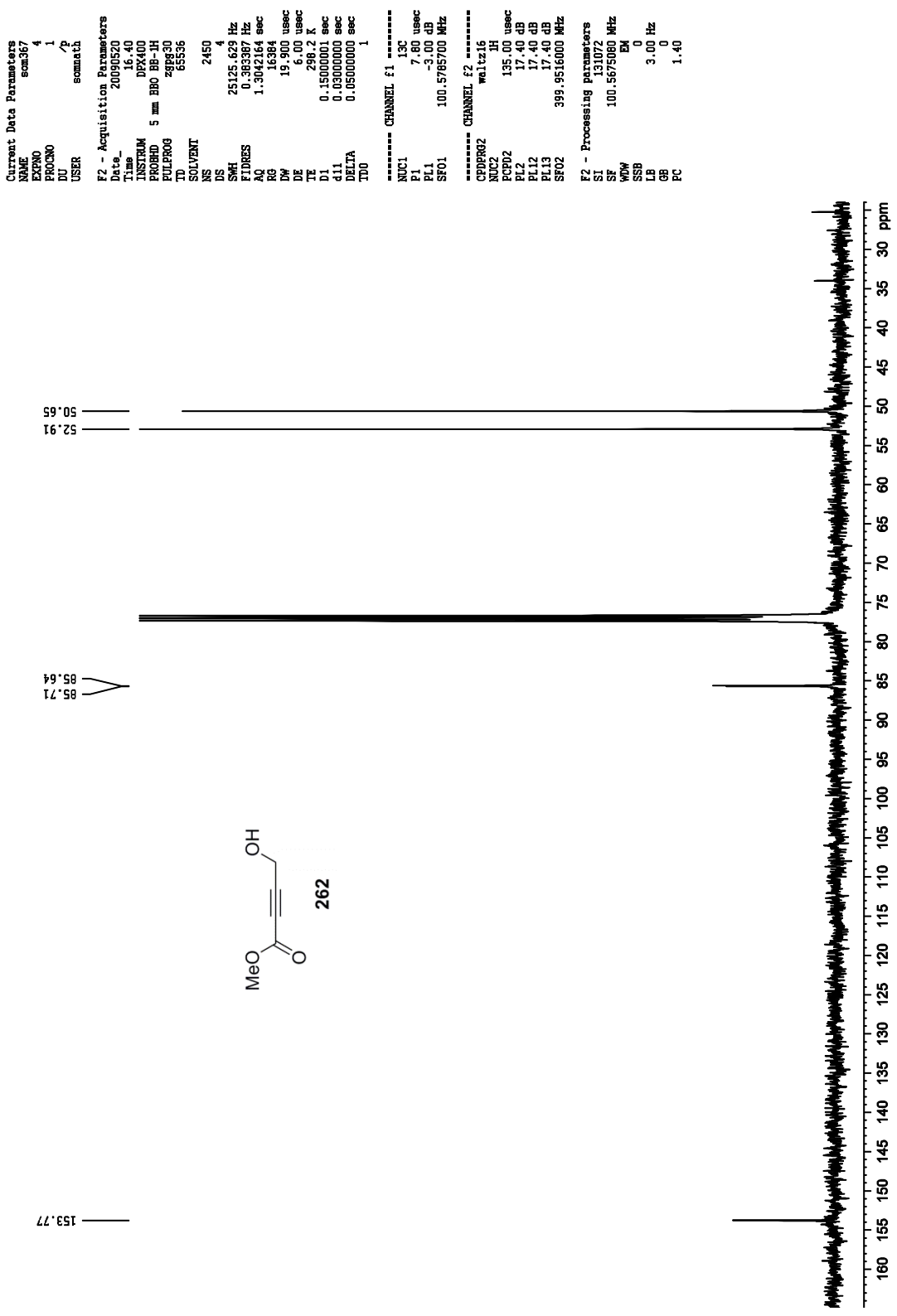

Current Data Parameters
NAME sma365
EXPNO 1
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20090513
Time 12.33
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 161.3
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9528000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
OTHP
260
1.00
2.10
1.09
1.12
0.95
2.36
4.71
ppm

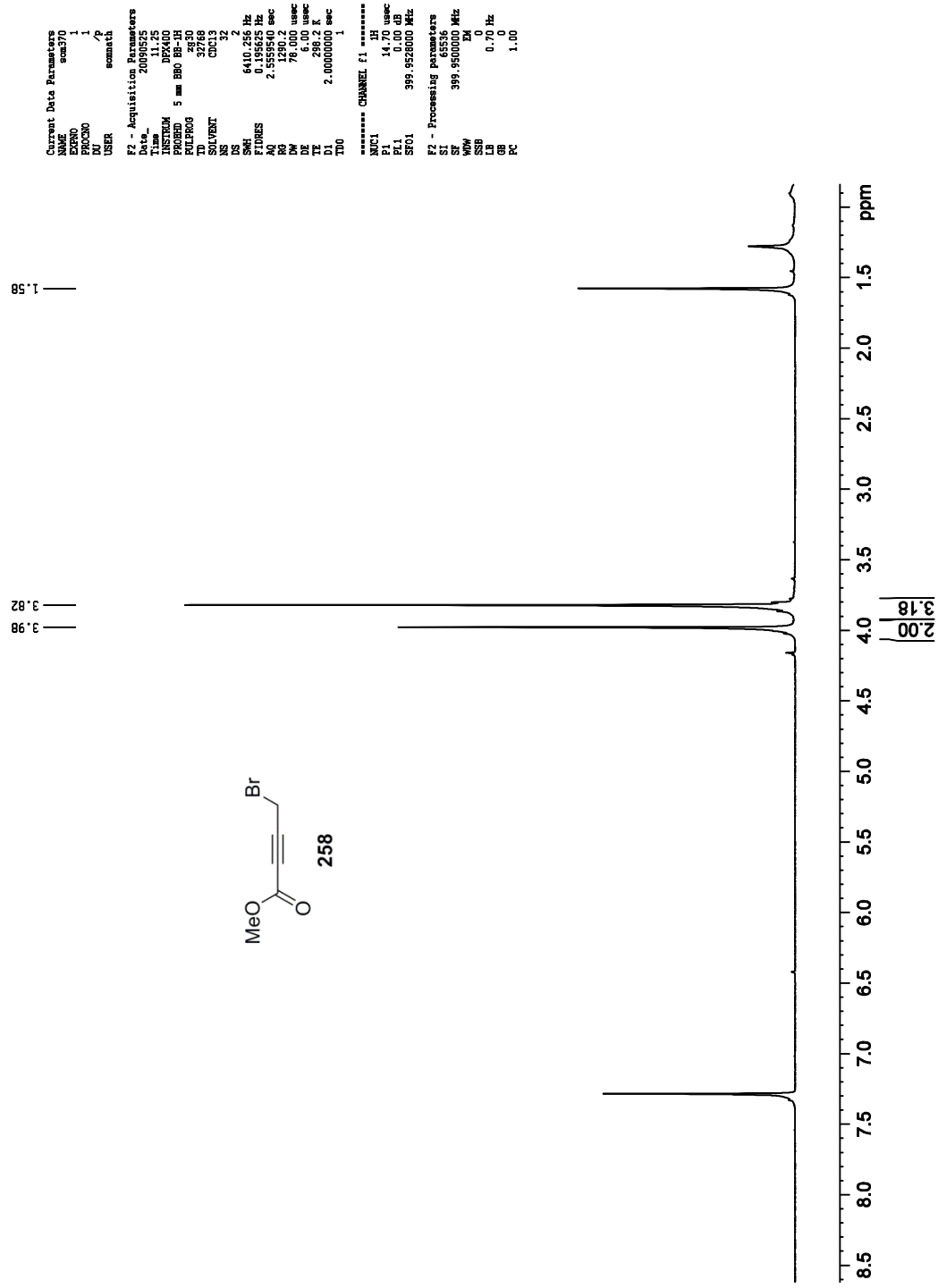

Current Data Parameters
NAME scm365
EXPNO 5
PROCNO 1
DU /p
USER somnath
F2 - Acquisition Parameters
Date_ 20090513
Time 14.31
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 2450
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 1310072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
18.99
25.33
30.21
53.99
62.00
73.98
76.72
77.03
77.35
79.78
96.84
OTHP
260
ppm

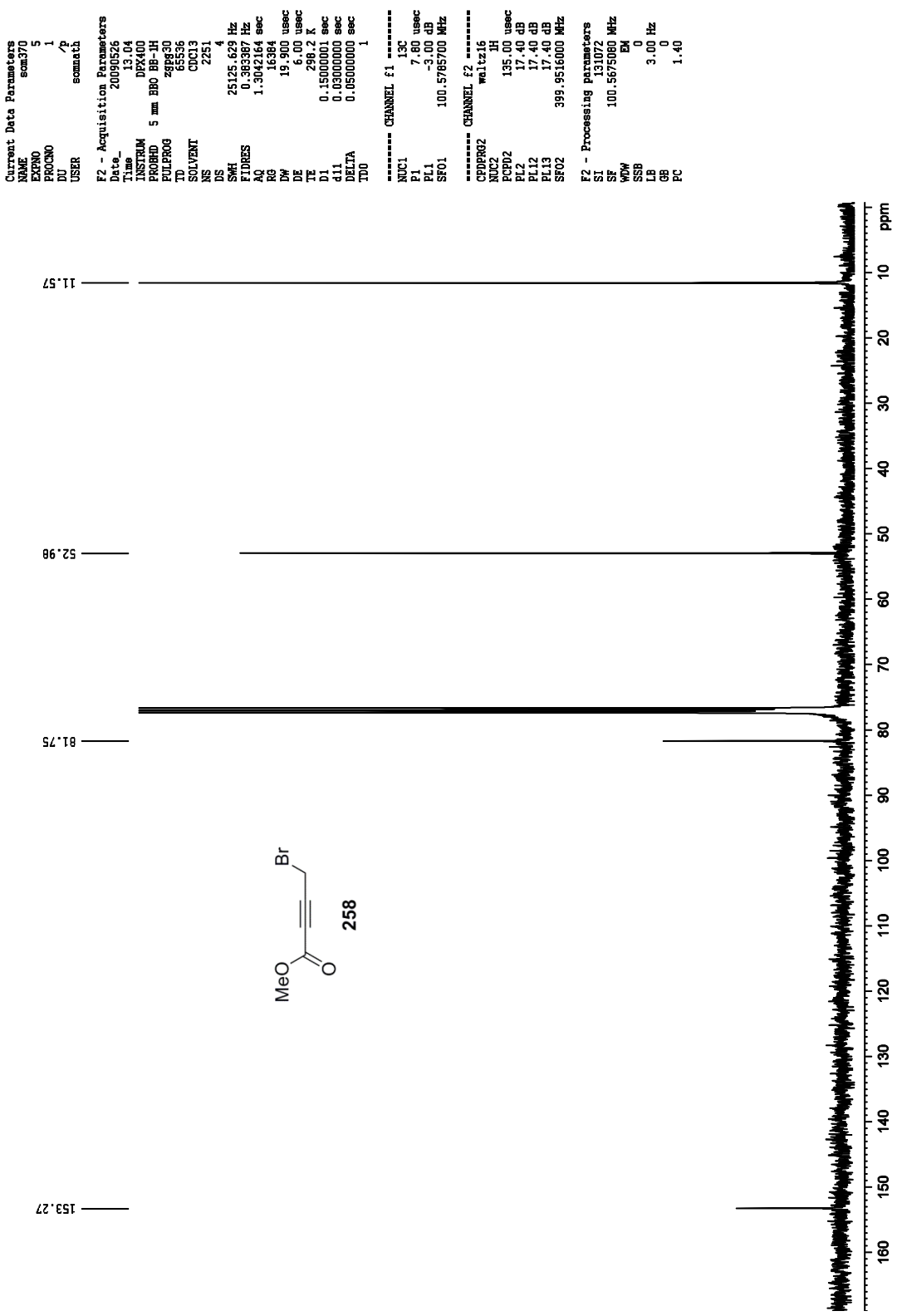

Current Data Parameters
NAME Scm366
EXPNO 1
PROCNO 1
DU /o/diels
USER scmsith
F2 - Acquisition Parameters
Date_ 20090514
Time 14.29
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 24
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 406.4
DW 104.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.541
1.546
1.562
1.566
1.575
1.581
1.607
1.619
1.628
1.647
1.660
1.671
1.675
1.720
1.740
1.751
1.763
1.783
1.794
1.804
1.809
1.816
3.542
3.547
3.565
3.571
3.580
3.583
3.797
3.828
3.836
4.399
4.813
4.822
4.831
7.201
OTHP
MeO
O
261
7.03
1.08
4.18
2.02
1.00
ppm

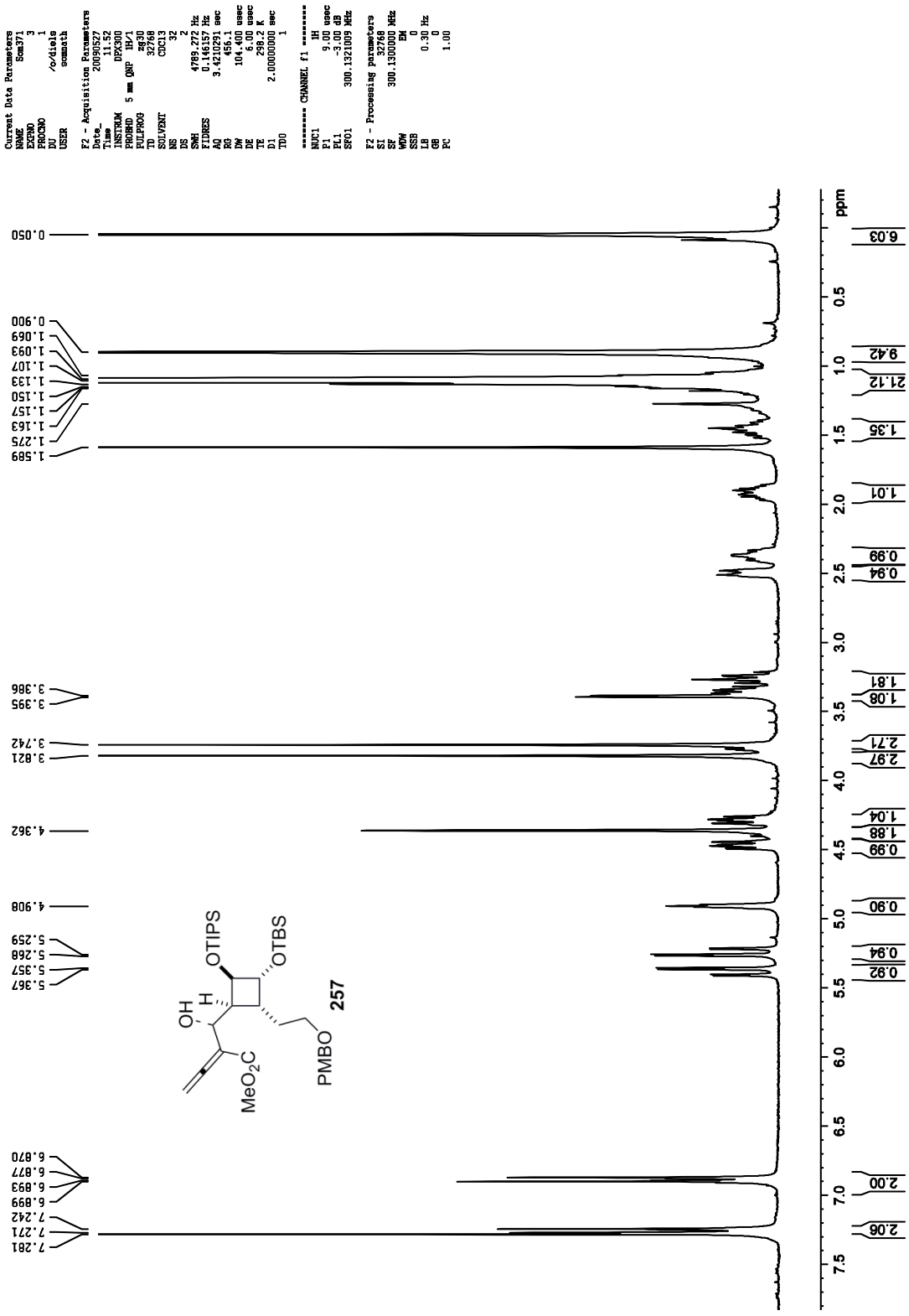

Current Data Parameters
NAME scm366
EXPNO 5
PROCNO 1
DU /p
USER somnath
F2 - Acquisition Parameters
Data_ 20090514
Time_ 20.05
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 2450
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 1310072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
153.63
97.15
83.98
61.97
53.61
52.78
30.04
25.24
18.78
OTHP
MeO
O
261
ppm
78
77
76
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

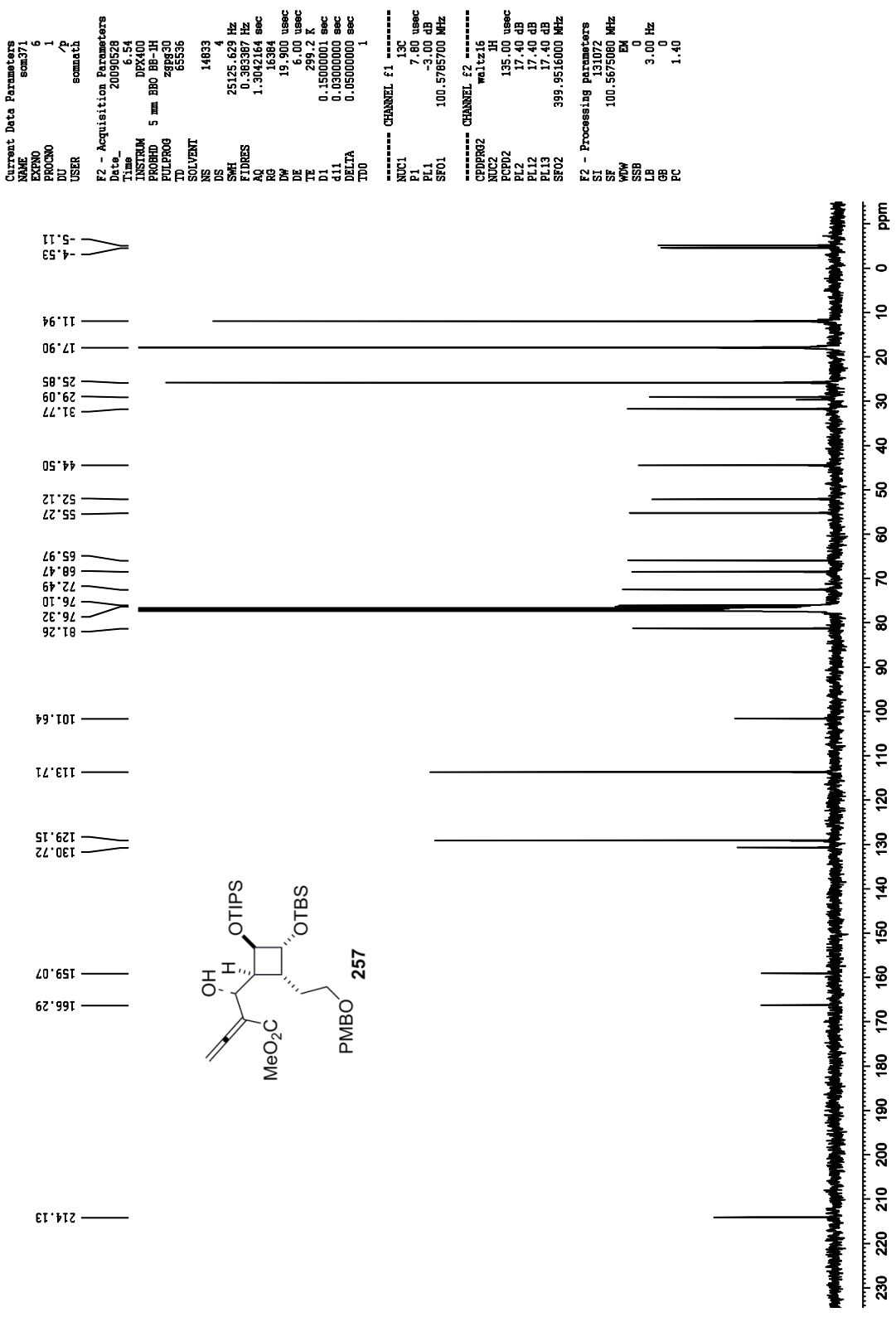

Current Data Parameters
NAME sun357
EXPNO 1
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20090520
Time 15.06
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 13
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.55559540 sec
RG 512
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9528000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
3.81
4.42
OH
MeO
O
262
3.05
2.00
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0

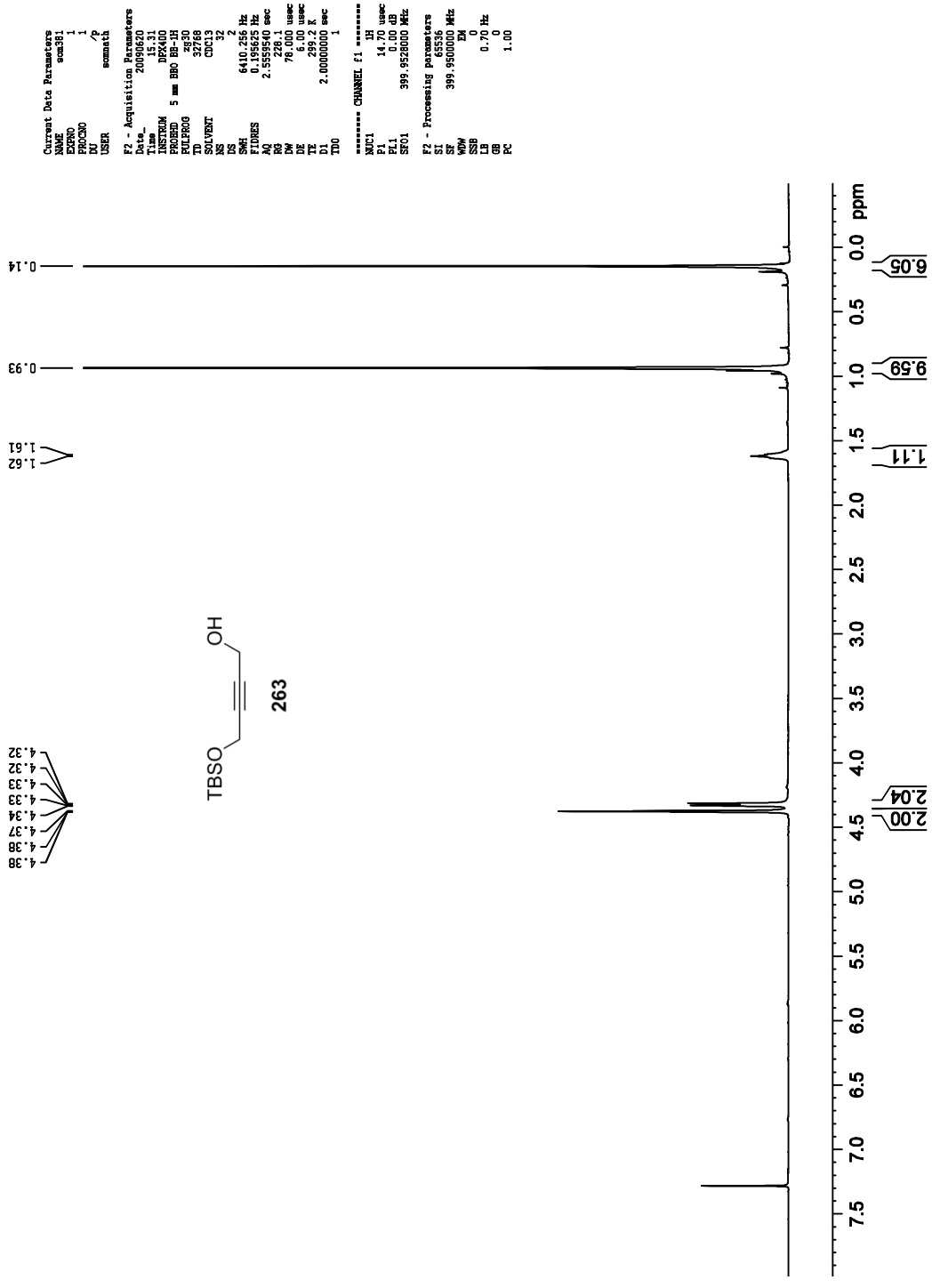

Current Data Parameters
NAME scm367
EXPNO 4
PROCNO 1
DU /p
USER somnath
F2 - Acquisition Parameters
Date_ 20090520
Time 16.40
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 2450
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
153.77
85.71
85.64
52.91
50.65
OH
MeO
O
262
ppm

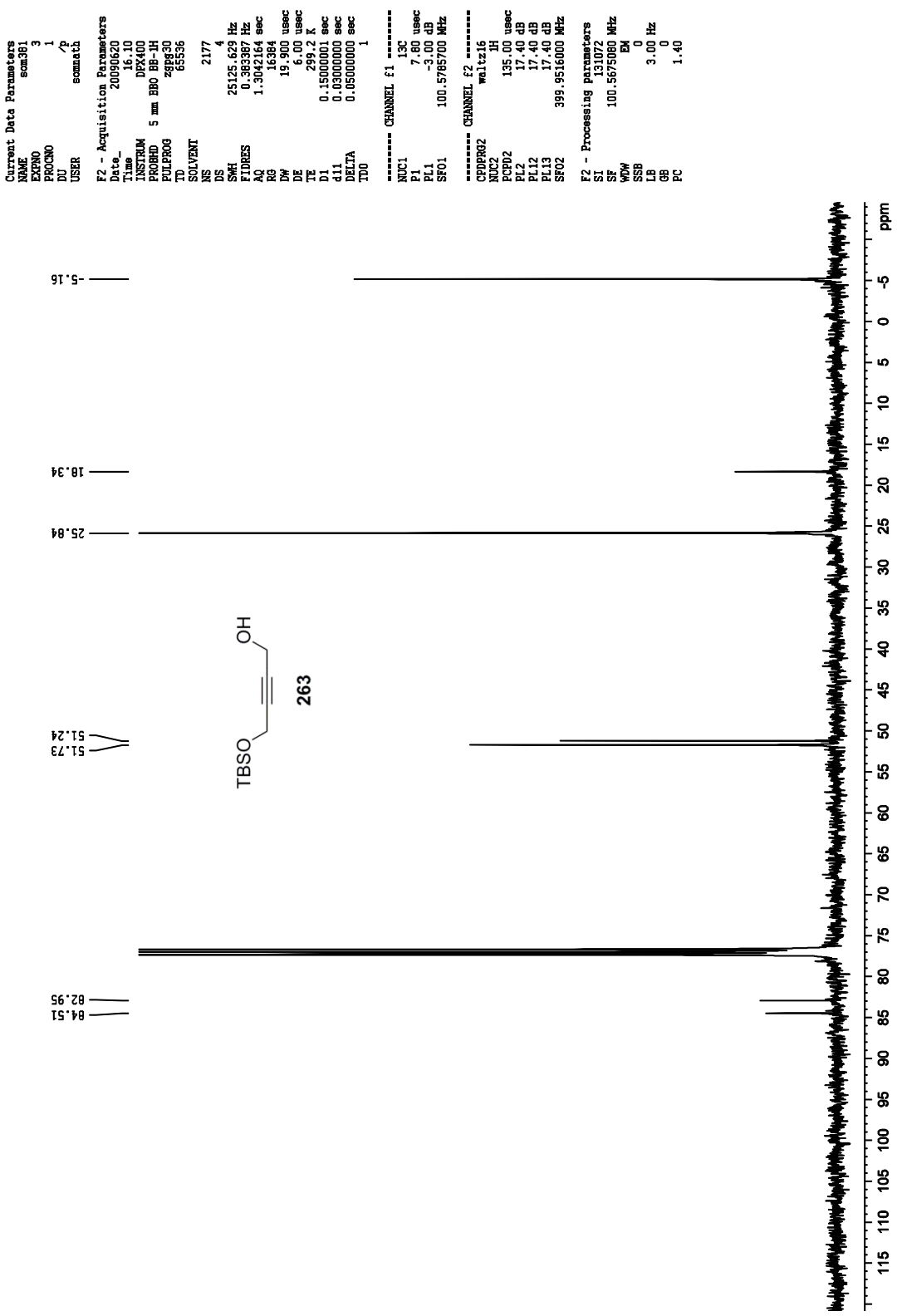

Current Data Parameters
NAME sam370
EXPNO 1
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20090525
Time 11.25
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 1290.2
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9528000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
1.58
3.82
3.98
2.00
3.18
ppm
Br
MeO
O
258

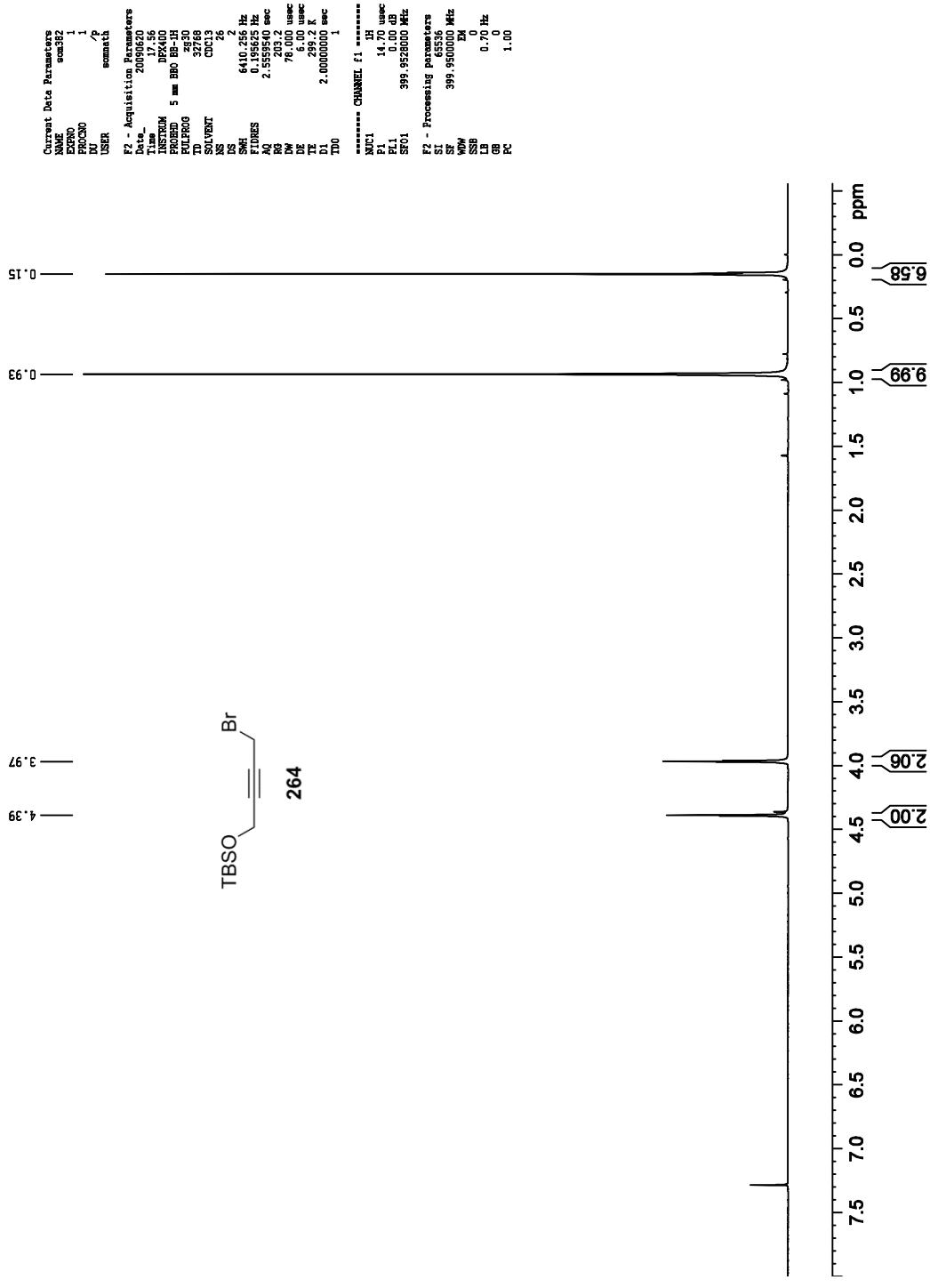

Current Data Parameters
NAME scm370
EXPNO 5
PROCNO 1
DU /p
USER somnath
F2 - Acquisition Parameters
Date_ 20090526
Time 13.04
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2251
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
153.27
81.75
52.98
11.57
ppm
Br
MeO
O
258

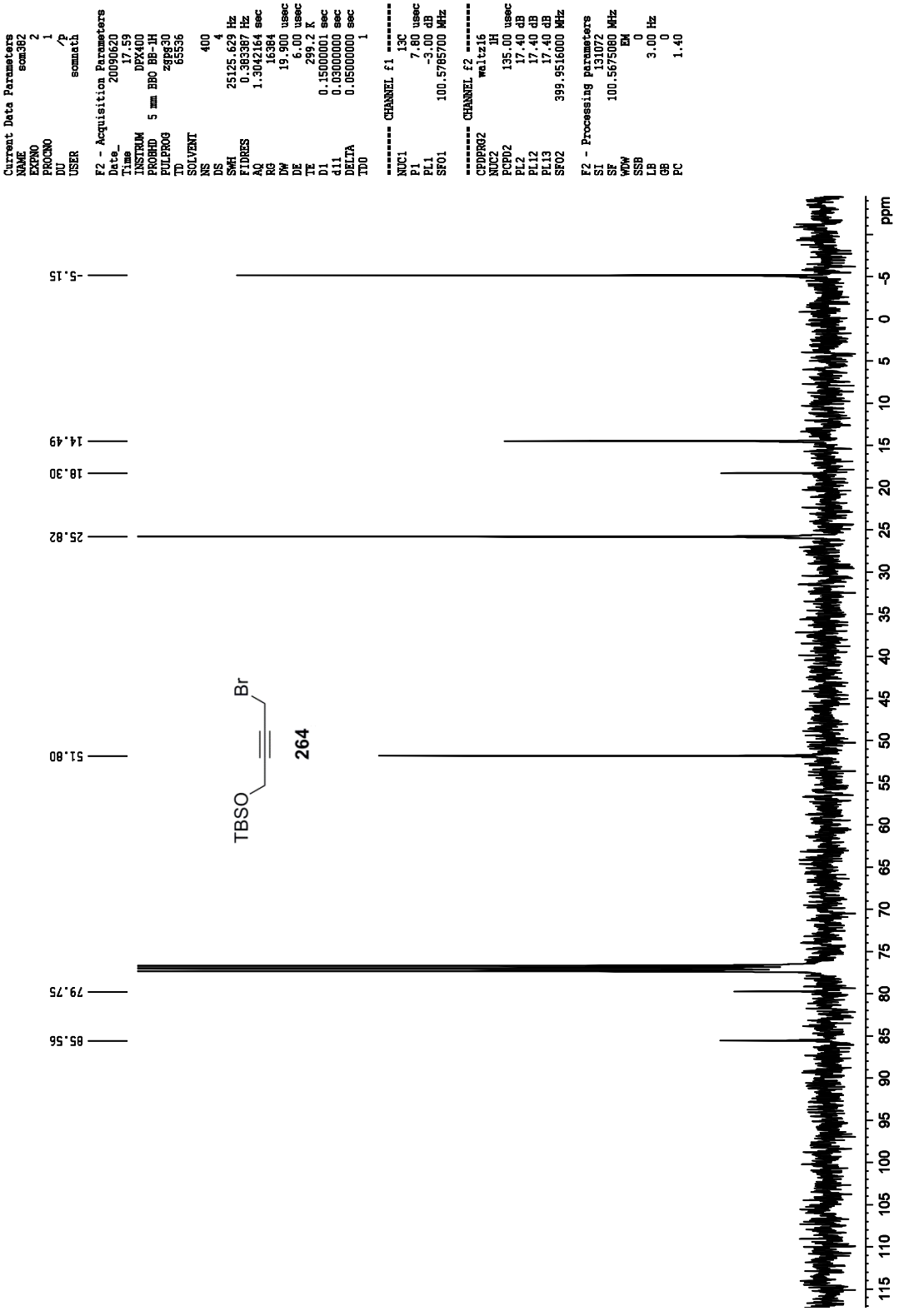

Current Data Parameters
NAME 5ca371
EXPNO 3
PROCNO 1
DU /o/diels
USER somath
F2 - Acquisition Parameters
Date_ 20090527
Time 11.52
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 456.1
DW 104.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.050
0.900
1.069
1.093
1.107
1.133
1.150
1.157
1.163
1.275
1.589
3.386
3.395
3.742
3.821
4.362
4.908
5.259
5.268
5.357
5.367
6.870
6.877
6.893
6.899
7.242
7.271
7.281
OH
H
OTIPS
OTBS
MeO2C
PMBO
257
ppm
6.03
9.42
21.12
1.35
1.01
0.94
0.99
1.81
1.08
2.71
2.97
1.04
1.88
0.99
0.90
0.94
0.92
2.00
2.06

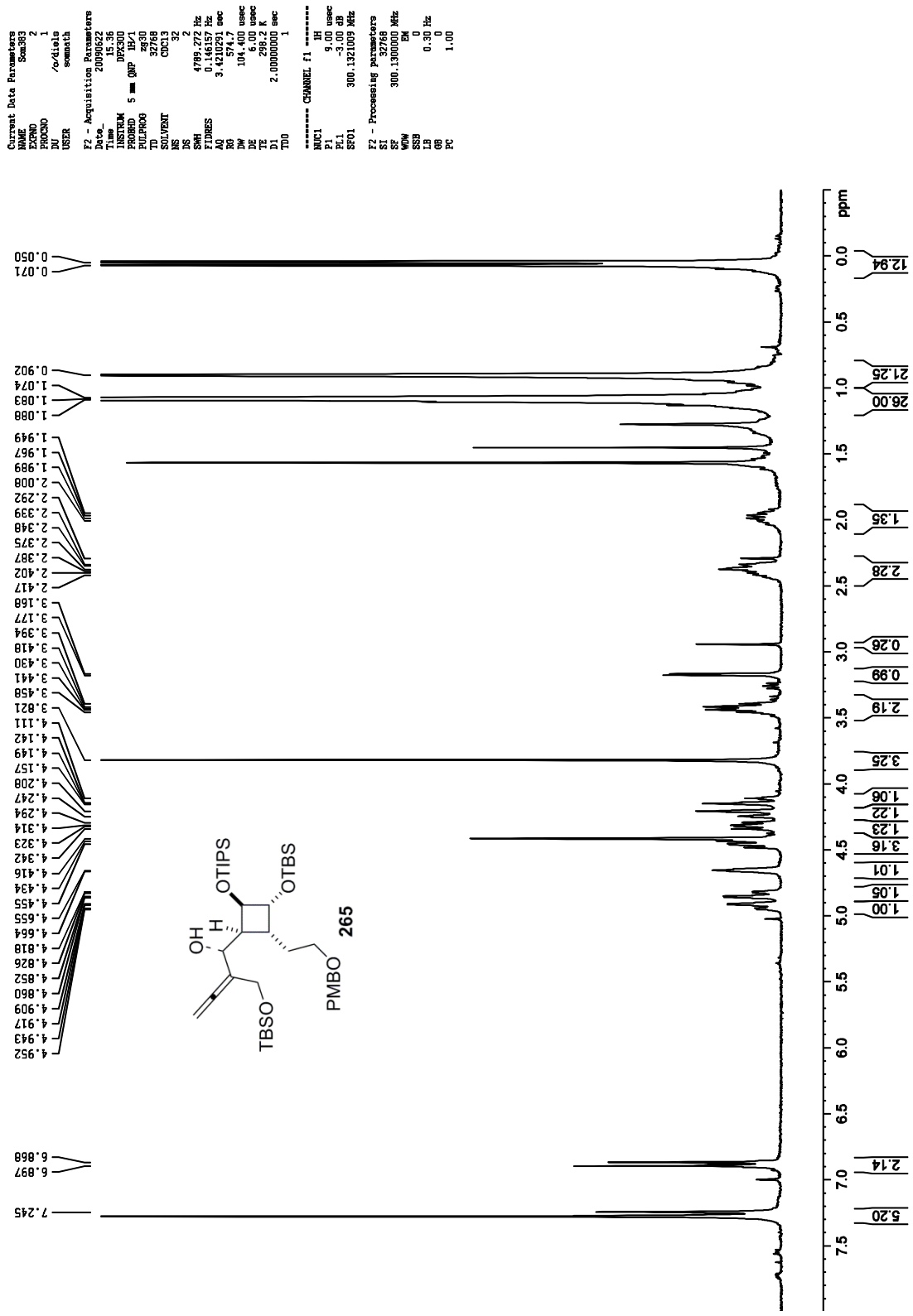

Current Data Parameters
NAME scm371
EXPNO 6
PROCNO 1
DU /p
USER somnath
F2 - Acquisition Parameters
Data_ 20090528
Time 6.54
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 1403
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 299.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.11
-4.53
11.94
17.90
25.85
29.09
31.77
44.50
52.12
55.27
65.97
68.47
72.49
76.10
76.32
81.26
101.64
113.71
129.15
130.72
159.07
166.29
214.13
OH
H
OTIPS
OTBS
MeO2C
PMBO
257
ppm

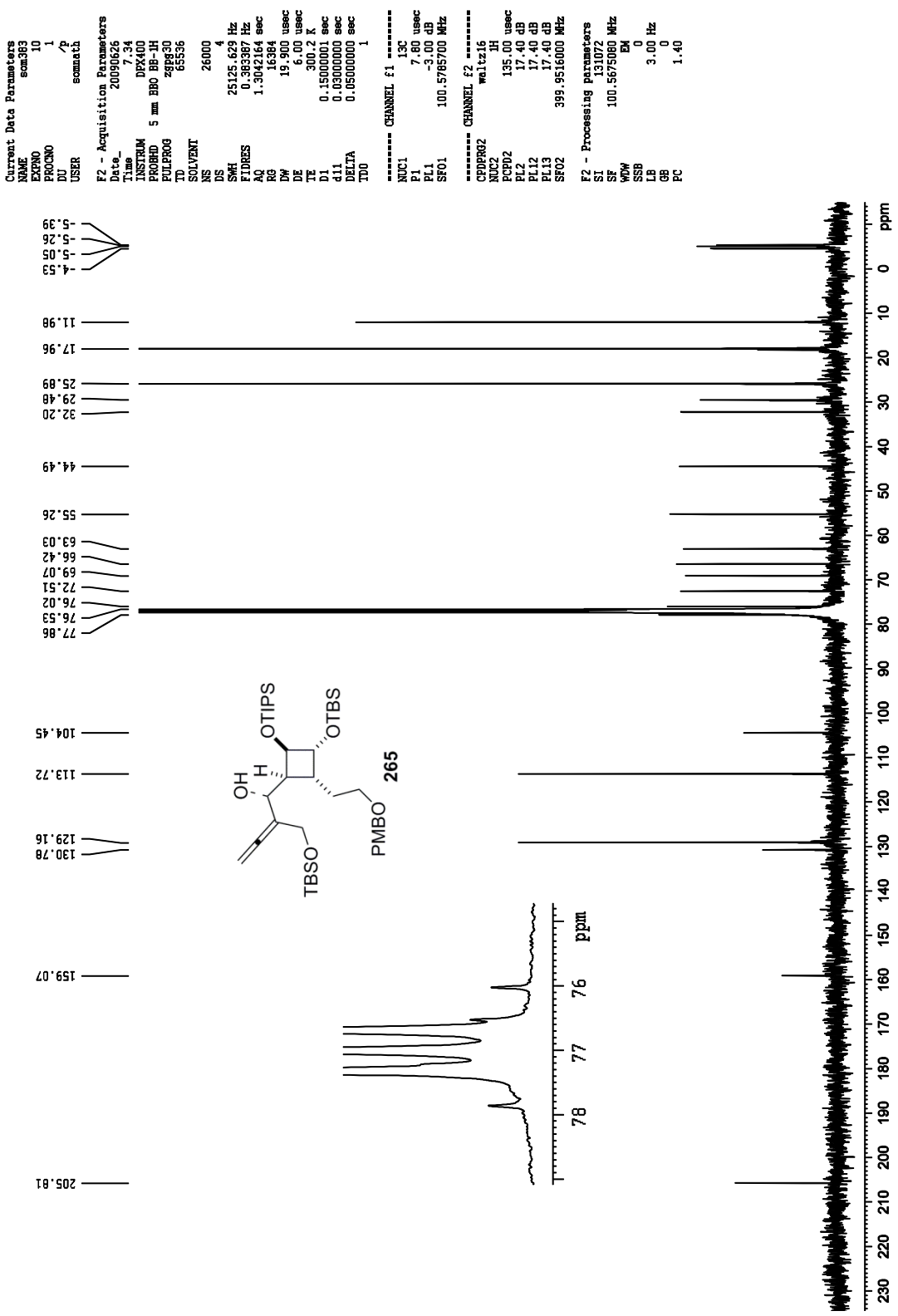

Current Data Parameters
NAME sam381
EXPNO 1
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20090620
Time 15.31
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.55559540 sec
RG 228.1
DW 78.000 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9528000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
0.14
0.93
1.62
1.61
4.38
4.32
4.32
4.33
4.33
4.34
4.37
4.38
4.38
TBSO
OH
263
6.05
9.59
1.11
2.00
2.04
ppm

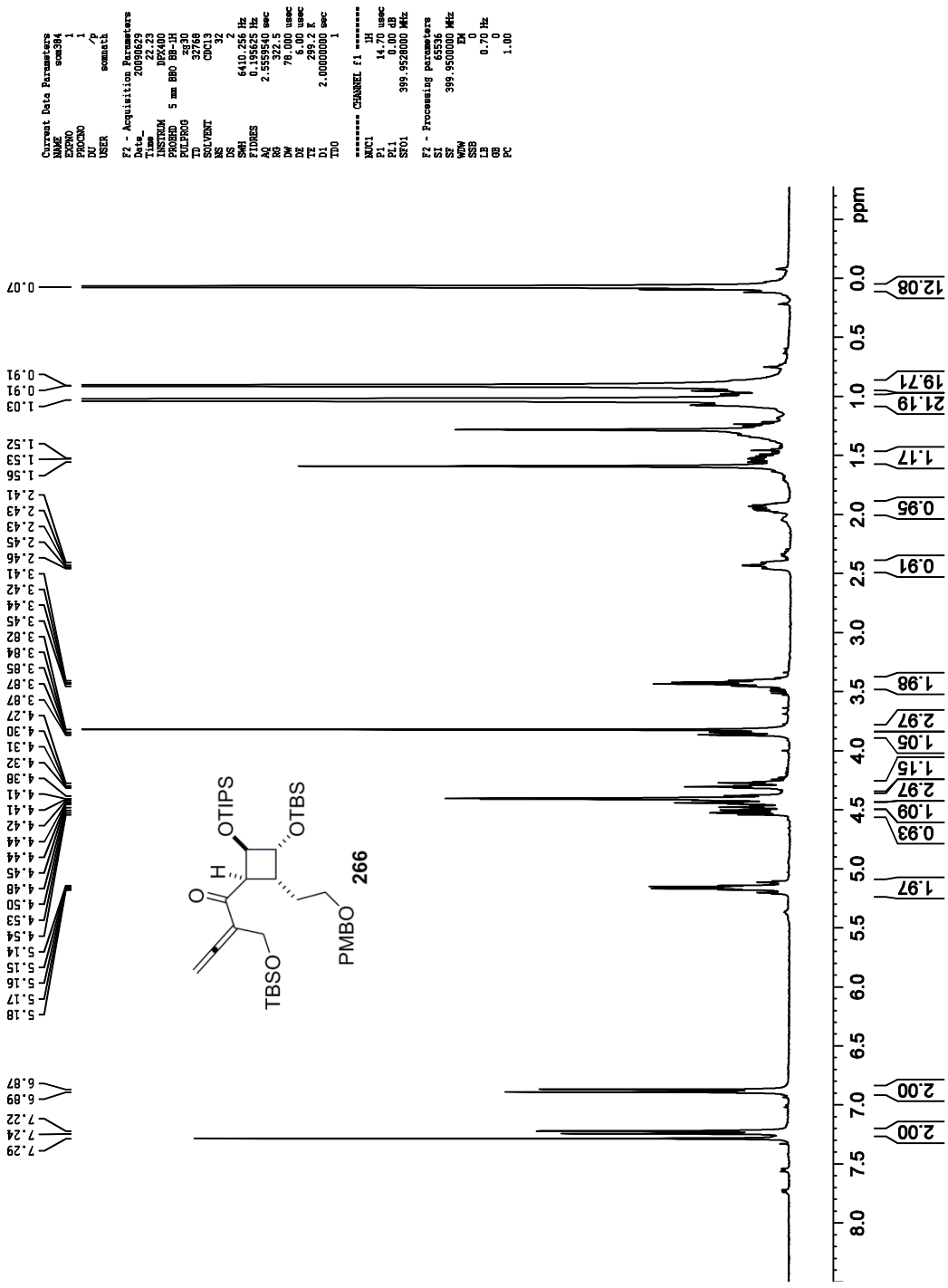

Current Data Parameters
NAME scm381
EXPNO 3
PROCNO 1
DU /p
USER somnath
F2 - Acquisition Parameters
Date_ 20090620
Time 16.10
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 2177
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 299.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 1310072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.16
18.34
25.84
51.73
51.24
82.95
84.51
TBSO
OH
263
ppm

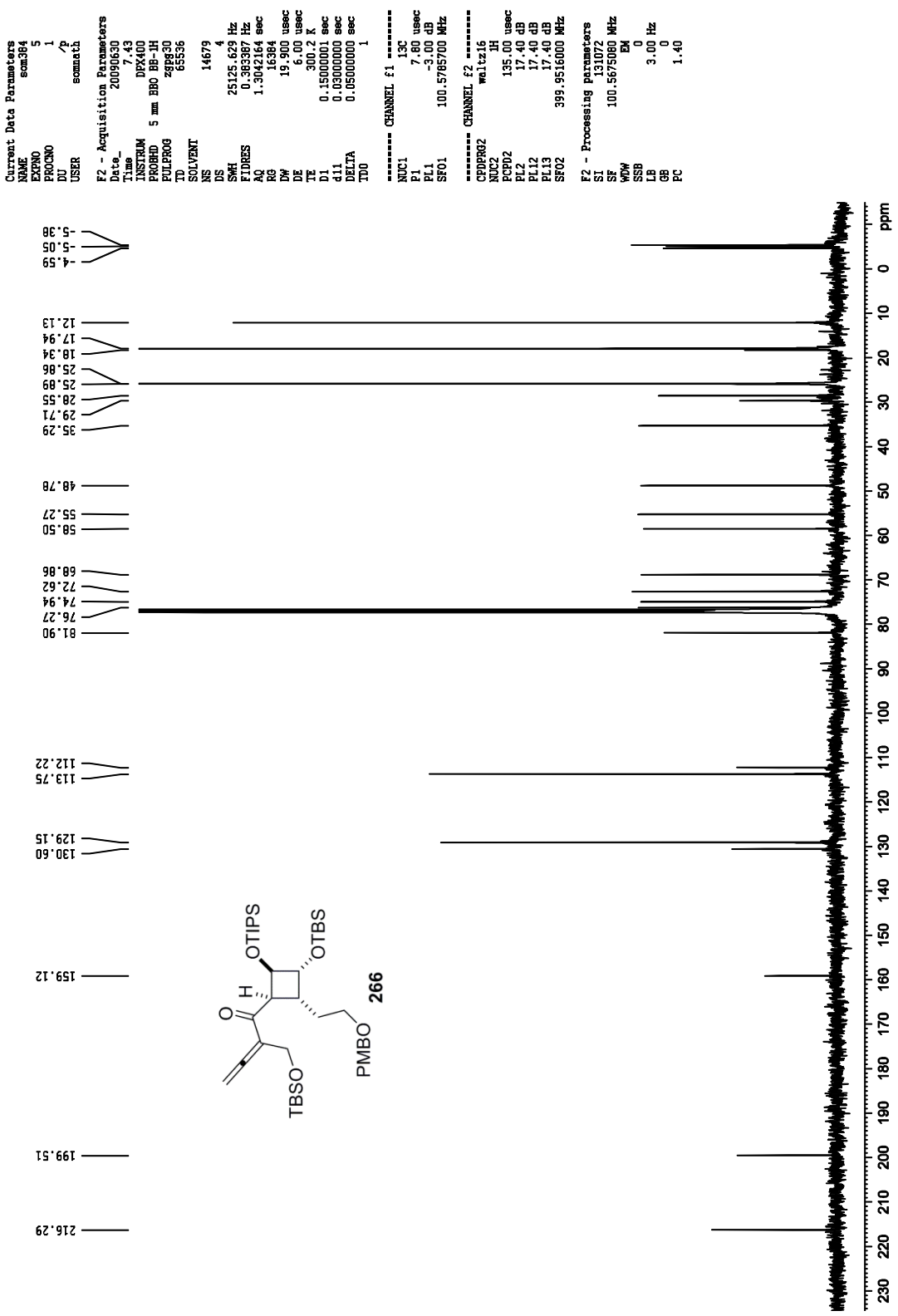

Current Data Parameters
NAME sam382
EXPNO 1
PROCNO 1
DU /p
USER somath
F2 - Acquisition Parameters
Date_ 20090620
Time 17.36
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 26
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 203.2
DW 78.000 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9528000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
0.15
0.93
3.97
4.39
TBSO
Br
264
6.58
9.99
2.06
2.00
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

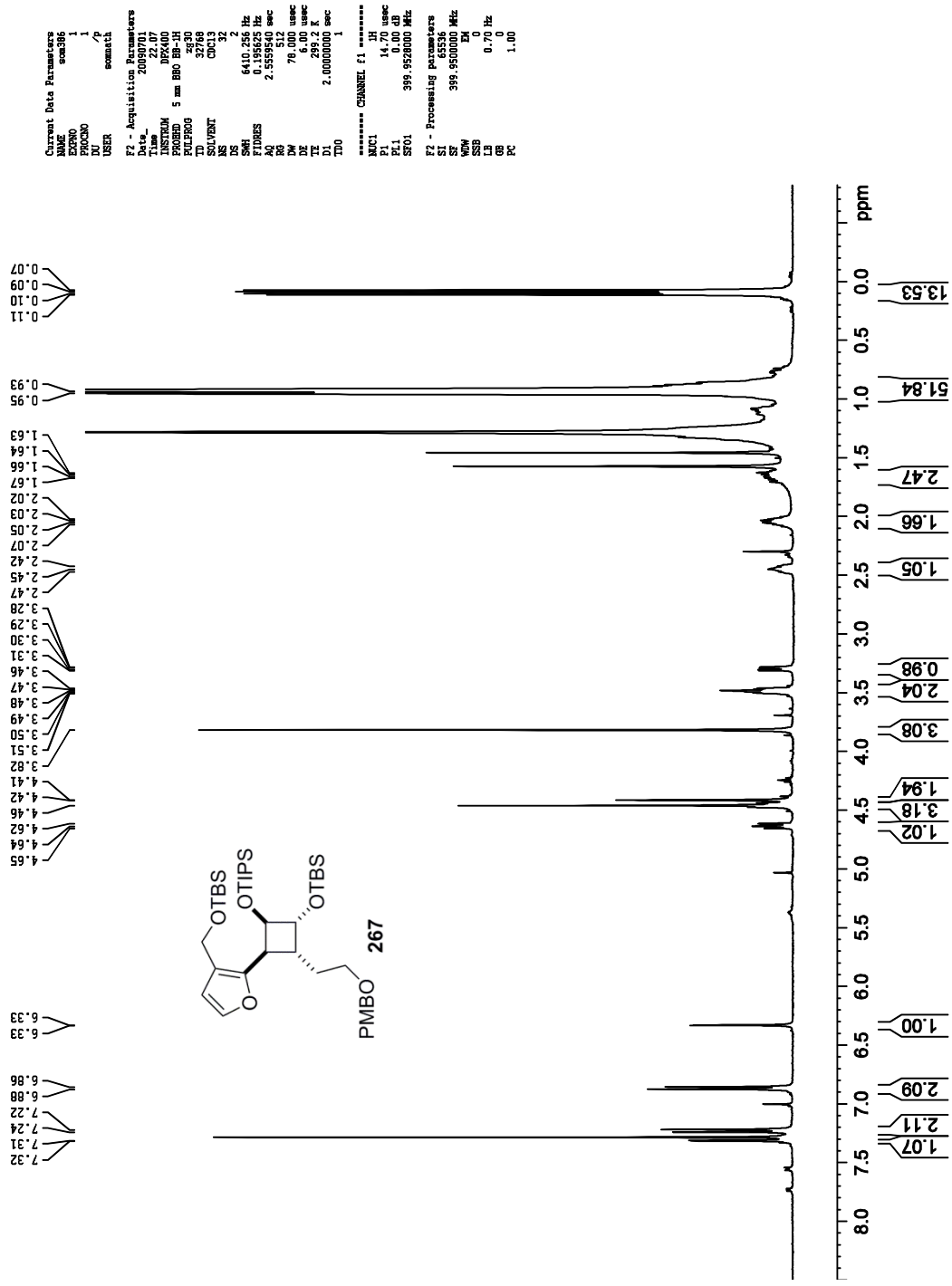

Current Data Parameters
NAME scm382
EXPNO 2
PROCNO 1
DU /p
USER somnath
F2 - Acquisition Parameters
Date_ 20090620
Time 17.59
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 400
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 299.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TDO 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.15
14.49
18.30
25.82
51.80
79.75
85.56
TBSO
Br
264
ppm

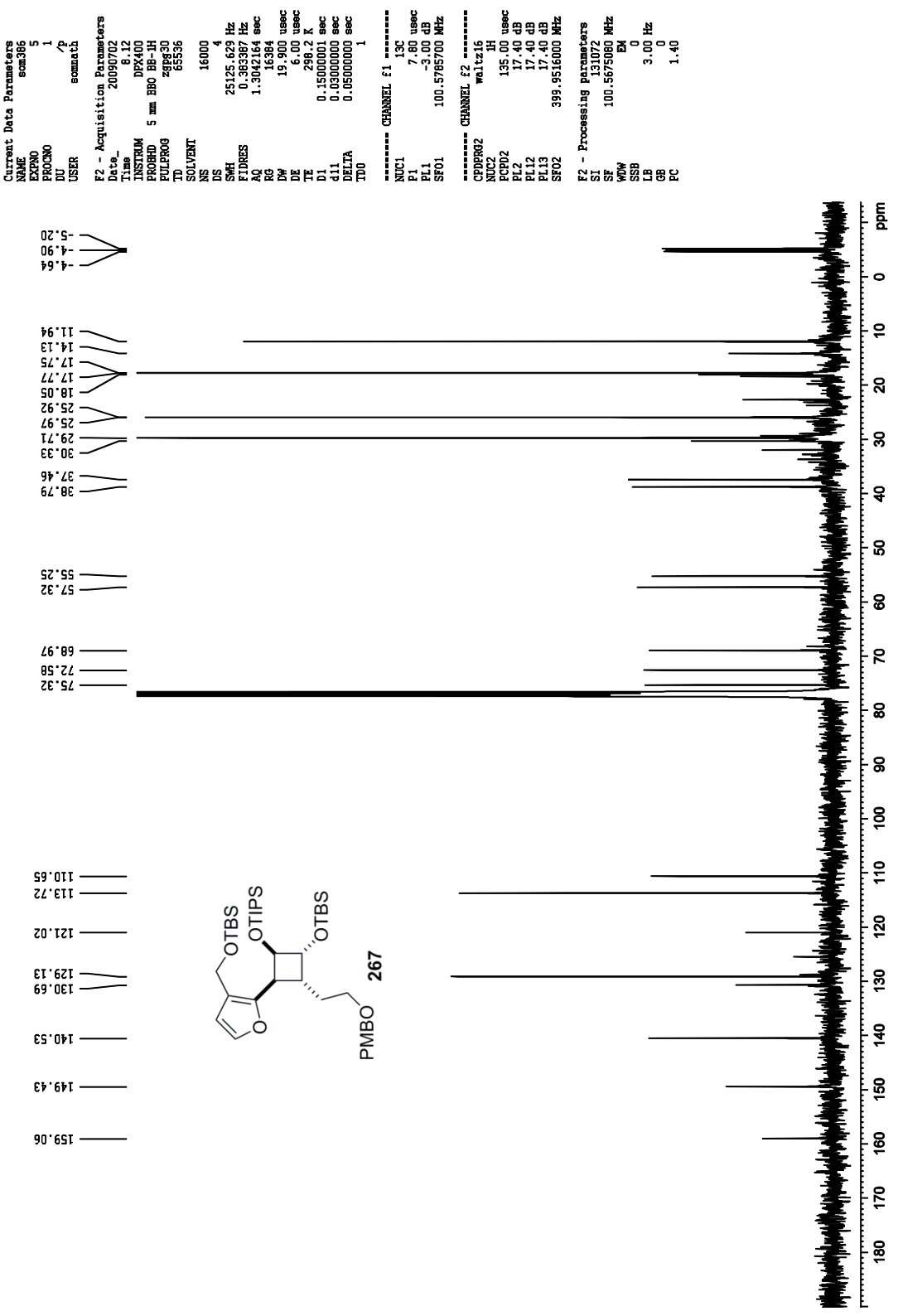

Current Data Parameters
NAME Sca383
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Data_ 20090622
Time 15.36
INSTRUM DPX300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 574.7
DW 104.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -3.00 dB
SFO1 300.1321009 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
H
OTIPS
OTBS
TBSO
PMBO
265
ppm

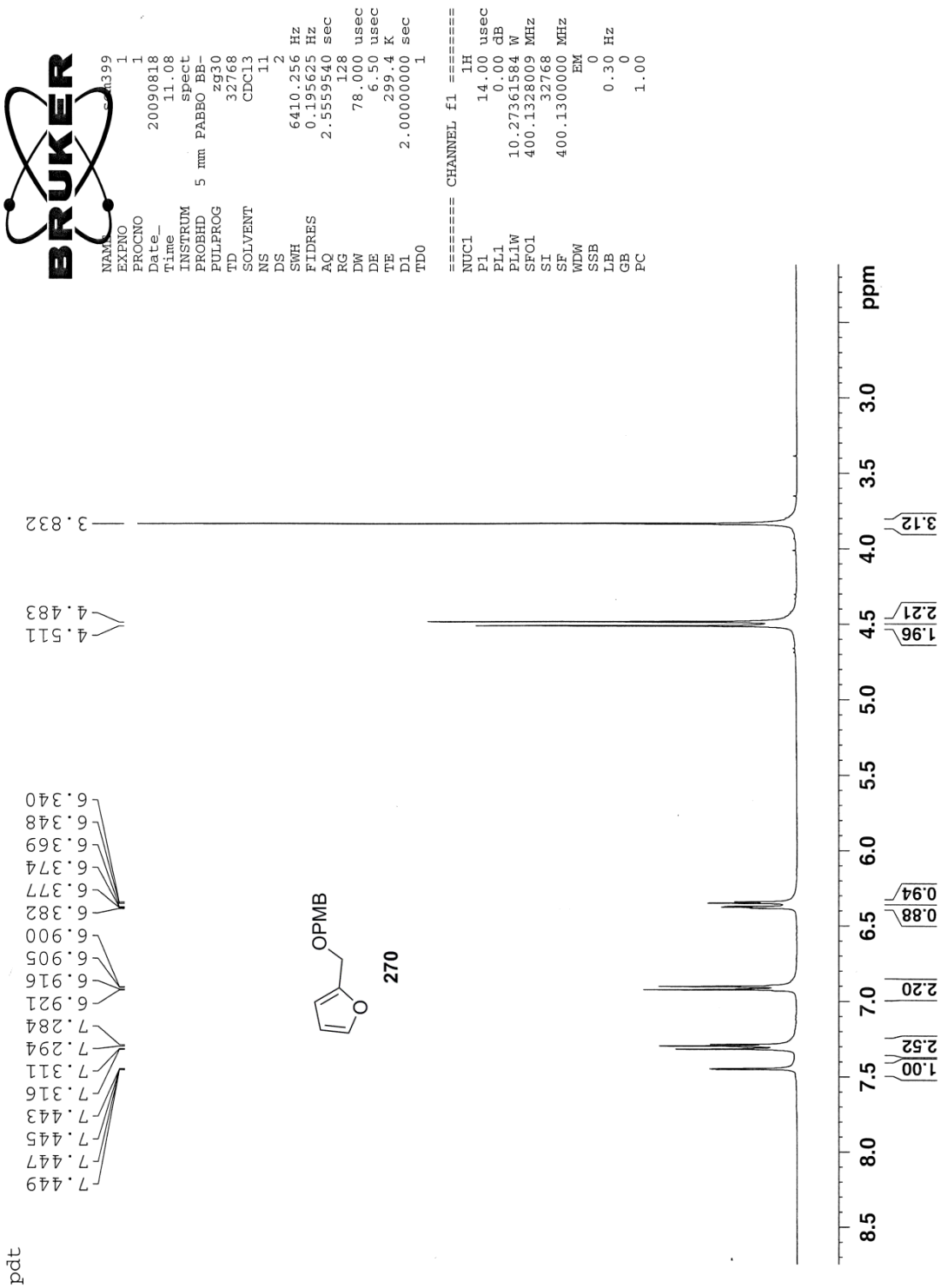

Current Data Parameters
NAME scm383
EXPNO 10
PROCNO 1
DU /p
USER somnath
F2 - Acquisition Parameters
Data_ 20090626
Time 7.34
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 26000
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 300.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-4.53
-5.05
-5.26
-5.39
11.98
17.96
25.89
29.48
32.20
44.49
55.26
63.03
66.42
69.07
72.51
76.02
76.53
77.86
104.45
113.72
129.16
130.78
159.07
205.81
OTIPS
OTBS
OH
H
TBSO
PMBO
265
78
77
76
ppm
ppm

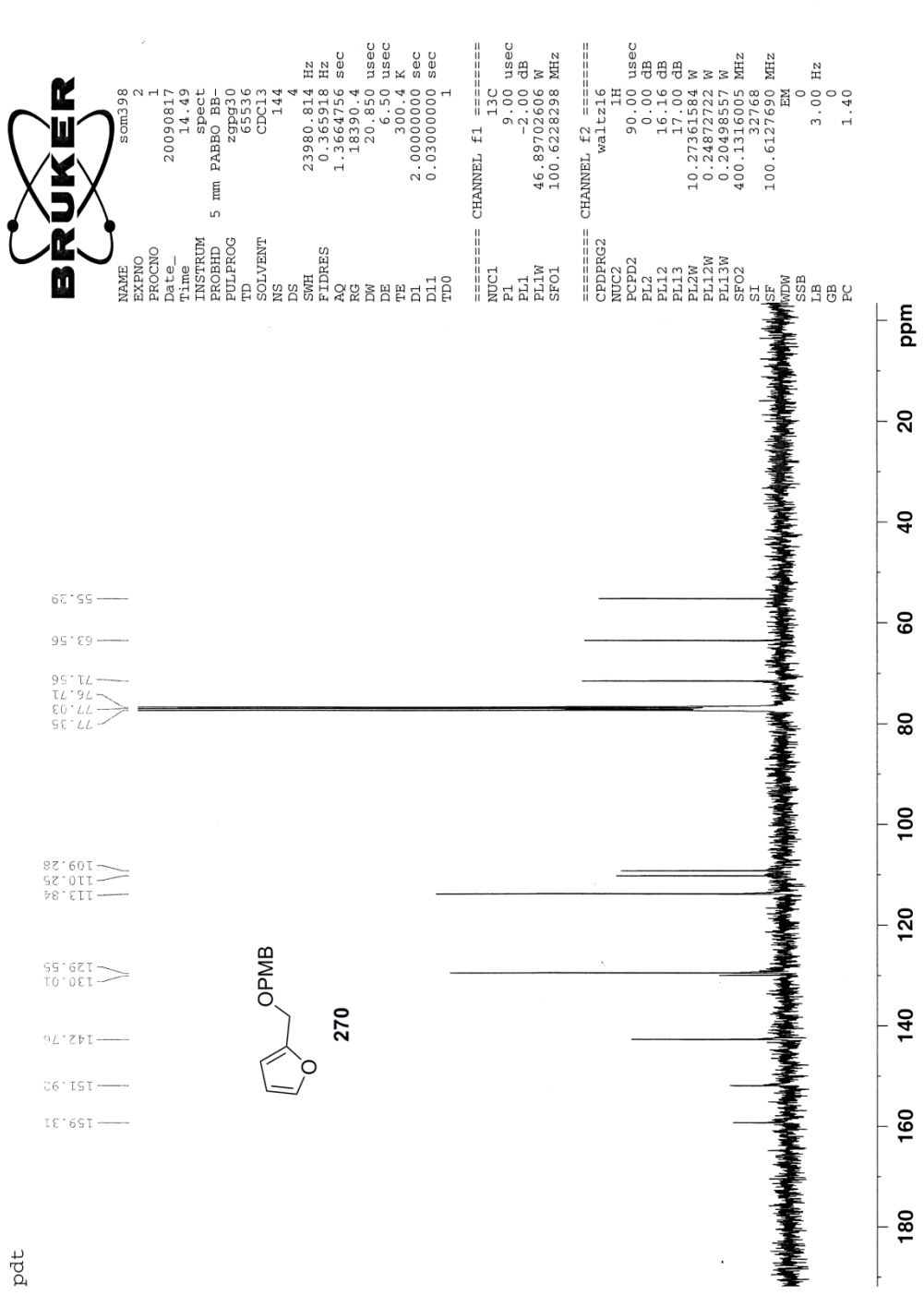

Current Data Parameters
NAME scm384
EXPNO 1
PROCNO 1
DU /p
USER scmatch
F2 - Acquisition Parameters
Date_ 20091629
Time 22.23
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 37.5
DW 78.000 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9520000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
OTIPS
OTBS
H
O
TBSO
PMBO
266
ppm
12.08
19.71
21.19
1.17
0.95
0.91
1.98
2.97
1.05
1.15
2.97
0.93
1.09
1.97
2.00
2.00


Current Data Parameters
NAME scm384
EXPNO 5
PROCNO 1
DU /p
USER somnath
F2 - Acquisition Parameters
Data_ 20090630
Time_ 7.43
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 14679
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 300.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.38
-5.05
-4.59
12.13
17.94
18.34
25.86
25.89
28.55
29.71
35.29
48.78
55.27
58.50
68.86
72.62
74.94
76.27
81.90
112.22
113.75
129.15
130.60
159.12
199.51
216.29
ppm
OTIPS
OTBS
H
O
TBSO
PMBO
266

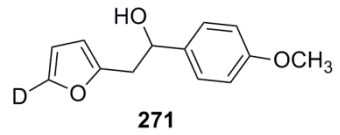

Current Data Parameters
NAME scm396
EXPNO 1
PROCNO 1
DU /p
USER scmatch
F2 - Acquisition Parameters
Date_ 20091701
Time 22.27
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 52
DW 78.000 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
SFO1 399.9520000 MHz
F2 - Processing parameters
SI 65536
SF 399.9500000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00
OTBS
OTIPS
OTBS
PMBO
267
ppm
13.53
51.84
2.47
1.66
1.05
0.98
2.04
3.08
1.94
3.18
1.02
1.00
2.09
2.11
1.07


Current Data Parameters
NAME scm386
EXPNO 5
PROCNO 1
DU /p
USER somnath
F2 - Acquisition Parameters
Data_ 20090702
Time 8.12
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 16000
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.20
-4.90
-4.64
11.94
14.13
17.75
17.77
18.05
25.92
25.97
29.71
30.33
37.46
38.79
55.25
57.32
68.97
72.58
75.32
110.65
113.72
121.02
129.13
130.69
140.53
149.43
159.06
OTBS
OTIPS
OTBS
O
PMBO
267
ppm


BRUKER
NAME pdt399
EXPNO 1
PROCNO 1
Date_ 20090818
Time 11.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 11
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 128
DW 78.000 usec
DE 6.50 usec
TE 299.4 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
PL1W 10.27361584 W
SFO1 400.1328009 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
pdt
7.449
7.447
7.445
7.443
7.316
7.311
7.294
7.284
6.921
6.916
6.905
6.900
6.382
6.377
6.374
6.369
6.348
6.340
4.511
4.483
3.832
OPMB
O
270
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
1.00
2.52
2.20
0.94
0.88
1.96
2.21
3.12


pdt
BRUKER
NAME som398
EXPNO 2
PROCNO 1
Date_ 20090817
Time 14.49
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 144
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 18390.4
DW 20.850 usec
DE 6.50 usec
TE 300.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -2.00 dB
PL1W 46.89702606 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 16.16 dB
PL13 17.00 dB
PL2W 10.27361584 W
PL12W 0.24872722 W
PL13W 0.20498557 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
OPMB
270
159.31
151.92
142.76
130.01
129.55
113.84
110.25
109.28
77.35
77.03
76.71
71.56
63.56
55.29
180
160
140
120
100
80
60
40
20
ppm

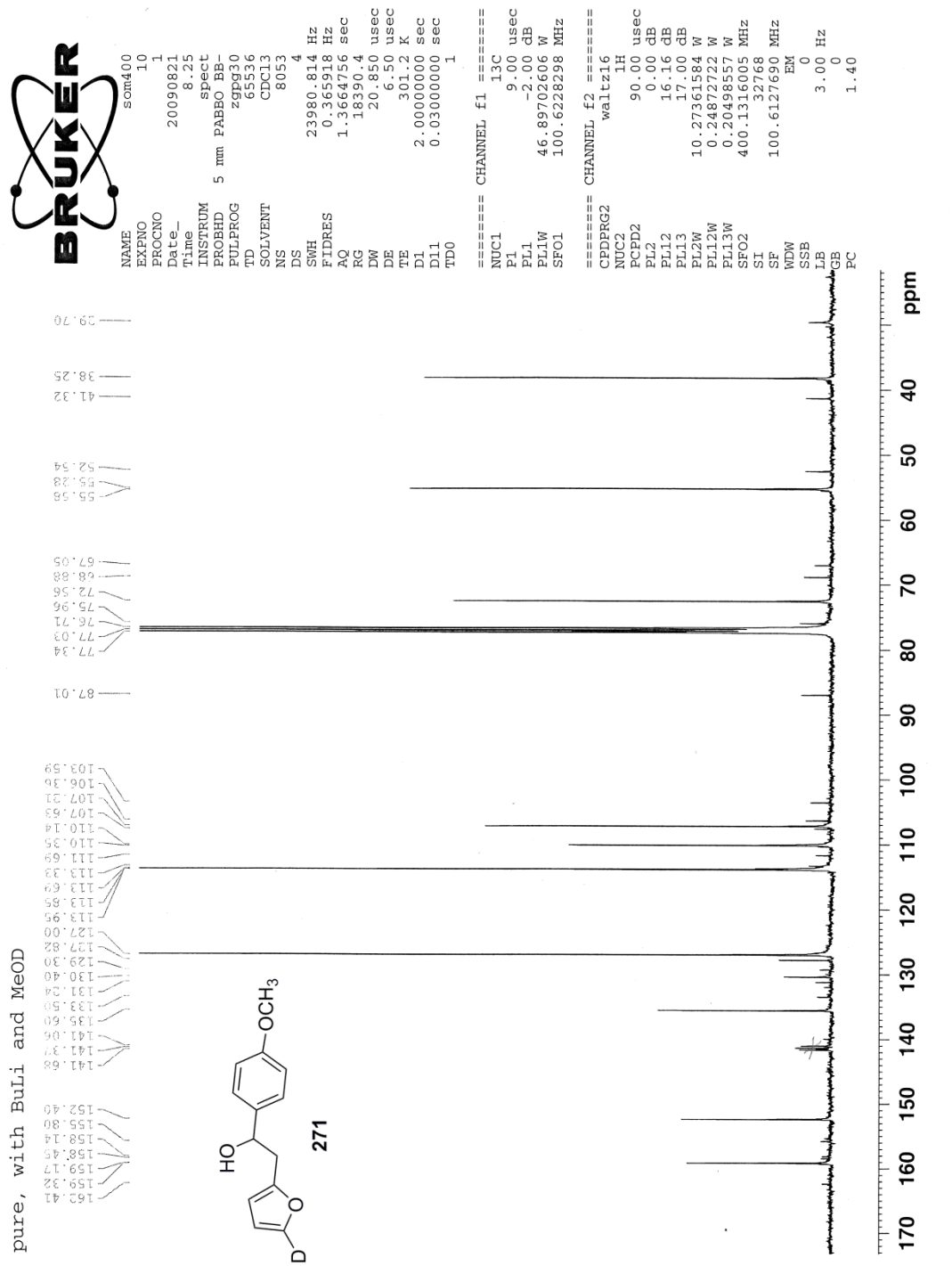
crude, with BuLi and MeOD

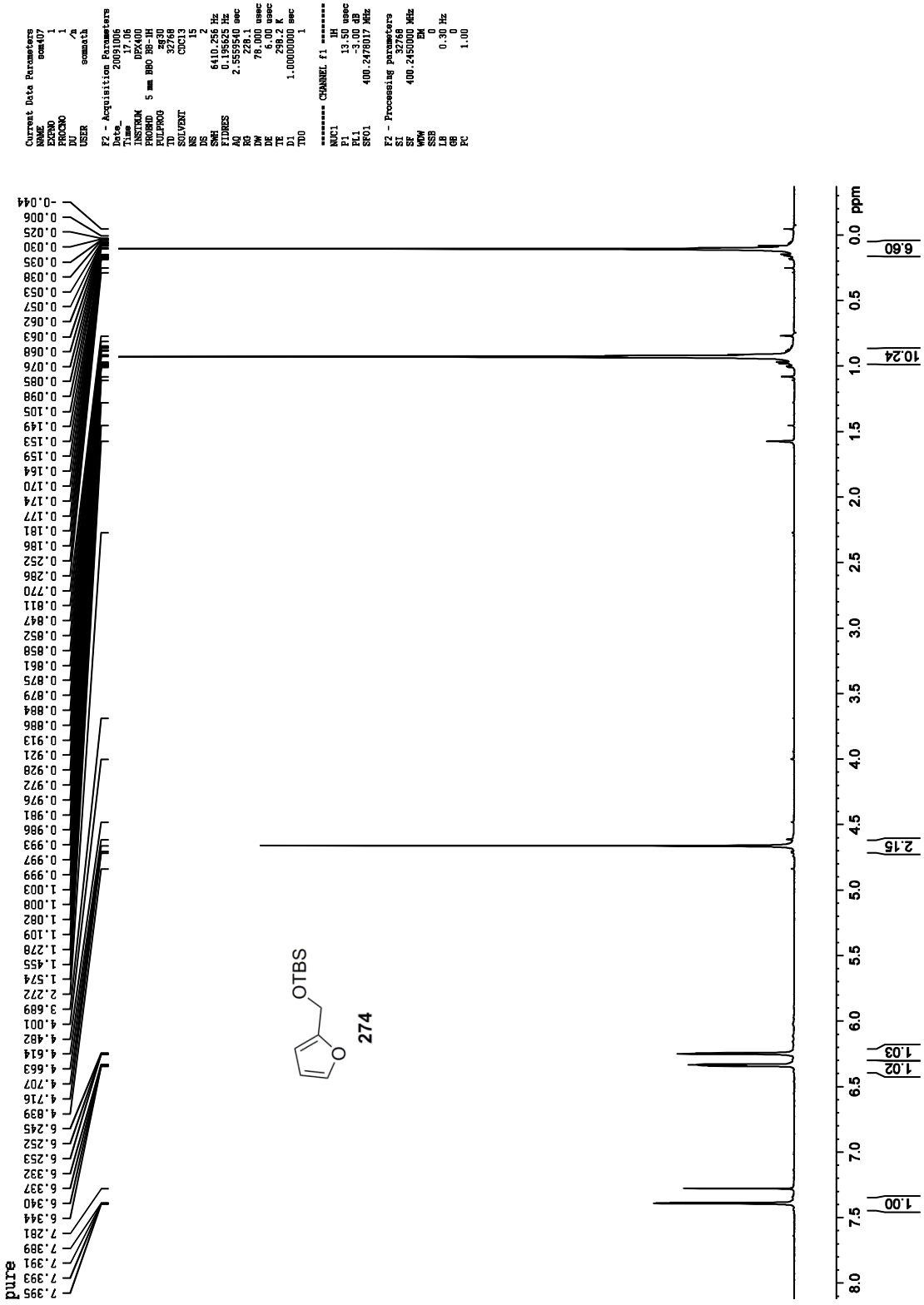


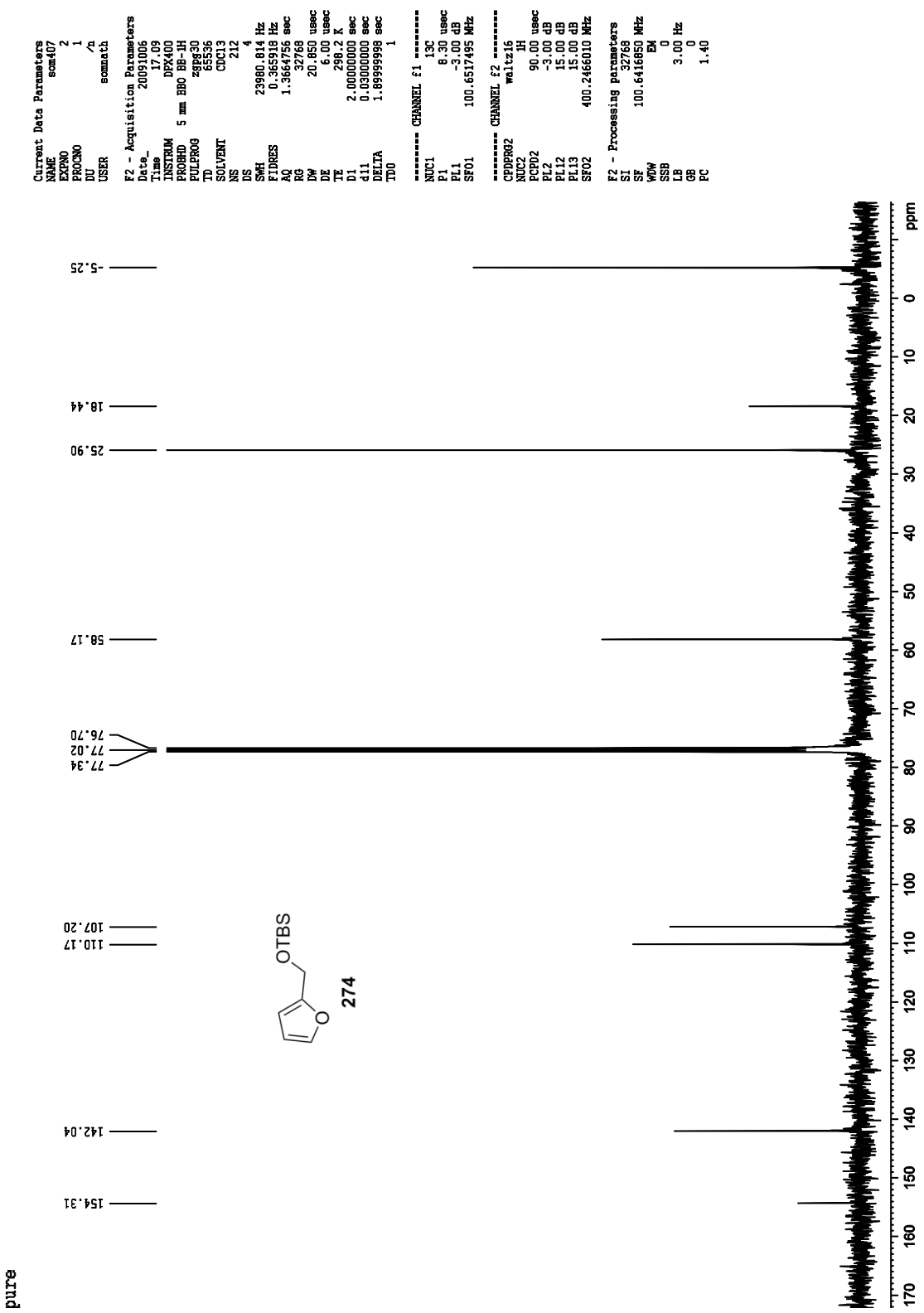
271

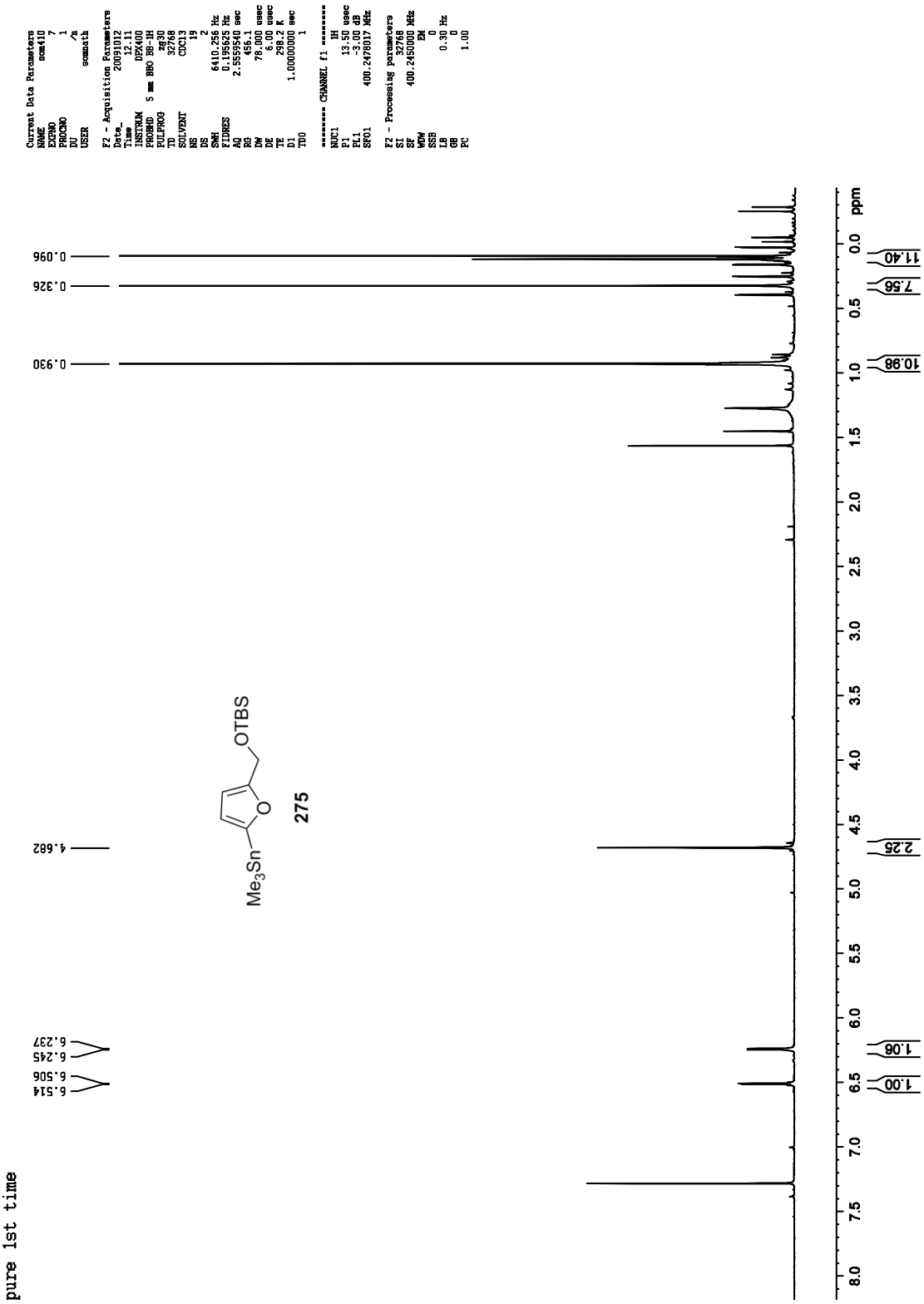
BRUKER

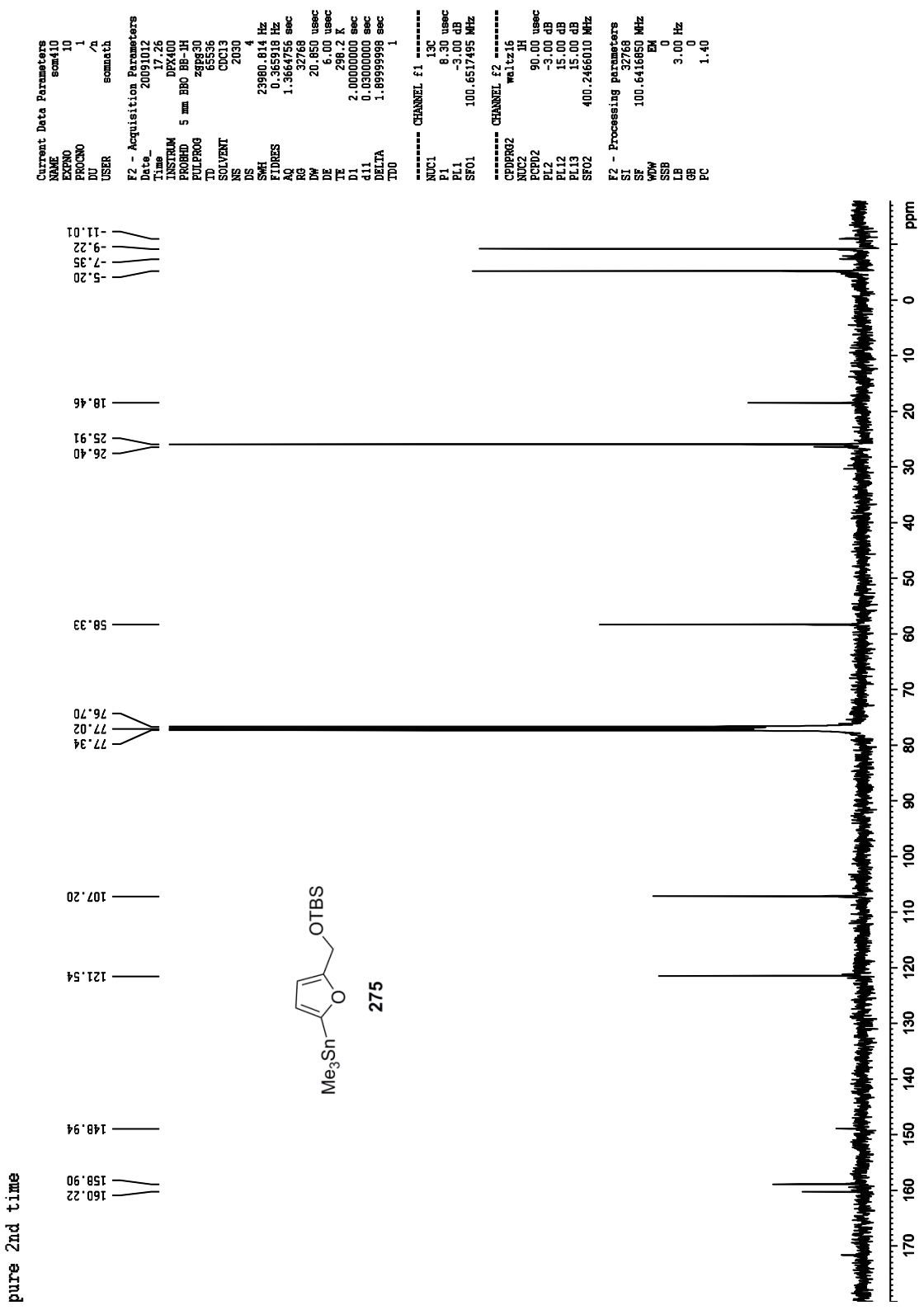
NAME	som400
EXPNO	3
PROCNO	1
Date_	20090820
Time	9.03
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	2
SWH	6410.256 Hz
FIDRES	0.195625 Hz
AQ	2.5559540 sec
RG	114
DW	78.000 usec
DE	6.50 usec
TE	299.5 K
D1	2.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.00 usec
PL1	0.00 dB
PL1W	10.27361584 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

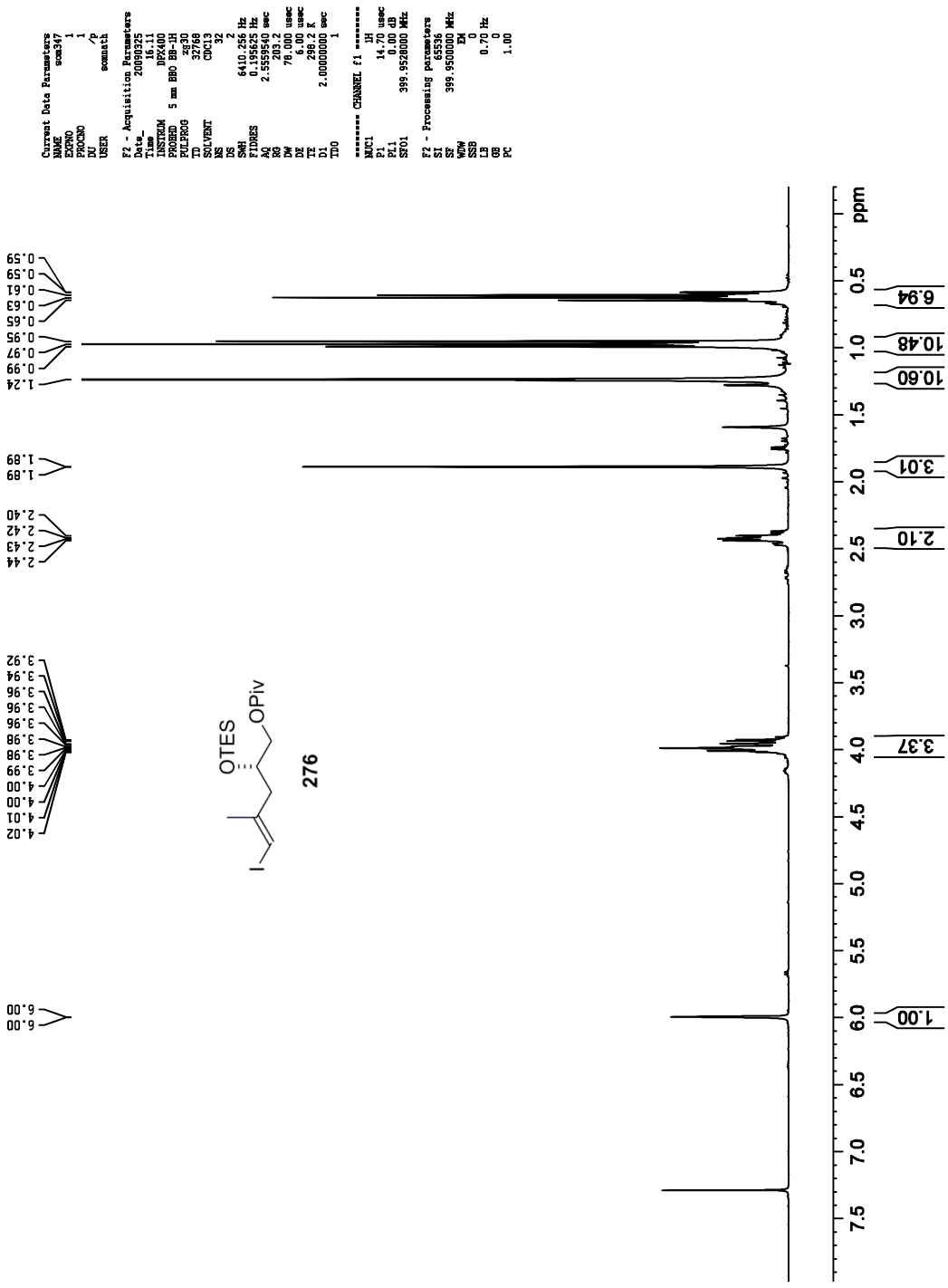

pure, with BuLi and MeOD
271
OCH3
HO
D
ppm

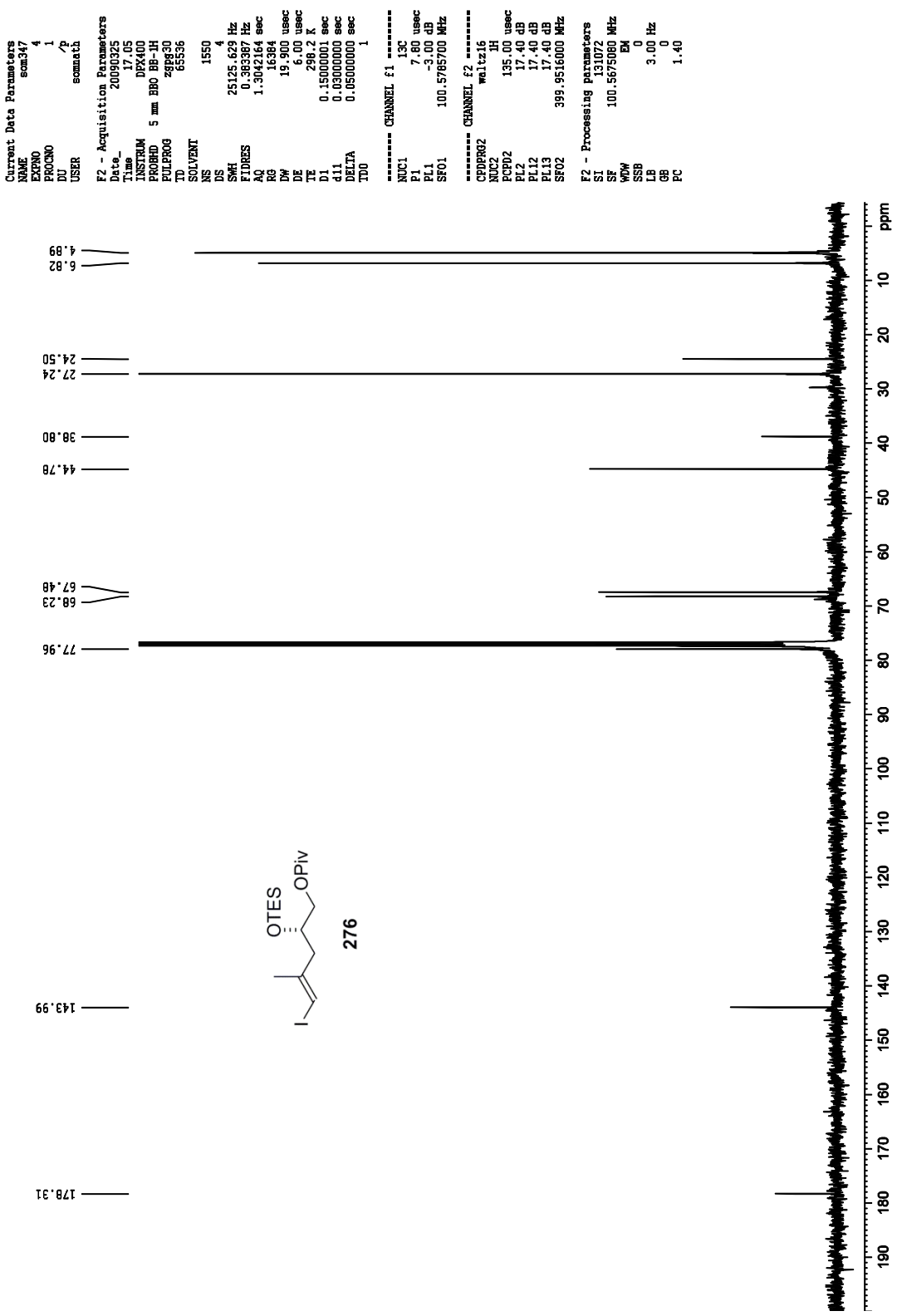

Current Data Parameters
NAME scott07
EXPNO 1
PROCNO 1
DU /a
USER somsath
F2 - Acquisition Parameters
Date_ 20091006
Time 17.06
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 15
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 228.1
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
274
pure
6.60
10.24
2.15
1.03
1.02
1.00
ppm

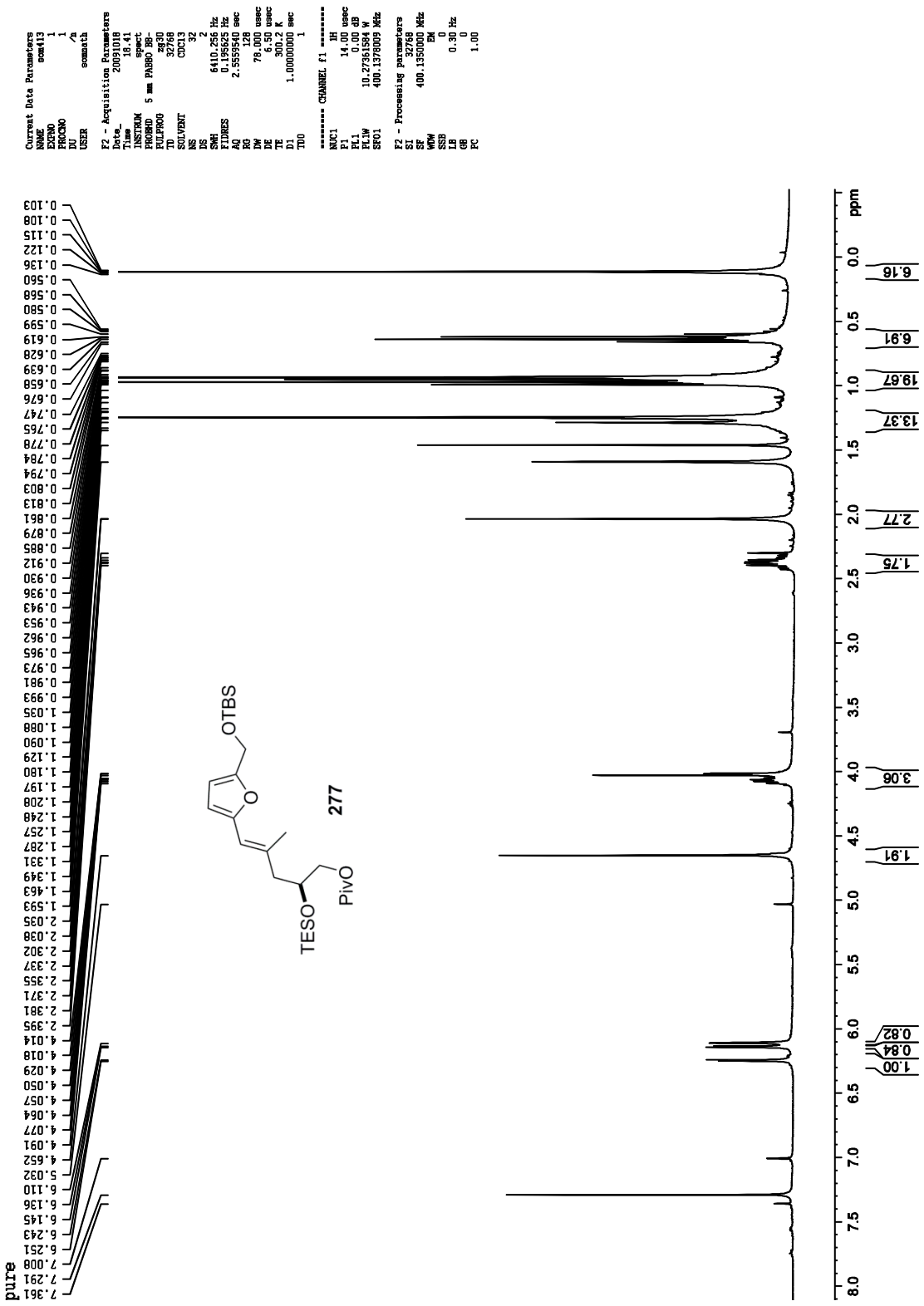

Current Data Parameters
NAME scm407
EXPNO 2
PROCNO 1
DU /n
USER somnath
F2 - Acquisition Parameters
Date_ 20091006
Time 17.09
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 212
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 32768
DW 20.850 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.25
18.44
25.90
58.17
76.70
77.02
77.34
107.20
110.17
142.04
154.31
OTBS
O
274
ppm
pure

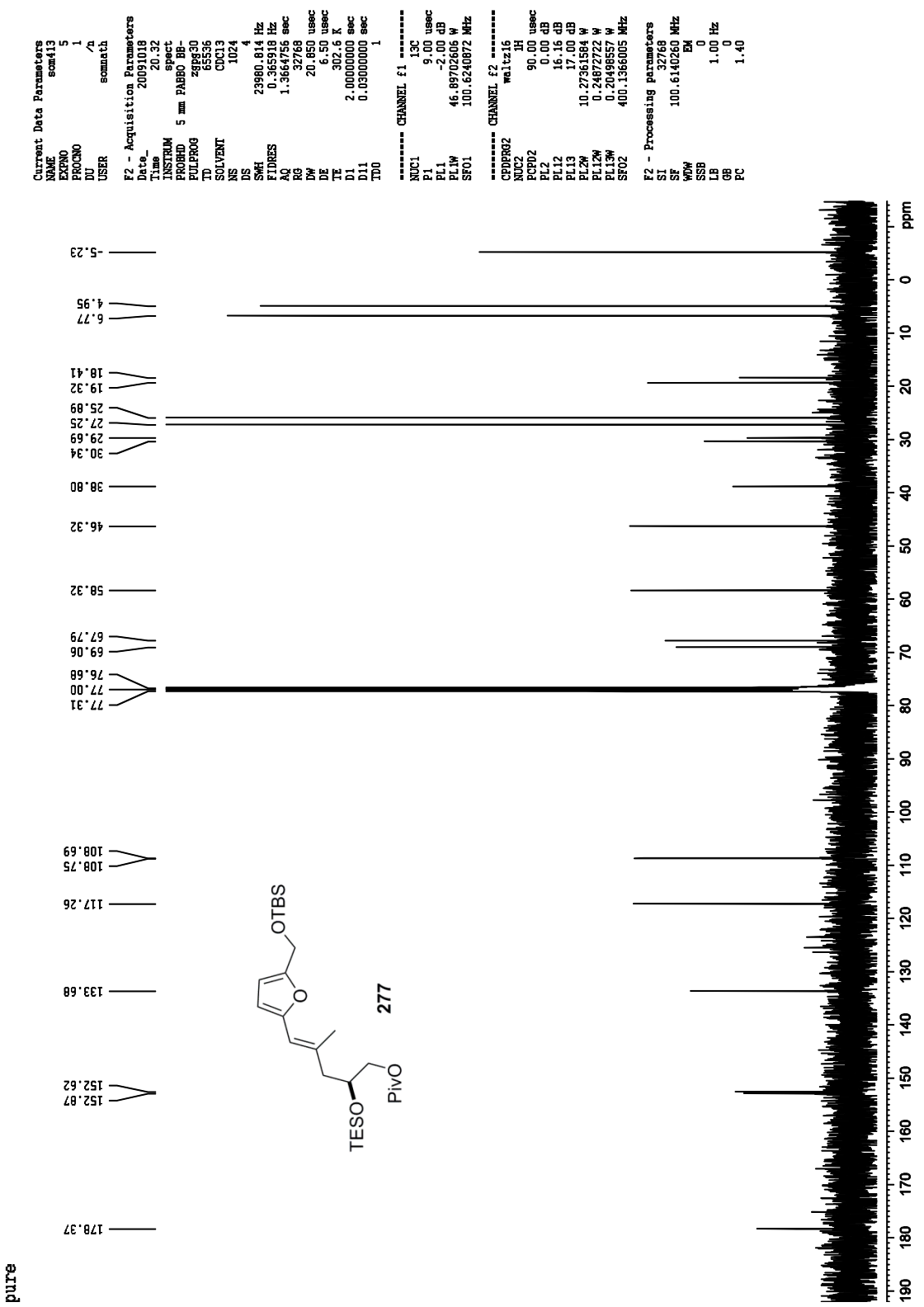

pure 1st time
Current Data Parameters
NAME scott10
EXPNO 7
PROCNO 1
DU /a
USER scomath
F2 - Acquisition Parameters
Date_ 20091012
Time 12.11
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 456.1
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
Me3Sn
O
275
0.096
0.326
0.930
4.682
6.237
6.245
6.506
6.514
11.40
7.56
10.98
2.25
1.06
1.00
ppm

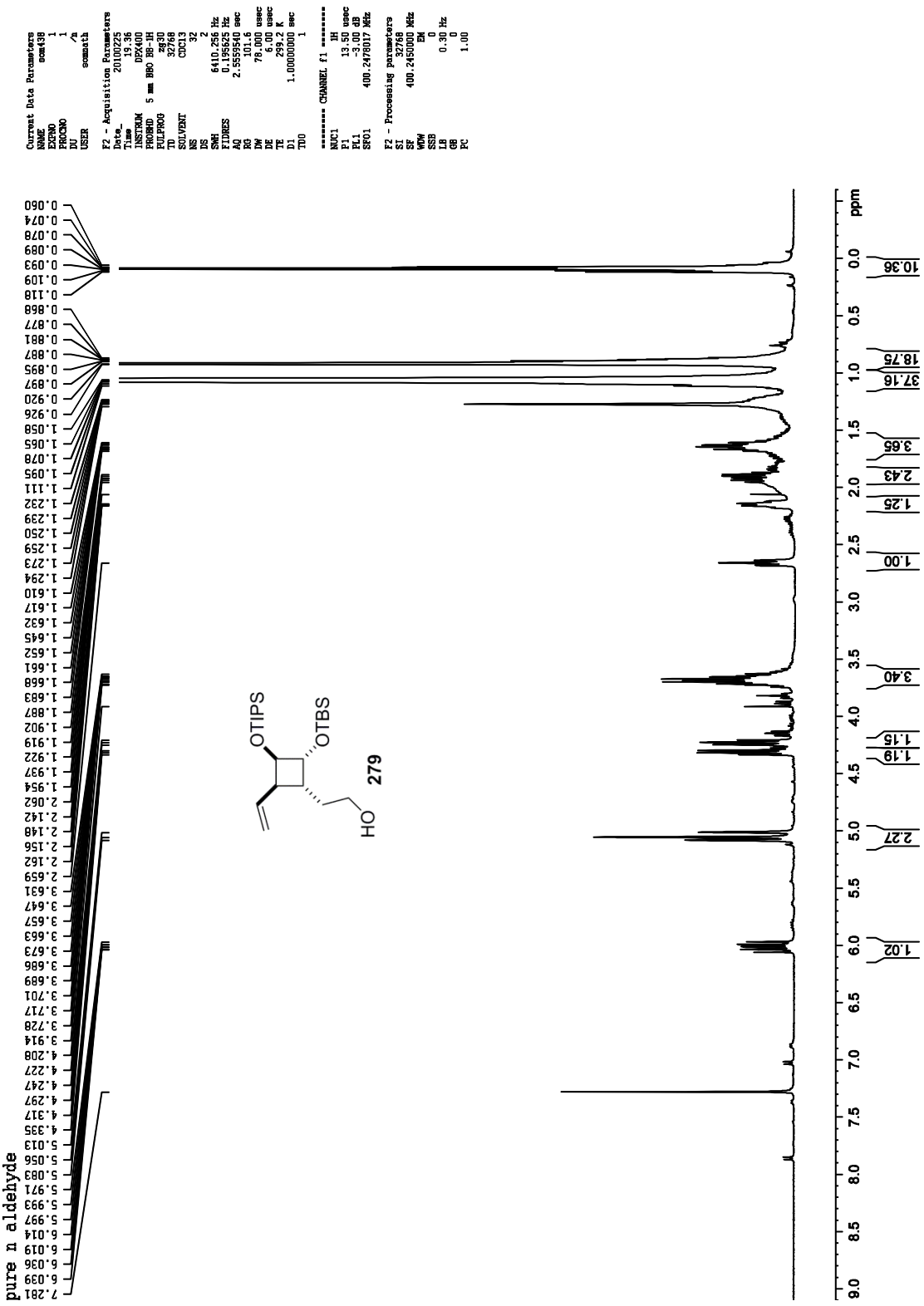

pure 2nd time
Current Data Parameters
NAME scm410
EXPNO 10
PROCNO 1
DU /n
USER somnath
F2 - Acquisition Parameters
Date_ 20091012
Time 17.26
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2030
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.36664756 sec
RG 32768
DW 20.850 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-11.01
-9.22
-7.35
-5.20
18.46
25.91
26.40
58.33
76.70
77.02
77.34
107.20
121.54
148.94
158.90
160.22
OTBS
O
Me3Sn
275
ppm

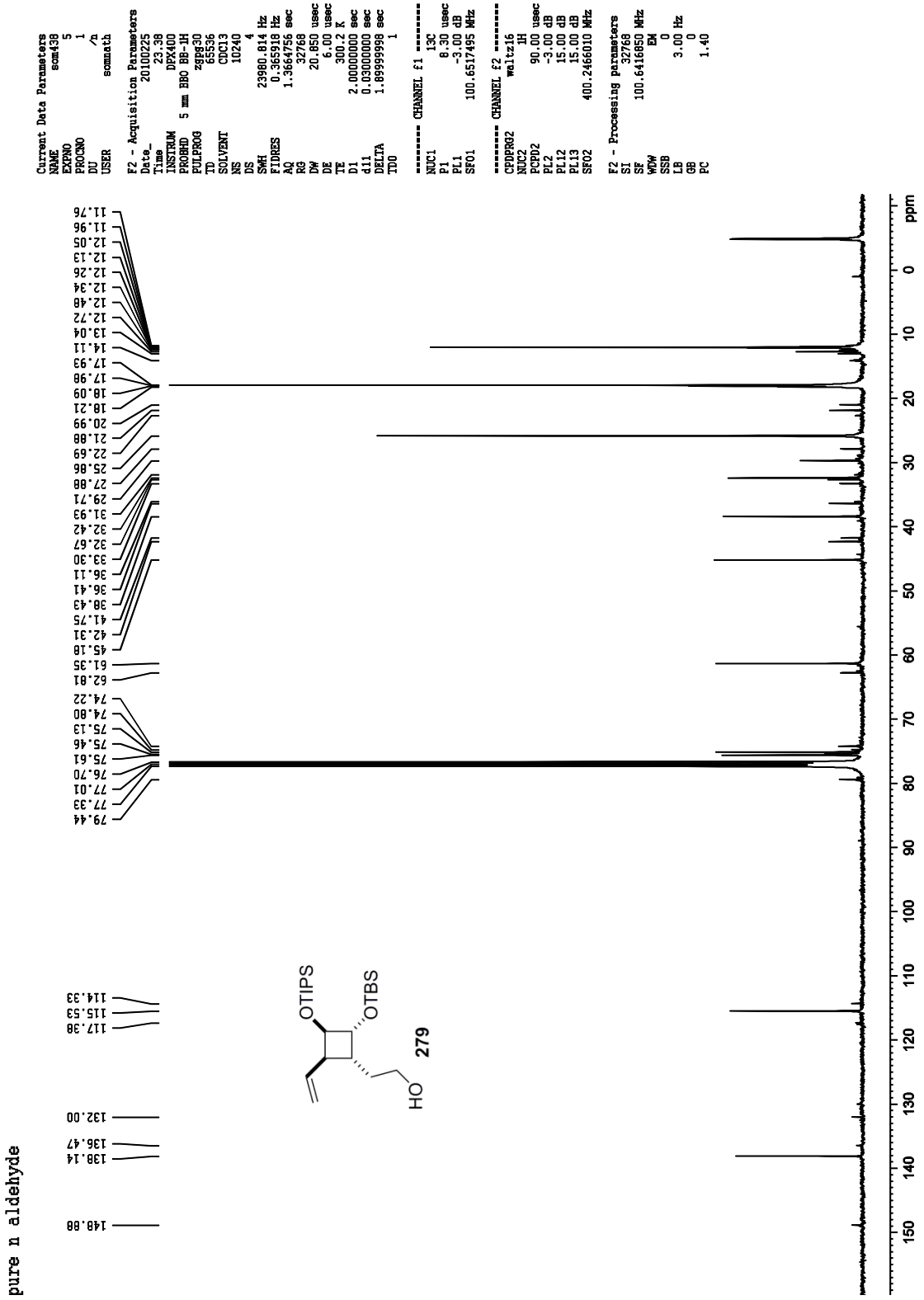

OTES
OPiv
I
276
ppm
6.94
10.48
10.60
3.01
2.10
3.37
1.00

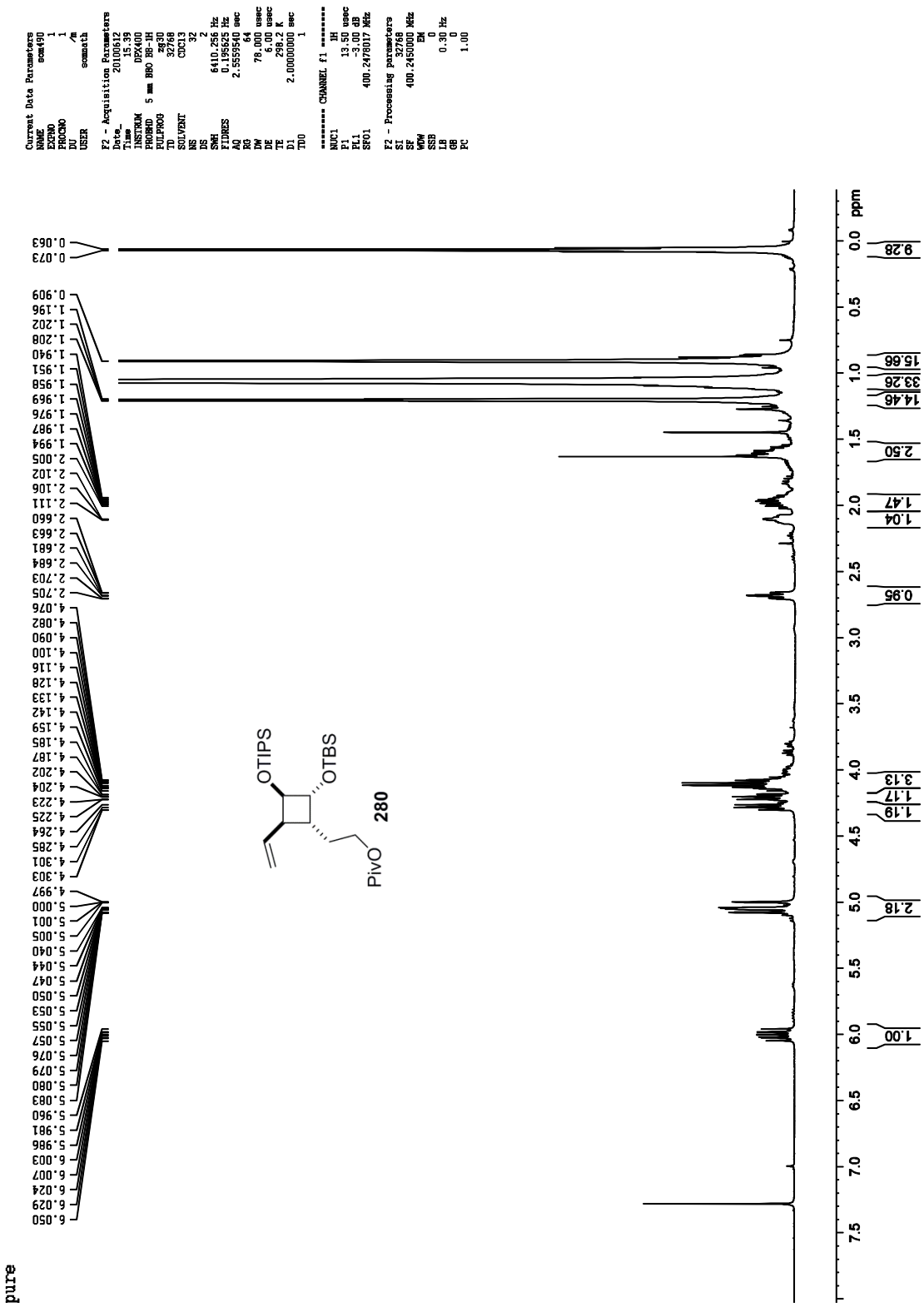

Current Data Parameters
NAME scm347
EXPNO 4
PROCNO 1
DU /p
USER scmnath
F2 - Acquisition Parameters
Data_ 20090325
Time_ 17.05
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT
NS 1550
DS 4
SWH 25125.623 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 298.2 K
D1 0.15000001 sec
d11 0.03000000 sec
DELTA 0.05000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 -3.00 dB
SFO1 100.5785700 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 135.00 usec
PL2 17.40 dB
PL12 17.40 dB
PL13 17.40 dB
SFO2 399.9516000 MHz
F2 - Processing parameters
SI 131072
SF 100.5675080 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
4.89
6.82
24.50
27.24
38.80
44.78
67.48
68.23
77.96
143.99
178.31
OTES
OPiv
I
276
ppm

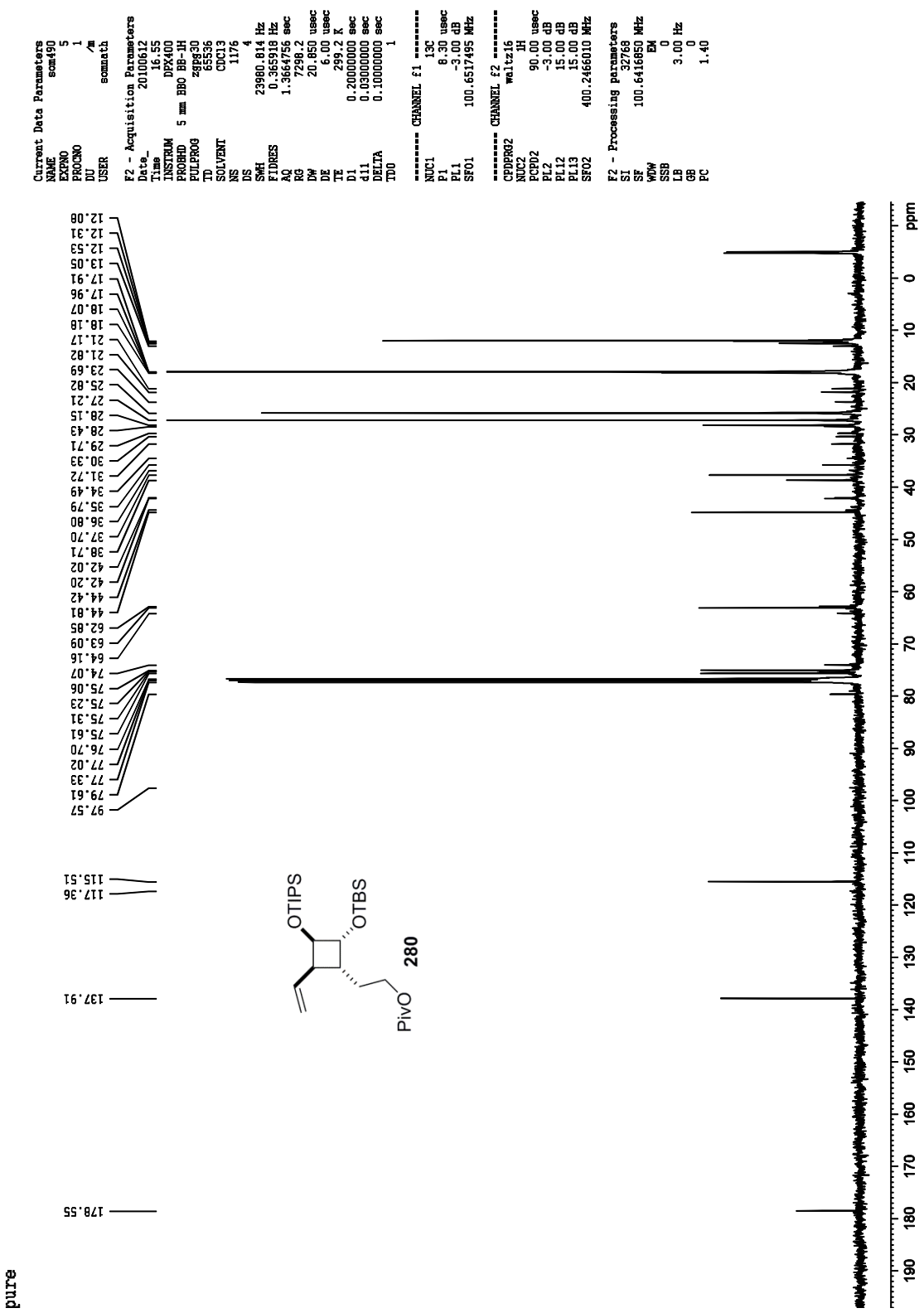

Current Data Parameters
NAME scott3
EXPNO 1
PROCNO 1
DU /a
USER somuath
F2 - Acquisition Parameters
Date_ 20091018
Time 18.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 128
DW 78.000 usec
DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
PL1W 10.27361584 W
SFO1 400.1378009 MHz
F2 - Processing parameters
SI 32768
SF 400.1350000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
O
TESO
PivO
277
pure
ppm
6.16
6.91
19.67
13.37
2.77
1.75
3.06
1.91
1.00
0.84
0.82

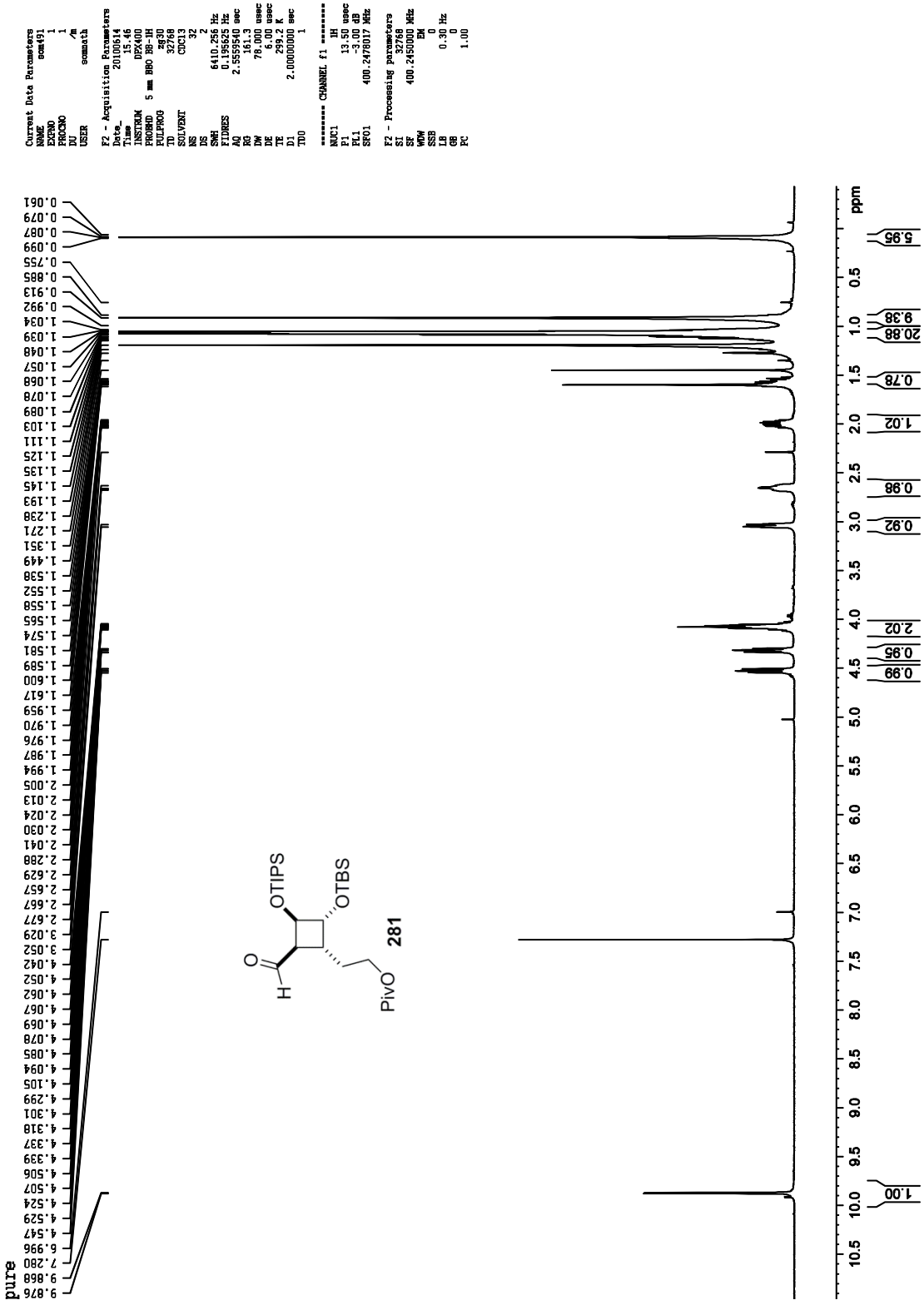

pure
Current Data Parameters
NAME scm413
EXPNO 5
PROCNO 1
DU /n
USER somnath
F2 - Acquisition Parameters
Data_ 20091018
Time 20.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 32768
DW 20.850 usec
DE 6.50 usec
TE 302.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -2.00 dB
PL1W 46.89702606 W
SFO1 100.6240872 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 16.16 dB
PL13 17.00 dB
PL2W 10.27361584 W
PL12W 0.24872722 W
PL13W 0.20498557 W
SFO2 400.1366005 MHz
F2 - Processing parameters
SI 32768
SF 100.6140260 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
-5.23
4.95
6.77
18.41
19.32
25.89
27.25
29.69
30.34
38.80
46.32
58.32
67.79
69.06
76.68
77.00
77.31
108.69
108.75
117.26
133.68
152.62
152.87
178.37
OTBS
O
TESO
PivO
277
ppm

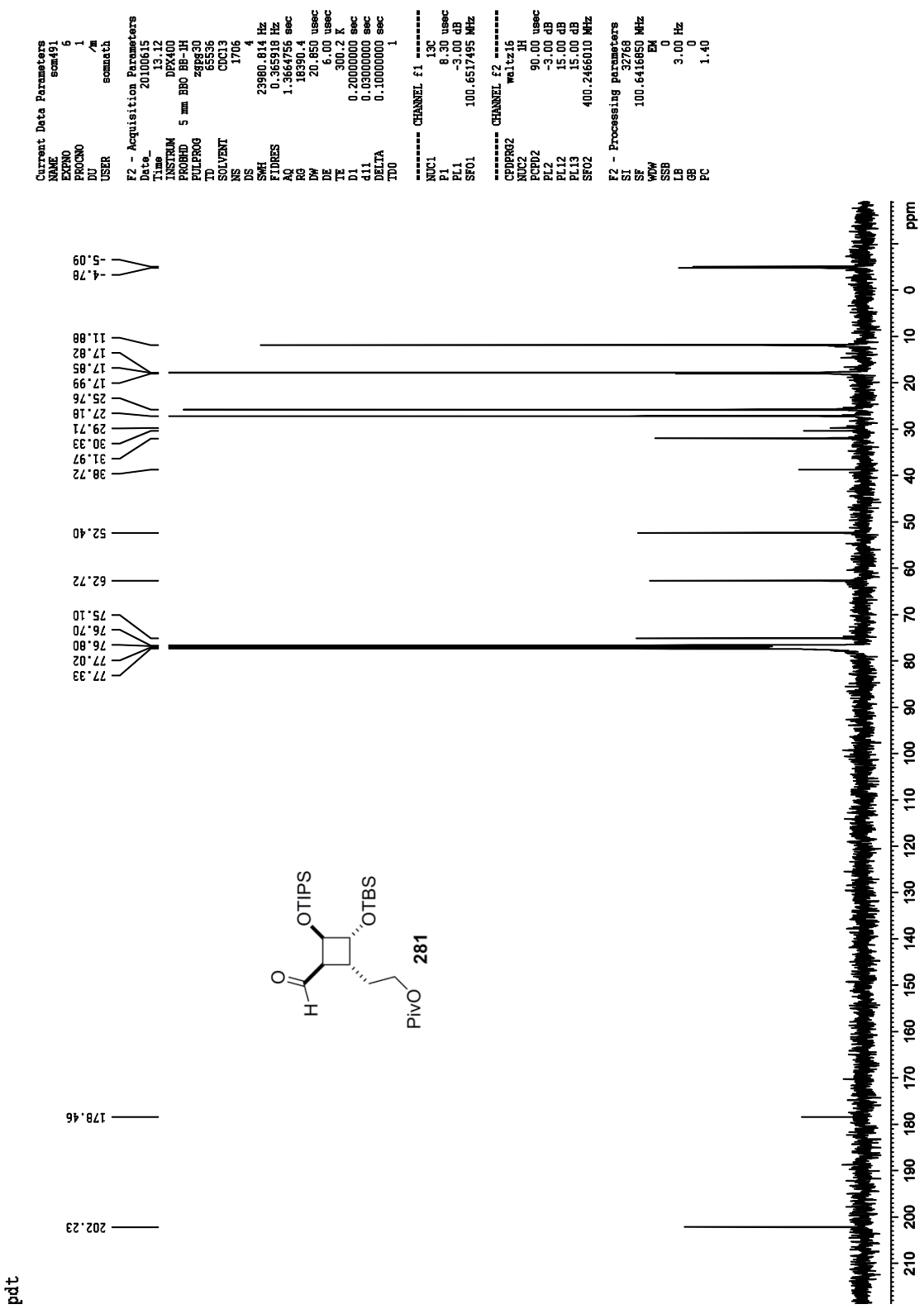

pure n aldehyde
Current Data Parameters
NAME som438
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Data_ 20100225
Time_ 19.36
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 101.6
DW 78.000 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTIPS
OTBS
HO
279
10.36
18.75
37.16
3.65
2.43
1.25
1.00
3.40
1.15
1.19
2.27
1.02
ppm

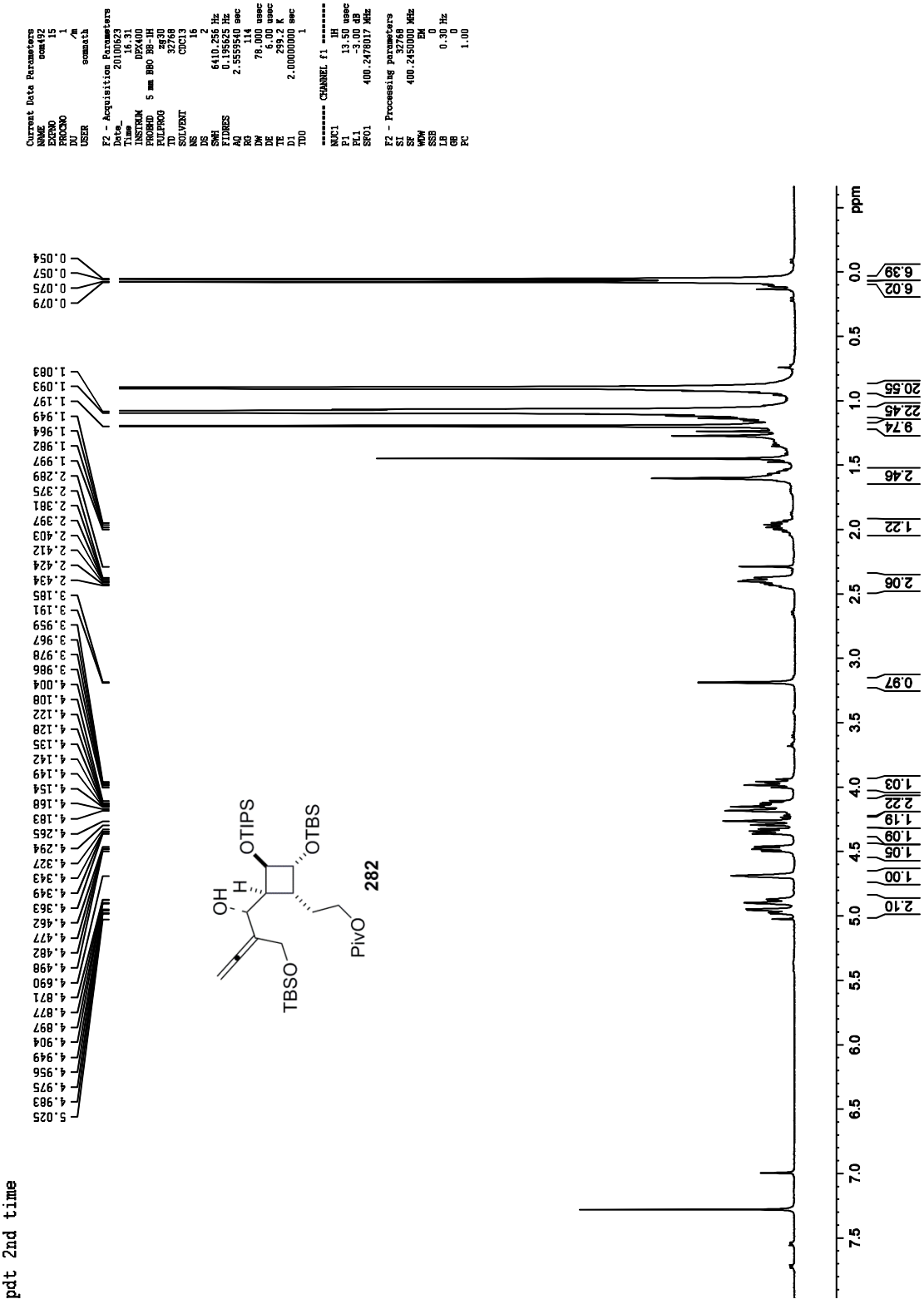

pure n aldehyde
Current Data Parameters
NAME scm438
EXPNO 5
PROCNO 1
DU /n
USER scmath
F2 - Acquisition Parameters
Date_ 20100225
Time 23.38
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10240
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.36664756 sec
RG 32768
DW 20.850 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
OTIPS
OTBS
HO
279
ppm

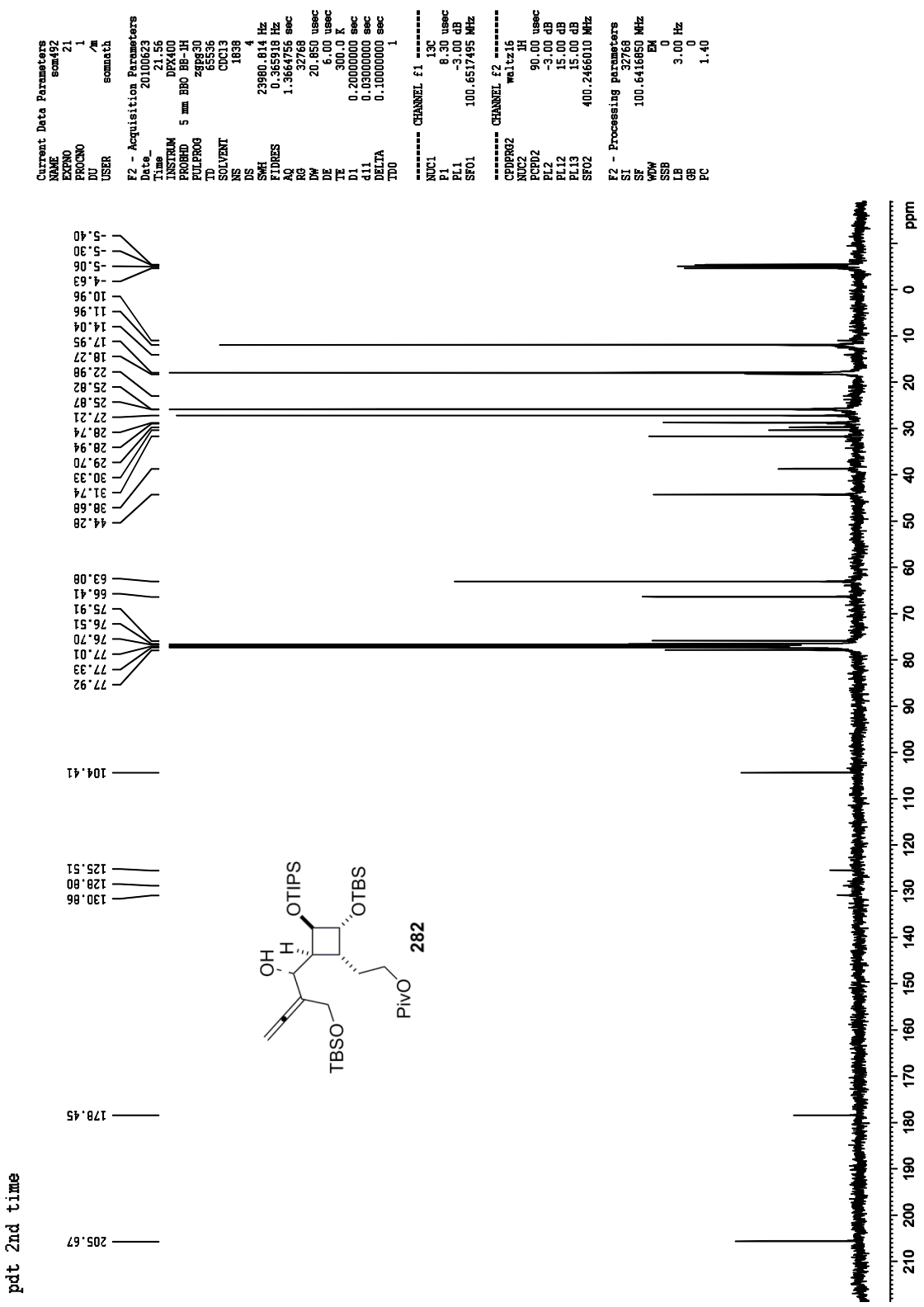

pure
Current Data Parameters
NAME scott90
EXPNO 1
PROCNO 1
DU /m
USER somnath
F2 - Acquisition Parameters
Date_ 20100612
Time 15.39
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 64
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTIPS
OTBS
PivO
280
ppm
9.28
15.66
33.26
14.46
2.50
1.04
1.47
0.85
3.13
1.17
1.19
2.18
1.00

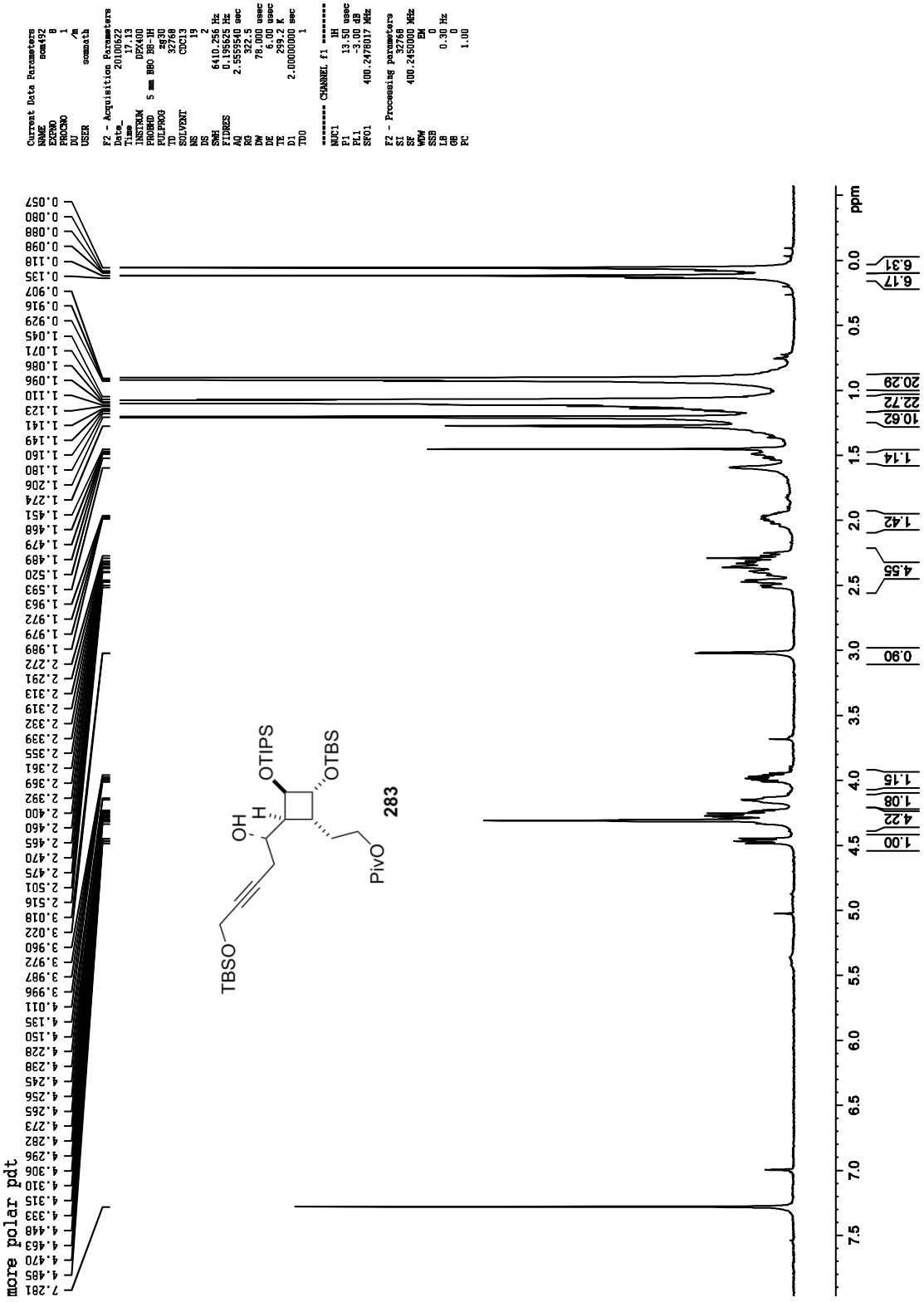

Current Data Parameters
NAME scm490
EXPNO 5
PROCNO 1
DU /m
USER somnath
F2 - Acquisition Parameters
Date_ 20100612
Time 16.55
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1176
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 7298.2
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
OTIPS
OTBS
PivO
280
pure
ppm

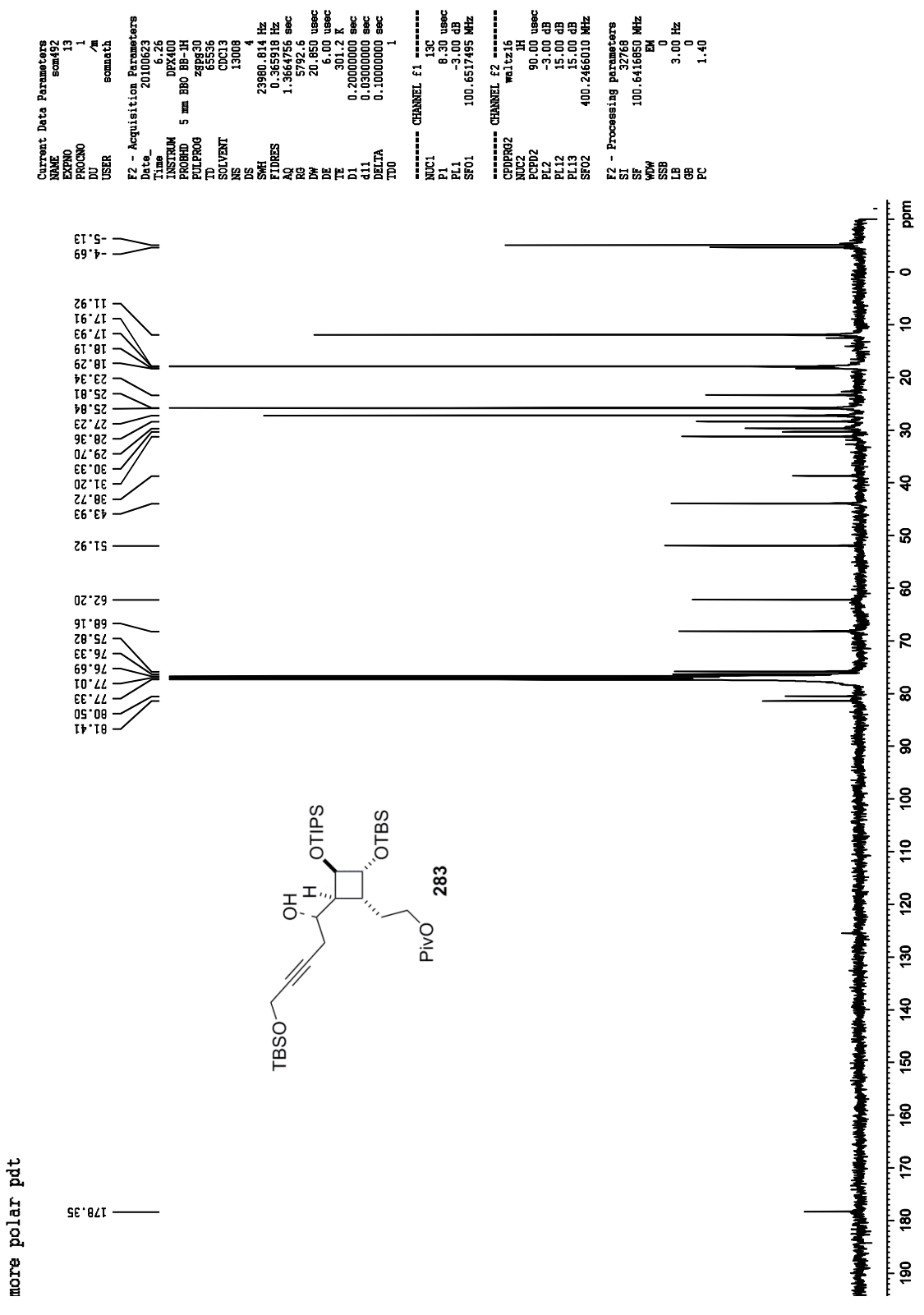

Current Data Parameters
NAME scott91
EXPNO 1
PROCNO 1
DU /m
USER scottath
F2 - Acquisition Parameters
Date_ 20100614
Time 15.46
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 161.3
DW 78.000 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
pure
OTIPS
OTBS
PivO
281
ppm
5.95
9.38
20.88
0.78
1.02
0.98
0.92
2.02
0.95
0.99
1.00

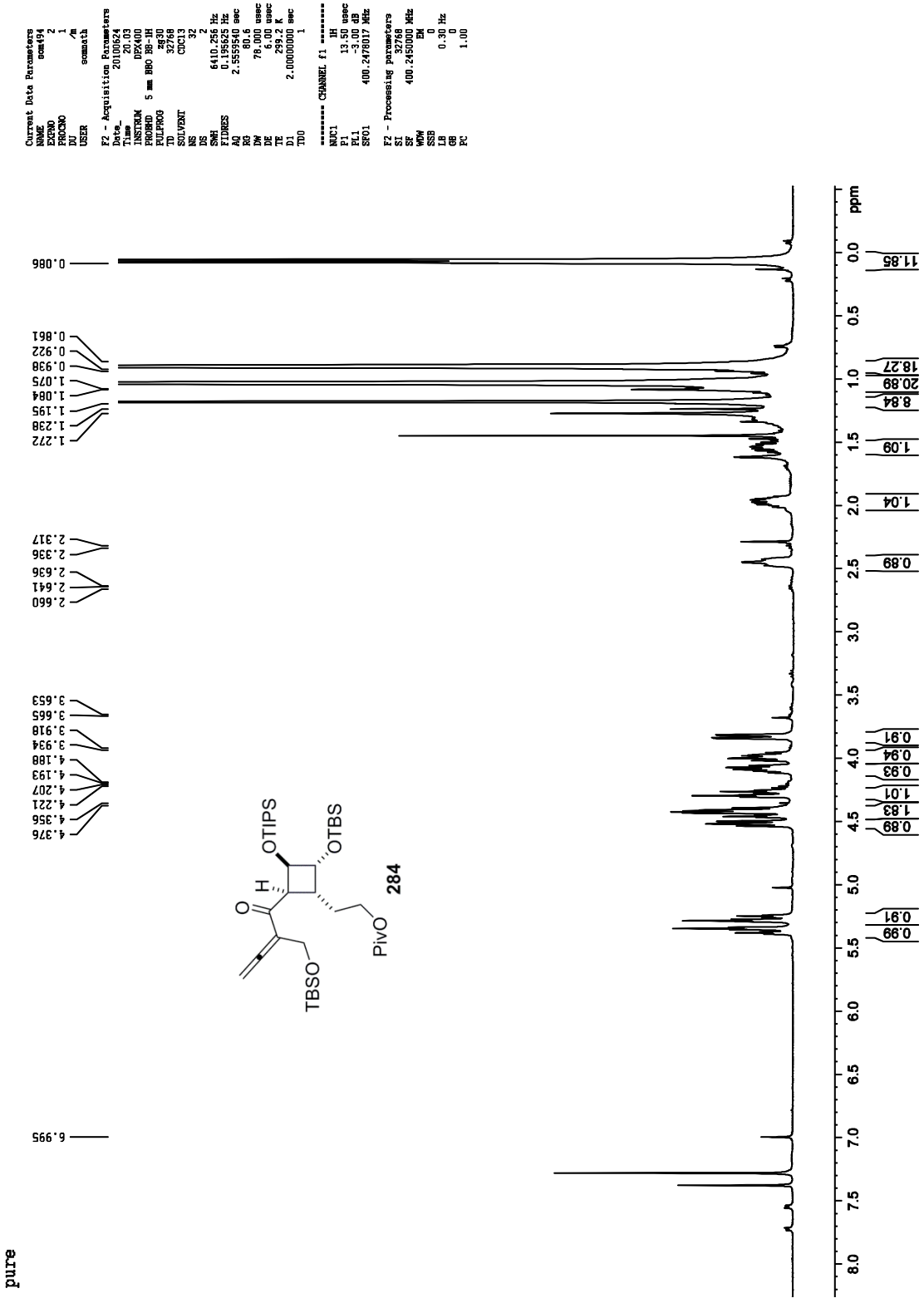

Current Data Parameters
NAME scm491
EXPNO 6
PROCNO 1
DU /m
USER somnath
F2 - Acquisition Parameters
Data_ 20100615
Time_ 13.12
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1706
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 18390.4
DW 20.850 usec
DE 6.00 usec
TE 300.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TDO 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.09
-4.78
11.88
17.82
17.85
17.99
25.76
27.18
29.71
30.33
31.97
38.72
52.40
62.72
75.10
76.70
76.80
77.02
77.33
178.46
202.23
OTIPS
OTBS
O
H
PivO
281
ppm
pdt

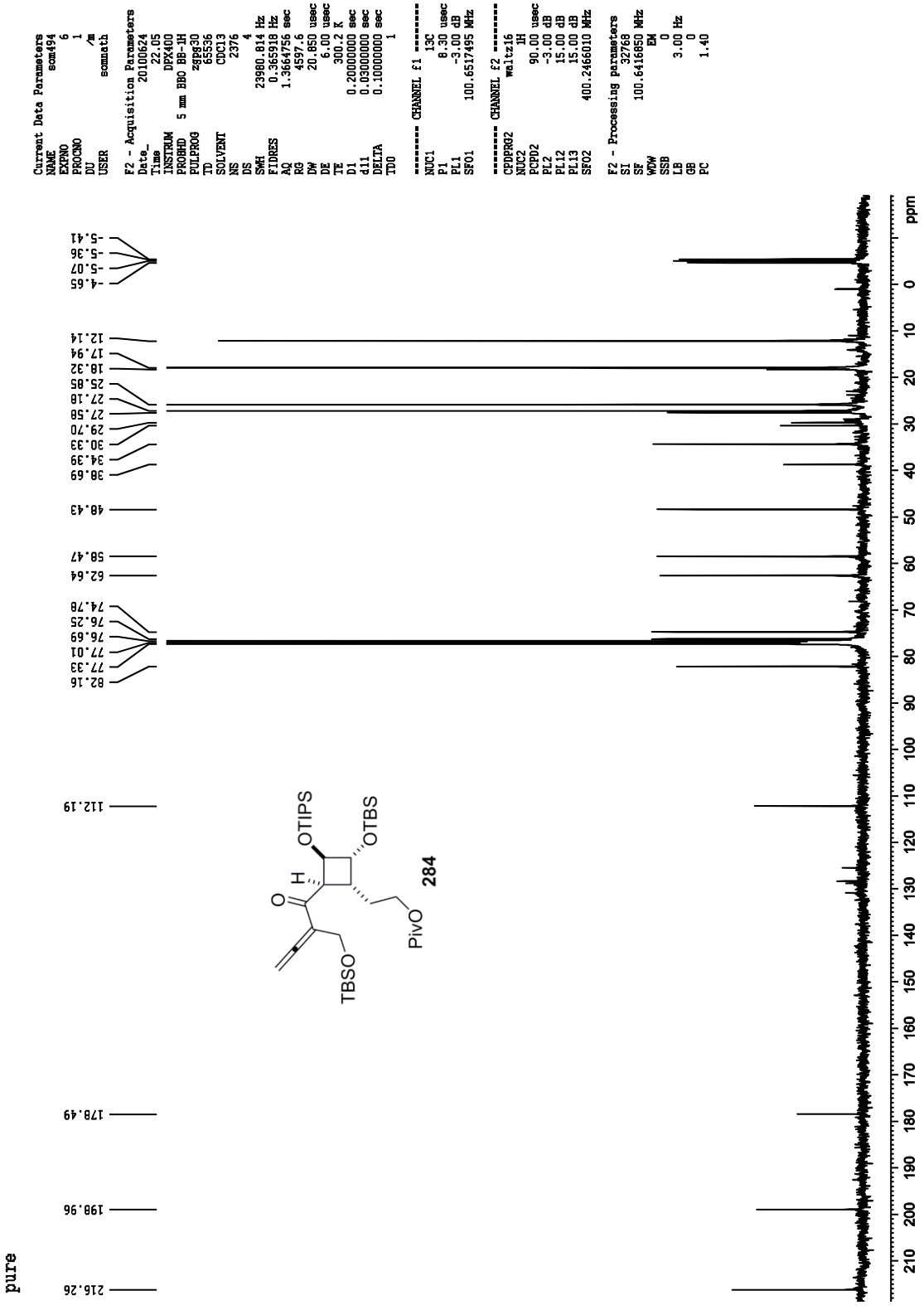

pdt 2nd time
Current Data Parameters
NAME som472
EXPNO 15
PROCNO 1
DU /n
USER somuath
F2 - Acquisition Parameters
Date_ 20100623
Time 16.31
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 114
DW 78.000 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
H
OTIPS
OTBS
TBSO
PivO
282
ppm
6.39
6.02
20.55
22.45
9.74
2.46
1.22
2.06
0.97
1.03
2.22
1.19
1.09
1.05
1.00
2.10

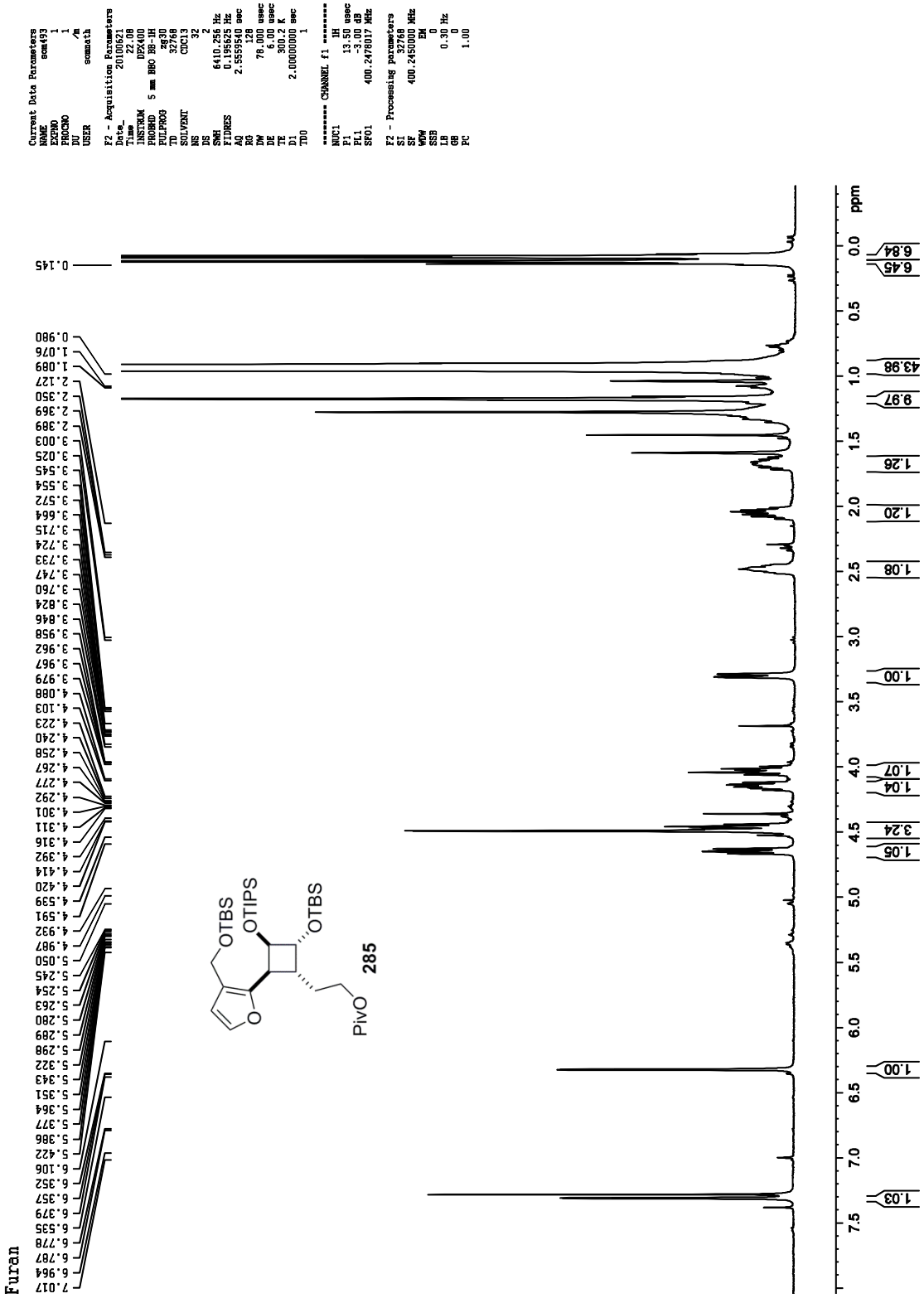

pdt 2nd time
Current Data Parameters
NAME som492
EXPNO 21
PROCNO 1
DU /m
USER somath
F2 - Acquisition Parameters
Date_ 20100623
Time 21.56
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1838
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 32768
DW 20.850 usec
DE 6.00 usec
TE 300.0 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.40
-5.30
-5.06
-4.63
10.96
11.96
14.04
17.95
18.27
22.96
25.82
25.87
27.21
28.74
28.94
29.70
30.33
31.74
38.68
44.28
63.08
66.41
75.91
76.51
76.70
77.01
77.33
77.92
104.41
125.51
128.80
130.86
178.45
205.67
OH
H
OTIPS
OTBS
TBSO
PivO
282
ppm

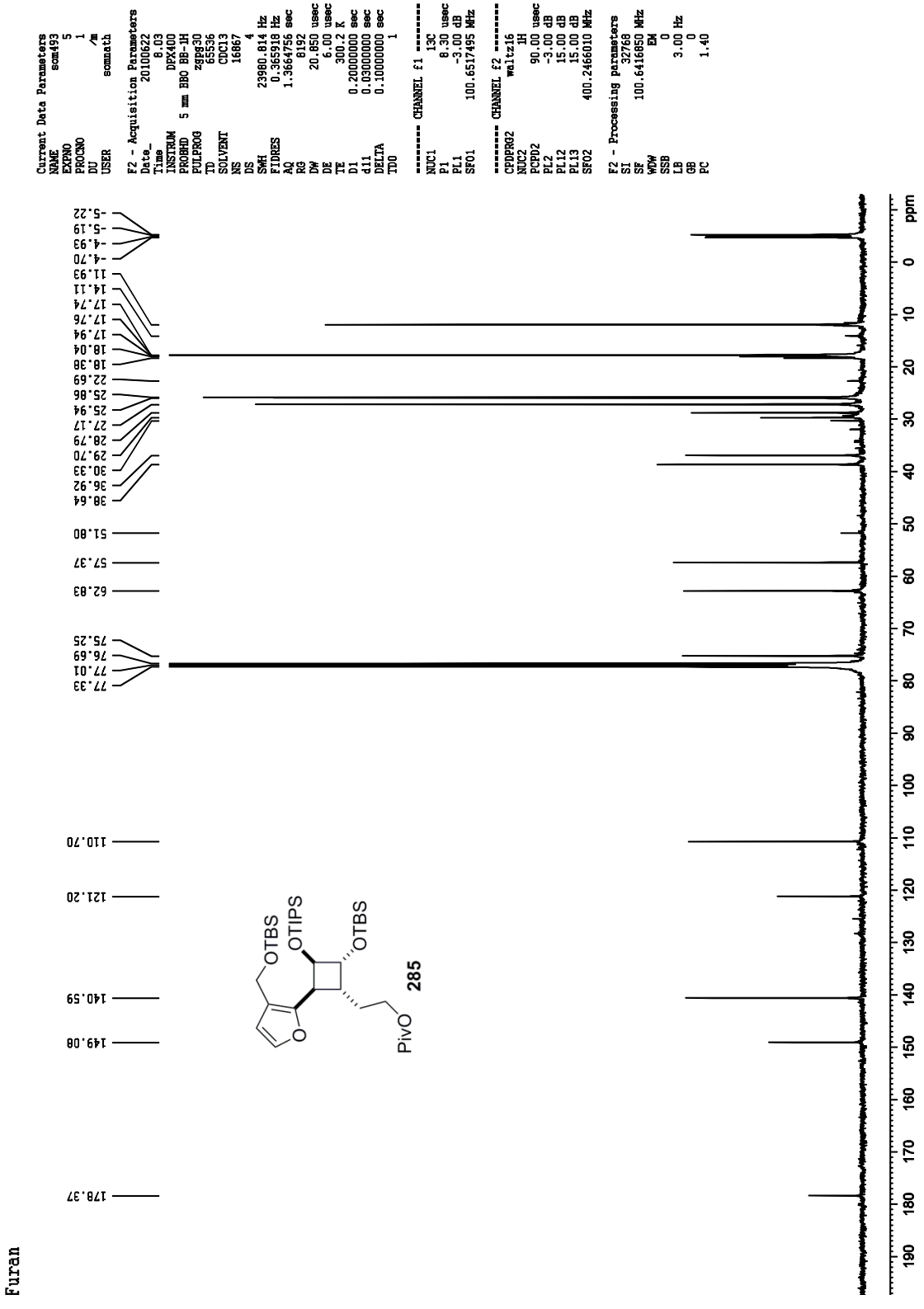

Current Data Parameters
NAME som492
EXPNO 8
PROCNO 1
F2 - Acquisition Parameters
Data_ 20100622
Time_ 17.13
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 2
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 322.5
DW 78.000 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
more polar pdt
TBSO
OH
H
OTIPS
OTBS
PivO
283
ppm
6.31
6.17
20.29
22.72
10.62
1.14
1.42
4.55
0.90
1.15
1.08
4.22
1.00

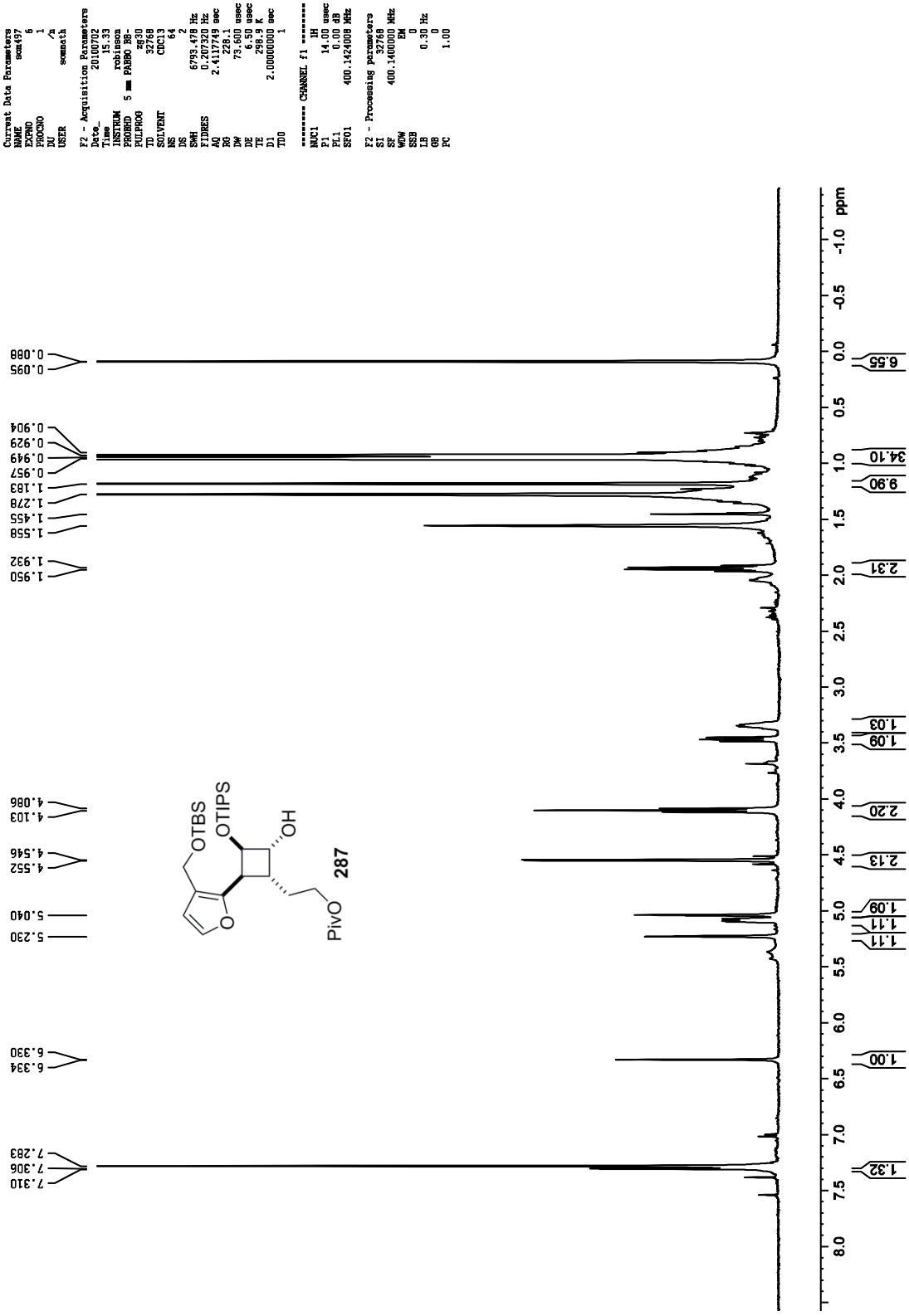

more polar pdt
Current Data Parameters
NAME scm492
EXPNO 13
PROCNO 1
DU /m
USER somnath
F2 - Acquisition Parameters
Date_ 20100623
Time 6.26
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1300
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 5792.6
DW 20.850 usec
DE 6.00 usec
TE 301.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.13
-4.69
11.92
17.91
17.93
18.19
18.29
23.34
25.81
25.84
27.23
28.36
29.70
30.33
31.20
38.72
43.93
51.92
62.20
68.16
75.82
76.33
76.69
77.01
77.33
80.50
81.41
178.35
TBSO
OH
H
OTIPS
OTBS
PivO
283
ppm

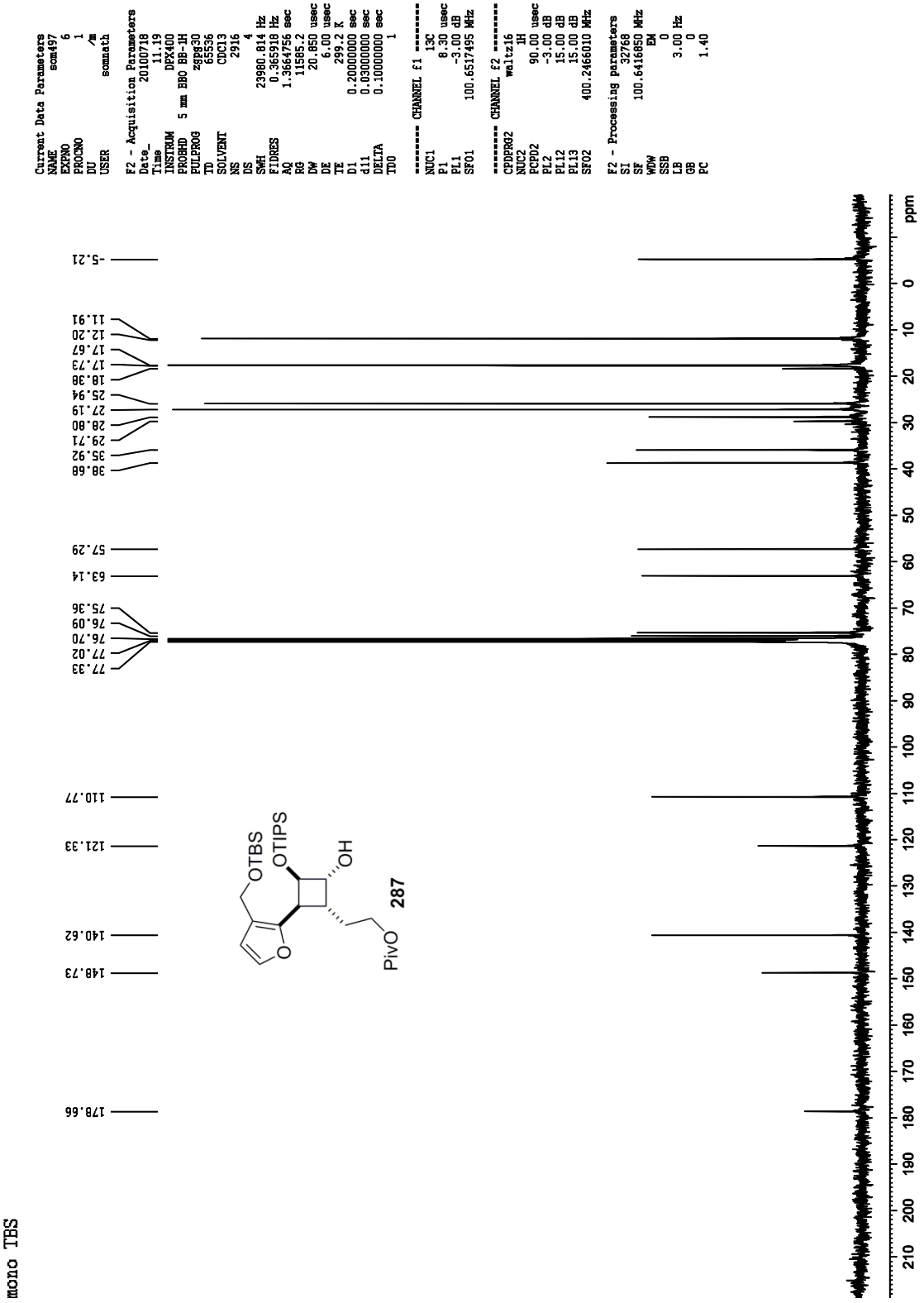

Current Data Parameters
NAME scott44
EXPNO 2
PROCNO 1
DU /m
USER scottath
F2 - Acquisition Parameters
Date_ 20100624
Time 20.03
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 80.6
DW 78.000 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
pure
6.995
4.376
4.356
4.221
4.207
4.193
4.188
3.934
3.918
3.665
3.653
2.660
2.641
2.636
2.336
2.317
1.272
1.238
1.195
1.084
1.075
0.938
0.922
0.861
0.086
OTIPS
OTBS
H
O
TBSO
PivO
284
ppm
11.85
18.27
20.89
8.84
1.09
1.04
0.89
0.91
0.94
0.93
1.01
1.83
0.89
0.91
0.99

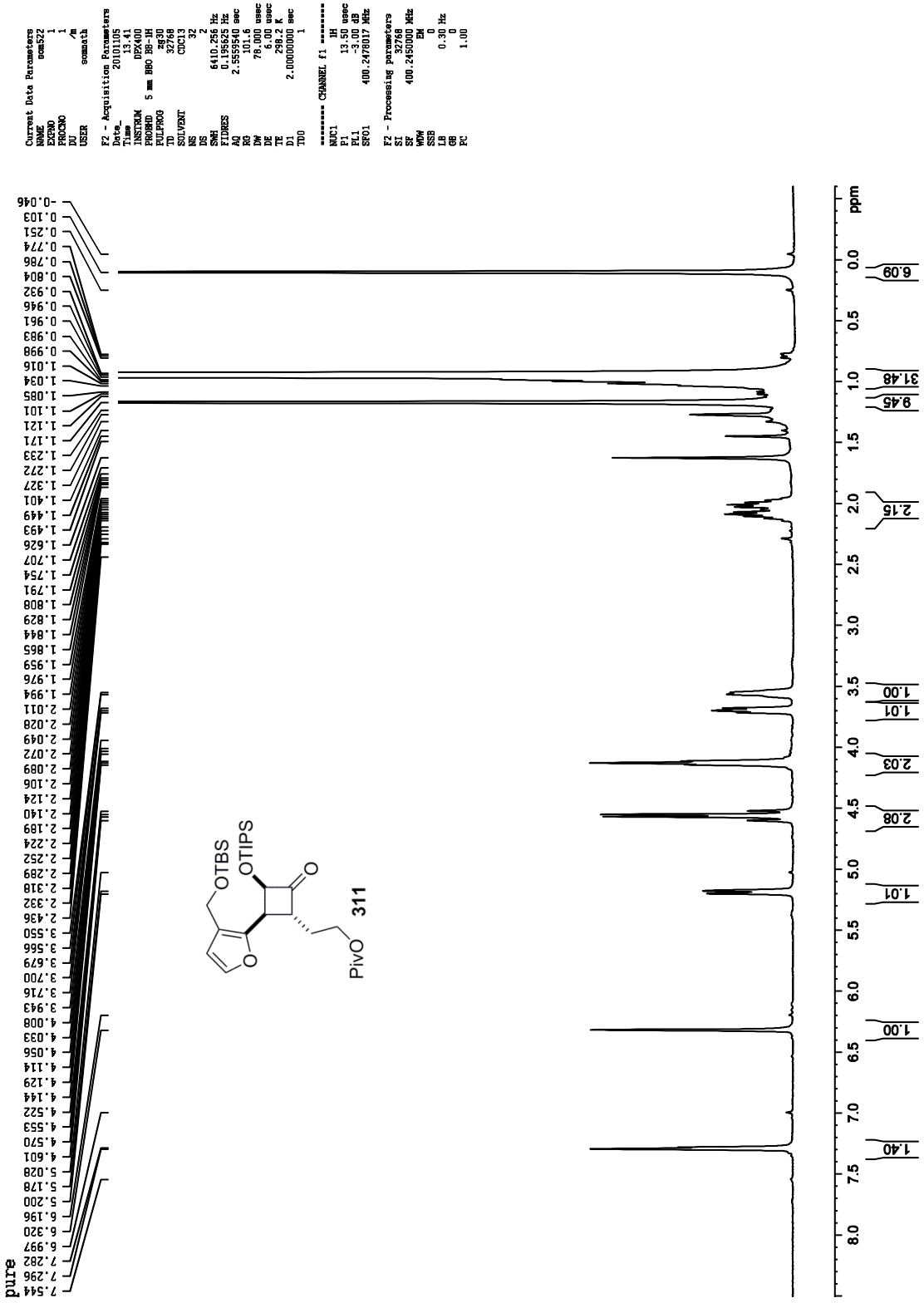

Current Data Parameters
NAME scan494
EXPNO 6
PROCNO 1
DU /m
USER somnath
F2 - Acquisition Parameters
Data_ 20100624
Time_ 22.05
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2376
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 4597.6
DW 20.850 usec
DE 6.00 usec
TE 300.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.41
-5.36
-5.07
-4.65
12.14
17.94
18.32
25.85
27.18
27.58
29.70
30.33
34.39
38.69
48.43
58.47
62.64
74.78
76.25
76.69
77.01
77.33
82.16
112.19
178.49
198.96
216.26
OTIPS
OTBS
H
O
TBSO
PivO
284
ppm
pure

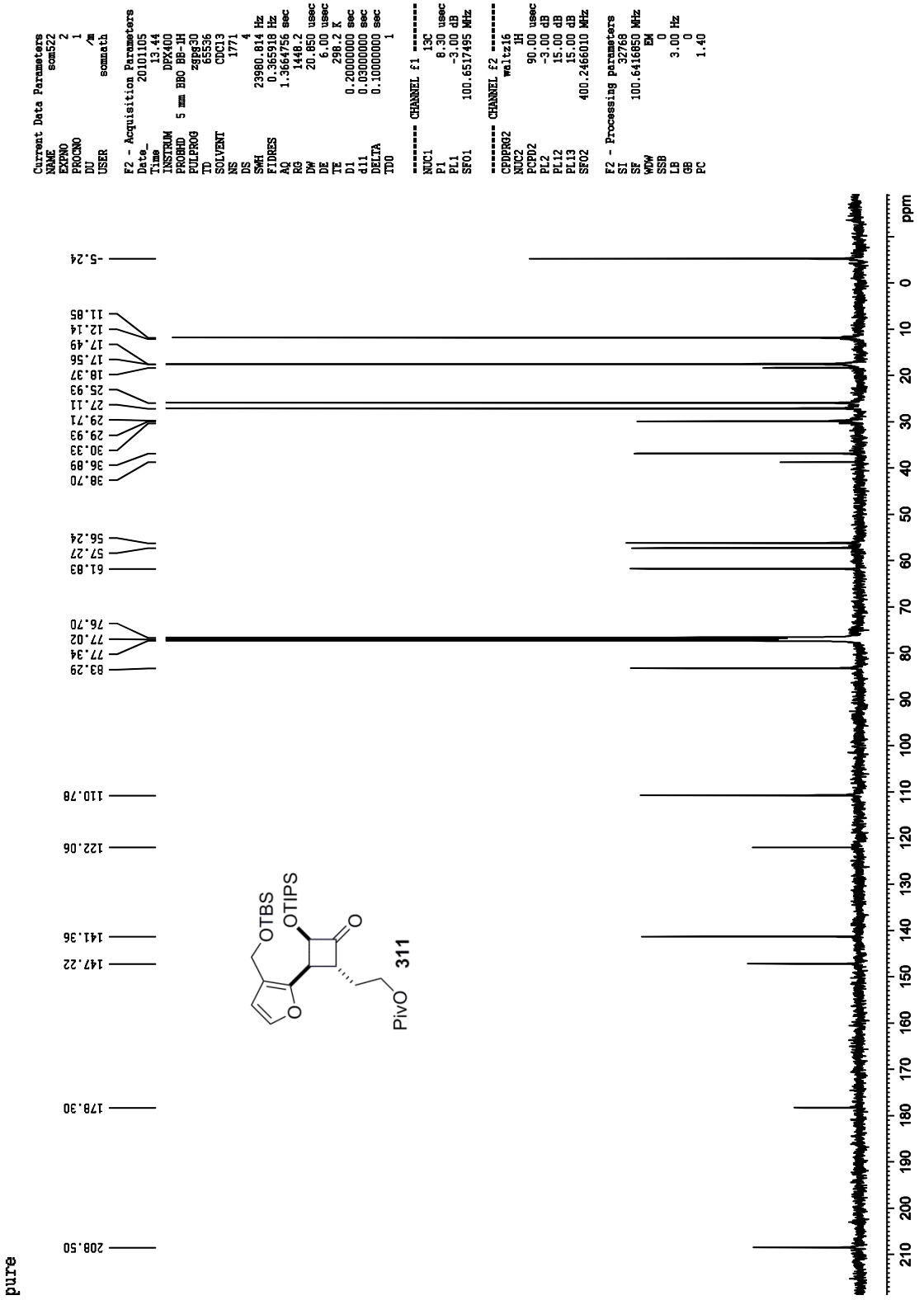

Current Data Parameters
NAME som493
EXPNO 1
PROCNO 1
DATA /m
USER sommath
F2 - Acquisition Parameters
Date_ 20100621
Time 22.08
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 228
DW 78.000 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Furan
OTBS
OTIPS
OTBS
PivO
285
ppm

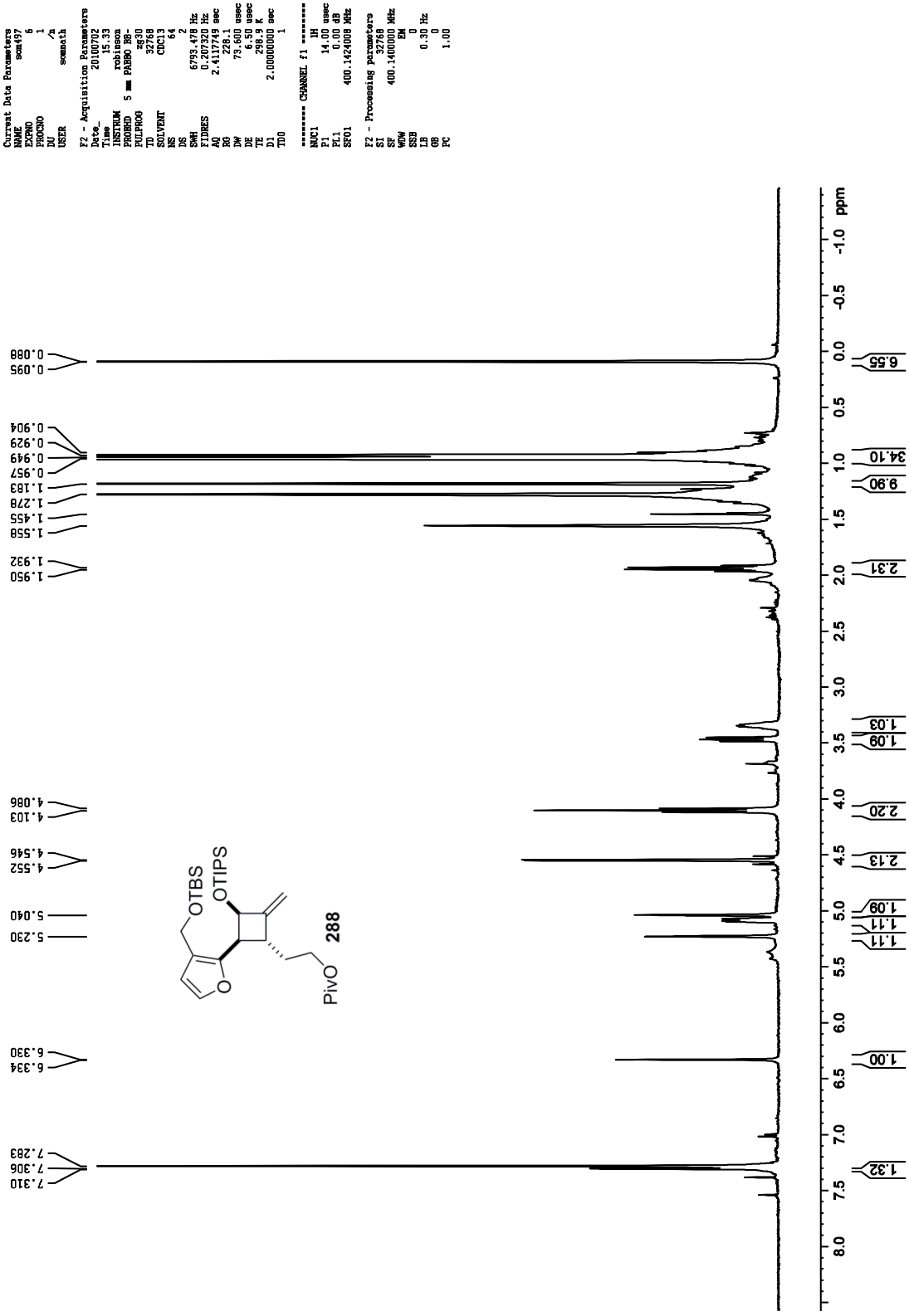

Furan
Current Data Parameters
NAME som493
EXPNO 5
PROCNO 1
DU /m
USER somath
F2 - Acquisition Parameters
Date_ 20100622
Time 8.03
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16867
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 8192
DW 20.850 usec
DE 6.00 usec
TE 300.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.22
-5.19
-4.93
-4.70
11.93
14.11
17.74
17.76
17.94
18.04
18.38
22.69
25.86
25.94
27.17
28.79
29.70
30.33
36.92
38.64
51.80
57.37
62.83
75.25
76.69
77.01
77.33
110.70
121.20
140.59
149.08
178.37
OTBS
OTIPS
OTBS
O
PivO
285
ppm

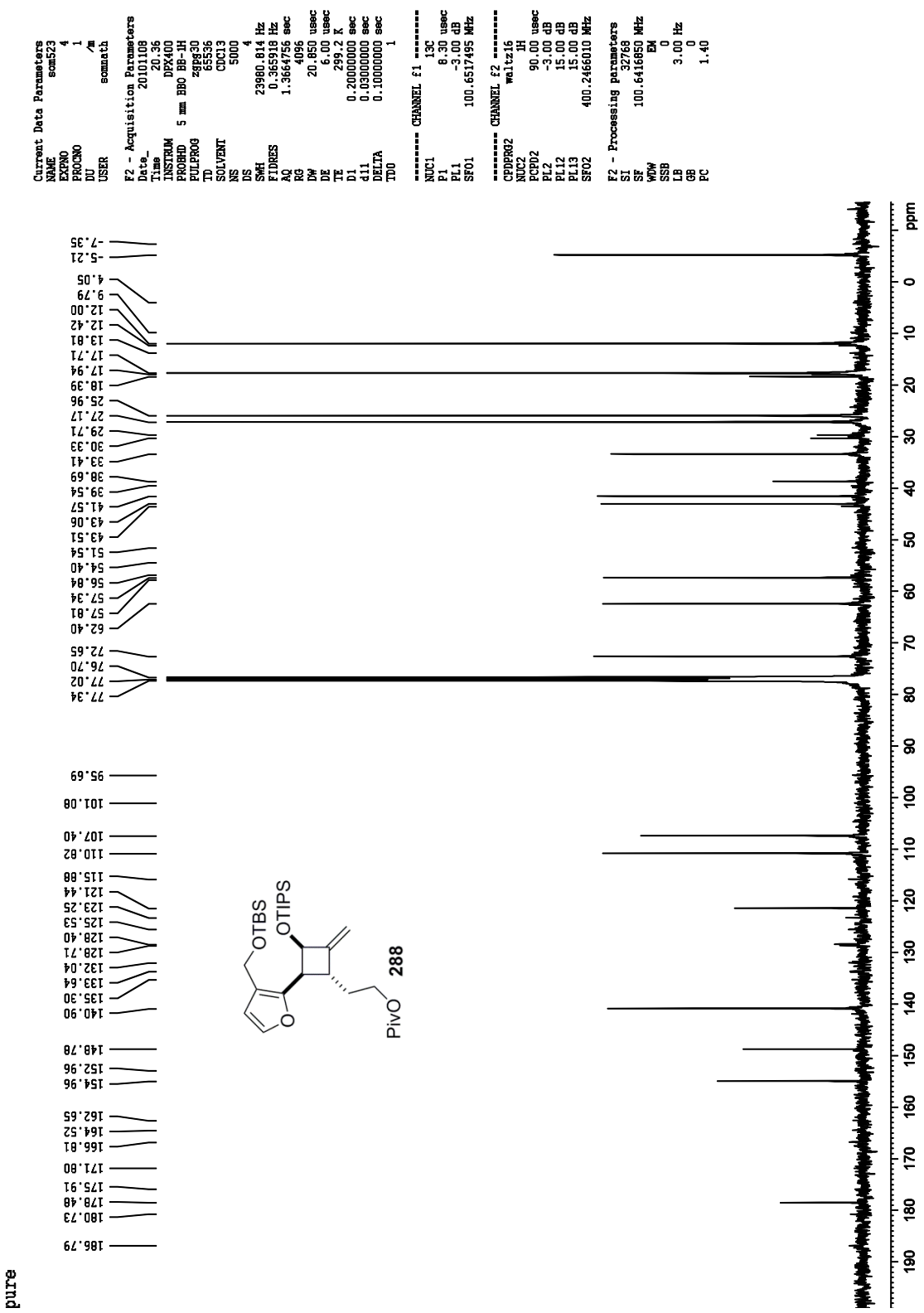

Current Data Parameters
NAME scs497
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Data_ 20100702
Time 15.33
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 2
SWH 6793.478 Hz
FIDRES 0.207320 Hz
AQ 2.4117749 sec
RG 228.1
DW 73.600 usec
DE 6.50 usec
TE 298.9 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1424009 MHz
F2 - Processing parameters
SI 32768
SF 400.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
OTIPS
OH
PivO
287
ppm

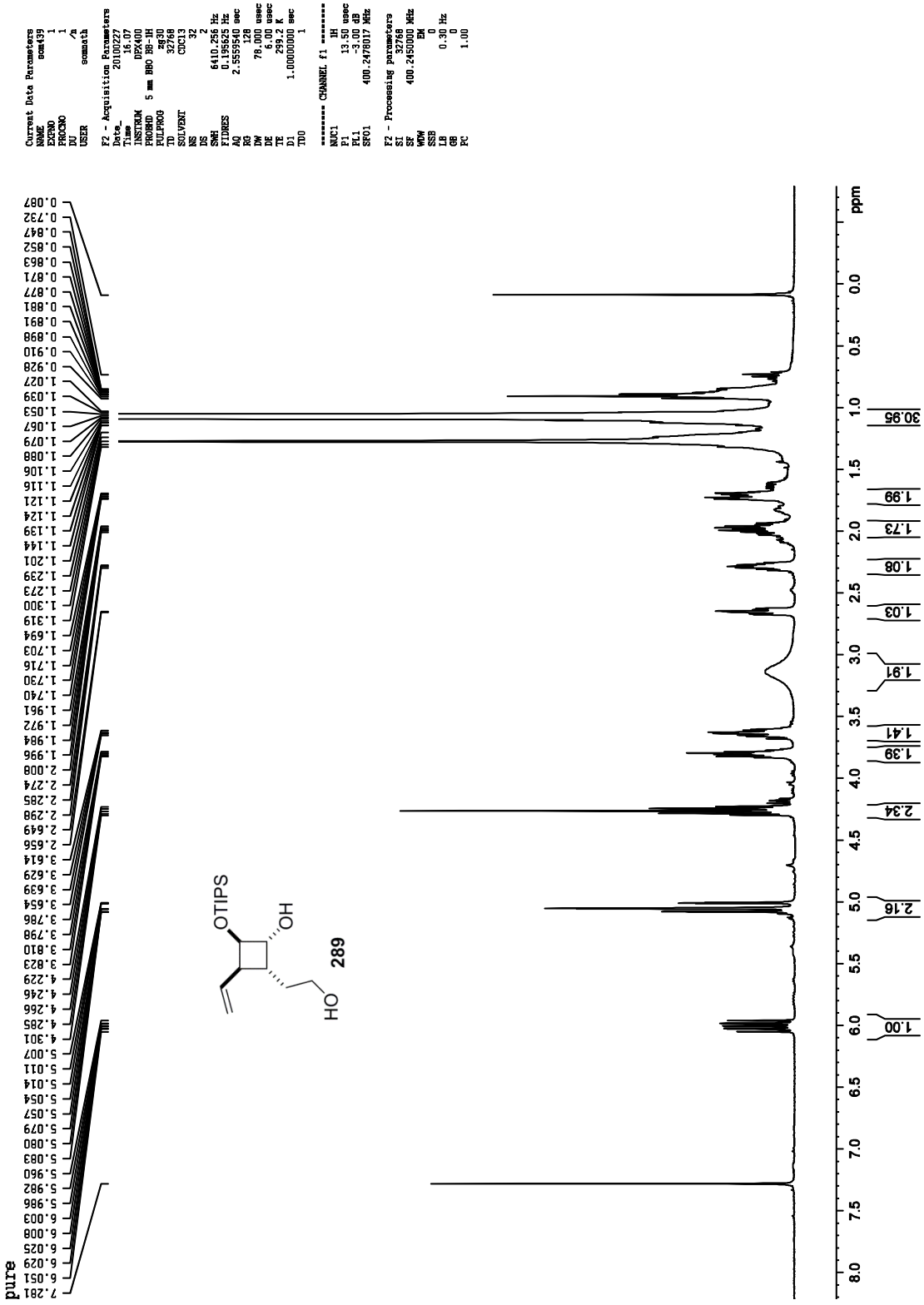

mono TBS
Current Data Parameters
NAME scm497
EXPNO 6
PROCNO 1
DU /m
USER scmath
F2 - Acquisition Parameters
Date_ 20110718
Time 11.19
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2916
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 11585.2
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.21
11.91
12.20
17.67
17.73
18.36
25.94
27.19
28.80
29.71
35.92
38.68
57.29
63.14
75.36
76.09
76.70
77.02
77.33
110.77
121.33
140.62
148.73
178.66
OTBS
OTIPS
OH
PivO
287
ppm

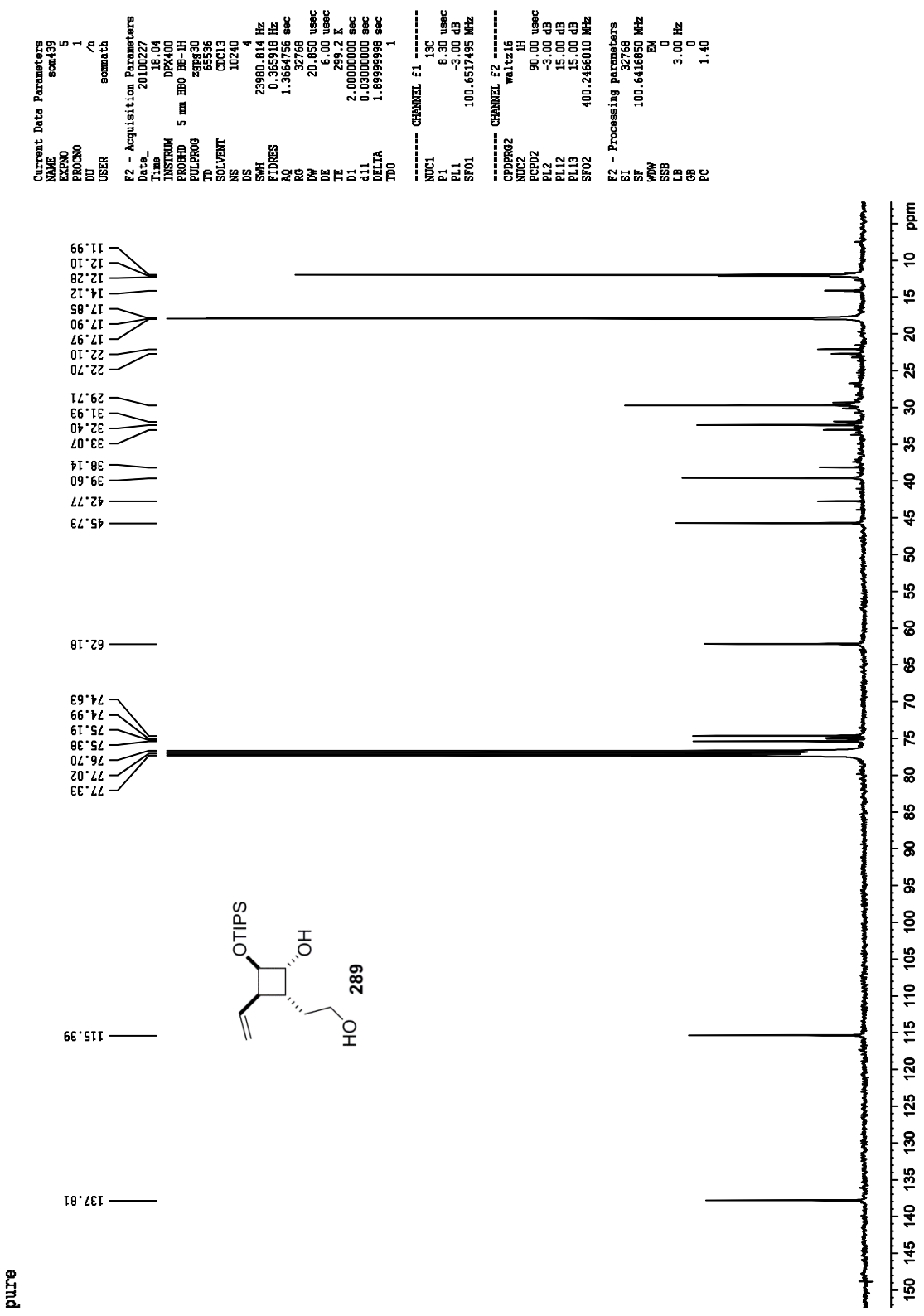

Current Data Parameters
NAME som522
EXPNO 1
PROCNO 1
DU /m
USER somuth
F2 - Acquisition Parameters
Date_ 20101105
Time 13.41
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 101.6
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
OTIPS
PivO
311
pure
ppm
6.09
31.48
9.45
2.15
1.00
1.01
2.03
2.08
1.01
1.00
1.40

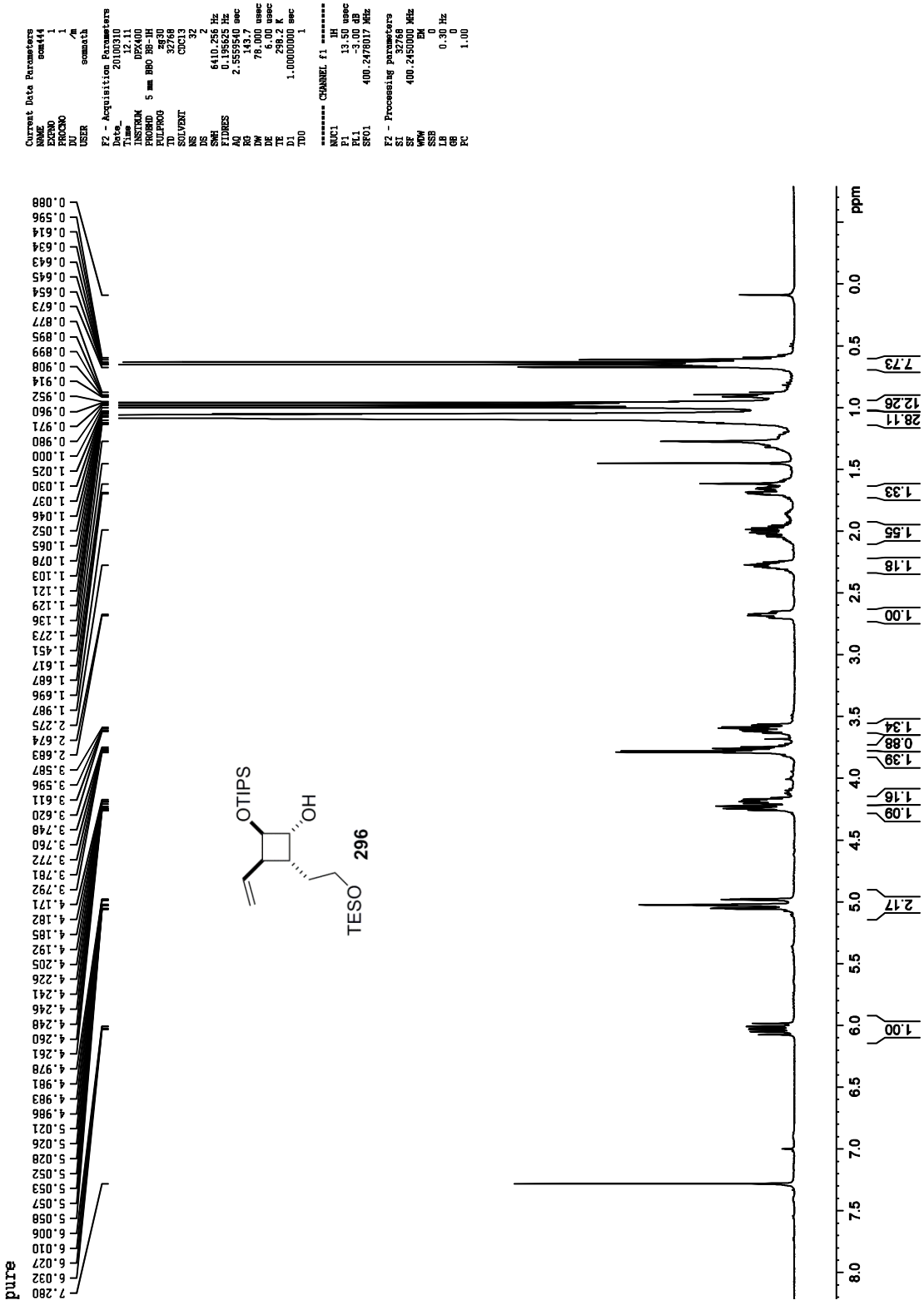

Current Data Parameters
NAME scm522
EXPNO 2
PROCNO 1
DU /m
USER somnath
F2 - Acquisition Parameters
Date_ 20101105
Time 13.44
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1771
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 1448.2
DW 20.850 usec
DE 6.00 usec
TE 298.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.24
11.85
12.14
17.49
17.56
18.37
25.93
27.11
29.71
29.93
30.33
36.89
38.70
56.24
57.27
61.83
76.70
77.02
77.34
83.29
110.78
122.06
141.36
147.22
178.30
208.50
OTBS
OTIPS
O
O
PivO
311
ppm
pure

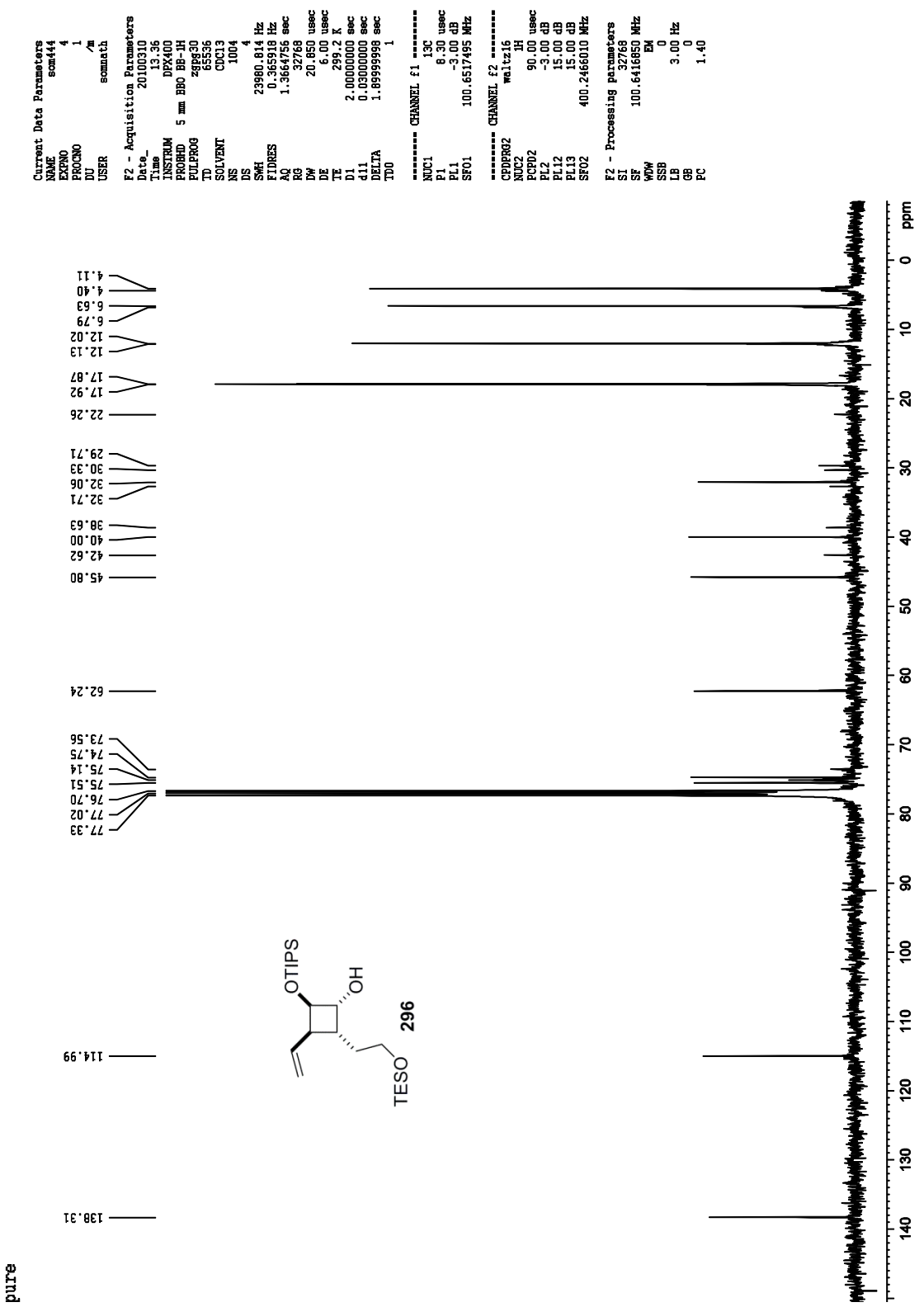

Current Data Parameters
NAME sonk97
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Data_ 20100702
Time 15.33
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 2
SWH 6793.478 Hz
FIDRES 0.207320 Hz
AQ 2.4117749 sec
RG 228.1
DW 73.600 usec
DE 6.50 usec
TE 298.9 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1424009 MHz
F2 - Processing parameters
SI 32768
SF 400.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
OTIPS
PivO
288
ppm

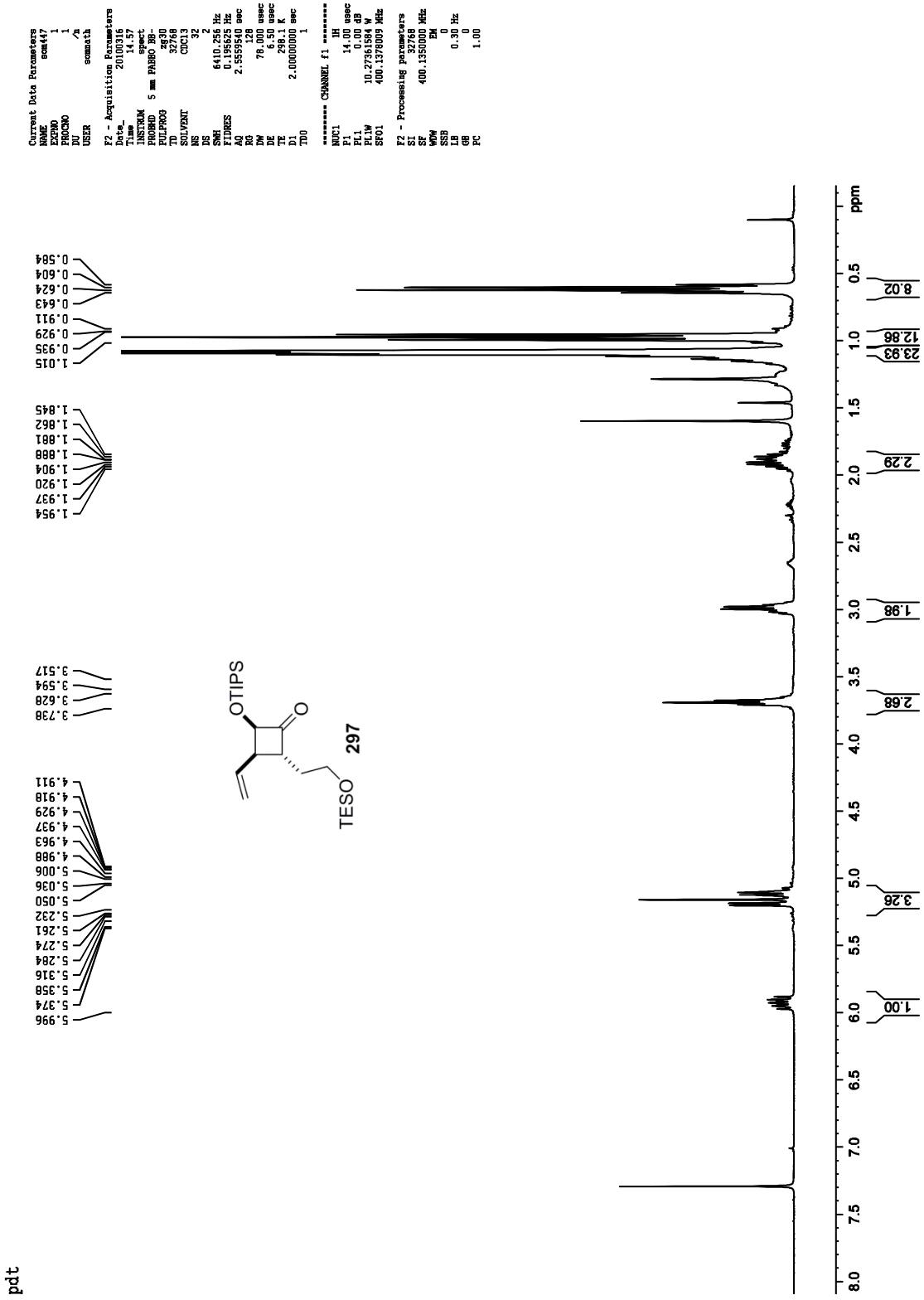

Current Data Parameters
NAME scm523
EXPNO 4
PROCNO 1
DU /m
USER somnath
F2 - Acquisition Parameters
Date_ 20101108
Time 20.36
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 5000
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 4096
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-7.35
-5.21
4.05
9.79
12.00
12.42
13.81
17.71
17.94
18.39
25.96
27.17
29.71
30.33
33.41
38.69
39.54
41.57
43.06
43.51
51.54
54.40
56.84
57.34
57.81
62.40
72.65
76.70
77.02
77.34
95.69
101.08
107.40
110.82
115.88
121.44
123.25
125.53
128.40
128.71
132.04
133.64
135.30
140.90
148.78
152.96
154.96
162.65
164.52
166.81
171.80
175.91
178.48
180.73
186.79
OTBS
OTIPS
O
PivO
288
pure
ppm

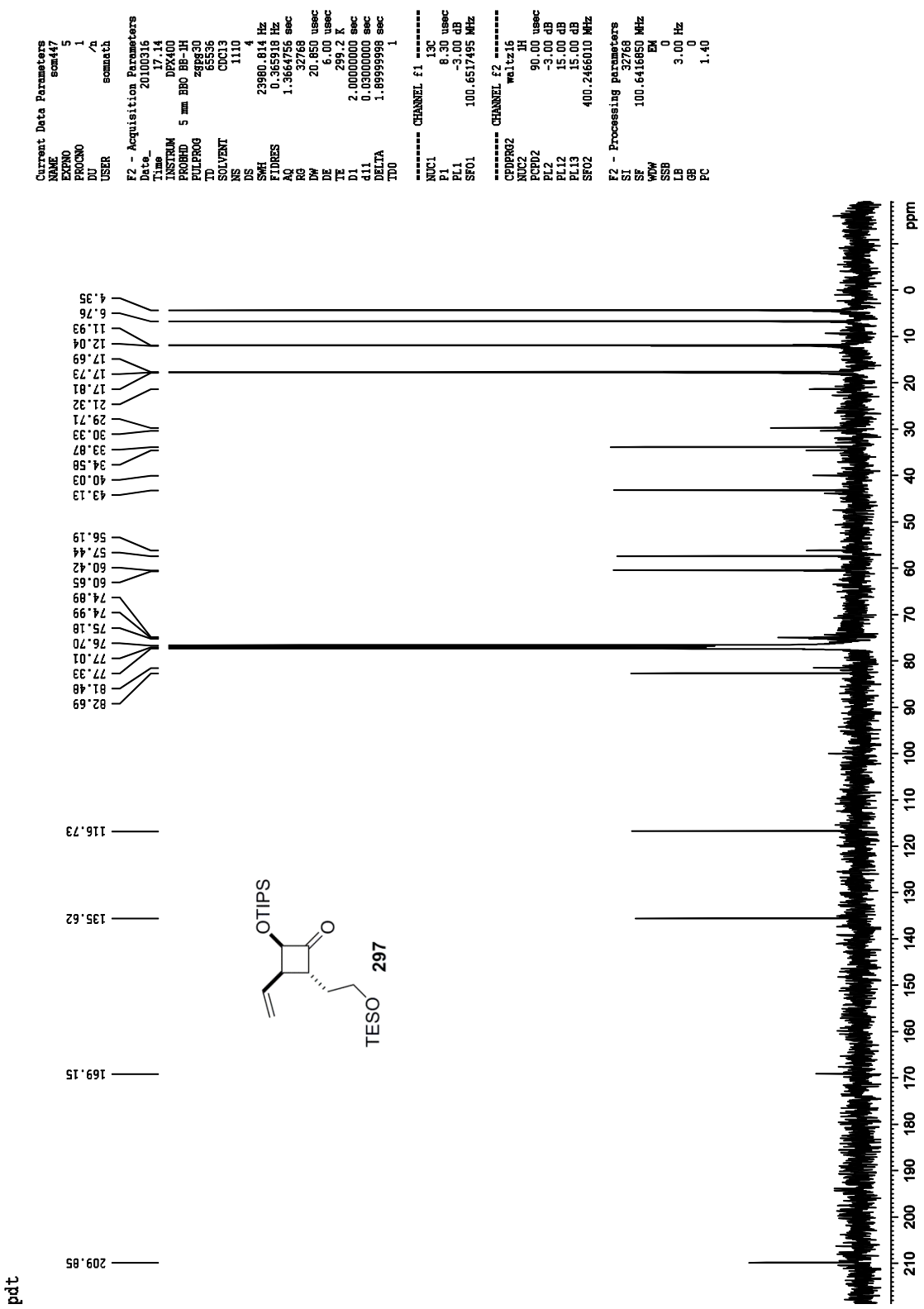

Current Data Parameters
NAME somi49
EXPNO 1
PROCNO 1
DU /a
USER somuth
F2 - Acquisition Parameters
Date_ 20100227
Time 16.07
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 128
DW 78.000 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
pure
OTIPS
OH
HO
289
ppm
30.95
1.99
1.73
1.08
1.03
1.91
1.41
1.39
2.34
2.16
1.00

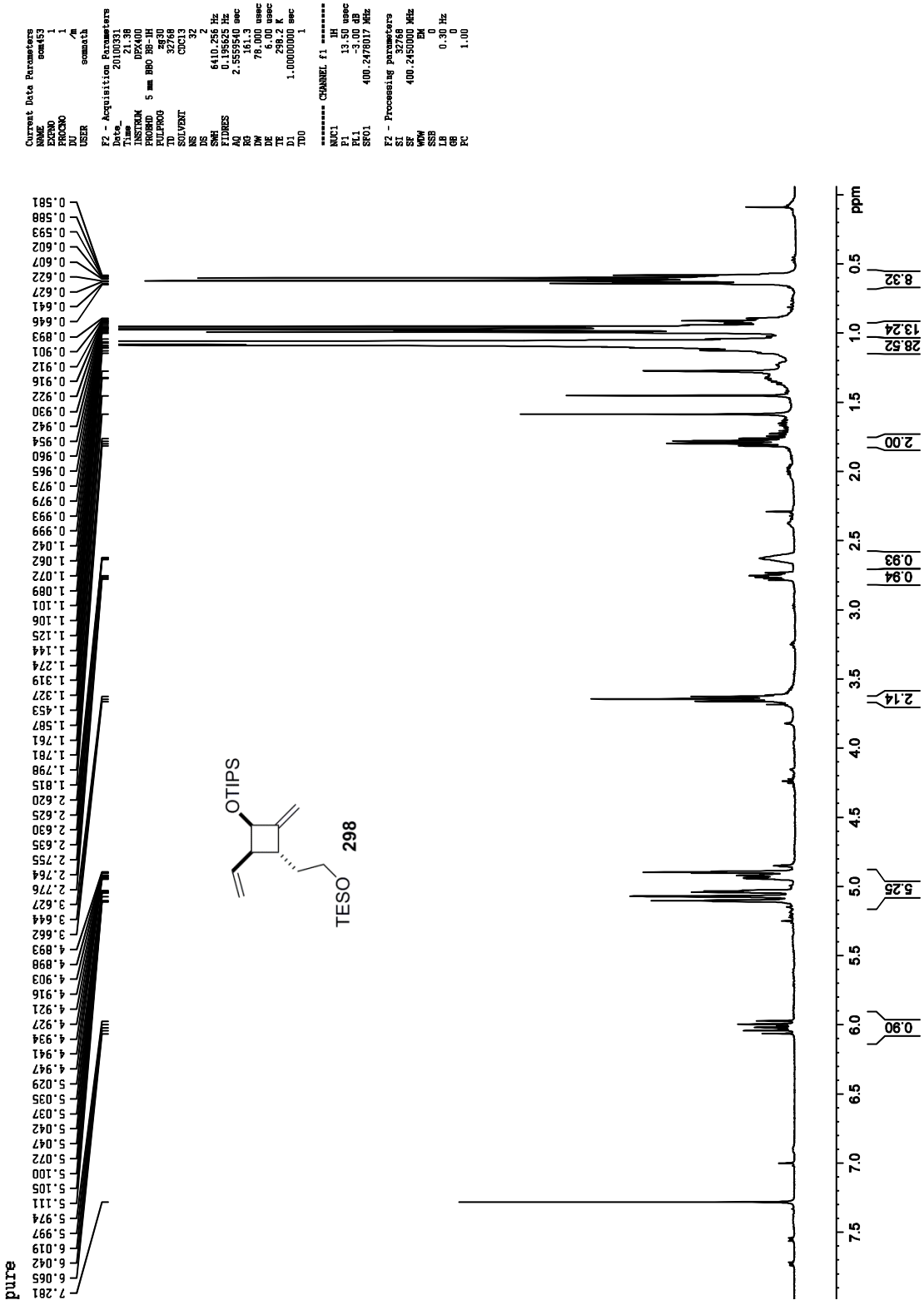

Current Data Parameters
NAME scm439
EXPNO 5
PROCNO 1
DU /n
USER somnath
F2 - Acquisition Parameters
Data_ 20100227
Time 18.04
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10240
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 32768
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
137.81
115.39
77.33
77.02
76.70
75.38
75.19
74.99
74.63
62.18
45.73
42.77
39.60
38.14
33.07
32.40
31.93
29.71
22.70
22.10
17.97
17.90
17.85
14.12
12.28
12.10
11.99
OTIPS
OH
HO
289
ppm
pure

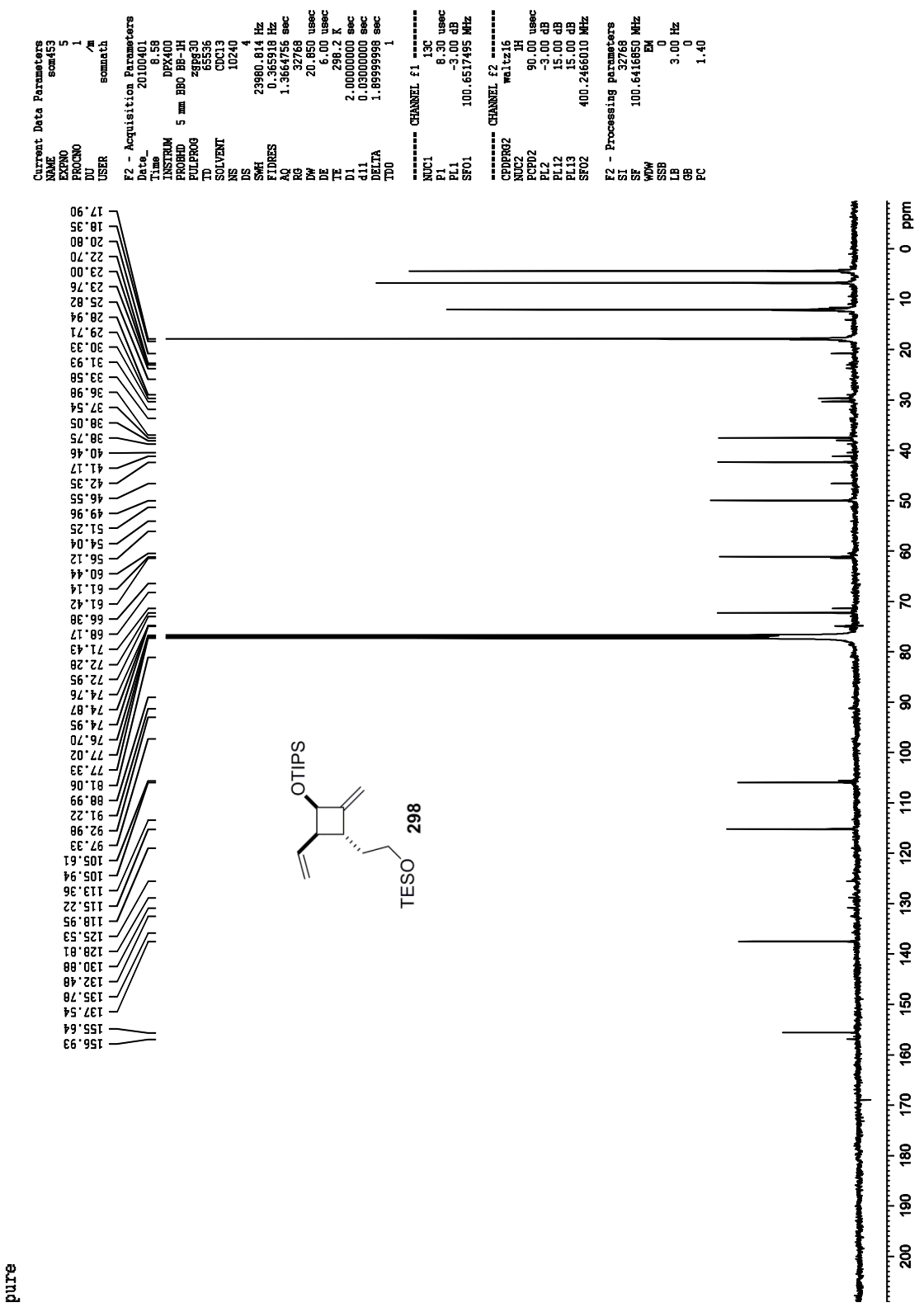

pure
OTIPS
OH
TESO
296
ppm
7.73
12.26
28.11
1.33
1.55
1.18
1.00
1.34
0.88
1.39
1.16
1.09
2.17
1.00

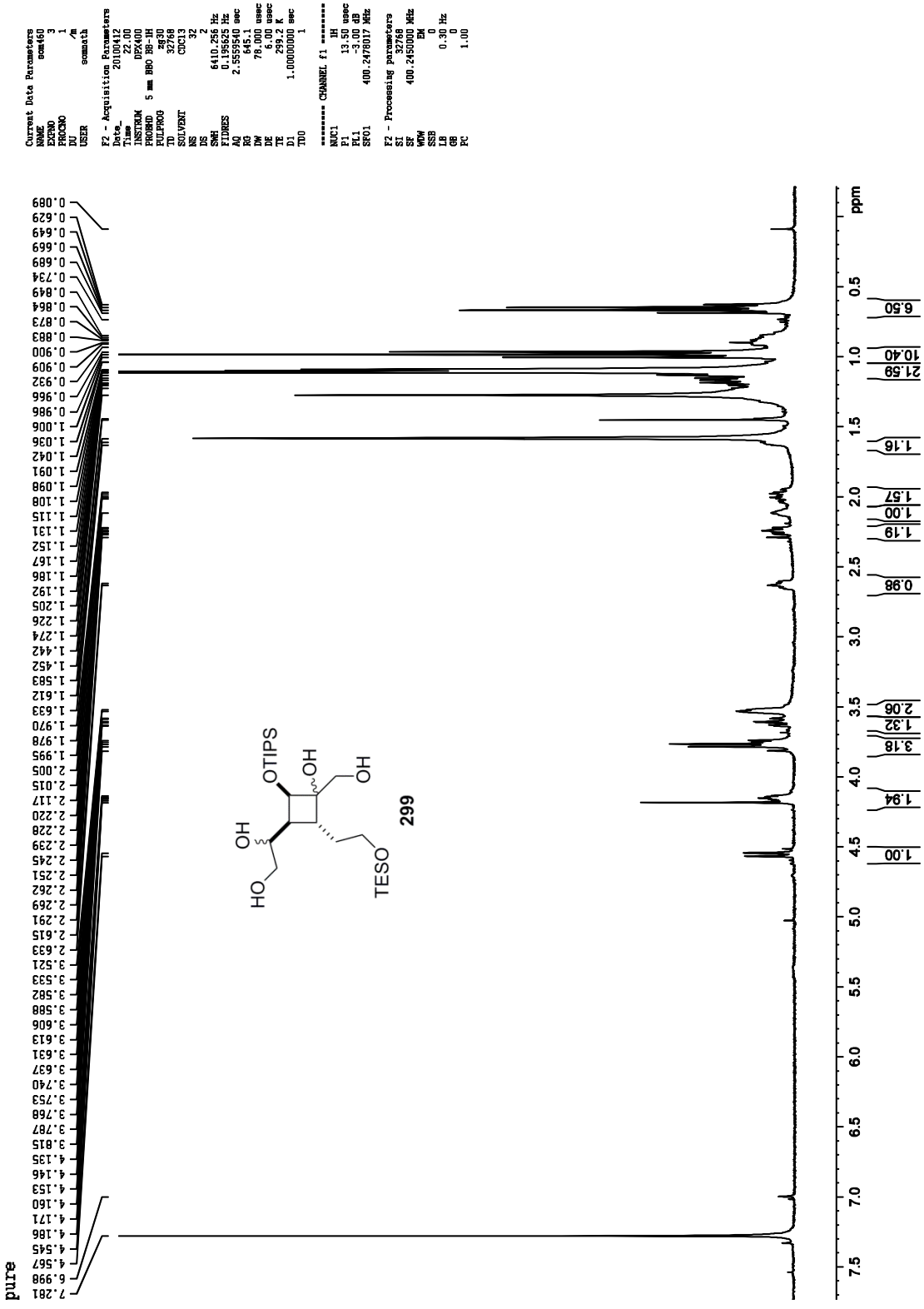

Current Data Parameters
NAME scm444
EXPNO 4
PROCNO 1
DU /m
USER somnath
F2 - Acquisition Parameters
Date_ 20100310
Time 13.36
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1004
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 32768
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
4.11
4.40
6.63
6.79
12.02
12.13
17.87
17.92
22.26
29.71
30.33
32.06
32.71
38.63
40.00
42.62
45.80
62.24
73.56
74.75
75.14
75.51
76.70
77.02
77.33
114.99
138.31
OTIPS
OH
TESO
296
pure
ppm

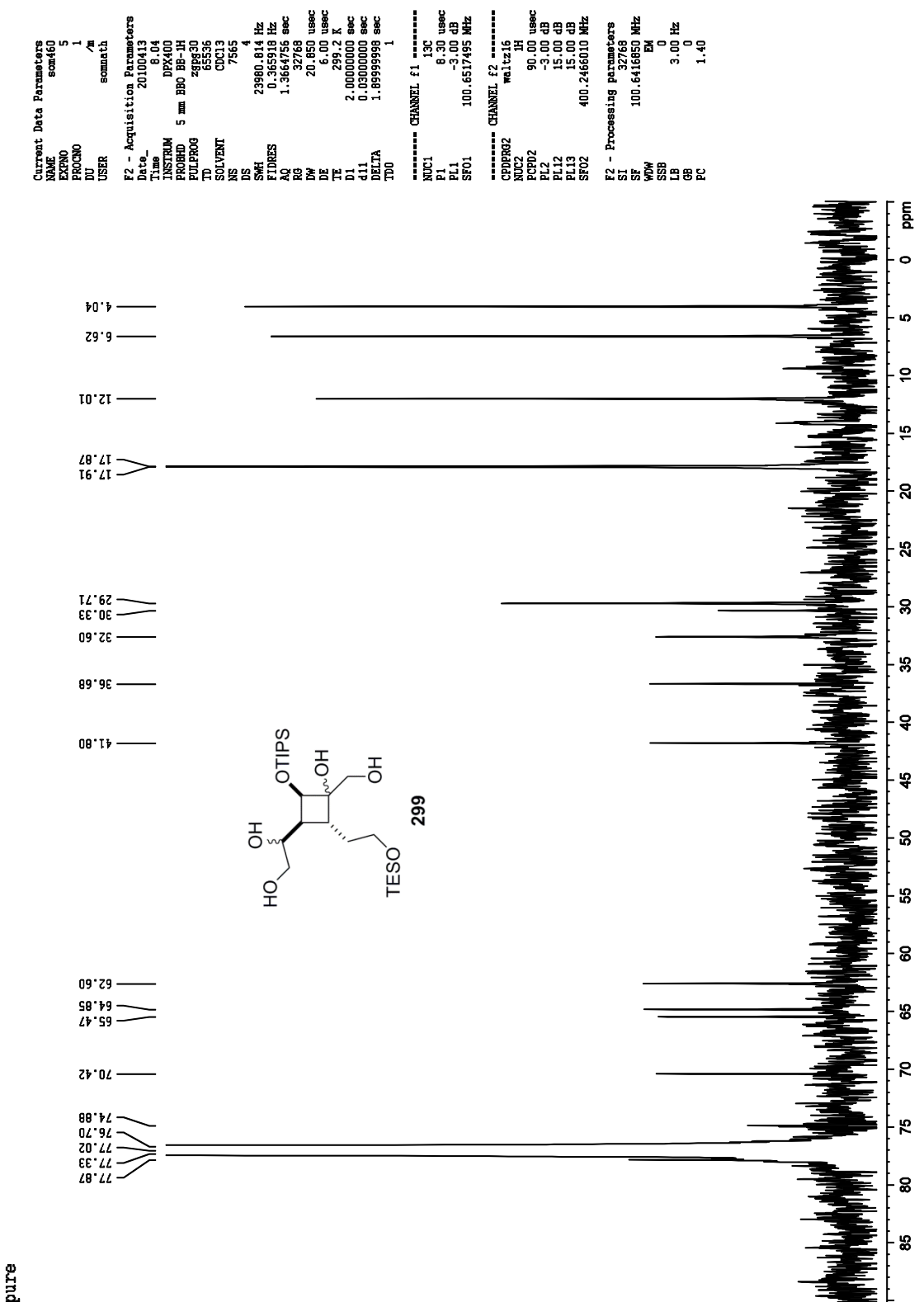

Current Data Parameters
NAME sca447
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100316
Time 14.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 228
DW 78.000 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
PL1W 10.27361584 W
SFO1 400.1378009 MHz
F2 - Processing parameters
SI 32768
SF 400.1350000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTIPS
O
TESO
297
pdt
ppm
8.02
12.86
23.93
2.29
1.98
2.66
3.26
1.00

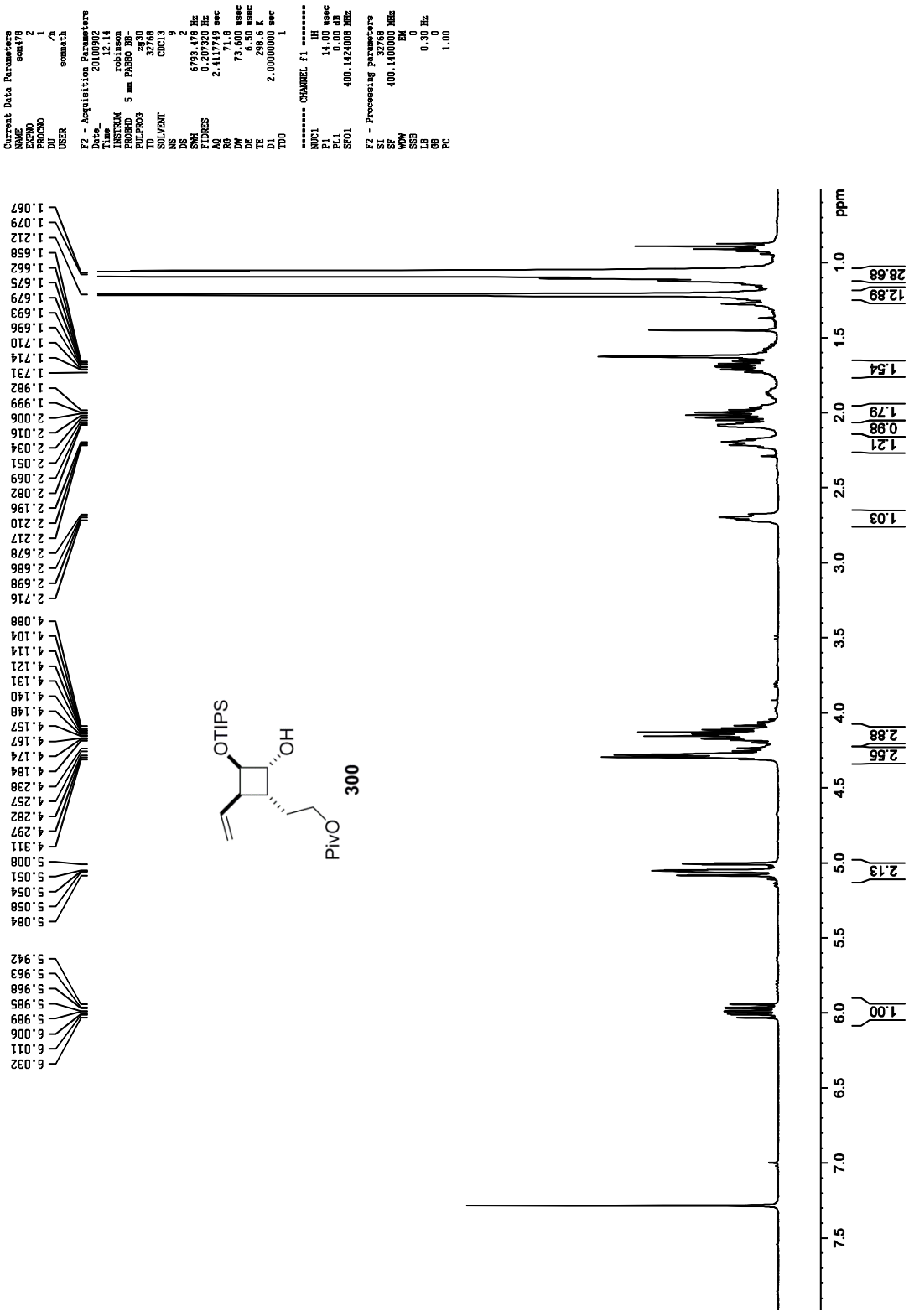

Current Data Parameters
NAME scm447
EXPNO 5
PROCNO 1
DU /n
USER somnath
F2 - Acquisition Parameters
Date_ 20100316
Time 17.14
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1110
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 32768
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
4.35
6.76
11.93
12.04
17.69
17.73
17.81
21.32
29.71
30.33
33.87
34.58
40.03
43.13
56.19
57.44
60.42
60.65
74.89
74.99
75.18
76.70
77.01
77.33
81.48
82.69
116.73
135.62
169.15
209.85
OTIPS
O
TESO
297
pdt
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

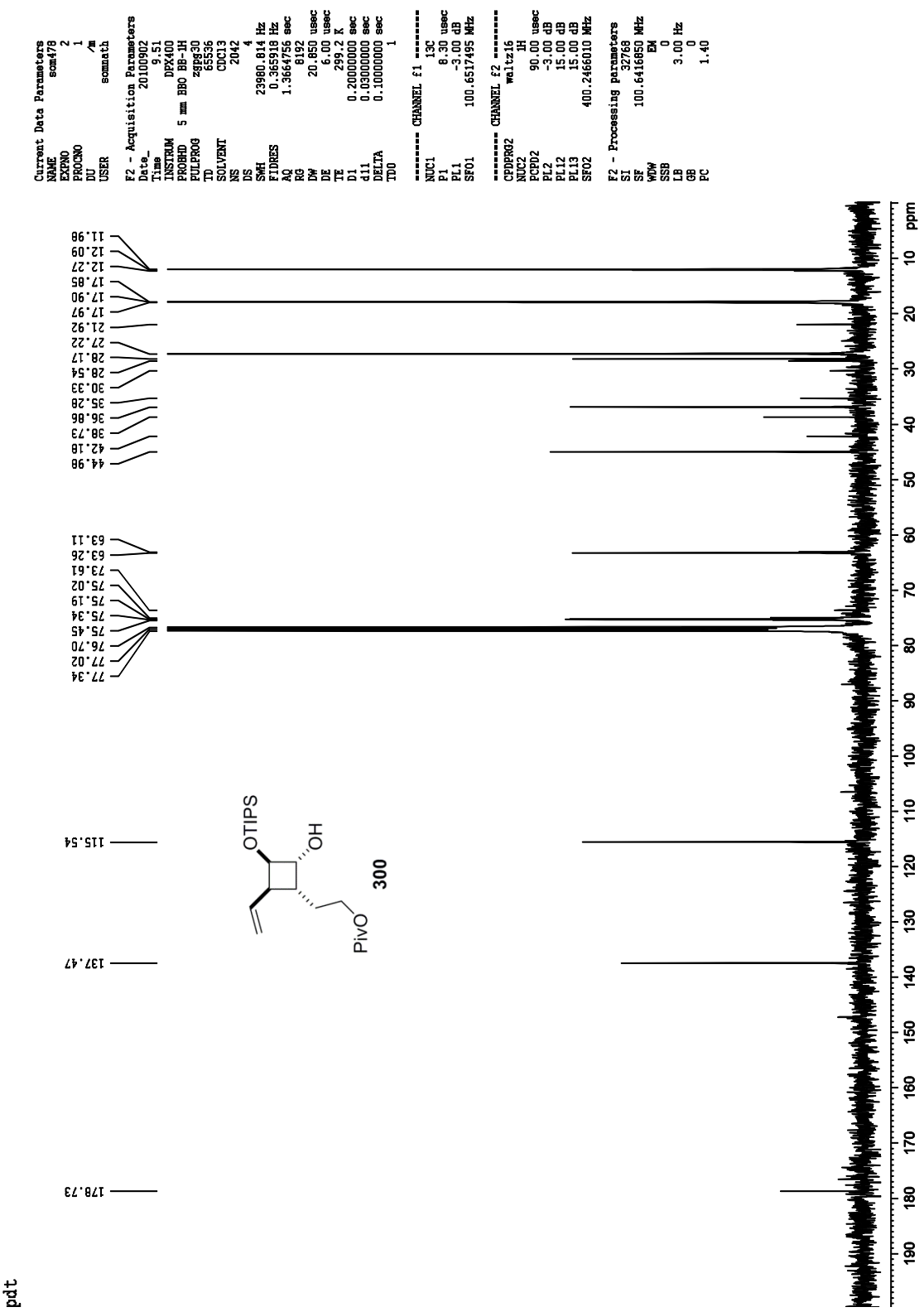

Current Data Parameters
NAME som453
EXPNO 1
PROCNO 1
DU /m
USER somnath
F2 - Acquisition Parameters
Date_ 20100331
Time 21.38
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 161.3
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTIPS
TESO
298
pure
ppm
8.32
13.24
28.52
2.00
0.94
0.93
2.14
5.25
0.90


Current Data Parameters
NAME scm453
EXPNO 5
PROCNO 1
DU /m
USER somnath
F2 - Acquisition Parameters
Date_ 20100401
Time 8.58
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10240
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 32768
DW 20.850 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
OTIPS
TESO
298
ppm

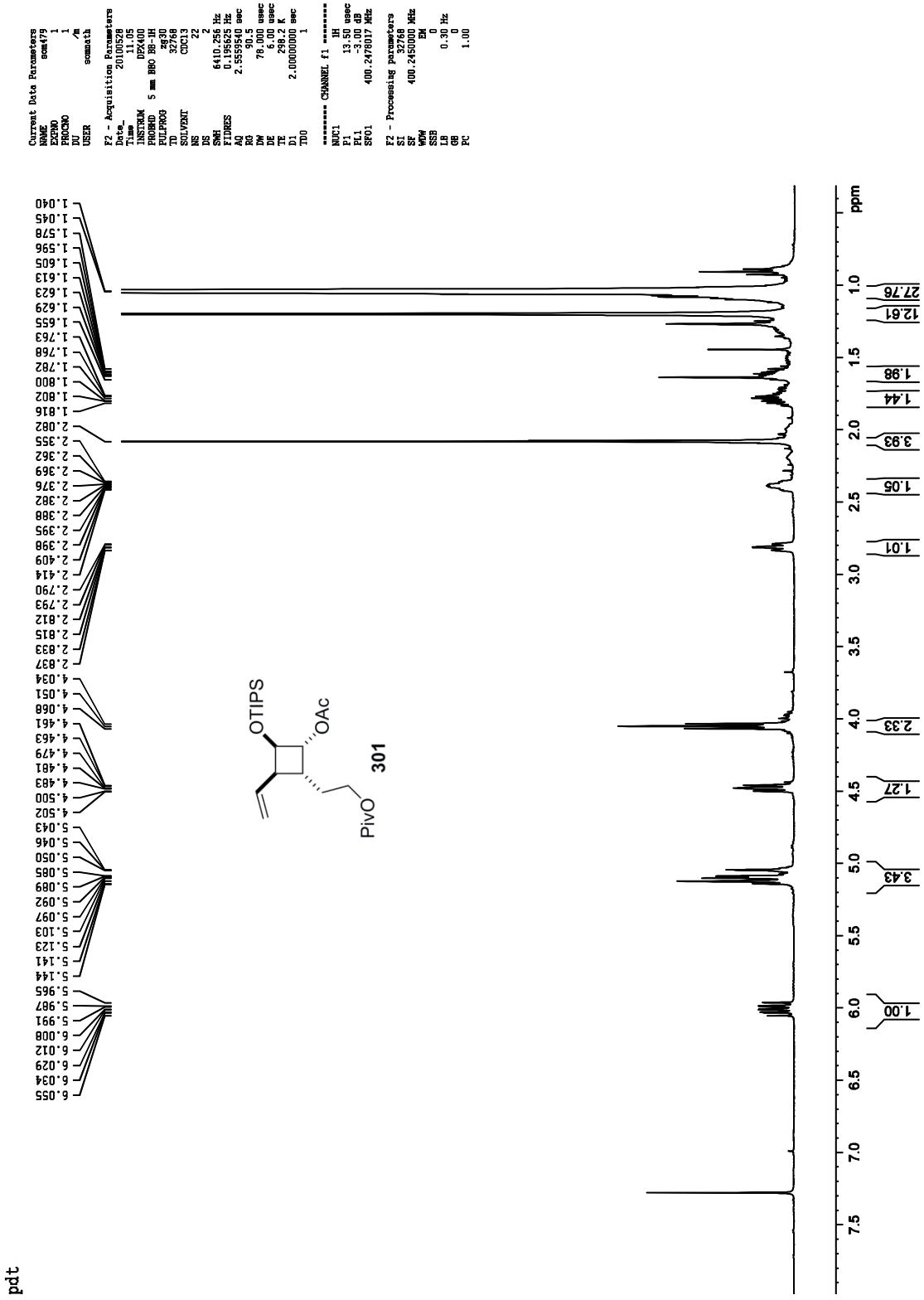

Current Data Parameters
NAME scm460
EXPNO 3
PROCNO 1
DU /m
USER scmauth
F2 - Acquisition Parameters
Date_ 20100412
Time 22.00
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 645.1
DW 78.000 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTIPS
OH
OH
OH
HO
TESO
299
pure
ppm
6.50
10.40
21.59
1.16
1.57
1.00
1.19
0.98
2.06
1.32
3.18
1.94
1.00

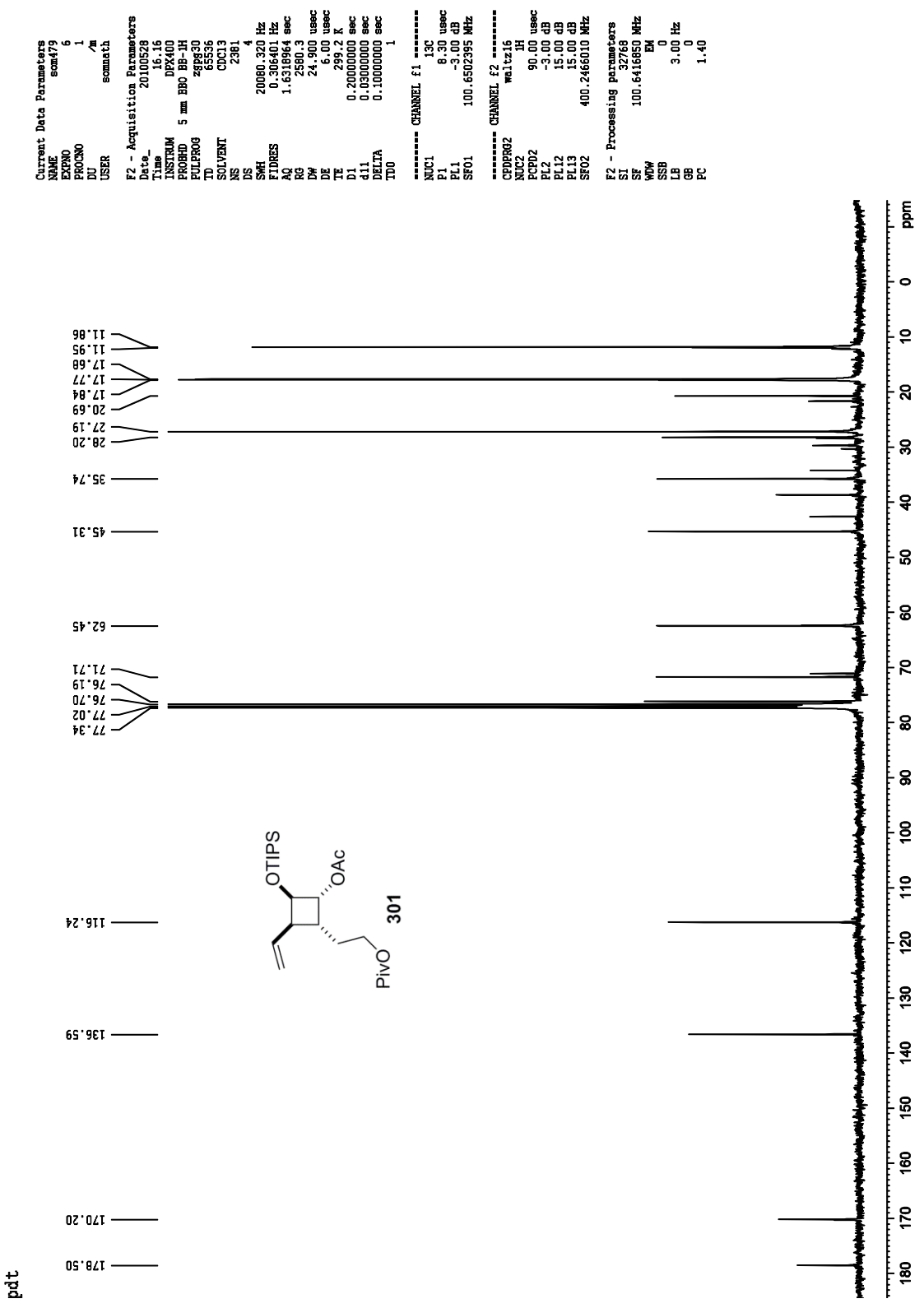

Current Data Parameters
NAME scm460
EXPNO 5
PROCNO 1
DU /m
USER somnath
F2 - Acquisition Parameters
Date_ 20100413
Time 8.04
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 7565
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 32768
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
4.04
6.62
12.01
17.87
17.91
29.71
30.33
32.60
36.68
41.80
62.60
64.85
65.47
70.42
74.88
76.70
77.02
77.33
77.87
OTIPS
OH
OH
HO
OH
TESO
299
ppm
pure

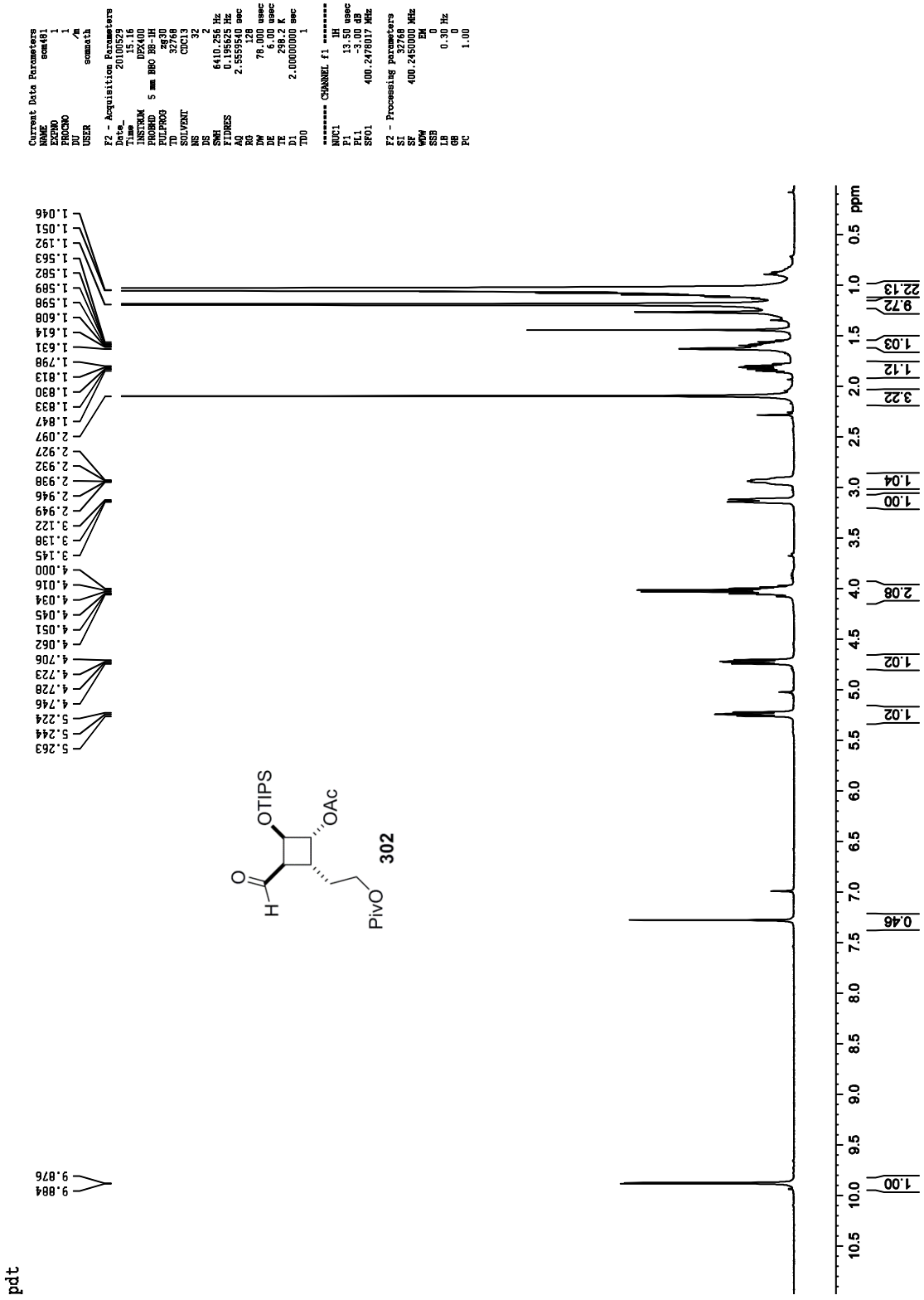

Current Data Parameters
NAME sonf9
EXPNO 2
PROCNO 1
DU /a
USER sonnath
F2 - Acquisition Parameters
Date_ 20100902
Time 12.14
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 2
DS 2
SWH 6793.476 Hz
FIDRES 0.207320 Hz
AQ 2.4117749 sec
RG 71.8
DW 73.600 usec
DE 6.50 usec
TE 298.6 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1424008 MHz
F2 - Processing parameters
SI 32768
SF 400.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTIPS
OH
PivO
300
ppm
28.68
12.89
1.54
1.79
0.98
1.21
1.03
2.88
2.55
2.13
1.00

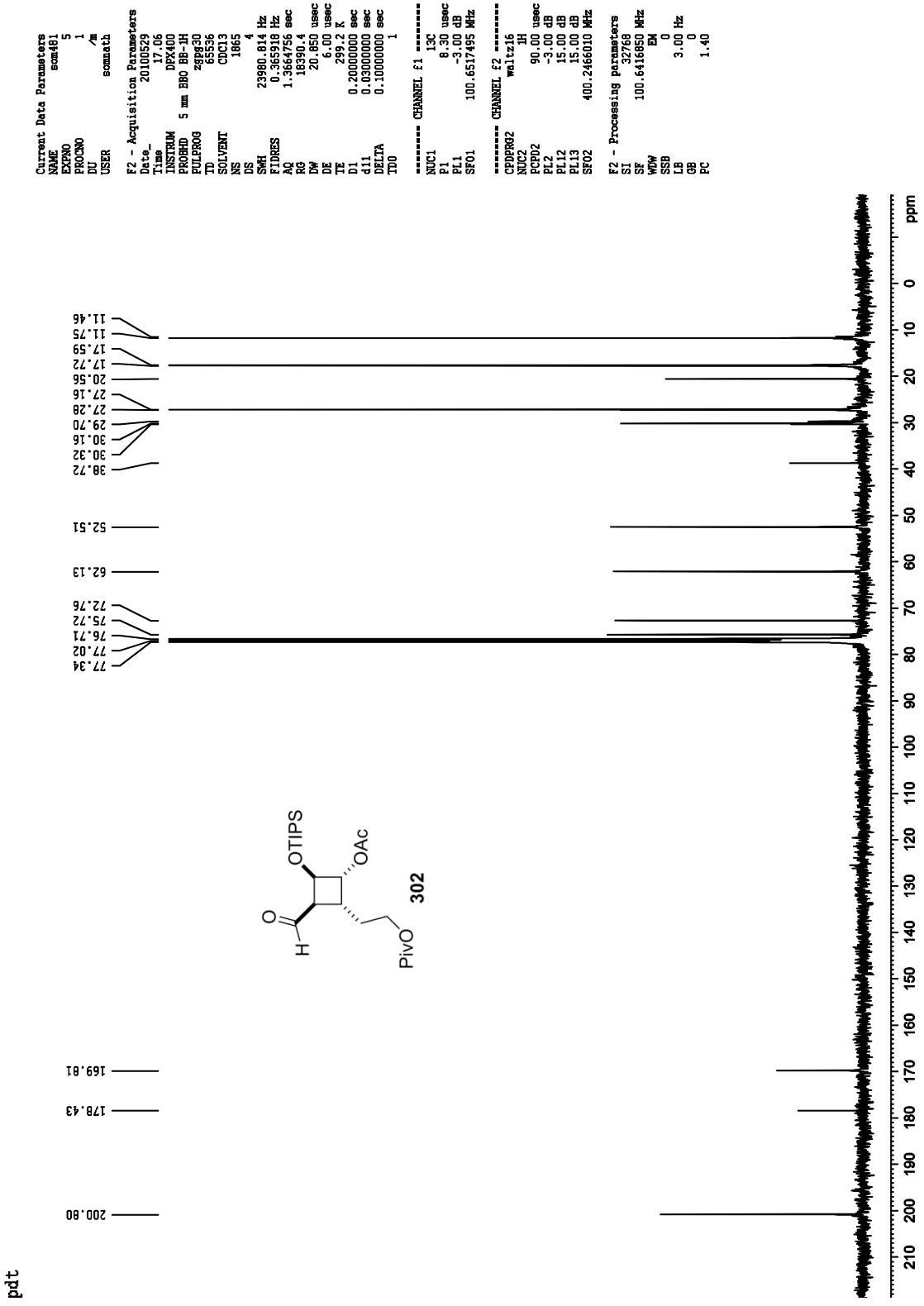

Current Data Parameters
NAME scm478
EXPNO 2
PROCNO 1
DU /m
USER somnath
F2 - Acquisition Parameters
Date_ 20100902
Time 9.51
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2042
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 8192
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
11.98
12.09
12.27
17.85
17.90
17.97
21.92
27.22
28.17
28.54
30.33
35.28
36.86
38.73
42.18
44.98
63.11
63.26
73.61
75.02
75.19
75.34
75.45
76.70
77.02
77.34
115.54
137.47
178.73
OTIPS
OH
PivO
300
ppm

pdt

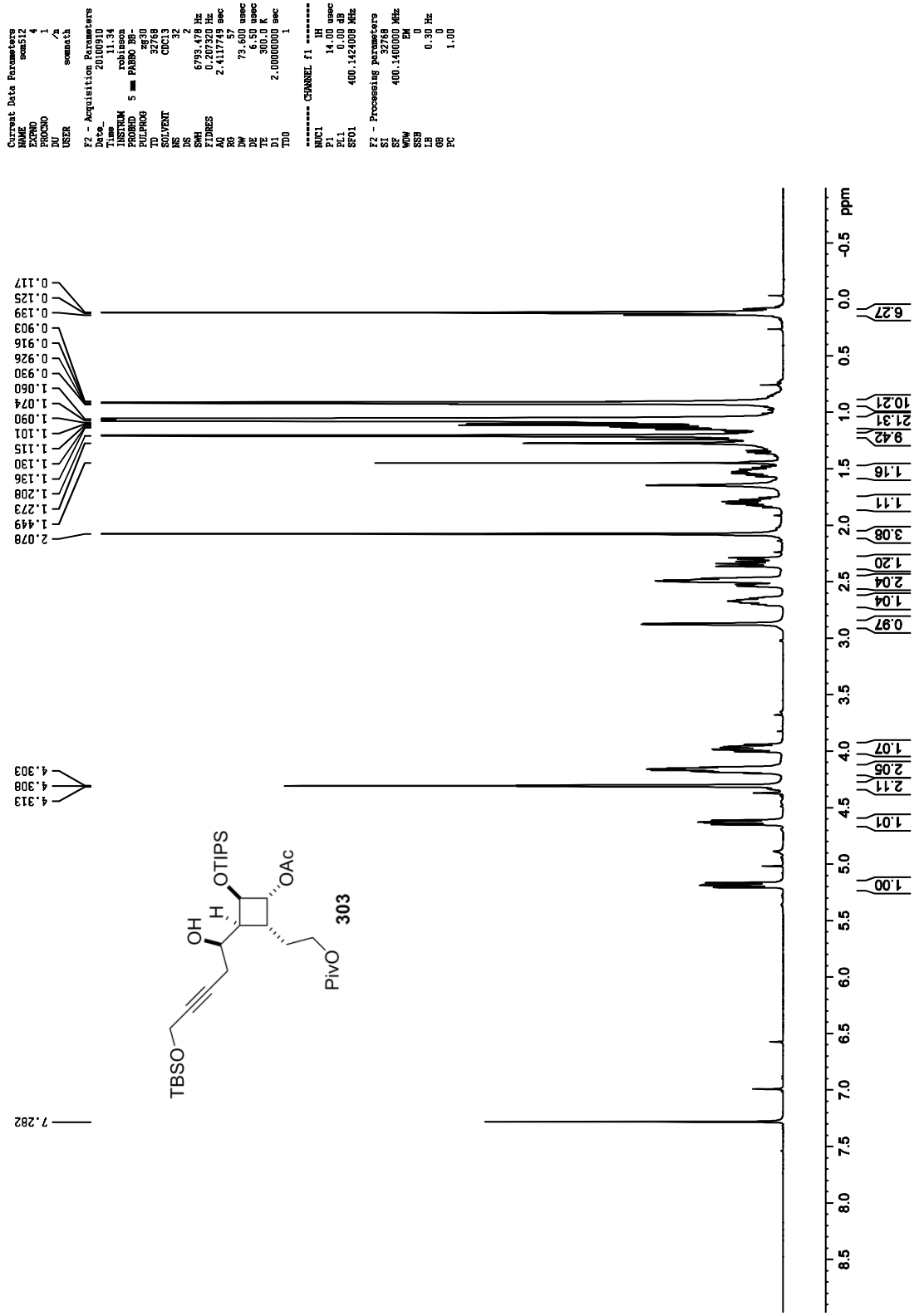

Current Data Parameters
NAME som479
EXPNO 1
PROCNO 1
DATA /m
USER sommath
F2 - Acquisition Parameters
Date_ 20100528
Time 11.05
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 22
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 203.5
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTIPS
OAc
PivO
301
pdt
ppm
1.00
3.43
1.27
2.33
4.00
1.01
1.05
3.93
2.00
1.44
1.98
12.61
27.76

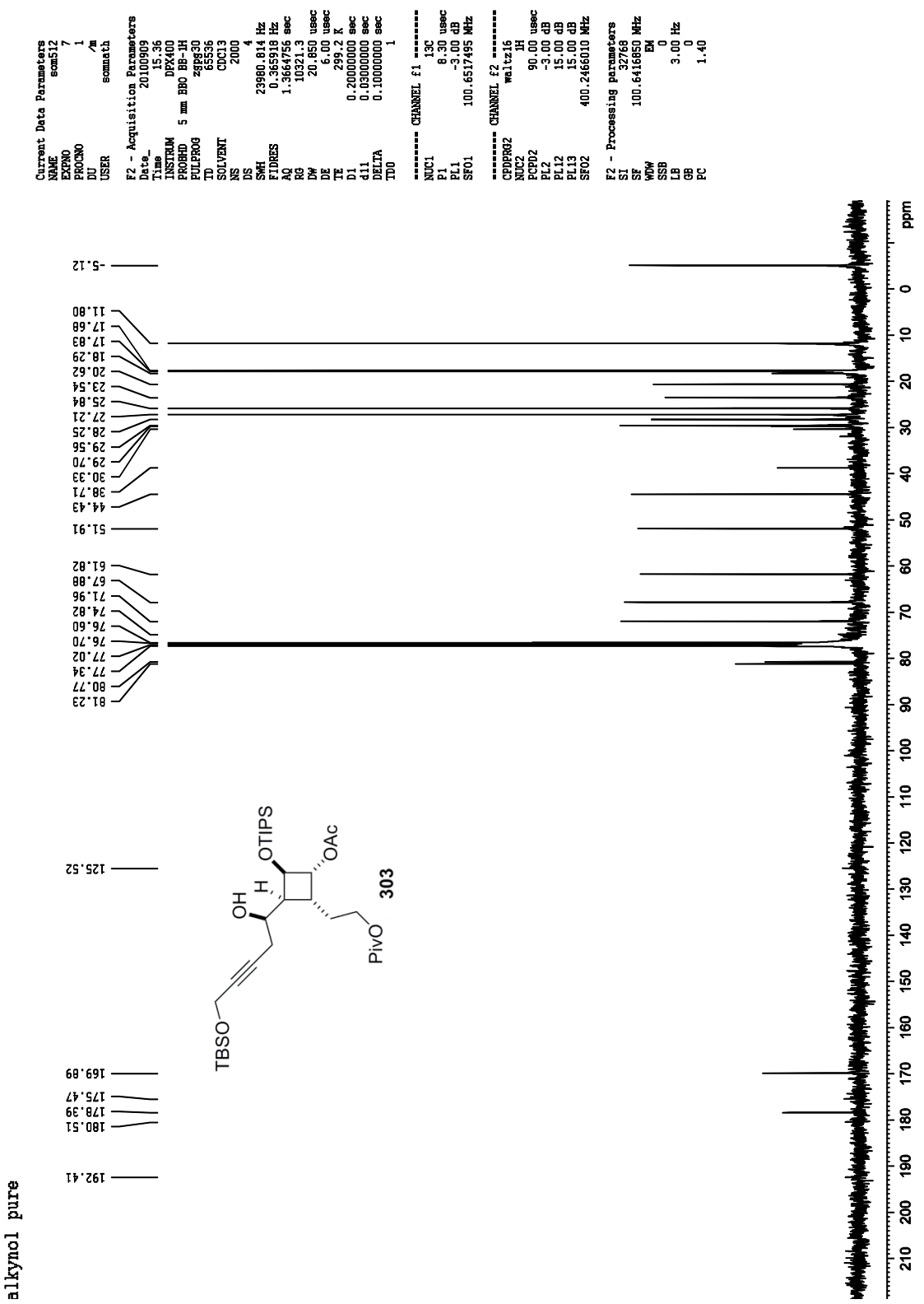

Current Data Parameters
NAME scm479
EXPNO 6
PROCNO 1
DU /m
USER somnath
F2 - Acquisition Parameters
Data_ 20100528
Time_ 16.16
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2381
DS 4
SWH 20080.320 Hz
FIDRES 0.306401 Hz
AQ 1.6318964 sec
RG 2580.3
DW 24.900 usec
DE 6.00 usec
TE 299.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6502395 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
pdt
178.50
170.20
136.59
116.24
77.34
77.02
76.70
76.19
71.71
62.45
45.31
35.74
28.20
27.19
20.69
17.84
17.77
17.68
11.95
11.86
OTIPS
OAc
PivO
301
ppm

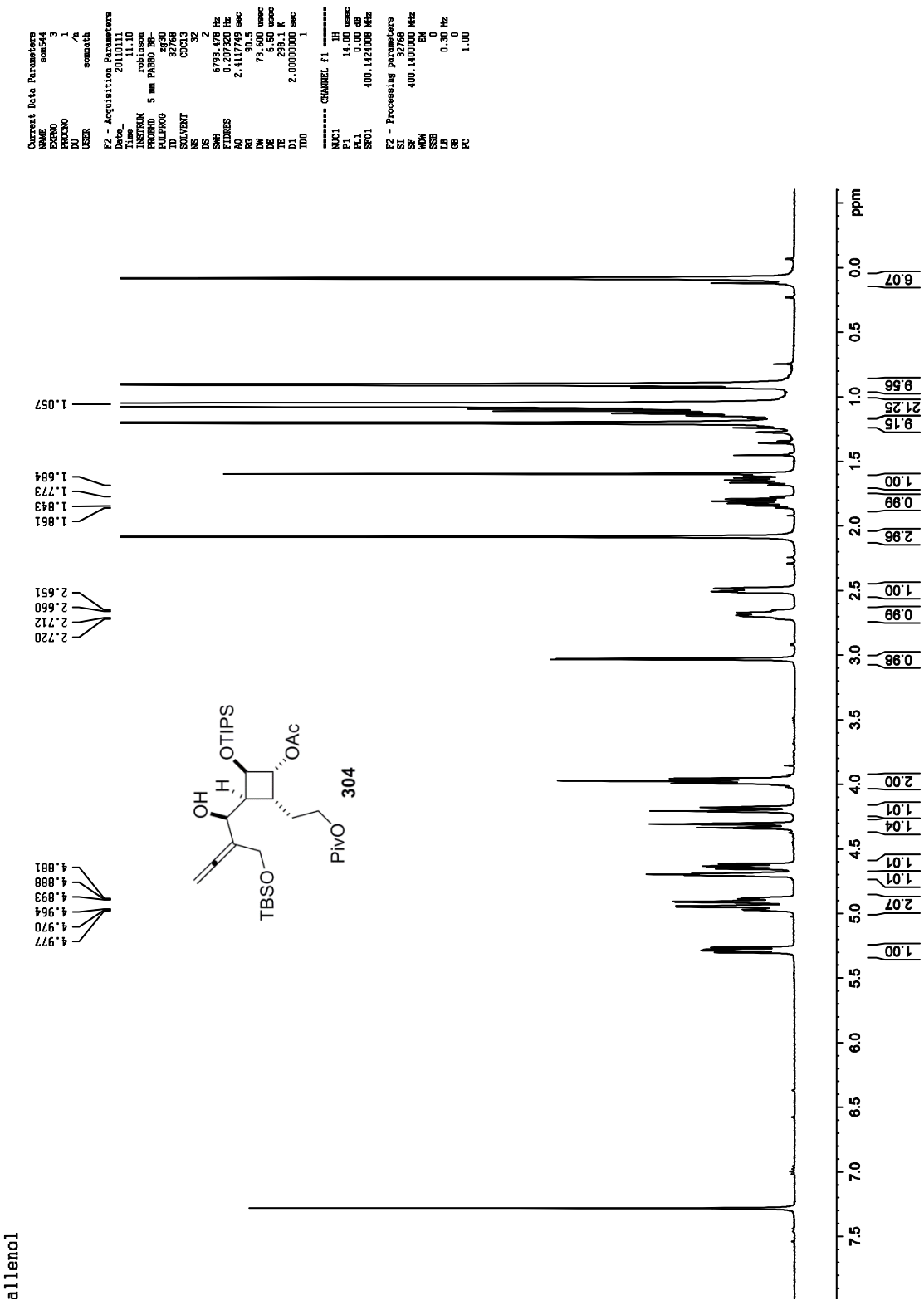

Current Data Parameters
NAME som401
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Data_ 20100529
Time_ 15.16
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 228
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.876
9.864
5.263
5.244
5.224
4.746
4.728
4.723
4.706
4.062
4.051
4.045
4.034
4.016
4.000
3.145
3.138
3.122
2.949
2.946
2.938
2.932
2.927
2.097
1.847
1.833
1.830
1.813
1.798
1.631
1.614
1.608
1.598
1.589
1.582
1.563
1.192
1.051
1.046
OTIPS
OAc
O
H
PivO
302
pdt
ppm
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
8.5
9.0
9.5
10.0
10.5
1.00
0.46
1.02
1.02
1.00
2.08
1.04
1.00
3.22
1.12
1.03
9.72
22.13

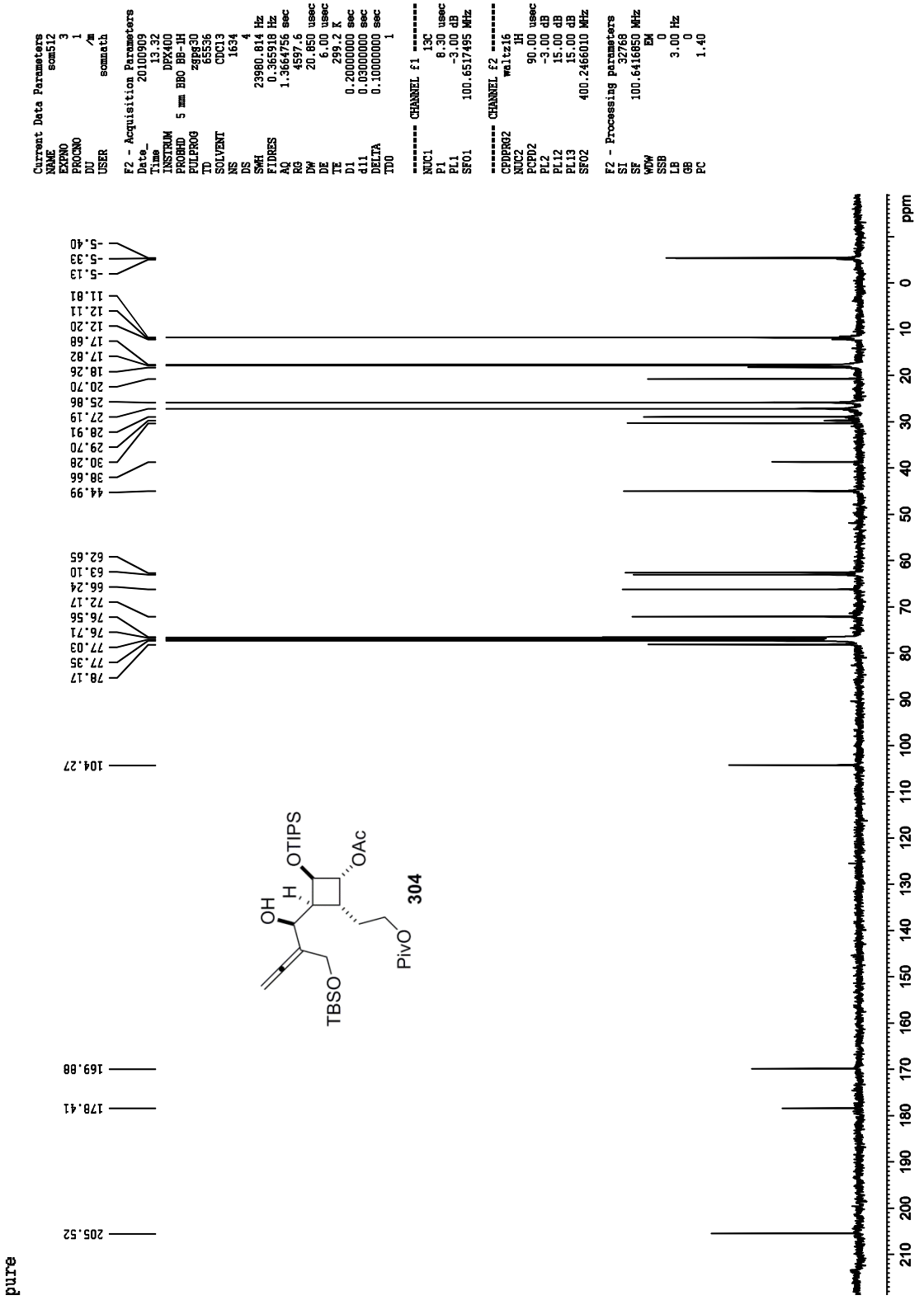

Current Data Parameters
NAME scm481
EXPNO 5
PROCNO 1
DU /m
USER sommath
F2 - Acquisition Parameters
Data_ 20100529
Time_ 17.06
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1865
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 18390.4
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
11.46
11.75
17.59
17.72
20.56
27.16
27.28
29.70
30.16
30.32
38.72
52.51
62.13
72.76
75.72
76.71
77.02
77.34
169.81
178.43
200.80
OTIPS
OAc
O
H
PivO
302
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

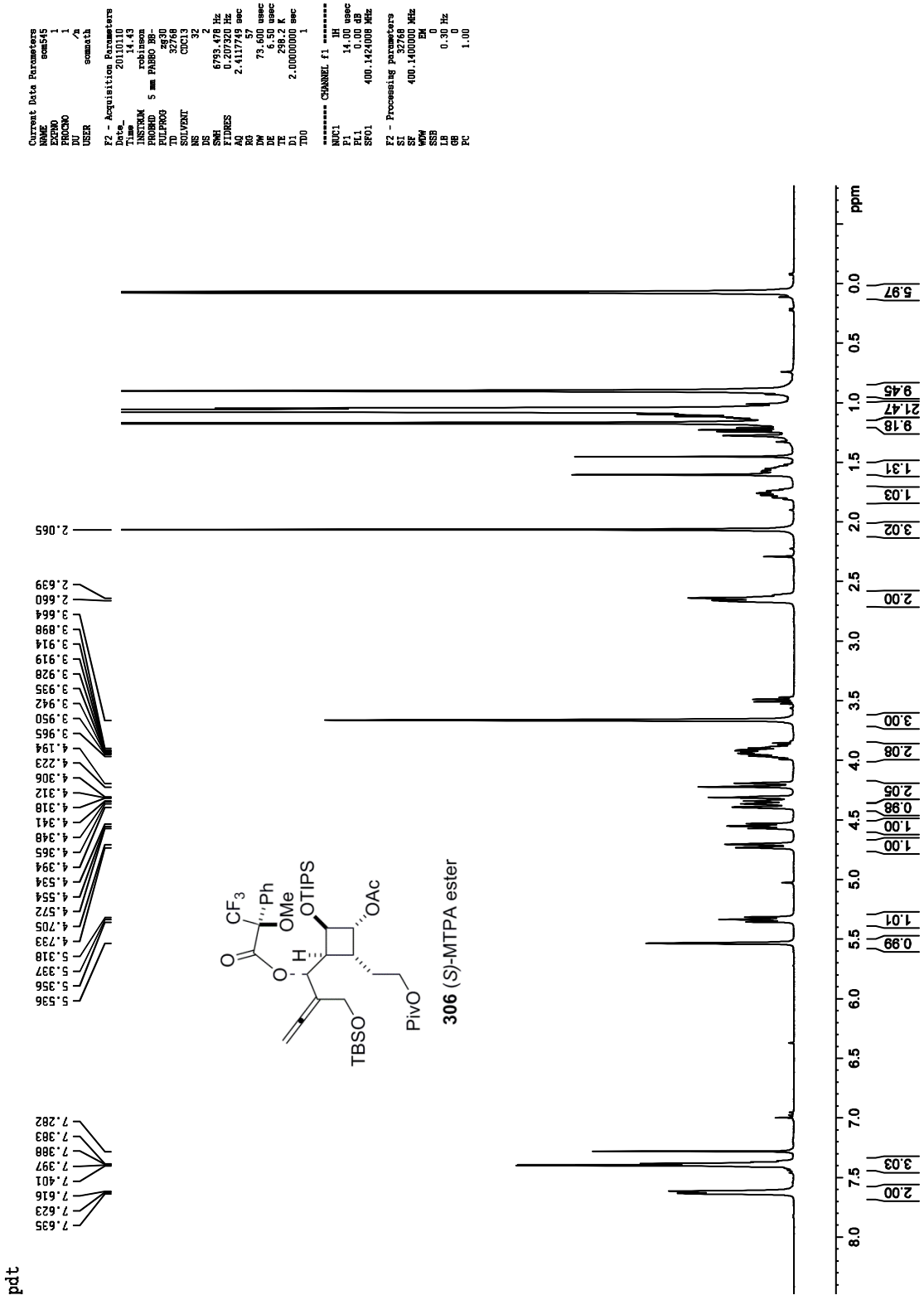
pdt

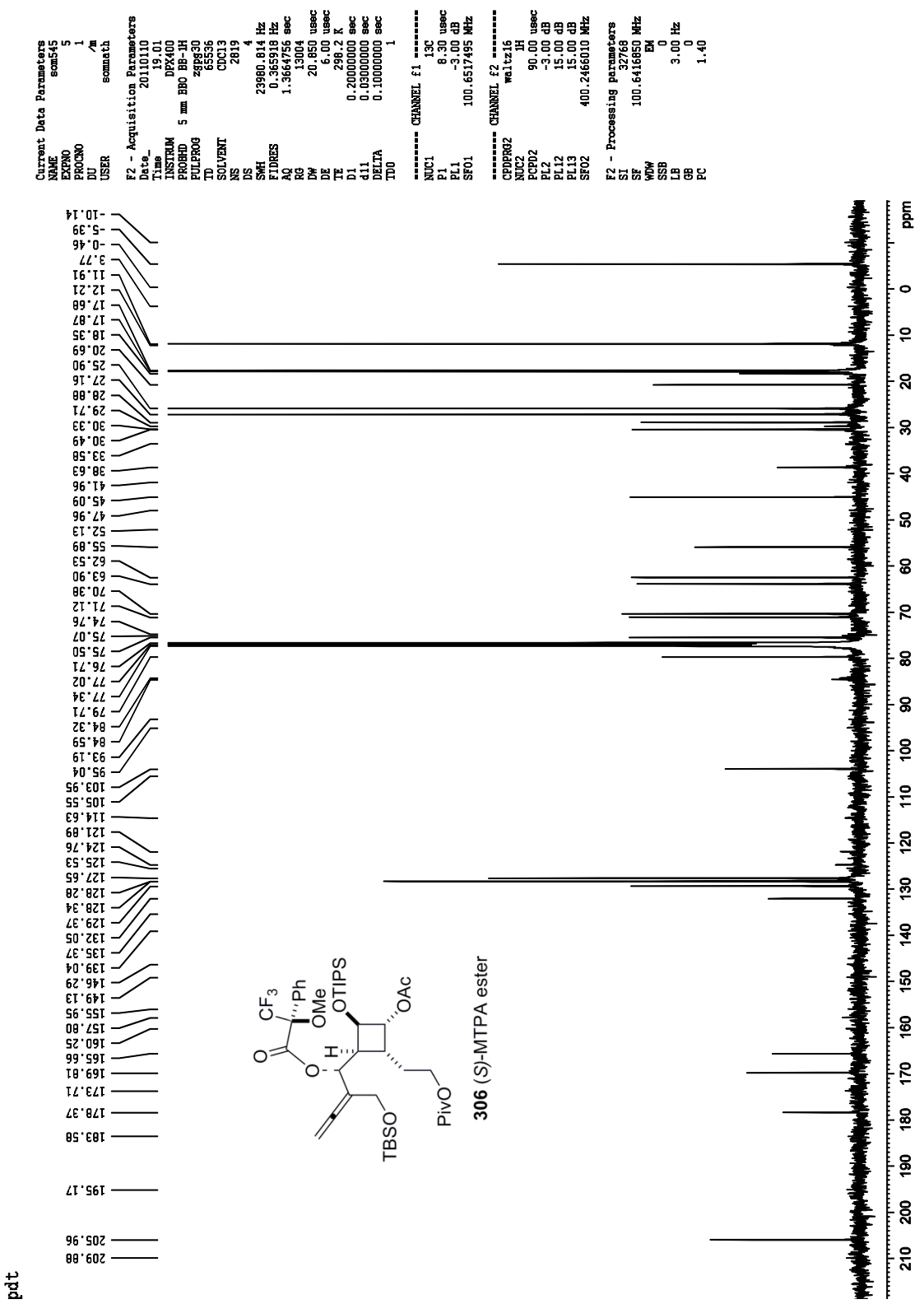

Current Data Parameters
NAME scm512
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Data_ 20100910
Time 11.34
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6793.478 Hz
FIDRES 0.207320 Hz
AQ 2.4117749 sec
RG 57
DW 73.600 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1424009 MHz
F2 - Processing parameters
SI 32768
SF 400.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
TBSO
OH
H
OTIPS
OAc
PivO
303
ppm

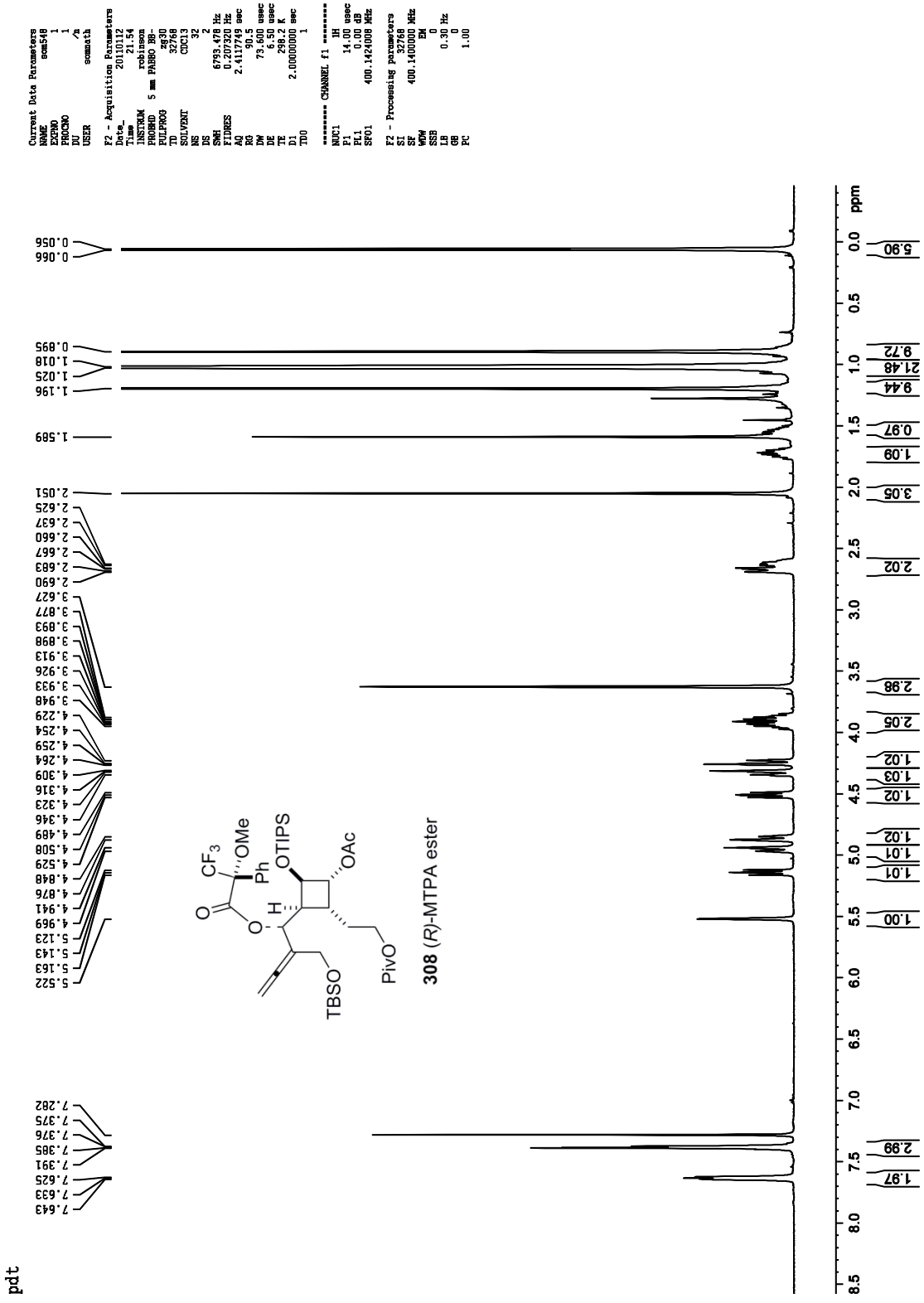

alkynol pure
Current Data Parameters
NAME scm512
EXPNO 7
PROCNO 1
DU /m
USER somnath
F2 - Acquisition Parameters
Data_ 20100909
Time 15.36
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2000
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 10321.3
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.12
11.80
17.68
17.83
18.29
20.62
23.54
25.84
27.21
28.25
29.56
29.70
30.33
38.71
44.43
51.91
61.82
67.88
71.96
74.82
76.60
76.70
77.02
77.34
80.77
81.23
125.52
169.89
175.47
178.39
180.51
192.41
TBSO
OH
H
OTIPS
OAc
PivO
303
ppm

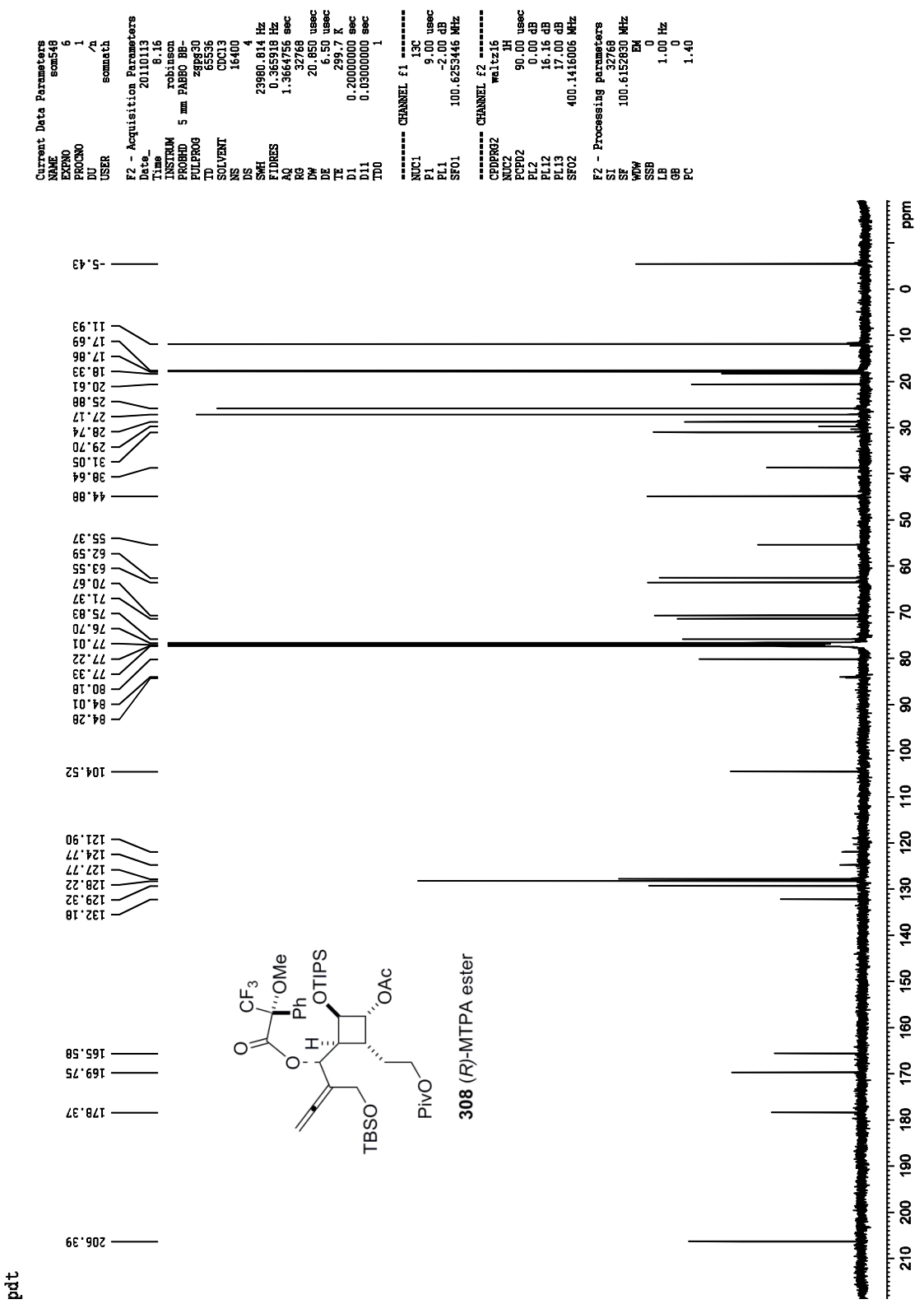

allenol
Current Data Parameters
NAME sam544
EXPNO 3
PROCNO 1
DU /a
USER somnath
F2 - Acquisition Parameters
Date_ 20110111
Time 11.10
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6793.478 Hz
FIDRES 0.207320 Hz
AQ 2.4117749 sec
RG 90.5
DW 73.600 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1424008 MHz
F2 - Processing parameters
SI 32768
SF 400.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
4.977
4.970
4.964
4.893
4.888
4.881
2.720
2.712
2.660
2.651
1.861
1.843
1.773
1.684
1.057
OH
H
OTIPS
OAc
PivO
TBSO
304
6.07
9.56
21.25
9.15
1.00
0.99
2.96
1.00
0.99
0.98
2.00
1.04
1.01
1.01
1.01
2.07
1.00
ppm

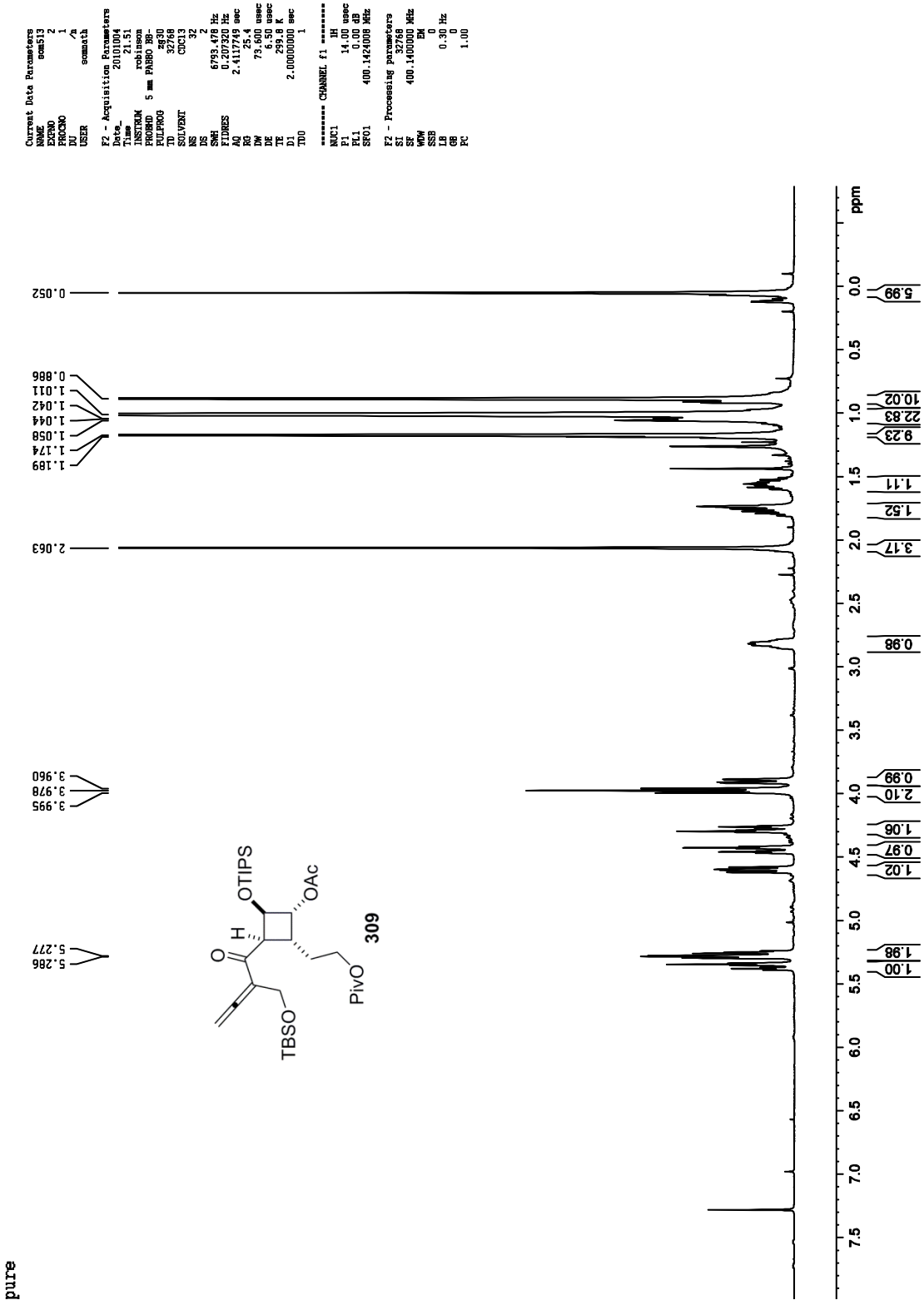

Current Data Parameters
NAME scm512
EXPNO 3
PROCNO 1
DU /m
USER sommath
F2 - Acquisition Parameters
Date_ 20100909
Time 13.32
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1634
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 4597.6
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.40
-5.33
-5.13
11.81
12.11
12.20
17.68
17.82
18.26
20.70
25.86
27.19
28.91
29.70
30.28
38.66
44.99
62.65
63.10
66.24
72.17
76.56
76.71
77.03
77.35
78.17
104.27
169.88
178.41
205.52
OH
H
OTIPS
OAc
PivO
TBSO
304
pure
ppm

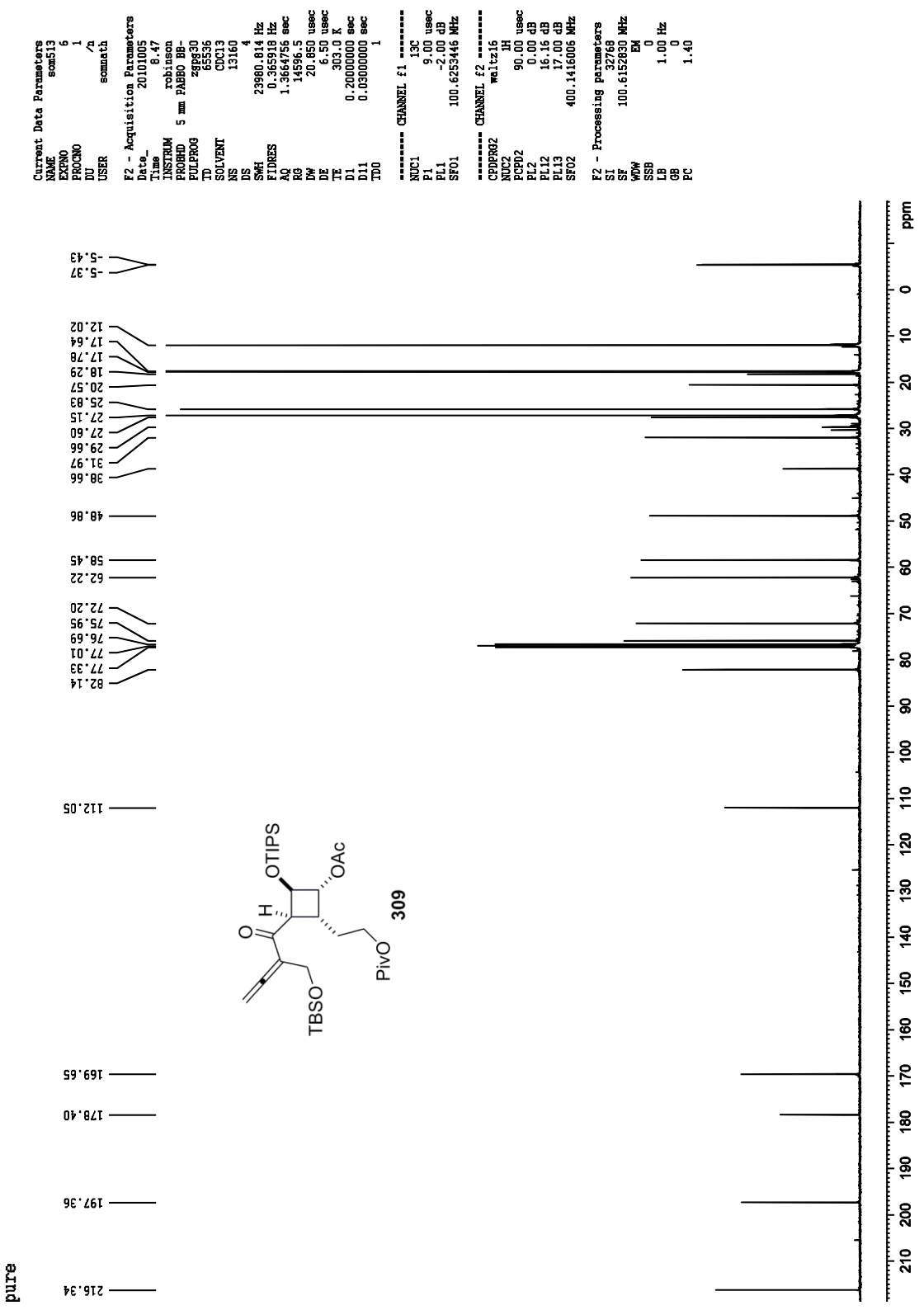

Current Data Parameters
NAME som545
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Data_ 20110110
Time 14.43
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6793.478 Hz
FIDRES 0.207320 Hz
AQ 2.4117749 sec
RG 57
DW 73.600 usec
DE 6.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1424008 MHz
F2 - Processing parameters
SI 32768
SF 400.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
pdt
306 (S)-MTPA ester
ppm


Current Data Parameters
NAME scm545
EXPNO 5
PROCNO 1
DU /m
USER sommath
F2 - Acquisition Parameters
Data_ 20110110
Time 19.01
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2019
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 13004
DW 20.850 usec
DE 6.00 usec
TE 298.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
pdt
-10.14
-5.39
-0.46
3.77
11.91
12.21
17.68
17.87
18.35
20.69
25.90
27.16
28.88
29.71
30.33
30.49
33.58
38.63
41.96
45.09
47.96
52.13
55.89
62.53
63.90
70.38
71.12
74.76
75.07
75.50
76.71
77.02
77.34
79.71
84.32
84.59
93.19
95.04
103.95
105.55
114.63
121.89
124.76
125.53
127.65
128.28
128.34
129.37
132.05
135.37
139.04
146.29
149.13
155.95
157.80
160.25
165.66
169.81
173.71
178.37
183.58
195.17
205.96
209.88
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
CF3
Ph
OMe
O
H
OTIPS
OAc
TBSO
PivO
306 (S)-MTPA ester


Current Data Parameters
NAME sos548
EXPNO 1
PROCNO 1
DATA /n
USER sosmath
F2 - Acquisition Parameters
Date_ 20110112
Time 21.54
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6793.478 Hz
FIDRES 0.207320 Hz
AQ 2.4111719 sec
RG 90.5
DW 73.600 usec
DE 6.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1424008 MHz
F2 - Processing parameters
SI 32768
SF 400.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
pdt
0.056
0.066
0.895
1.018
1.025
1.196
1.589
2.051
2.625
2.637
2.660
2.667
2.683
2.690
3.627
3.877
3.893
3.898
3.913
3.926
3.933
3.948
4.229
4.254
4.259
4.264
4.309
4.316
4.323
4.346
4.489
4.508
4.529
4.848
4.876
4.941
4.969
5.123
5.143
5.163
5.522
7.282
7.375
7.376
7.385
7.391
7.625
7.633
7.643
5.90
9.72
21.48
9.44
0.97
1.09
3.05
2.02
2.98
2.05
1.02
1.03
1.02
1.02
1.01
1.01
1.00
2.99
1.97
ppm
CF3
OMe
Ph
OTIPS
H
O
O
OAc
TBSO
PivO
308 (R)-MTPA ester


Current Data Parameters
NAME scm548
EXPNO 6
PROCNO 1
DU /n
USER sommath
F2 - Acquisition Parameters
Data_ 20110113
Time 8.16
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16400
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 32768
DW 20.850 usec
DE 6.50 usec
TE 299.7 K
D1 0.20000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -2.00 dB
SFO1 100.6253446 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 16.16 dB
PL13 17.00 dB
SFO2 400.1416006 MHz
F2 - Processing parameters
SI 32768
SF 100.6152830 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
-5.43
11.93
17.69
17.86
18.33
20.61
25.88
27.17
28.74
29.70
31.05
38.64
44.88
55.37
62.59
63.55
70.67
71.37
75.83
76.70
77.01
77.22
77.33
80.18
84.01
84.28
104.52
121.90
124.77
127.77
128.22
129.32
132.18
165.58
169.75
178.37
206.39
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
pdt
CF3
OMe
Ph
OTIPS
OAc
O
O
H
TBSO
PivO
308 (R)-MTPA ester


pure
Current Data Parameters
NAME som513
EXPNO 2
PROCNO 1
DU /a
USER somnath
F2 - Acquisition Parameters
Date_ 20101004
Time 21.51
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6793.478 Hz
FIDRES 0.207320 Hz
AQ 2.4117749 sec
RG 25.4
DW 73.600 usec
DE 6.50 usec
TE 299.8 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1424008 MHz
F2 - Processing parameters
SI 32768
SF 400.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.052
0.886
1.011
1.042
1.044
1.058
1.174
1.189
2.063
3.960
3.978
3.995
5.277
5.286
OTIPS
OAc
PivO
TBSO
309
5.99
10.02
22.83
9.23
1.11
1.52
3.17
0.98
0.99
2.10
1.06
0.97
1.02
1.00
1.98
ppm


Current Data Parameters
NAME scm513
EXPNO 6
PROCNO 1
DU /n
USER somnath
F2 - Acquisition Parameters
Data_ 20101005
Time 8.47
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 13160
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 14596.5
DW 20.850 usec
DE 6.50 usec
TE 303.0 K
D1 0.20000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -2.00 dB
SFO1 100.6253446 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 16.16 dB
PL13 17.00 dB
SFO2 400.1416006 MHz
F2 - Processing parameters
SI 32768
SF 100.6152830 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
-5.43
-5.37
12.02
17.64
17.78
18.29
20.57
25.83
27.15
27.60
29.66
31.97
38.66
48.86
58.45
62.22
72.20
75.95
76.69
77.01
77.33
82.14
112.05
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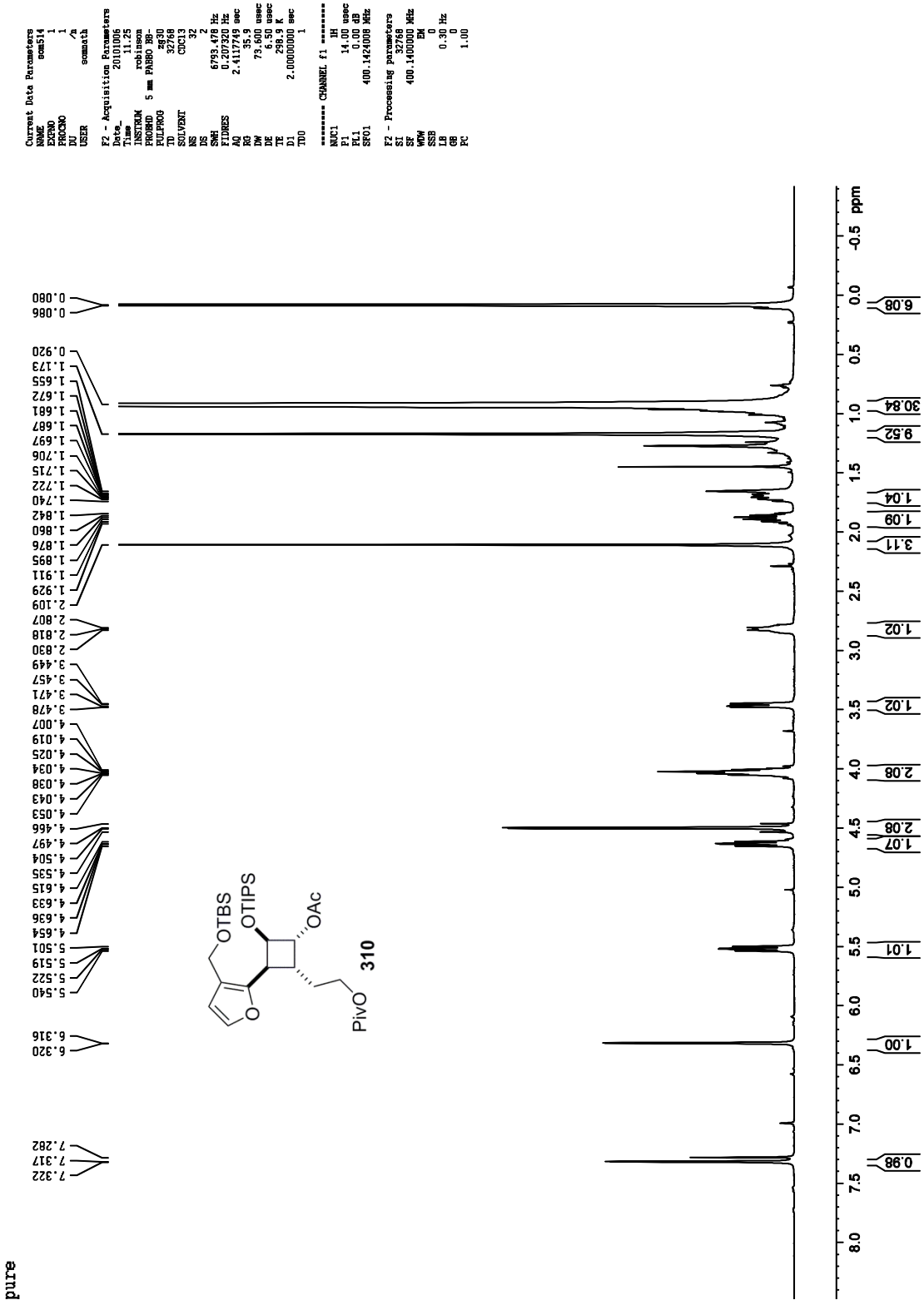
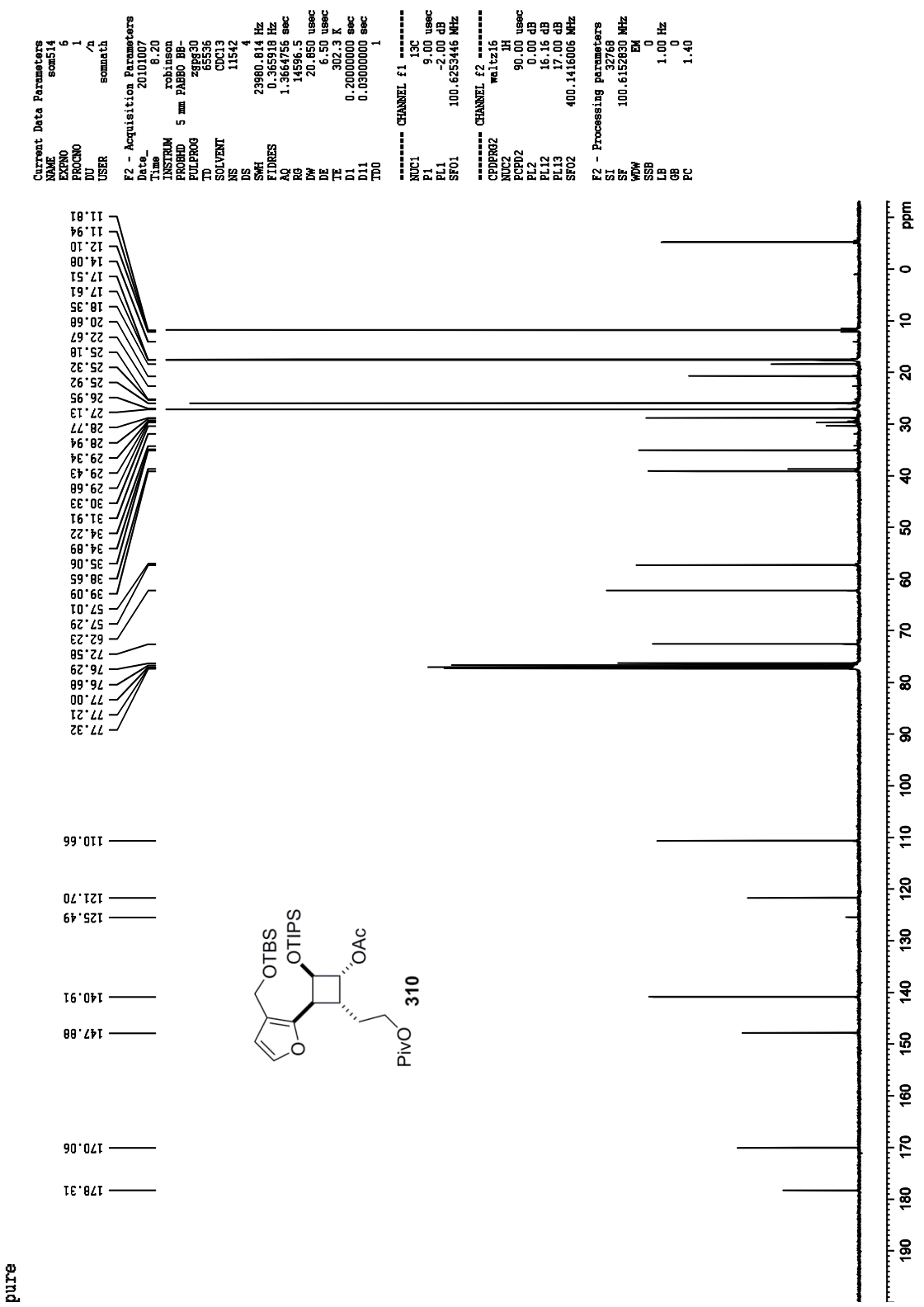
178.40
197.36
216.34
OTIPS
OAc
H
O
TBSO
PivO
309
ppm
pure


pure
Current Data Parameters
NAME scm514
EXPNO 1
PROCNO 1
DU /a
USER scmuth
F2 - Acquisition Parameters
Date_ 20101006
Time 11.25
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6793.478 Hz
FIDRES 0.207320 Hz
AQ 2.4117749 sec
RG 35.9
DW 73.600 usec
DE 6.50 usec
TE 298.9 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1424008 MHz
F2 - Processing parameters
SI 32768
SF 400.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
OTIPS
OAc
PivO
310
ppm


Current Data Parameters
NAME scm514
EXPNO 6
PROCNO 1
DU /n
USER sommath
F2 - Acquisition Parameters
Date_ 20101007
Time 8.20
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1152
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 14596.5
DW 20.850 usec
DE 6.50 usec
TE 302.3 K
D1 0.20000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -2.00 dB
SFO1 100.6253446 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 16.16 dB
PL13 17.00 dB
SFO2 400.1416006 MHz
F2 - Processing parameters
SI 32768
SF 100.6152830 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
11.81
11.94
12.10
14.08
17.51
17.61
18.35
20.68
22.67
25.18
25.32
25.92
26.95
27.13
28.77
28.94
29.34
29.43
29.68
30.33
31.91
34.22
34.89
35.06
38.65
39.09
57.01
57.29
62.23
72.58
76.29
76.68
77.00
77.21
77.32
110.66
121.70
125.49
140.91
147.88
170.06
178.31
OTBS
OTIPS
OAc
PivO
310
ppm
0
10
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70
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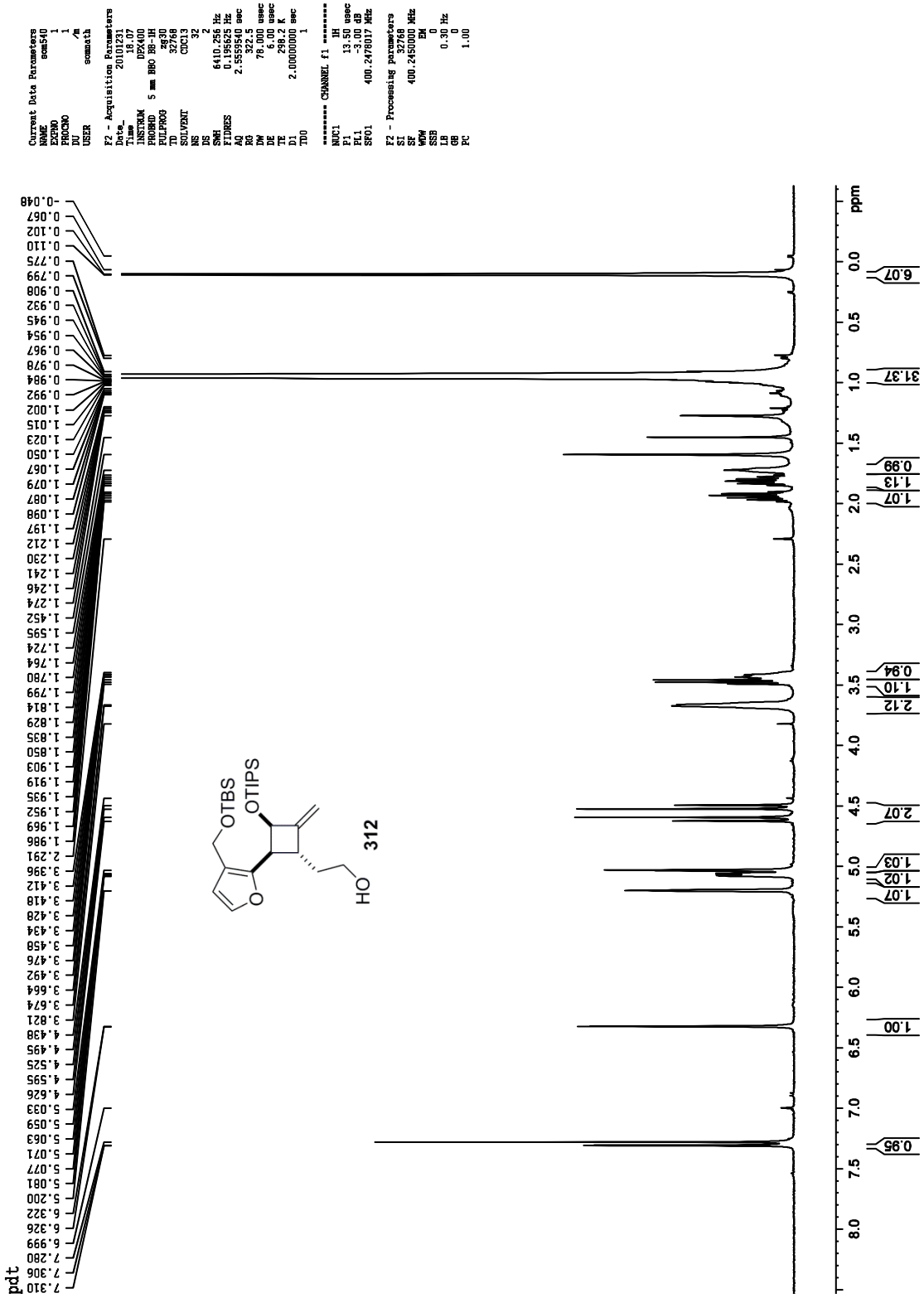
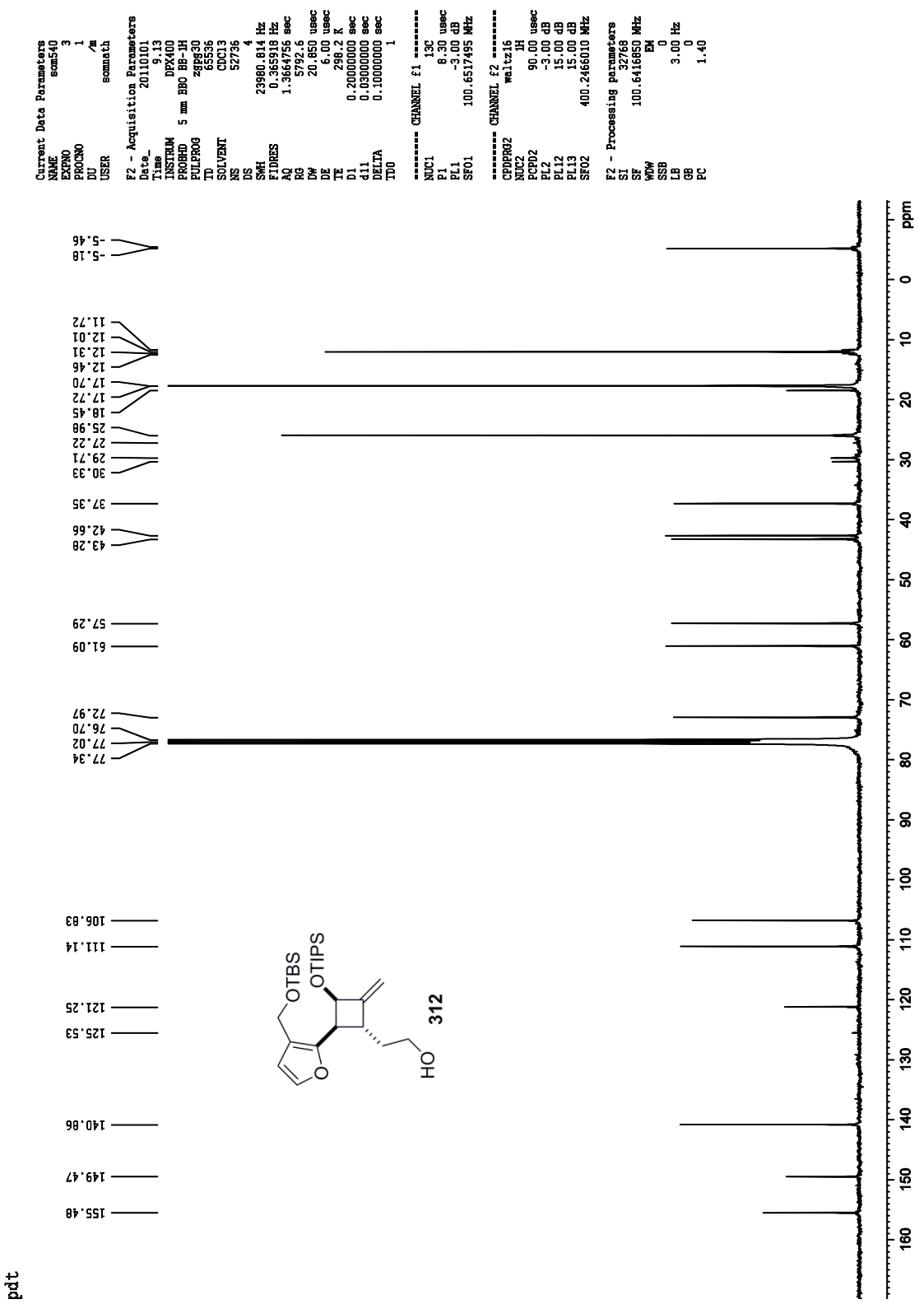
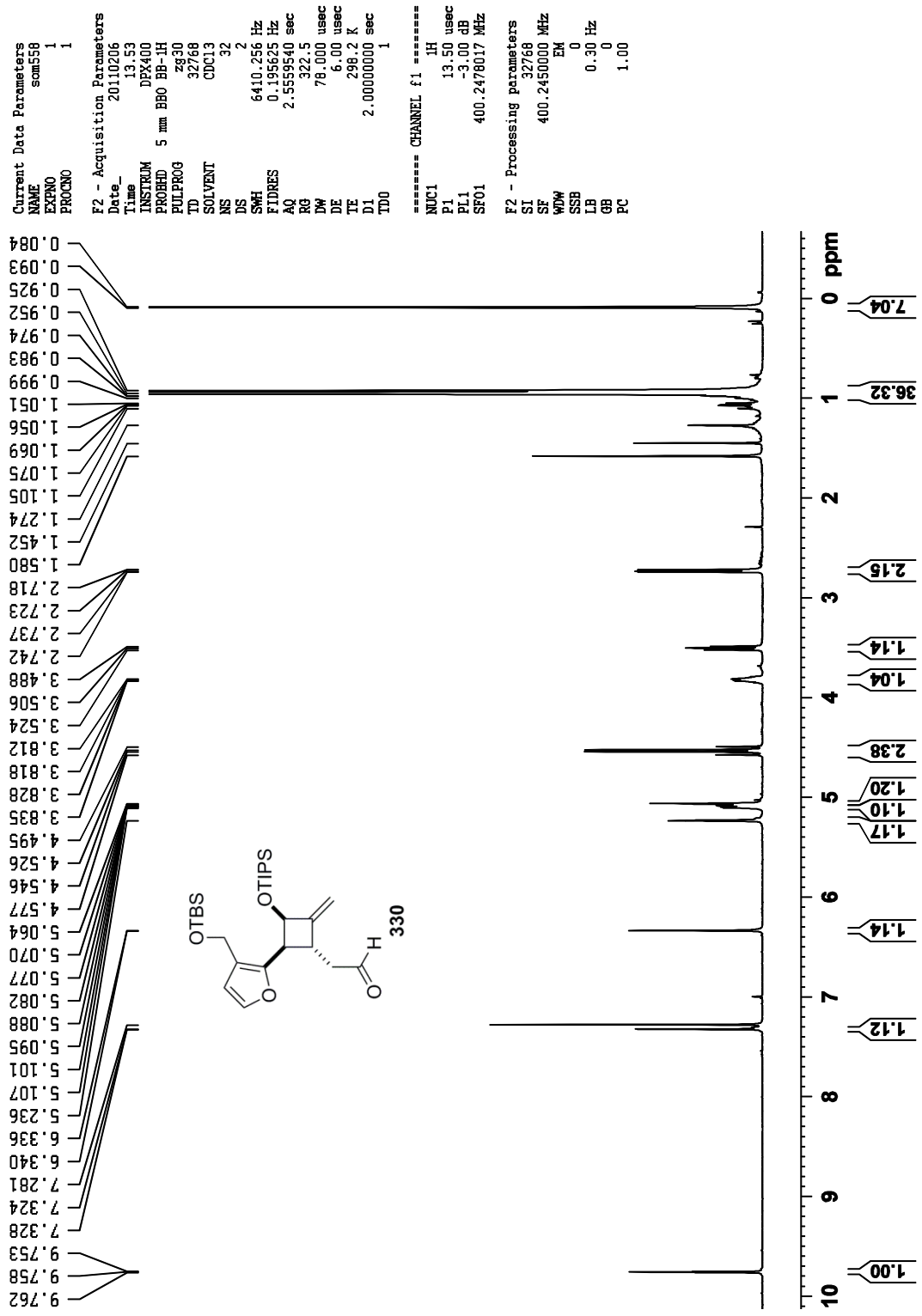
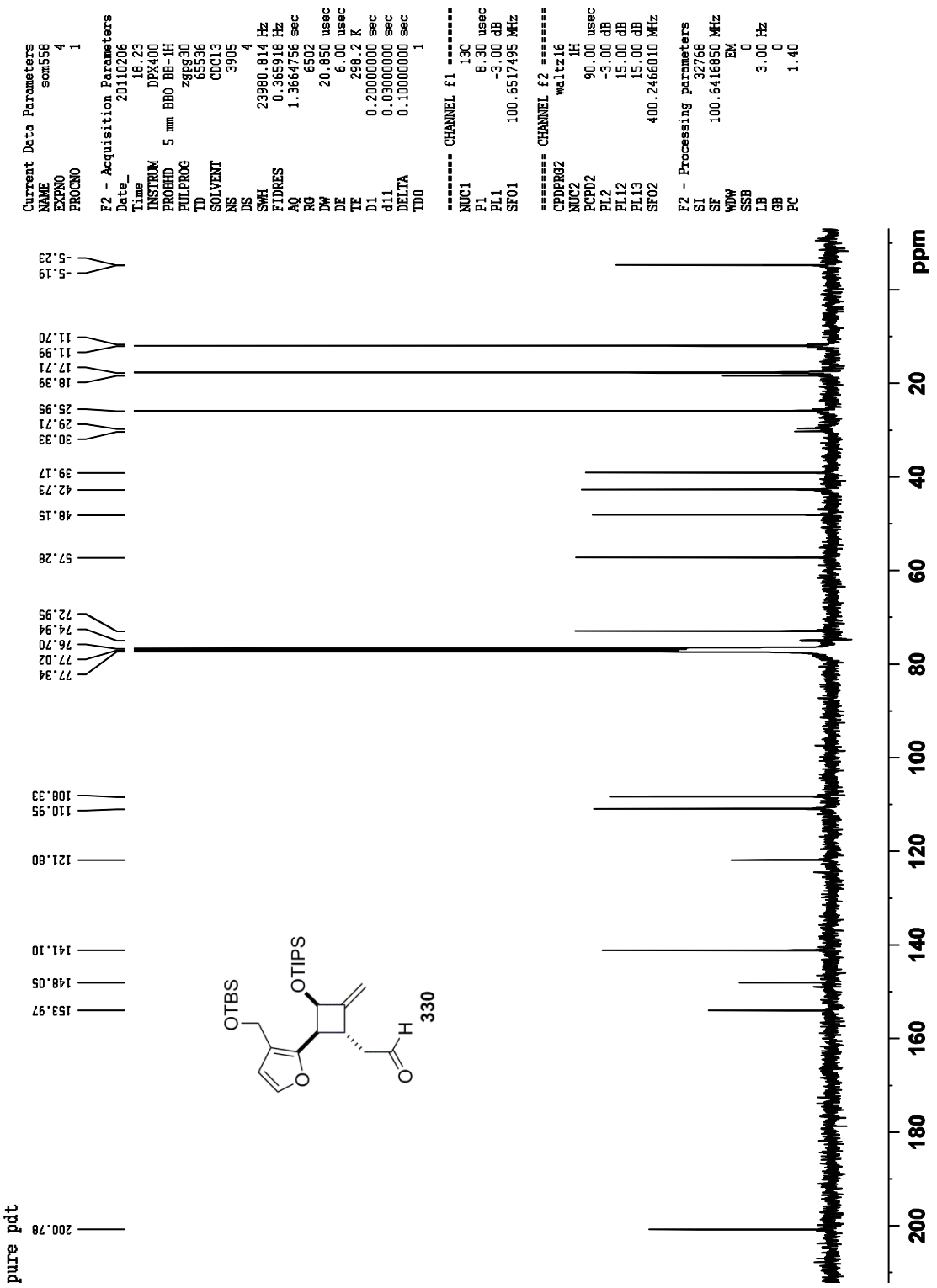
90
100
110
120
130
140
150
160
170
180
190

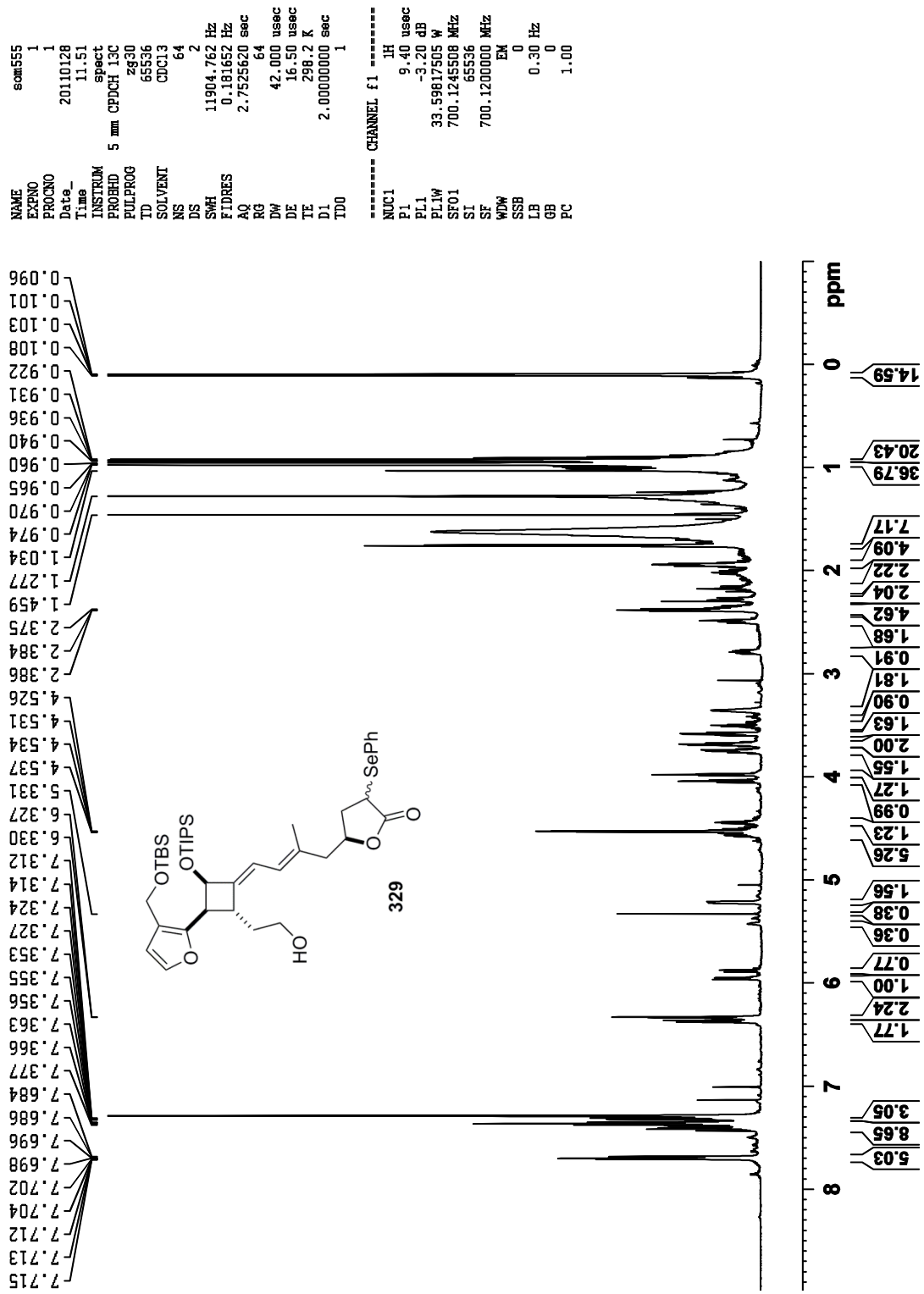
pure


Current Data Parameters
NAME sos540
EXPNO 1
PROCNO 1
DATA /m
USER sosmath
F2 - Acquisition Parameters
Date_ 20101231
Time 18.07
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 322.5
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
OTIPS
HO
312
pdt
ppm
6.07
31.37
0.99
1.13
1.07
0.94
1.10
2.12
2.07
1.03
1.02
1.07
1.00
0.95

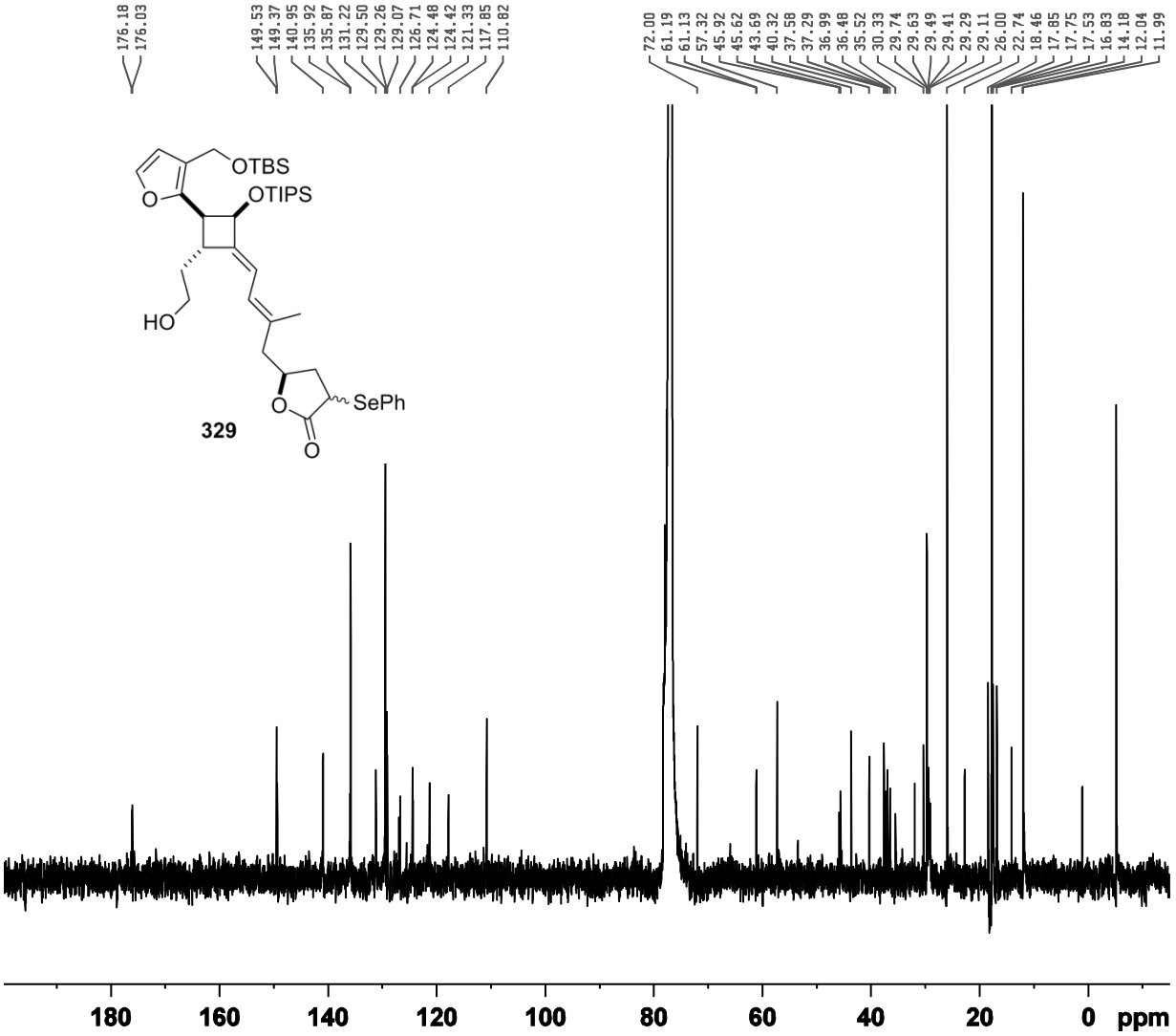

Current Data Parameters
NAME scm540
EXPNO 3
PROCNO 1
DU /m
USER somnath
F2 - Acquisition Parameters
Date_ 20110101
Time 9.13
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 52736
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 5792.6
DW 20.850 usec
DE 6.00 usec
TE 298.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.46
-5.18
11.72
12.01
12.31
12.46
17.70
17.72
18.45
25.98
27.22
29.71
30.33
37.35
42.66
43.28
57.29
61.09
72.97
76.70
77.02
77.34
106.83
111.14
121.25
125.53
140.86
149.47
155.48
OTBS
OTIPS
HO
312
ppm
pdt


Current Data Parameters
NAME scm558
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110206
Time 13.53
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 322.5
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -3.00 dB
SF01 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
OTIPS
O
O
H
330
ppm
0
1
2
3
4
5
6
7
8
9
10
7.04
36.32
2.15
1.14
1.04
2.38
1.20
1.10
1.17
1.14
1.12
1.00

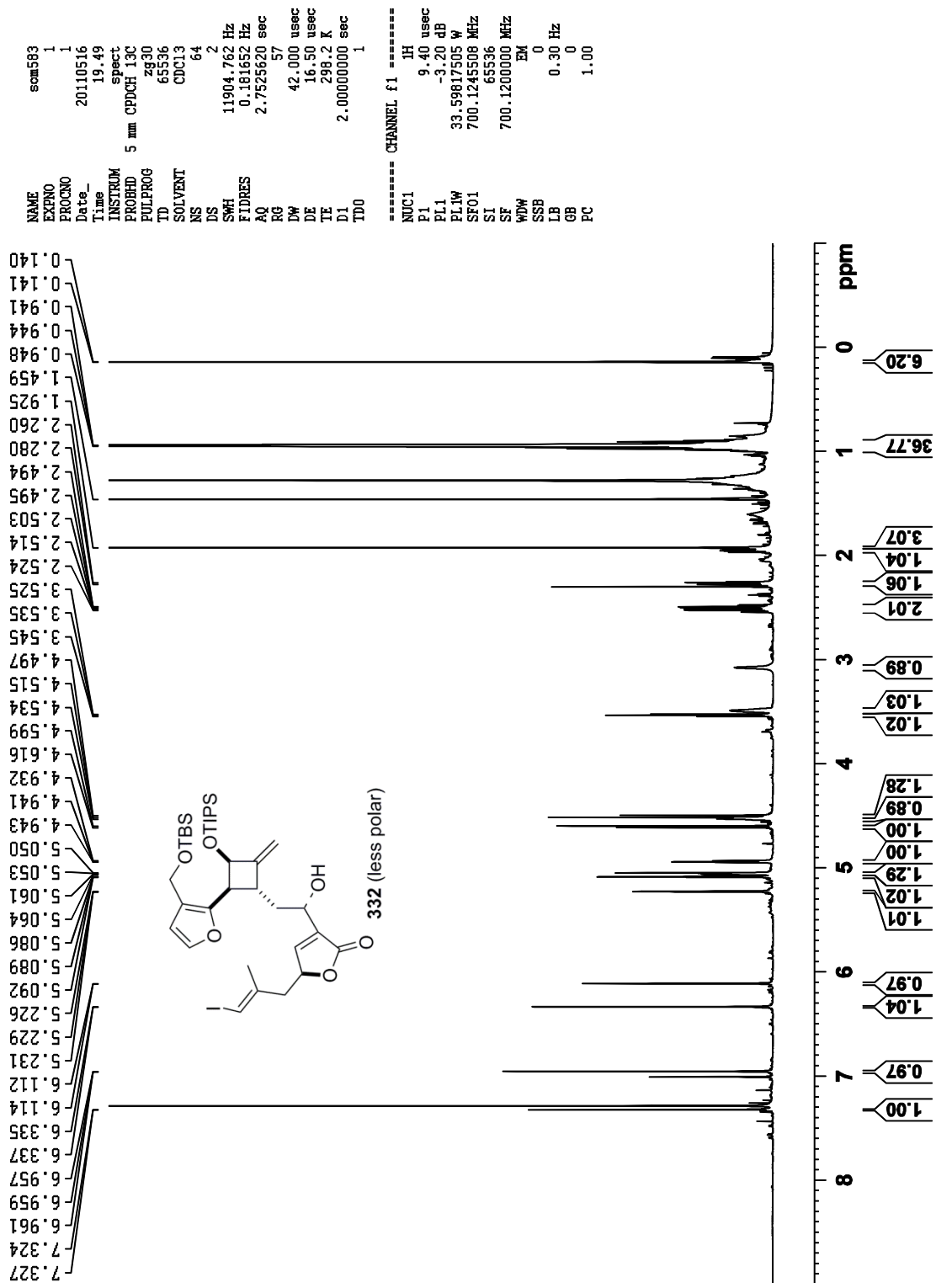

pure pdt
Current Data Parameters
NAME som558
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110206
Time 18.23
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3905
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 6502
DW 20.850 usec
DE 6.00 usec
TE 298.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.23
-5.19
11.70
11.99
17.71
18.39
25.95
29.71
30.33
39.17
42.73
48.15
57.28
72.95
74.94
76.70
77.02
77.34
108.33
110.95
121.80
141.10
148.05
153.97
200.78
OTBS
OTIPS
H
O
O
330
ppm
200
180
160
140
120
100
80
60
40
20

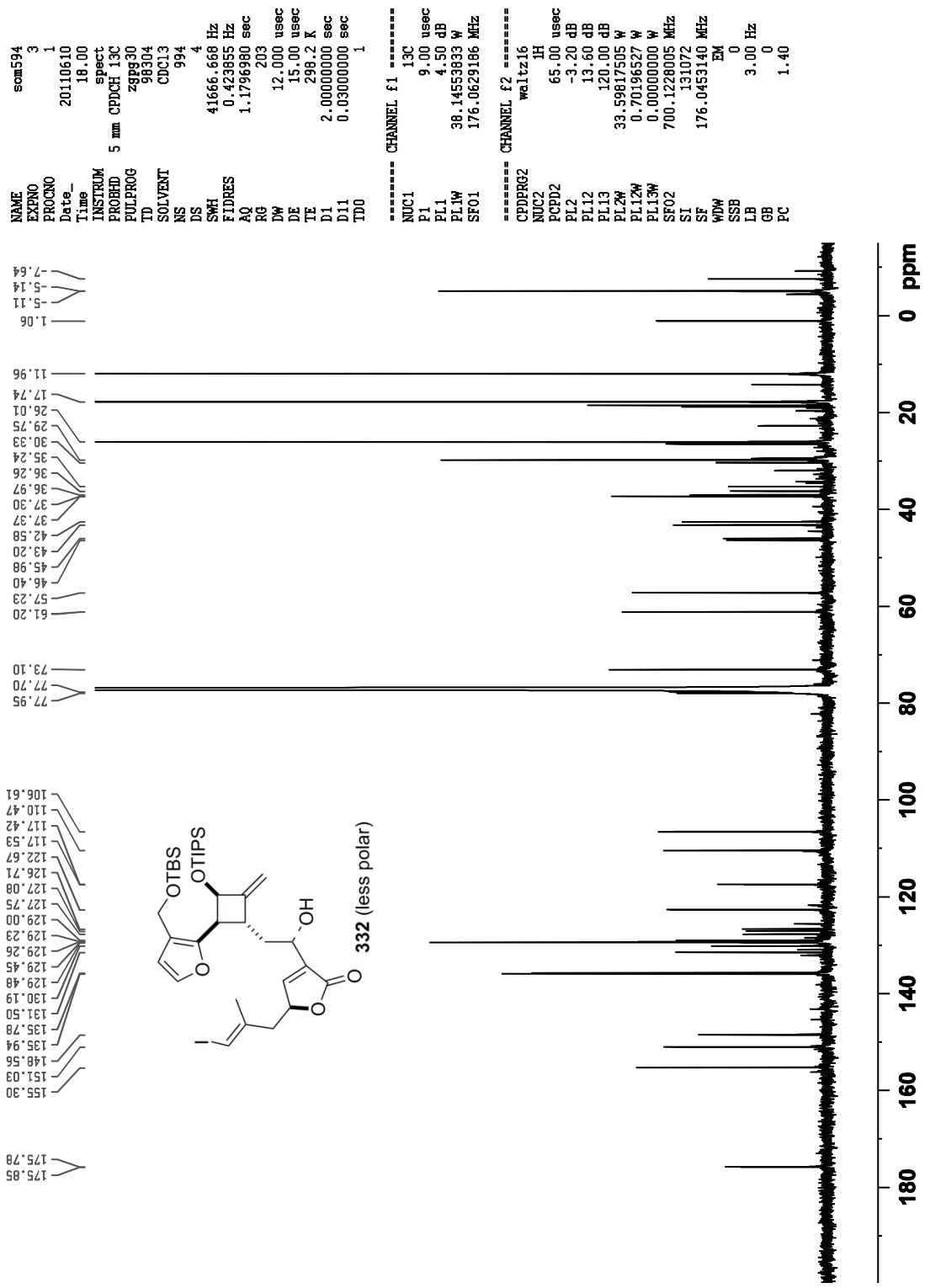

NAME sem555
EXPNO 1
PROCNO 1
Date_ 20110128
Time 11.51
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 11904.762 Hz
FIDRES 0.181652 Hz
AQ 2.7525620 sec
RG 64
DW 42.000 usec
DE 16.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 -3.20 dB
PL1W 33.59817505 W
SFO1 700.1245508 MHz
SI 65536
SF 700.1200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
OTIPS
SePh
HO
O
329
ppm

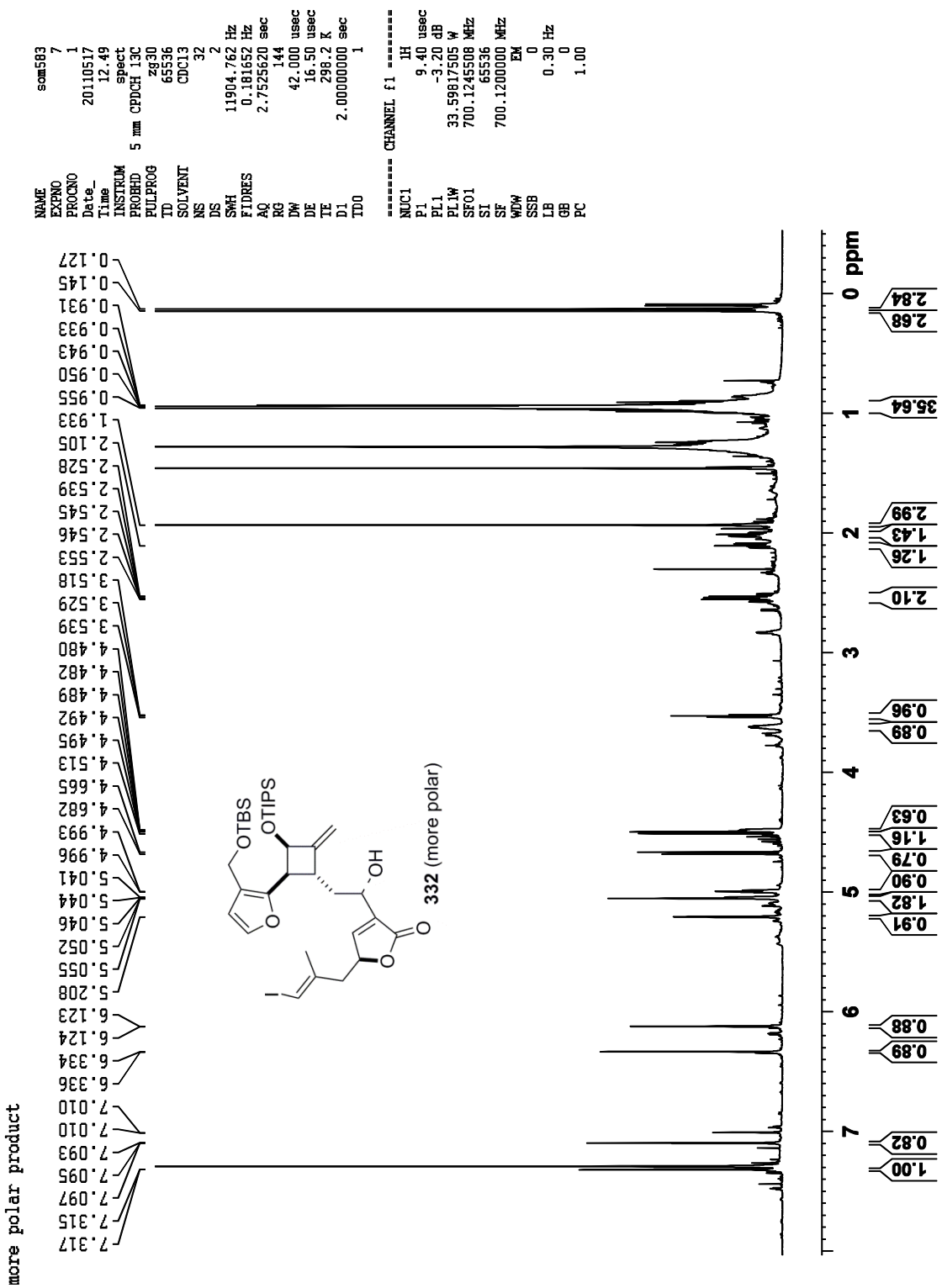
pdt

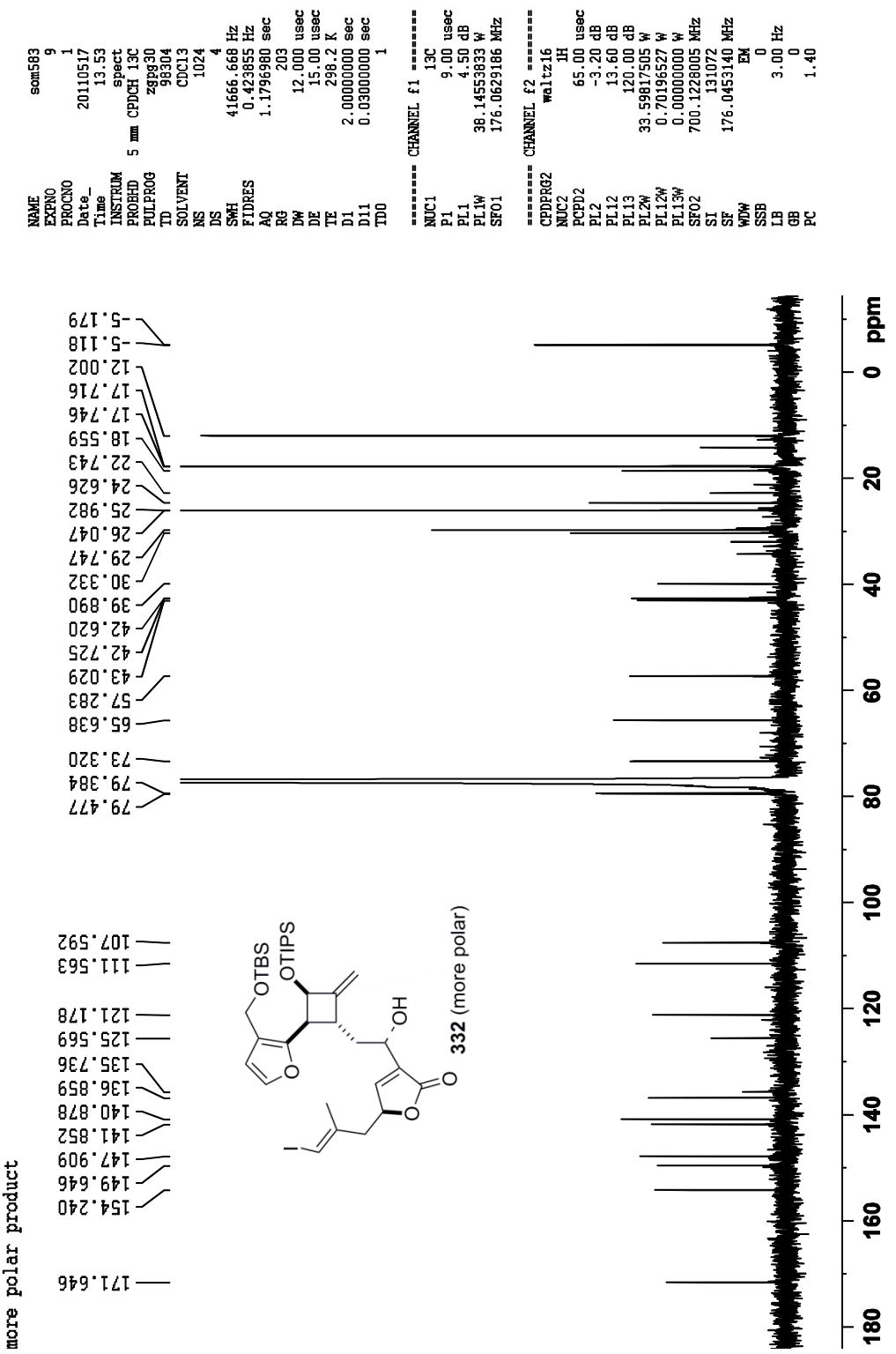


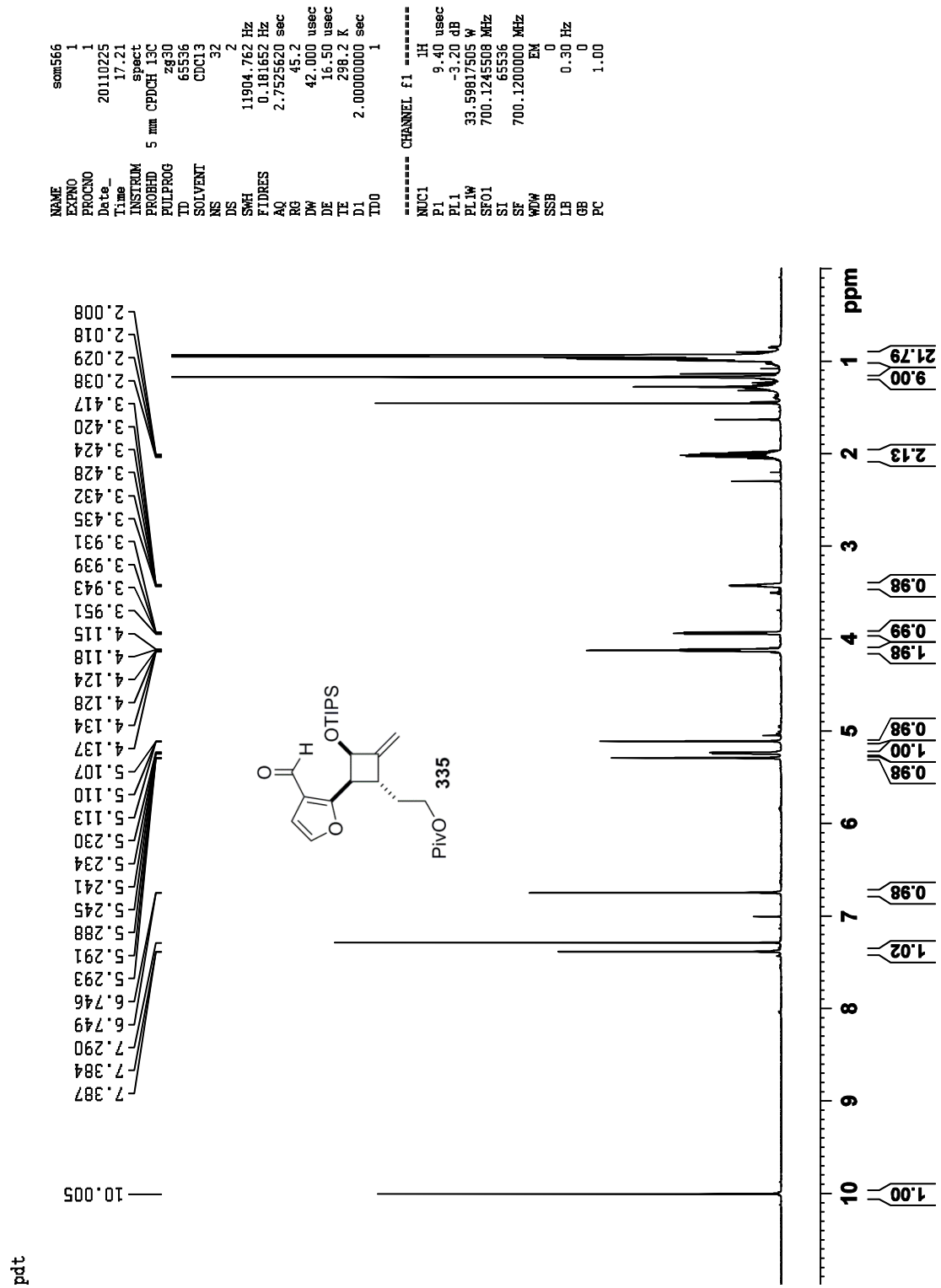
NAME	som555
EXPNO	3
PROCNO	1
Date_	20110128
Time	12.16
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	98304
SOLVENT	CDCl3
NS	2860
DS	4
SWH	41666.668 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	203
DW	12.000 usec
DE	15.00 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
--------	CHANNEL f1 --------
NUC1	13C
P1	9.00 usec
PL1	4.50 dB
PL1W	38.14553833 W
SFO1	176.0629186 MHz
--------	CHANNEL f2 --------
CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 usec
PL2	-3.20 dB
PL12	13.60 dB
PL13	120.00 dB
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1228005 MHz
SI	131072
SF	176.0453140 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

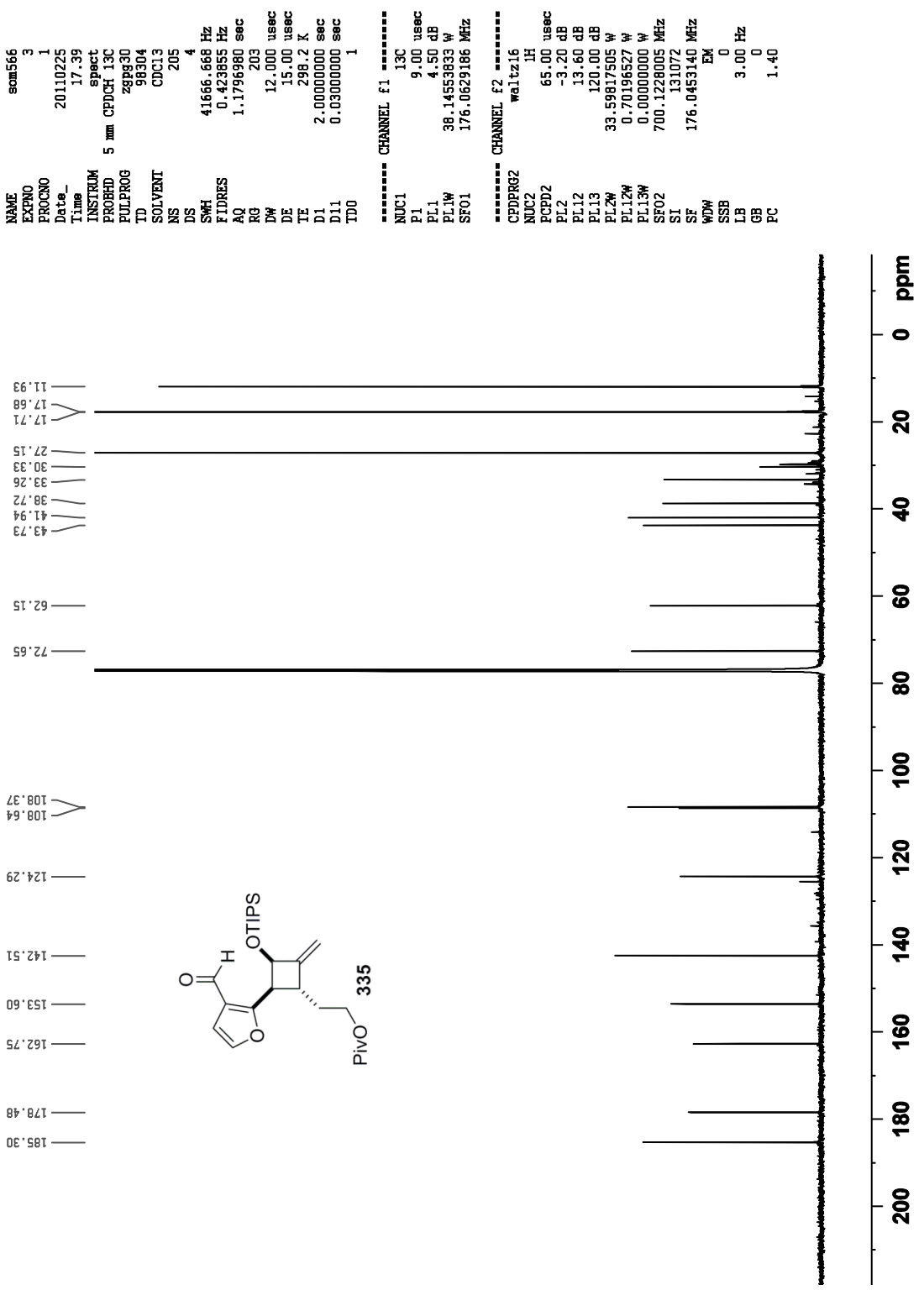

NAME scm583
EXPNO 1
PROCNO 1
Date_ 20110516
Time 19.49
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 11904.762 Hz
FIDRES 0.181652 Hz
AQ 2.7525620 sec
RG 57
DW 42.000 usec
DE 16.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 -3.20 dB
PL1W 33.59817505 W
SFO1 700.1245508 MHz
SI 65536
SF 700.1200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
OTIPS
OH
O
O
O
332 (less polar)
ppm
0.140
0.141
0.941
0.944
0.948
1.459
1.925
2.260
2.280
2.494
2.495
2.503
2.514
2.524
3.525
3.535
3.545
4.497
4.515
4.534
4.599
4.616
4.932
4.941
4.943
5.050
5.053
5.061
5.064
5.086
5.089
5.092
5.226
5.229
5.231
6.112
6.114
6.335
6.337
6.957
6.959
6.961
7.324
7.327
6.20
36.77
3.07
1.04
1.06
2.01
0.89
1.03
1.02
1.28
0.89
1.00
1.00
1.29
1.02
1.01
1.04
0.97
0.97
1.00

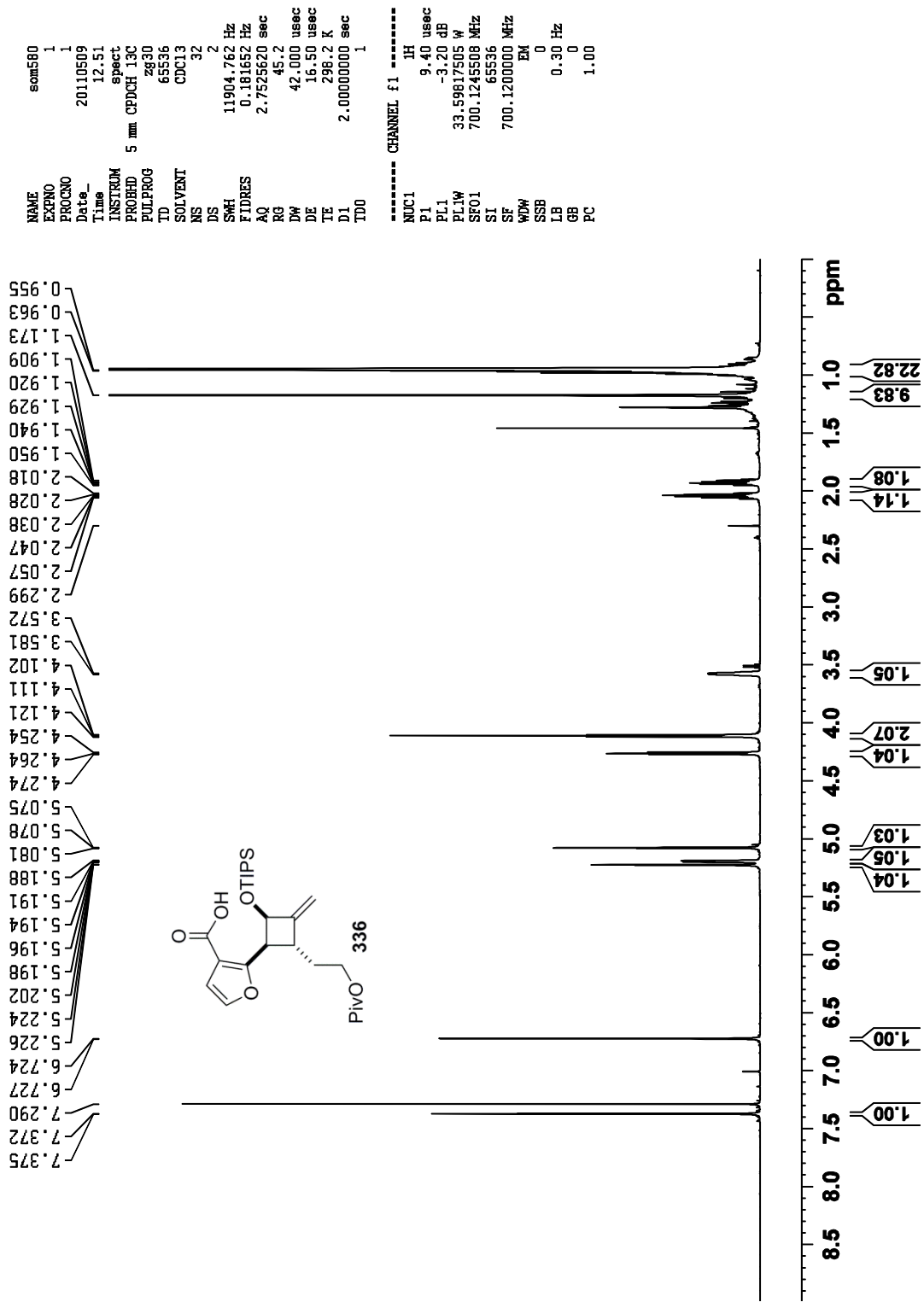

NAME scm594
EXPNO 3
PROCNO 1
Date_ 20110610
Time 18.00
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 98304
SOLVENT CDCl3
NS 994
DS 4
SWH 41666.668 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 203
DW 12.000 usec
DE 15.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 4.50 dB
PL1W 38.14553833 W
SFO1 176.0629186 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 usec
PL2 -3.20 dB
PL12 13.60 dB
PL13 120.00 dB
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1228005 MHz
SI 131072
SF 176.0453140 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
OTBS
OTIPS
OH
O
O
O
332 (less polar)
ppm


more polar product
NAME som583
EXPNO 7
PROCNO 1
Date_ 20110517
Time 12.49
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 11904.762 Hz
FIDRES 0.181652 Hz
AQ 2.7525620 sec
RG 144
DW 42.000 usec
DE 16.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 -3.20 dB
PL1W 33.59817505 W
SFO1 700.1245508 MHz
SI 65536
SF 700.1200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
OTIPS
OH
O
O
O
332 (more polar)
ppm


more polar product
171.646
154.240
149.646
147.909
141.852
140.878
136.859
135.736
125.569
121.178
111.563
107.592
79.477
79.384
73.320
65.638
57.283
43.029
42.725
42.620
39.890
30.332
29.747
26.047
25.982
24.626
22.743
18.559
17.746
17.716
12.002
-5.118
-5.179
OTBS
OTIPS
OH
O
O
O
332 (more polar)
NAME som583
EXPNO 9
PROCNO 1
Date_ 20110517
Time 13.53
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 98304
SOLVENT CDCl3
NS 1024
DS 4
SWH 41666.668 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 203
DW 12.000 usec
DE 15.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 4.50 dB
PL1W 38.14553833 W
SFO1 176.0629186 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 usec
PL2 -3.20 dB
PL12 13.60 dB
PL13 120.00 dB
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1228005 MHz
SI 131072
SF 176.0453140 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
0
ppm


NAME som566
EXPNO 1
PROCNO 1
Date_ 20110225
Time 17.21
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 11904.762 Hz
FIDRES 0.181652 Hz
AQ 2.7525620 sec
RG 45.2
DW 42.000 usec
DE 16.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 -3.20 dB
PL1W 33.59817505 W
SFO1 700.1245508 MHz
SI 65536
SF 700.1200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTIPS
H
O
O
PivO
335
ppm
21.79
9.00
2.13
0.98
0.99
1.98
0.98
1.00
0.98
0.98
1.02
1.00
10.005
7.387
7.384
7.290
6.749
6.746
5.293
5.291
5.288
5.245
5.241
5.234
5.230
5.113
5.110
5.107
4.137
4.134
4.128
4.124
4.118
4.115
3.951
3.943
3.939
3.931
3.435
3.432
3.428
3.424
3.420
3.417
2.038
2.029
2.018
2.008
pdt


NAME som566
EXPNO 3
PROCNO 1
Date_ 20110225
Time 17.39
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 98304
SOLVENT CDCl3
NS 205
DS 4
SWH 41666.668 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 203
DW 12.000 usec
DE 15.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 4.50 dB
PL1W 38.14553833 W
SFO1 176.0629186 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 usec
PL2 -3.20 dB
PL12 13.60 dB
PL13 120.00 dB
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1228005 MHz
SI 131072
SF 176.0453140 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
11.93
17.68
17.71
27.15
30.33
33.26
38.72
41.94
43.73
62.15
72.65
108.37
108.64
124.29
142.51
153.60
162.75
178.48
185.30
OTIPS
H
O
O
PivO
335
0
20
40
60
80
100
120
140
160
180
200
ppm


NAME som580
EXPNO 1
PROCNO 1
Date_ 20110509
Time 12.51
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 32
DS 2
SWH 11904.762 Hz
FIDRES 0.181652 Hz
AQ 2.7525620 sec
RG 45.2
DW 42.000 usec
DE 16.50 usec
TE 298.2 K
D1 2.00000000 sec
TDO 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 -3.20 dB
PL1W 33.59817505 W
SFO1 700.1245508 MHz
SI 65536
SF 700.1200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.955
0.963
1.173
1.909
1.920
1.929
1.940
1.950
2.018
2.028
2.038
2.047
2.057
2.299
3.572
3.581
4.102
4.111
4.121
4.254
4.264
4.274
5.075
5.078
5.081
5.188
5.191
5.194
5.196
5.198
5.202
5.224
5.226
6.724
6.727
7.290
7.372
7.375
OH
O
OTIPS
O
PivO
336
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
1.00
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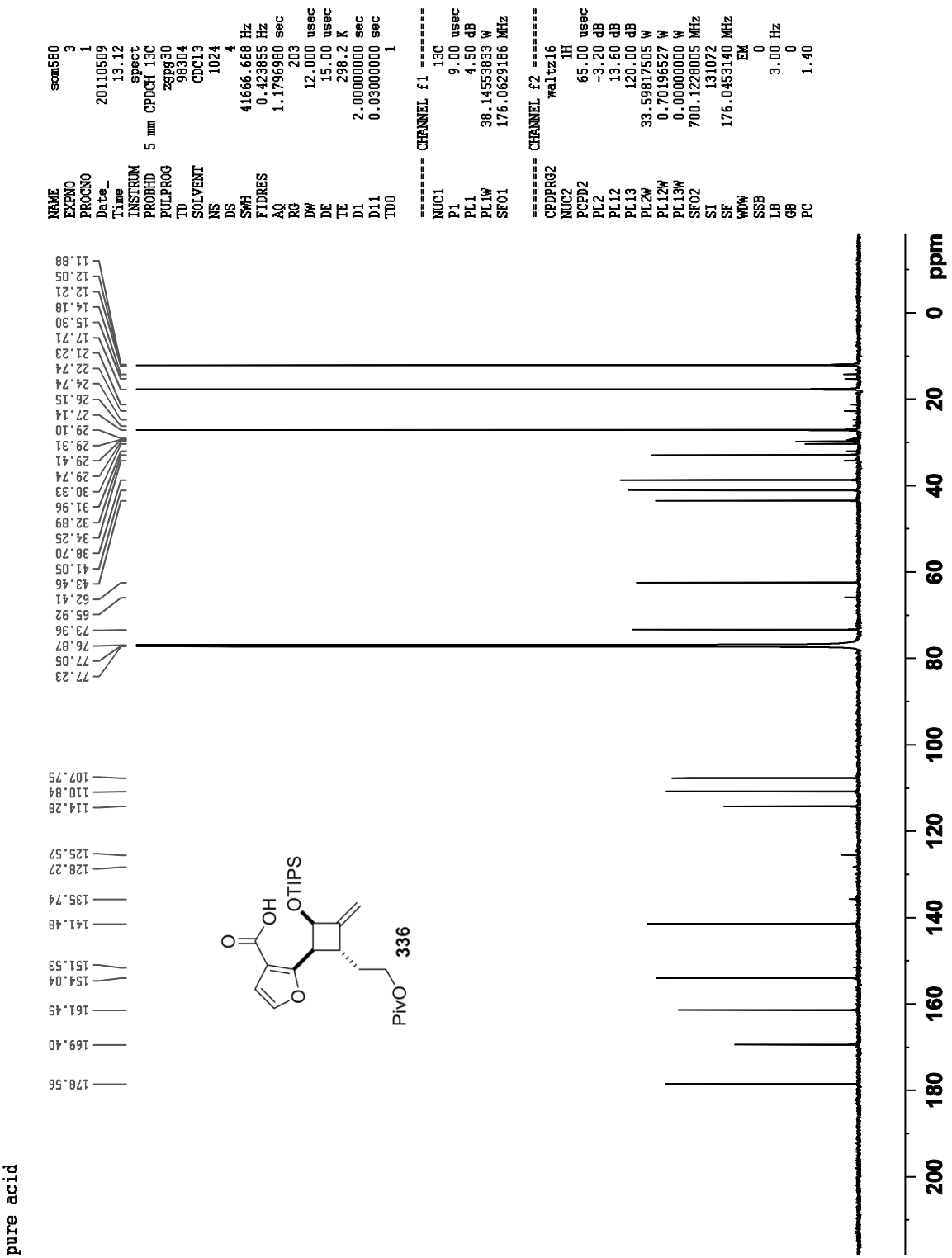
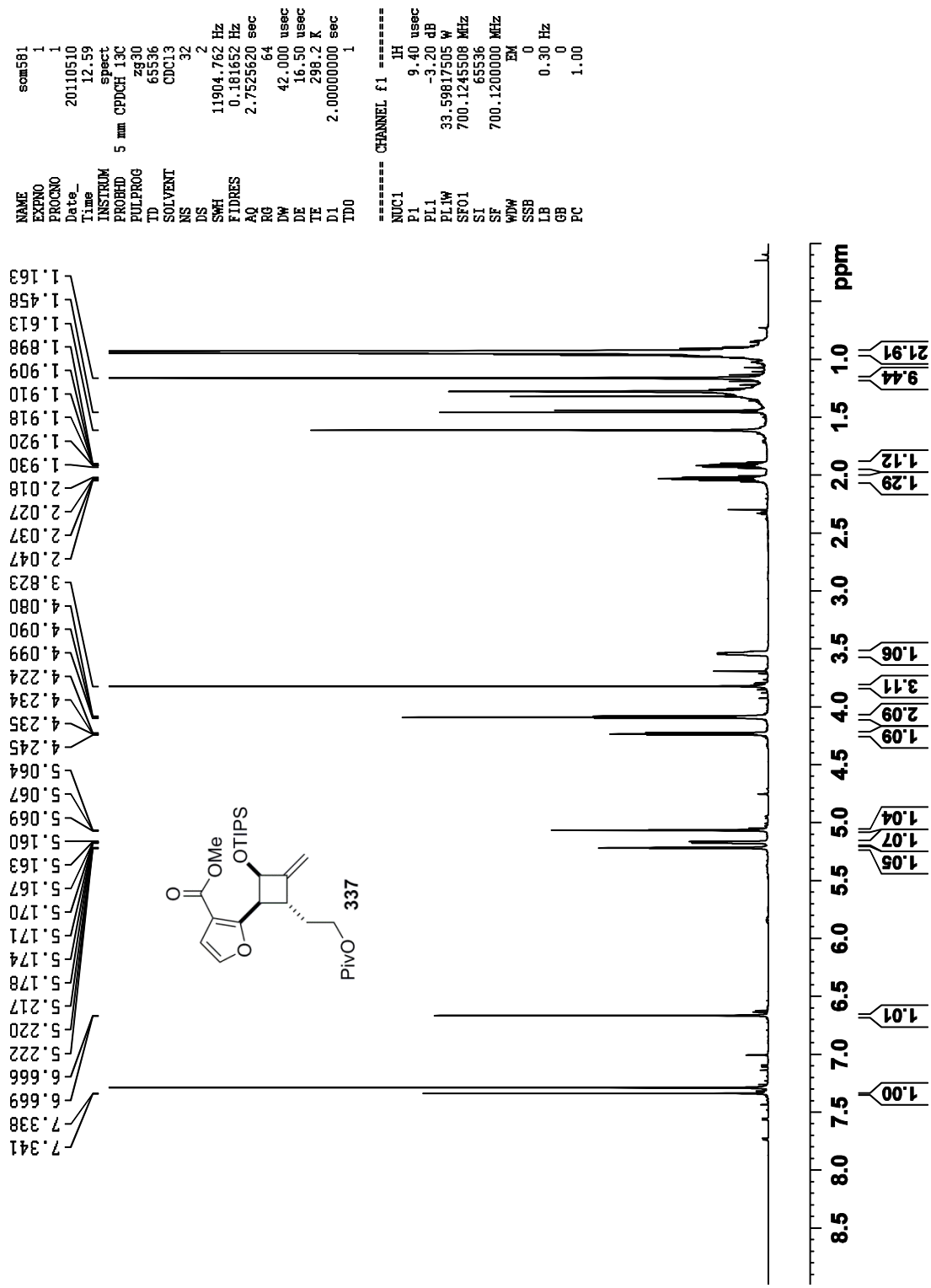
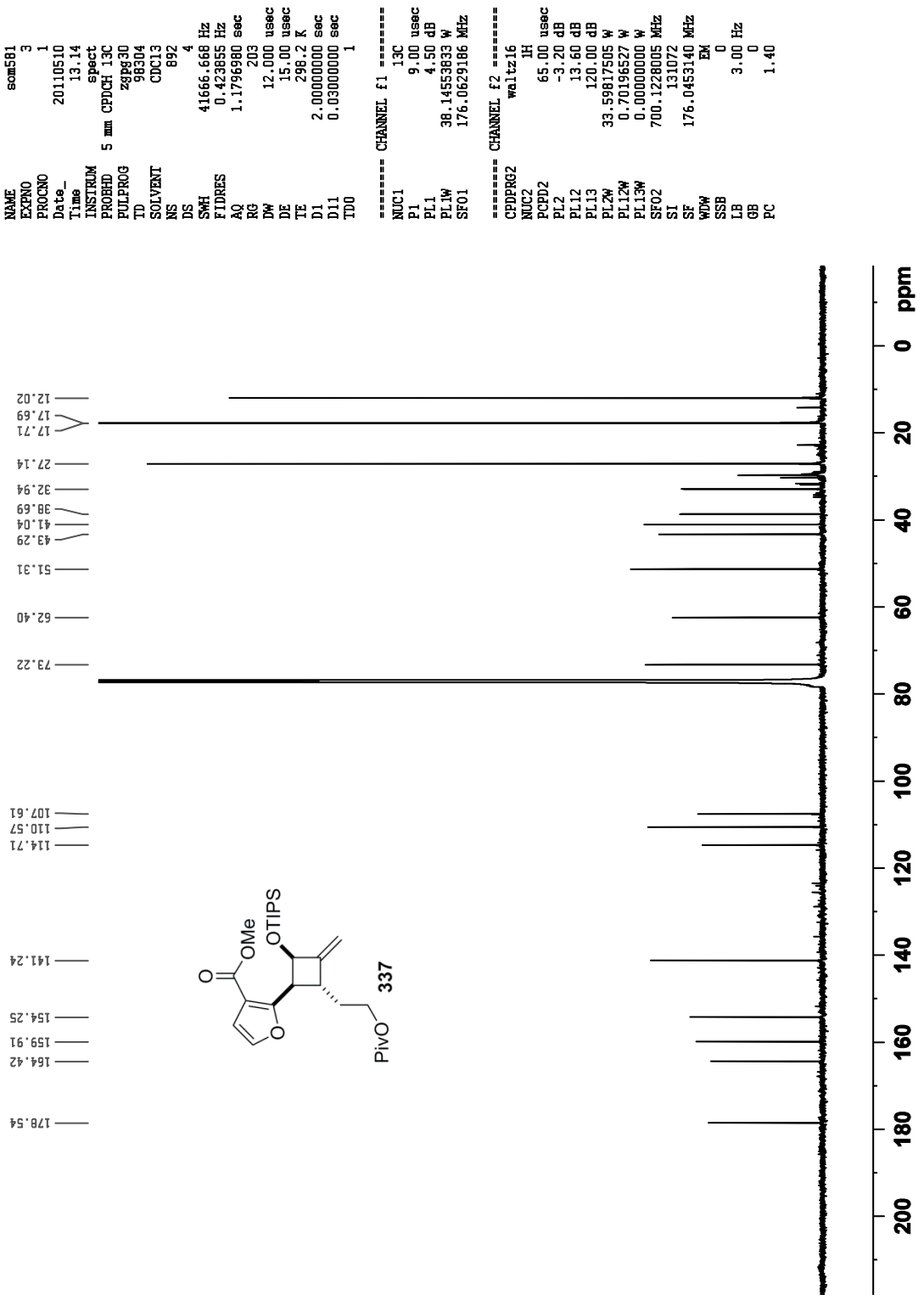
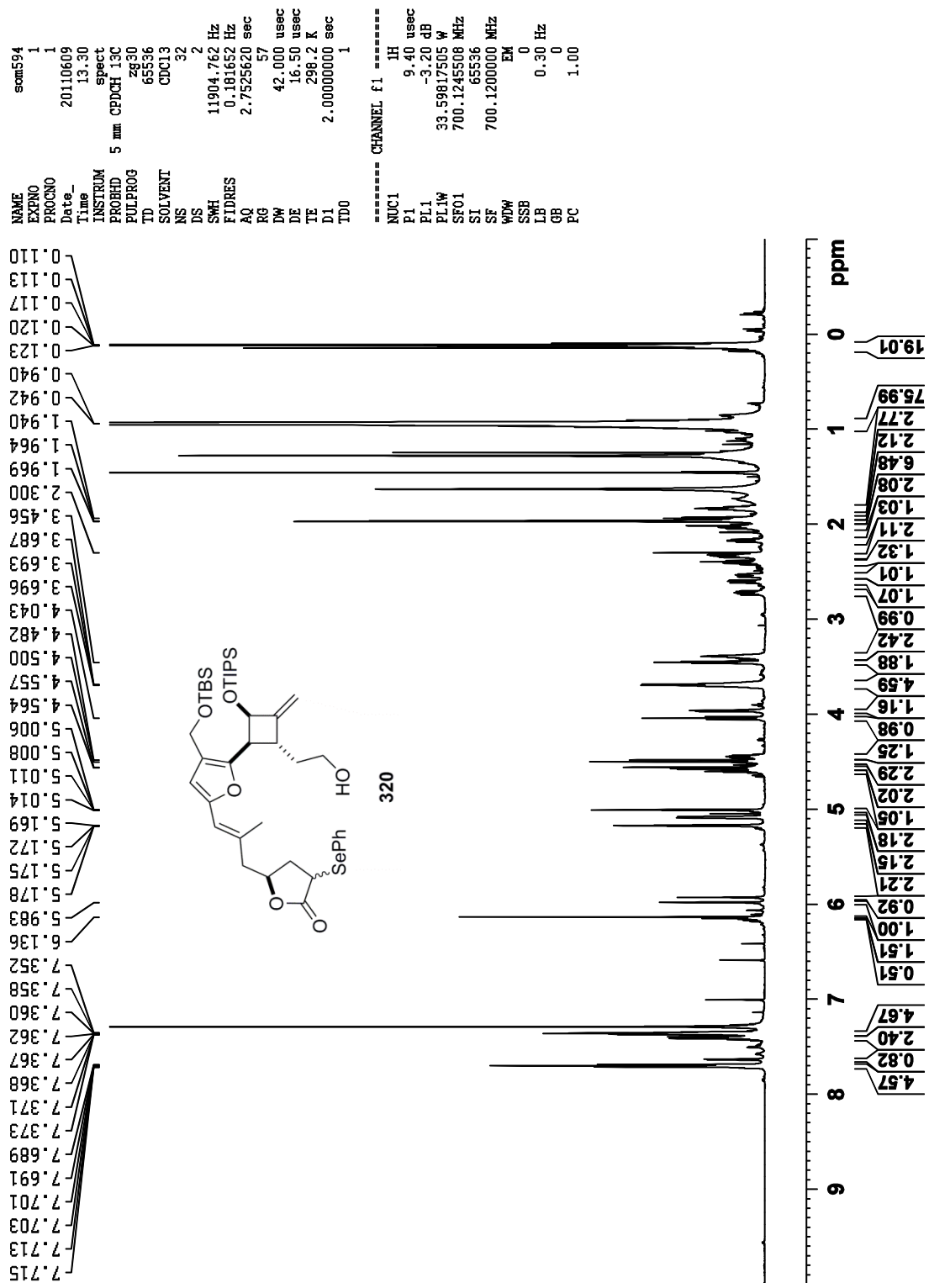
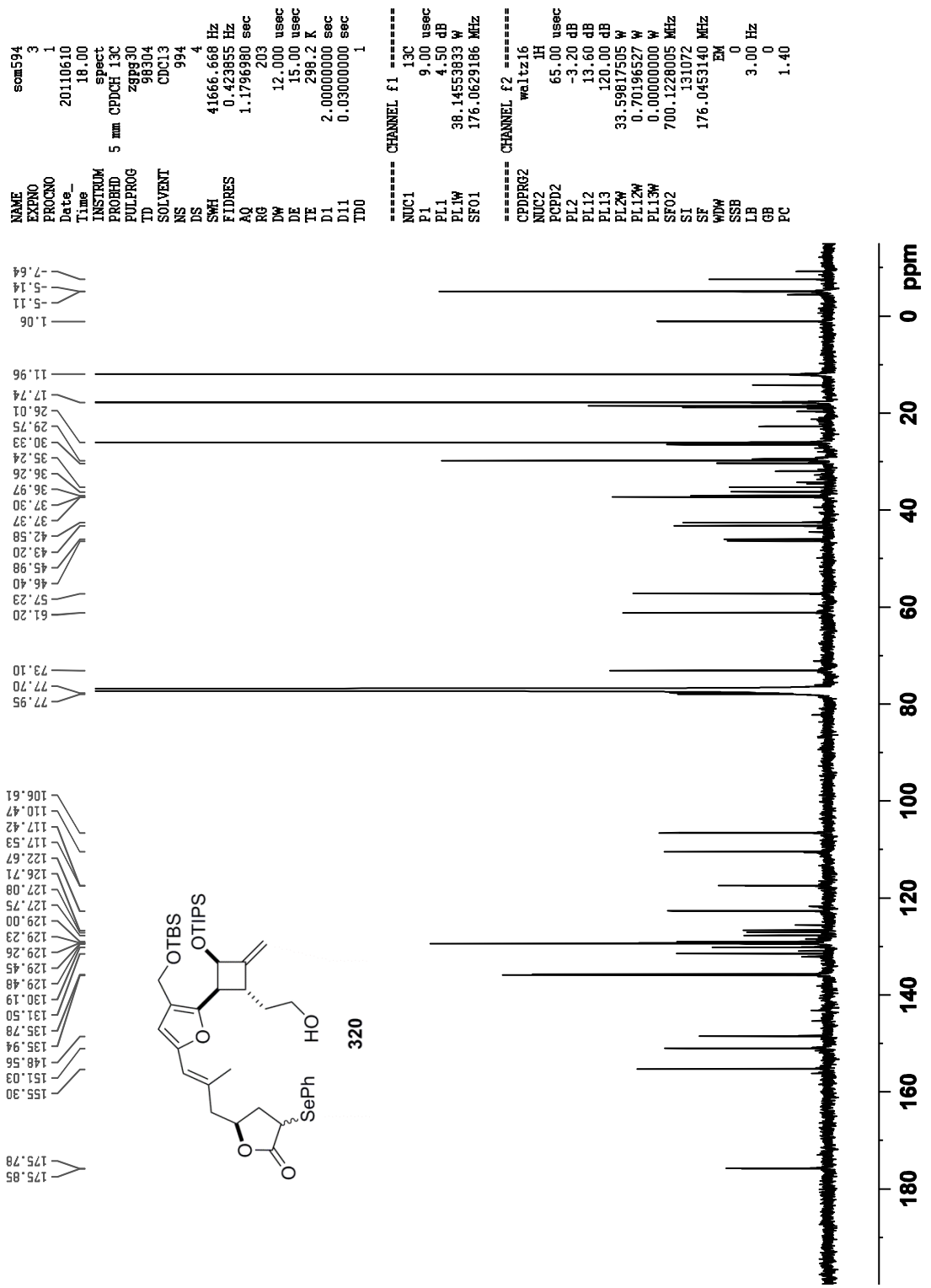
1.05
1.03
1.04
2.07
1.05
1.14
1.08
9.83
22.82

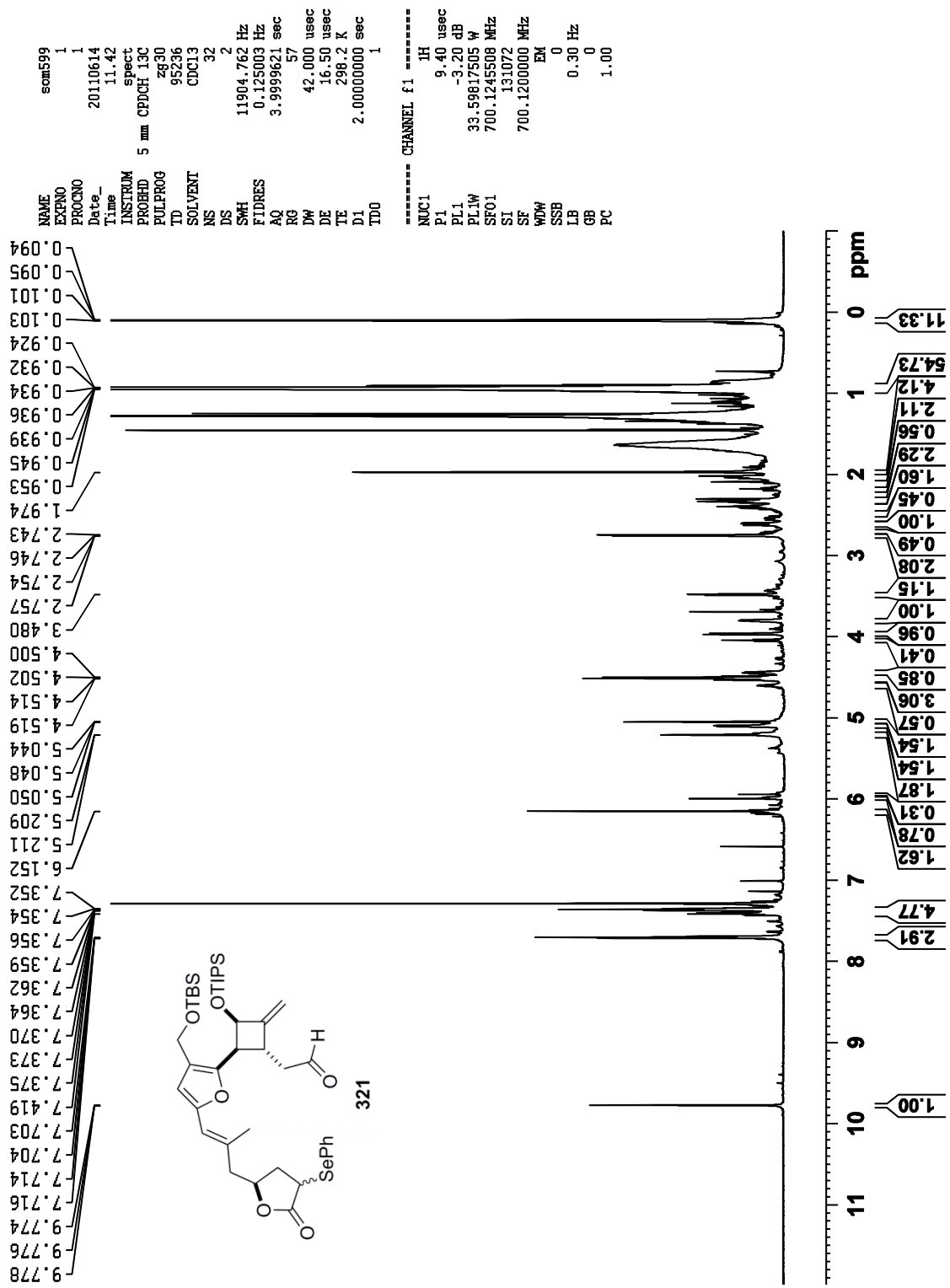

pure acid
NAME som580
EXPNO 3
PROCNO 1
Date_ 20110509
Time 13.12
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 98304
SOLVENT CDCl3
NS 1024
DS 4
SWH 41666.668 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 203
DW 12.000 usec
DE 15.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 4.50 dB
PL1W 38.14553833 W
SFO1 176.0629186 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 usec
PL2 -3.20 dB
PL12 13.60 dB
PL13 120.00 dB
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1228005 MHz
SI 131072
SF 176.0453140 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
11.88
12.05
12.21
14.18
15.30
17.71
21.23
22.74
24.74
26.15
27.14
29.10
29.31
29.41
29.74
30.33
31.96
32.89
34.25
38.70
41.05
43.46
62.41
65.92
73.36
76.87
77.05
77.23
107.75
110.84
114.28
125.57
128.27
135.74
141.48
151.53
154.04
161.45
169.40
178.56
OH
O
OTIPS
O
PivO
336
200
180
160
140
120
100
80
60
40
20
0
ppm

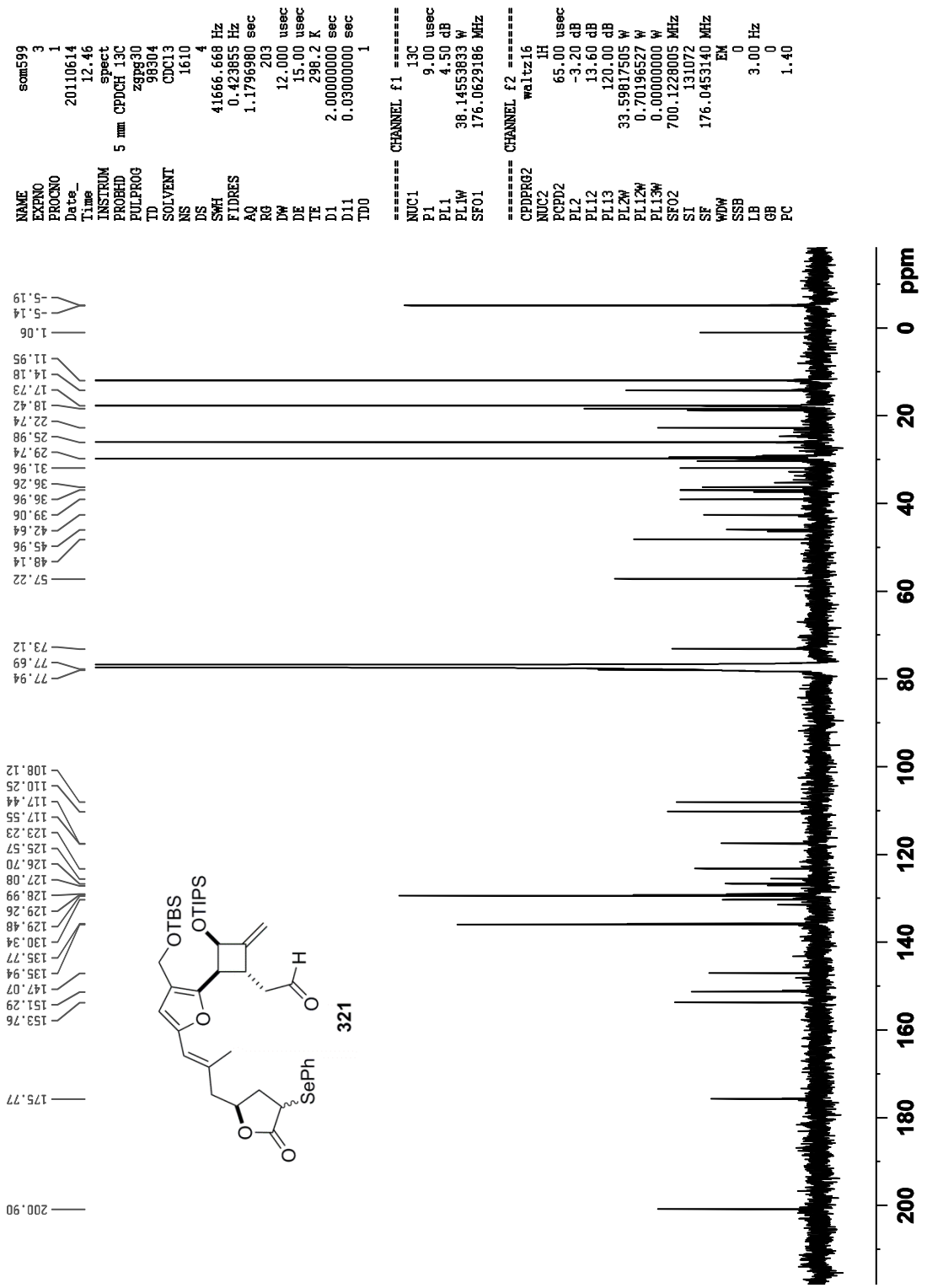

NAME scm581
EXPNO 1
PROCNO 1
Date_ 20110510
Time 12.59
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 11904.762 Hz
FIDRES 0.181652 Hz
AQ 2.7525620 sec
RG 64
DW 42.000 usec
DE 16.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 -3.20 dB
PL1W 33.59817505 W
SFO1 700.1245508 MHz
SI 65536
SF 700.1200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OMe
OTIPS
O
O
PivO
337
ppm
21.91
9.44
1.29
1.12
1.06
3.11
2.09
1.09
1.04
1.07
1.05
1.01
1.00

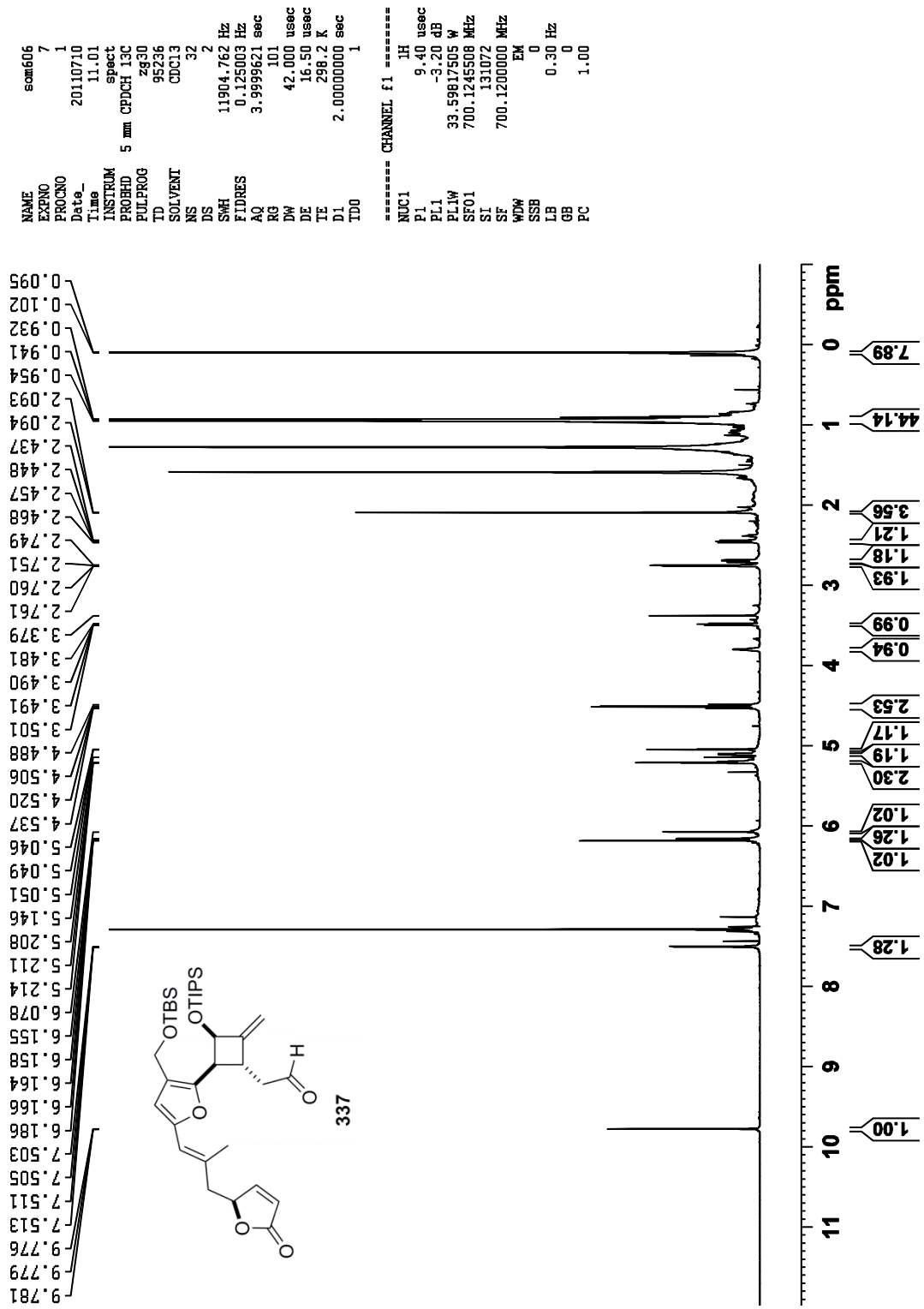

NAME som581
EXPNO 3
PROCNO 1
Date_ 20110510
Time 13.14
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 98304
SOLVENT CDC13
NS 892
DS 4
SWH 41666.668 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 203
DW 12.000 usec
DE 15.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 4.50 dB
PL1W 38.14553833 W
SFO1 176.0629186 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 usec
PL2 -3.20 dB
PL12 13.60 dB
PL13 120.00 dB
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1228005 MHz
SI 131072
SF 176.0453140 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
12.02
17.69
17.71
27.14
32.94
38.69
41.04
43.29
51.31
62.40
73.22
107.61
110.57
114.71
141.24
154.25
159.91
164.42
178.54
OMe
OTIPS
O
O
PivO
337
200
180
160
140
120
100
80
60
40
20
0
ppm

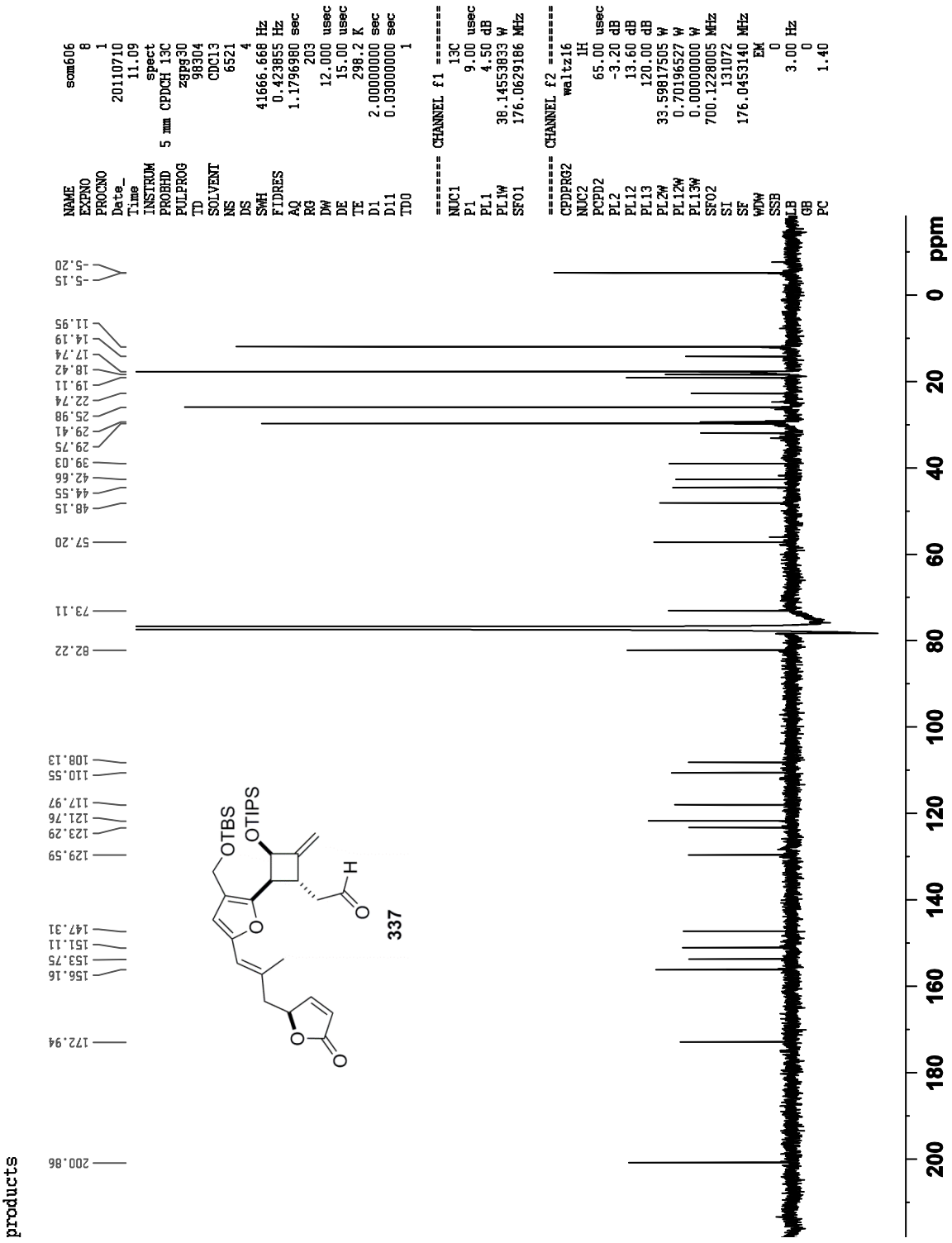

NAME scm594
EXPNO 1
PROCNO 1
Date_ 20110609
Time 13.30
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 11904.762 Hz
FIDRES 0.181652 Hz
AQ 2.7525620 sec
RG 57
DW 42.000 usec
DE 16.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 -3.20 dB
PL1W 33.59817505 W
SFO1 700.1245508 MHz
SI 65536
SF 700.1200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
OTIPS
HO
SePh
O
320
ppm


NAME scm594
EXPNO 3
PROCNO 1
Date_ 20110610
Time 18.00
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 98304
SOLVENT CDCl3
NS 994
DS 4
SWH 41666.668 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 203
DW 12.000 usec
DE 15.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 4.50 dB
PL1W 38.14553833 W
SFO1 176.0629186 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 usec
PL2 -3.20 dB
PL12 13.60 dB
PL13 120.00 dB
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1228005 MHz
SI 131072
SF 176.0453140 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
OTBS
OTIPS
HO
SePh
O
O
O
320
ppm


NAME scm599
EXPNO 1
PROCNO 1
Date_ 20110614
Time 11.42
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 32
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 57
DW 42.000 usec
DE 16.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 -3.20 dB
PL1W 33.59817505 W
SFO1 700.1245508 MHz
SI 131072
SF 700.1200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
OTIPS
H
O
O
O
SePh
O
321
ppm


NAME som599
EXPNO 3
PROCNO 1
Date_ 20110614
Time 12.46
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 98304
SOLVENT CDCl3
NS 1610
DS 4
SWH 41666.668 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 203
DW 12.000 usec
DE 15.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 4.50 dB
PL1W 38.14553833 W
SFO1 176.0629186 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 usec
PL2 -3.20 dB
PL12 13.60 dB
PL13 120.00 dB
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1228005 MHz
SI 1311072
SF 176.0453140 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.19
-5.14
1.06
11.95
14.18
17.73
18.42
22.74
25.98
29.74
31.96
36.26
36.96
39.06
42.64
45.14
48.14
57.22
73.12
77.69
77.94
108.12
110.25
117.44
117.55
123.23
125.57
126.70
127.08
128.99
129.26
129.48
130.34
135.77
135.94
147.07
151.29
153.76
175.77
200.90
OTBS
OTIPS
SePh
O
O
O
H
321
ppm
0
20
40
60
80
100
120
140
160
180
200


NAME scm606
EXPNO 7
PROCNO 1
Date_ 20110710
Time 11.01
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 32
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 101
DW 42.000 usec
DE 16.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 -3.20 dB
PL1W 33.59817505 W
SFO1 700.1245508 MHz
SI 131072
SF 700.1200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
OTIPS
H
O
337
ppm
7.89
44.14
3.56
1.21
1.18
1.93
0.99
0.94
2.53
1.17
1.19
2.30
1.02
1.26
1.02
1.28
1.00


products
NAME som606
EXPNO 8
PROCNO 1
Date_ 20110710
Time 11.09
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 98304
SOLVENT CDCl3
NS 6521
DS 4
SWH 41666.668 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 203
DW 12.000 usec
DE 15.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 4.50 dB
PL1W 38.14553833 W
SFO1 176.0629186 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 usec
PL2 -3.20 dB
PL12 13.60 dB
PL13 120.00 dB
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1228005 MHz
SI 131072
SF 176.0453140 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
-5.20
-5.15
11.95
14.19
17.74
18.42
19.11
22.74
25.98
29.41
29.75
39.03
42.66
44.55
48.15
57.20
73.11
82.22
108.13
110.55
117.97
121.76
123.29
129.59
147.31
151.11
153.75
156.16
172.94
200.86
OTBS
OTIPS
O
H
O
O
O
337
200
180
160
140
120
100
80
60
40
20
0
ppm