Open access • Journal Article • DOI:10.1021/JA309905J

Total Synthesis of (±)-Maoecrystal V — Source link

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Published on: 05 Nov 2012 - Journal of the American Chemical Society (American Chemical Society)

Topics: Ring (chemistry), Total synthesis and Intramolecular force

Total Synthesis of (±)Maoecrystal V

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Submitted in partial fulfillment of the

Requirements for the degree of

Doctor of Philosophy

in the Graduate School of Arts and Sciences

COLUMBIA UNIVERSITY

2012

Abstract

Total Synthesis of Maoecrystal V

Feng Peng

This thesis describes in detail our journey toward Maoecrystal V, a potential anti-cancer diterpenoid. Maoecrsytal V was isolated in 2004 from a Chinese herbal medicine. It has a highly congested structure, in which there are three continuous quaternary carbon center embedded within a rigid pentacyclic scaffold.

The first chapter of this thesis covers the isolation, bioactivity, and synthetic efforts from other groups. The second chapter discusses our first generation strategy toward Maoecrystal V. During our early studies, we successfully found the conditions for the key intramolecular Diels-Alder reaction. We also identified that the facial selectivity of this Diels-Alder reaction is a big challenge for our synthesis plan. The third chapter describes our solution to the core structure of Maoecrystal V. The exploration resulted in the discovery of a novel *exo*-glycal epoxide rearrangement. The last chapter describes the total synthesis of Maoecrystal V. The difficulties we met and our solution is discussed.

LIST OF ABBREVIATIONS

Ac	acetyl
AIBN	2, 2'-azo bisisobutyronitrile
Al	aluminum
aq.	Aqueous
B	boron
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthalene
BINOL	1, 1'-Bi-2-Naphthol
Bn	benzyl
n-BuLi	*n*-butyl lithium
Calcd.	calculated
CSA	camphor sulfonic acid
^{13}C NMR	carbon-13 magnetic resonance
°C	degree Celcius
DA	Diels-Alder
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	dichloromethane
DIBAL-H	diisobutylaluminum hydride
DMAP	4-dimethylaminopyridine
DMDO	2, 2-dimethyldioxirane
DME	1, 2-Dimethoxyethane

DMF	dimethylformamide
DMP	Dess-Martin periodinane
DMSO	methyl sulfoxide
E	Entgegen
Ee	enantiomeric excess
EI	electron impact
equiv.	equivalents
ES	electrospray
EtOH	ethanol
Et_2O	diethyl ether
Et	Ethyl
EtOAc	ethyl acetate
g	gram
h	hour
^{1}H NMR	Proton magnetic resonance
HRMS	high resolution mass spectrometry
IC_{50}	half maximal inhibitory concentration
IMDA	intramolecular Diels-Alder
i-Pr	Isopropyl
IR	infrared spectroscopy
Ir	Iridium
J	coupling constant
KHMDS	potassium bis(trimethylsilyl)amide

L.A.	Lewis acid
LDA	lithium diisopropylamide
LHMDS	lithium bis(trimethylsilyl)amide
Li	Lithium
Me	methyl group
MeOH	methanol
m-CPBA	*meta*-chloroperbenzoic acid
min	minutes
mL	milliliters
MOE	ethoxylmethyl
MOM	methoxylmethyl
Ms	mesyl (methanesulfonyl)
NIS	*N*-iodosuccinimide
OTf	fluoromethanesulfonate
Pd	Palladium
Ph	Phenyl
PIDA	phenyliodo(III) diacetate
PIFA	[bis(trifluoroacetoxy)iodo]benzene
PivCl	pivaloyl chloride
PPh_3	triphenylphosphine
Pt	Platinum
Py	pyridine
Rh	Rhodium

r.t.	room temperature
Si	Silicon
Sn	Tin
T	temperature
TASF	tris(dimethylamino)sulfonium difluorotrimethylsilicate
TBAF	tetrabutylammonium fluoride
TBDPS	*tert*-butylphenylsilyl
TBS	*tert*-butyldimethylsilyl
TBSOTf	*tert*-butyldimethylsilylrifluoromethanesufonate
TEA	triethyl amine
TFA	trifluoroacetic acid
TFDO	Methyl(trifluoromethyl)dioxirane
THF	tetrahydrofuran
Ti	Titanium
TMS	trimethylsilyl
TROSY	Transverse relaxation-optimized spectroscopy
W	Tungsten
Zn	Zinc
Z	Zusammen
δ	chemical shift downfield from TMS

Acknowledgements

I would like to thank my mentor, Professor Samuel J. Danishefsky, for his close supervision, continuous encouragement, and kind support during my Ph.D education. His rich wisdom about chemistry and philosophy has greatly inspired me during the past five years. I feel it is my great honor to work in Sam's group and I deeply appreciate Sam's teaching.

I am deeply grateful to Professor James Leighton, Scott A. Snyder, Tristan Lambert and Erik Sorensen for serving on my defense committee. In addition, I would like to thank Professor Leighton and Snyder for the suggestions on my research and job-hunting, which helped me a lot during my study at Columbia.

It is my great honor to study organic synthesis at Columbia University, which provided me a chance to learn chemistry from other great chemists here. I am in deep debt to Professor Stork and Professor Norton for their help suggestions on my research. I would also like to thanks Professor Breslow, Nakanishi, Katz, Nuckolls and Sames for their beautiful ideas and insightful thinking during the seminars and the Thursday Night Problem Sections.

Working in Sam's lab provided me a great opportunity to collaborate with a group of talent people. I would like to thank Dr. Benjamin J. Wright and Mr. John Hartung for

the collaboration on pluraflavin A project and for their friendship. They are very nice and patient with me, which help me a lot to learn English and culture in this country. Dr. Maolin Yu is thanked for his early exploration on Maoecrystal V project, which is very insightful for the further progress on this project. I would also like to thank Dr. Mingji Dai and Dr. Angie R. Angeles for the collaboration on the silyl enol ether isomerization project. I learned a lot from you guys. Dr. Robin E. Grote is thanked for her wonderful contribution to the Iso-Diels-Alder reaction project.

Working in Sam's lab also provided me a great opportunity to learn from other highly motivated chemists. I would like to thank Dr. Shengping Zheng, for teaching me the crazy mechanisms, for valuable suggestions on my research projects and for the friendship. I would like to thank Dr. Xuechen Li for the insightful discussion on chemistry and also on career development. I would like to thank Dr. Xiangyang Wu for the encouragement when I met difficulties in my research. I would like to thank Dr. Yandong Zhang for sharing with me about his beautiful chemistry and also his excellent professional skills. I would like to thank Dr. Zhang Wang for the insightful suggestions on my research projects. I would like to thank Dr. Suwei Dong for the help during my job hunting. I also want to express my gratitude to Dr. Alesandra Polara, Ms. Audrey Ross, Mr. Jordi Rull and Ms. Jessie Joussot, Dr. Jin Chen, Dr. Yu Yuan, Dr. Jianglong Zhu, Dr. Xiaohua Li, Dr. Ping Wang, Dr. Peter Park, Dr. Neeraj Sane, Dr. Karthik Iyer and all other MSKCC group members for the friendship and for the helps to my research.

I would like to thank Fay, Dana, and Laura for their management of the lab. Special thank goes to Rebecca for her wonderful work on manuscripts editing. I would also like to thank Professor William Berkowitz for his valuable help for literature searching.

During the past five years at Columbia, I am lucky to get help and support from a lot of great people. I would like to thank Alix and Dani who make my study smoothly here. I would also like to thanks John, Micheal and Yasuhiro for the NMR and Mass spectrum service. Without their support, a lot of important results would be missed. Special thanks goes to Aaron and Wes for their valuable help on the X-ray experiments. I would like to thank my classmates for the discussion and friendship. I would like to express my gratitude to Eli Lilly for a graduate fellowship.

Without support from my previous professors, I could not have the opportunity to study at Columbia. I would like to thank my Canada supervisor, Professor Dennis G. Hall, for his training and friendship. I would also like to thank Professor Zhen Yang and Professor Jiahua Chen at Peking University, for provided me an opportunity to study the frontier organic chemistry and for the guidance of my research. I would like to thank Professor He Li and Professor Ying Chen at Beijing Normal University for igniting my interest in organic chemistry.

Lastly, I would like to thank my family for endless support of my study. I thank my parents and my parents in-law for their love and encouragement. I especially thank

my wife, Ms. Yanqing Pan, for her love, understanding, and care. Without her support, I could not move forward in my career. I thank my son, Victor Peng, for all the happiness he brings to my family.

Chapter 1 Introduction

1.1 Isolation

Located in southern China, Yunnan province is considered as China's Botany Kingdom due to its rich plants resource. According to 2006's data, there were about 14590 different kinds of plants in Yunnan province, accounting for 48% of that in the whole China.[1] Most of these plants have been used as fork medicines for a long time.[1] With the development of natural product identification technologies in China, nowadays significant attention has been paid to the bioactive components of these herb medicines. Several research groups have already been engaged in the investigation of these plants. Among them, Professor Sun Han-Dong's team, who is from the Kunming Institute of Botany in the Yunnan province, is especially focused in the search for bioactive diterpenoids natural products from the genus *Isodon* plants of the Laiatae family.[2] Since 1976, his team has isolated and characterized more than 400 new diterpenoids. Most of these natural products share an *ent*-kaurane skeleton.[3]

Maoecrystal V was first isolated in 1994 from *Isodon eriocalyx* Hara, which is widely distributed in southern China. *Isodon eriocalyx* Hara has been used as a herbal medicine for a long time in Yunnan province. It has been used to treat sore throat, inflammation, and hypertension, etc. Since the X-ray structure was not obtained at that time, Professor Sun's group did not report Maoecrystal V. It was in 2004 that the group successfully acquired a single crystal of Maoecrystal V and its X-ray structure was reported on *Org. Lett.*[4] As shown (**Figure 1-1**), Maoecrystal V (1.1) featured two

contiguous quaternary carbon stereocenters and a tertiary alcohol, embedded within a rigid pentacyclic scaffold. The isolation chemists mentioned in the isolation paper, "Maoecrystal V is by far the most modified naturally occurring *ent*-kauranoid from Isodon species."[4] These factors make Maoecrystal V a very challenging target for total synthesis.

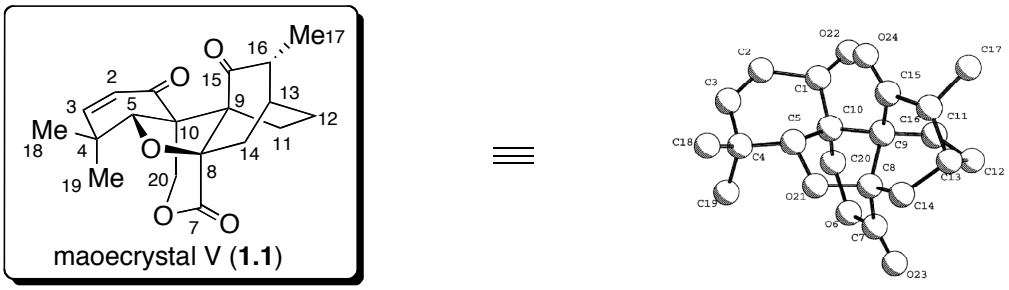
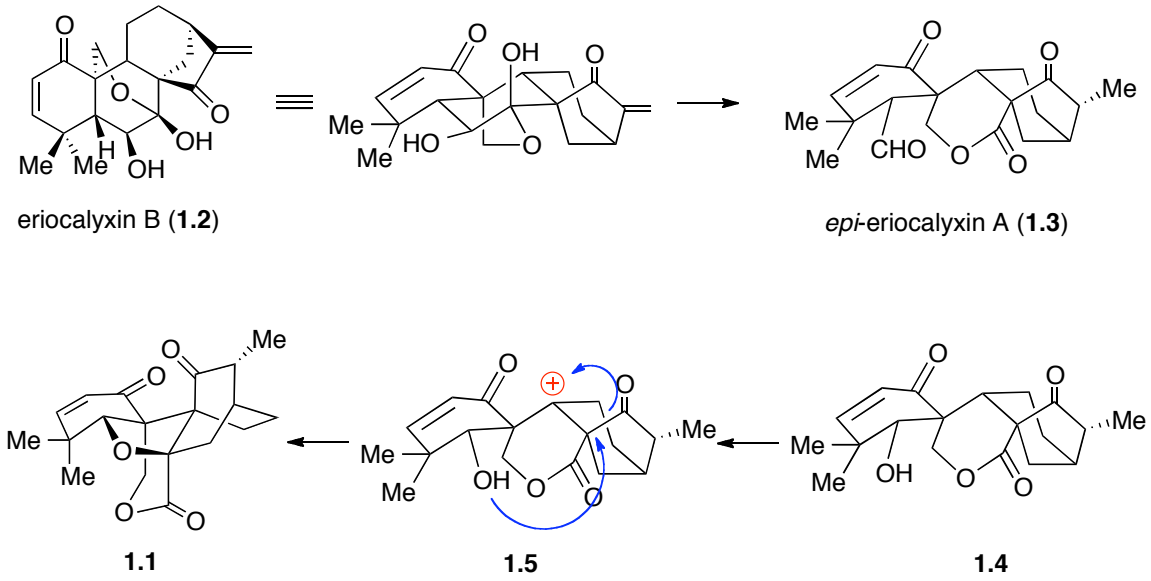


Figure 1-1 Structure of Maoecrystal V

1.2 Biosynthesis Hypothesis and Biological Activity

The isolation chemists proposed an interesting pathway accounting for the formation of Maoecrystal V from *eriocalyxin* B (Scheme 1-1).[5] An oxidative cleavage and selective reduction of *eriocalyxin* B would provide *epi-eriocalyxin* A(**1.3**). A Baeyer-Villager-type degradation of the aldehyde functional group of *epi-eriocalyxin* A(**1.3)** would generate the C-5 hydroxyl group with the retention of the stereochemistry (**1.4**). An enzymatic 1,2 carbon shift followed by tetrahedronfuran ring formation would afford Maoecrystal V.



Scheme 1-1 Biosynthesis of Maeocrystal V from Eriocalyxin B

Maoecrystal V was evaluated for its cytotoxicity against five human tumor cell lines.[4] Maoecrystal V showed high selective activity against the HeLa cell line with IC_{50} values as low as 20 ng/mL, while there is no significant cytotoxicity toward other four cell lines. These interesting results indicate that Maoecrystal V and its derivatives could potentially be lead anticancer agents.

1.3 Synthetic Studies toward Maoecrystal V

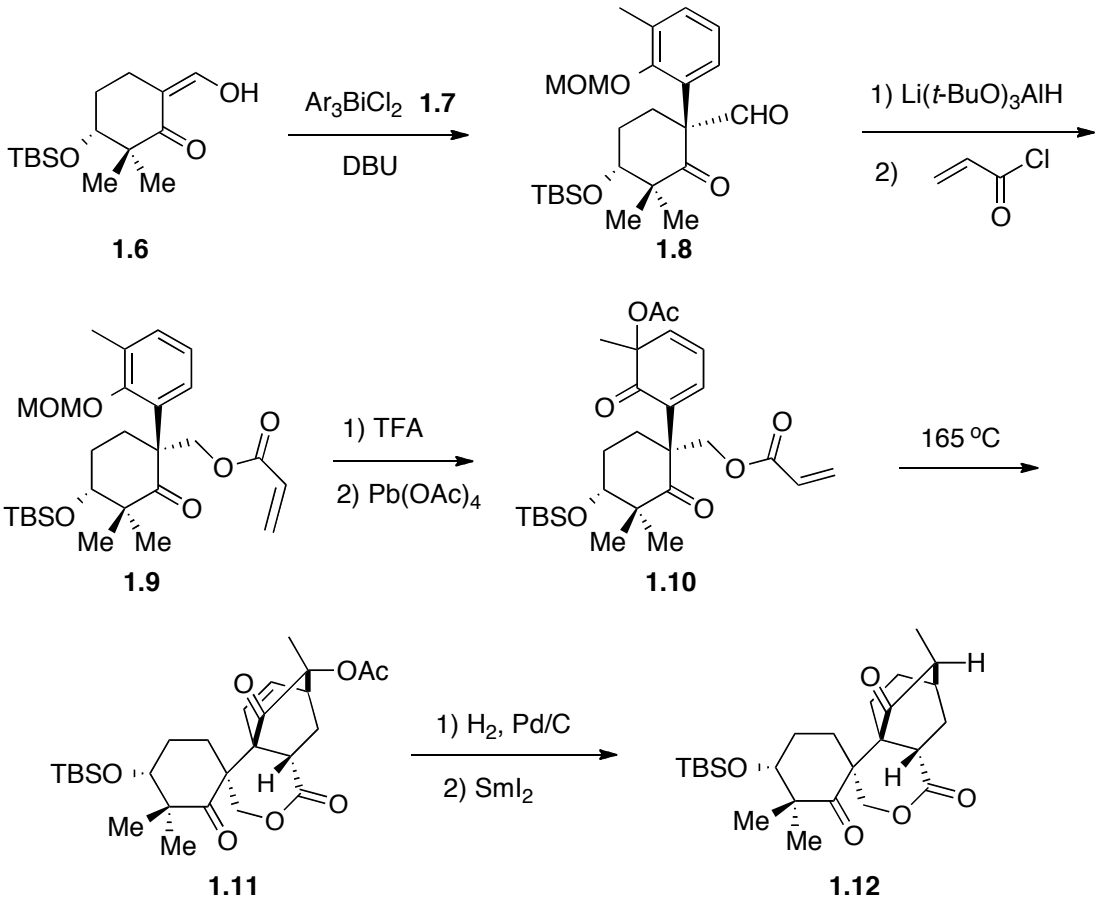
With a promising biological profile and an interesting structure, Maoecrystal V has gained significant attention from the synthetic organic community since its structure elucidation. More than 10 groups[6] have initiated synthetic programs toward this natural product with one total synthesis reported on 2010[22] from Professor Zhen Yang's group in

China. The proceeding section will highlight the chemistry involving the synthetic efforts towards Maoecrystal V by the synthetic community.

1.3.1 Professor Baran's Strategy toward Maoecrystal V[7]

Baran's group reported a creative approach toward Maoecrystal V based on their understanding of the problems in the maoecrystal V's synthesis in 2009. Their key reaction is an intramolecular Diels-Alder cyclization (**1.10** to **1.11**) to establish the skeleton. Within the DA strategy, there are three issues to be addressed: 1) what kind of diene and dienophile would work? 2) What kind of DA precursor is the best for this target? 3) How to control the stereoselectivity of this Diels-Alder reaction?

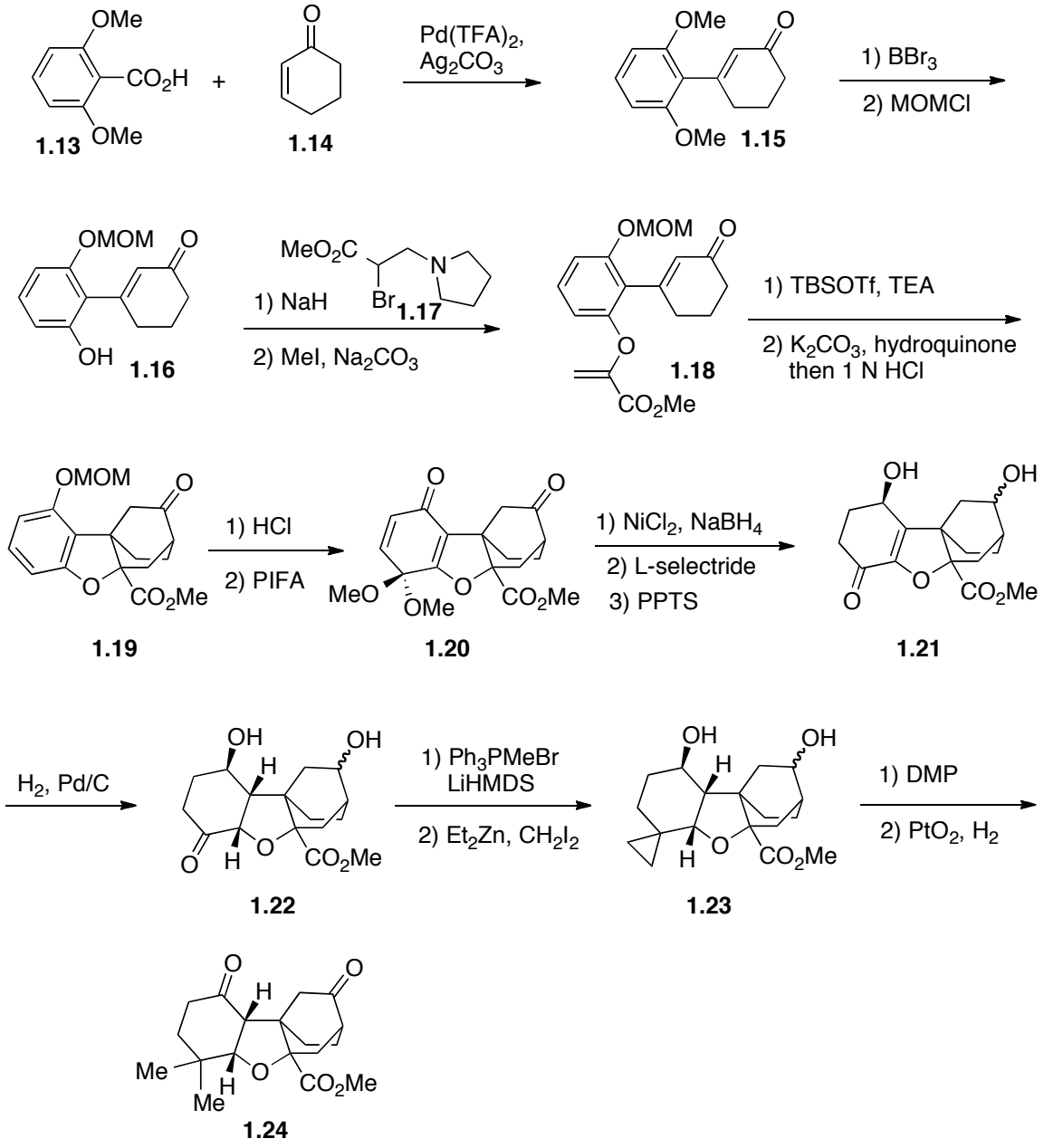
Baran's synthesis commenced with a Barton arylation reaction[8] between keto aldehyde **1.6** and an aryl bismuth compound **1.7**, which afforded **1.8** with the requisite quaternary carbon center. Reduction of the aldehyde and acylation of the resultant alcohol provided intermediate **1.9**. Unmasking of the phenol with TFA and subsequent Wessely oxidation with $Pb(OAc)_4$ gave the key Diels-Alder reaction precursor **1.10**. The thermal-induced IMDA proceeded smoothly to produce the desired *endo*-adduct **1.11**. This advanced intermediate was further transformed to compound **1.12** by hydrogenation and SmI_2 reduction. Baran's exploration on maoecrystal V provided a nice answer to the questions related to a Diels-Alder strategy toward Maoecrystal V considering their diene, DA precursor, and stereoselectivity. The chemistry left for a total synthesis is how to prepare the THF ring.



Scheme 1-2 Baran's Approach Toward Maoecrystal V

1.3.2 Professor Nicolaou and Professor Chen's Strategy toward Maoecrystal V [9, 10]

Nicolaou and Chen's group also investigated an intramolecular Diels-Alder strategy toward the total synthesis of Maoecrystal V. Their approach employed the ether-tethered IMDA precursor **1.18** instead of the lactone-tethered precursor such as Baran's compound **1.10**. Accordingly, the core THF ring (compound **1.19)** was prepared just after the IMDA reaction, presenting a very creative solution to the core THF ring problem of Maoecrystal V.



Scheme 1-3 Nicolaou/Chen's Approach toward Maoecrystal V

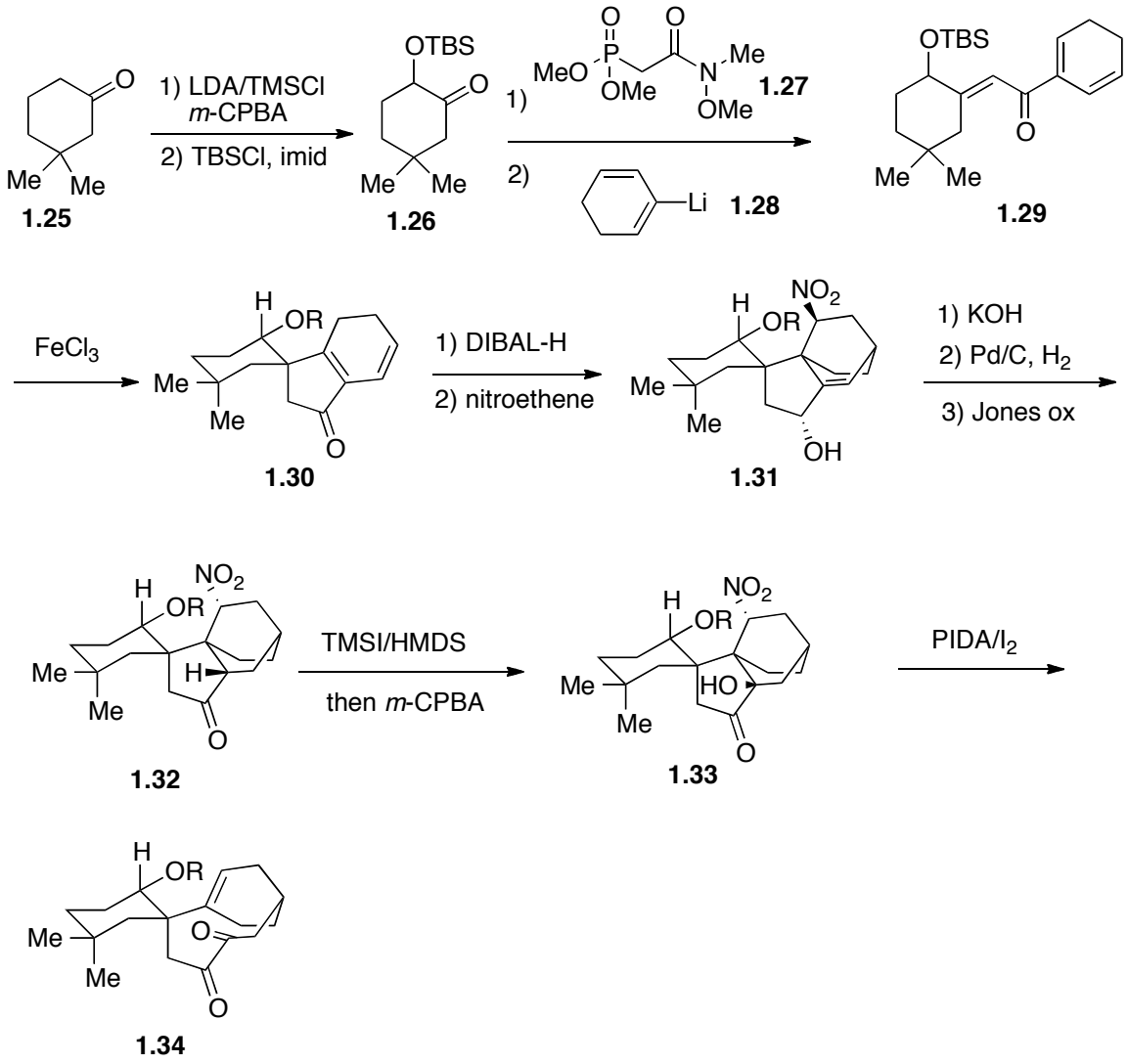
The synthesis commenced with a decarboxylative Heck coupling[11] to provide enone **1.15**. Protecting group manipulations of **1.15** afforded mono-phenol **1.16**. The mono-phenol **1.16** underwent an alkylation with bromide **1.17**, which afforded a

precursor for the dienophile. The resultant pyrollidine moiety was then alkylated with MeI and subsequent Hofmann elimination reaction furnished compound **1.18**. Compound **1.18** was then treated with TBSOTf and the resultant IMDA precursor was directly heated to furnish the desired *exo*-adduct. Subsequent deprotection gave compound **1.19**. This compound was then treated with aqueous HCl and the resultant phenol was oxidized with PIFA to furnished dearomatized compound **1.20**. To synthesize the correct C5 stereogenic center, compound **1.20** was further reduced to compound **1.21** using L-Selectride. A hydroxyl-directed hydrogenation with Pd/C afforded the compound **1.22** with the desired C5 stereochemistry.

The Nicolaou/Chen group demonstrated their solution to the gem-dimethyl functional group problem. As planned, compound **1.22** underwent Wittig reaction and subsequent Furukawa-modified Simmons-Smith cylopropanation of the *exo*-methylene provided the desired cyclopropane **1.23**. Global oxidation of compound **1.23** followed by hydrolysis indeed afforded the gem-dimethyl compound **1.24**. The remaining chemistry required toward a total synthesis of Maoecrystal V is how to construct the last lactone ring.

1.3.3 Professor Thomson's Strategy toward Maoecrystal V[12]

The Thomson group reported an interesting intermolecular Diels-Alder strategy toward Maoecrystal V (**1.30** to **1.31**). This strategy reminds me the Corey's synthesis of Antheridic Acid.[13] The synthesis started with a Rubottom oxidation[14] of ketone **1.25**. The resultant alcohol was protected as a TBS ether. The ketone **1.26** was then subjected to a Horner-Wadsworth-Emmons reaction condition using reagent **1.27**.



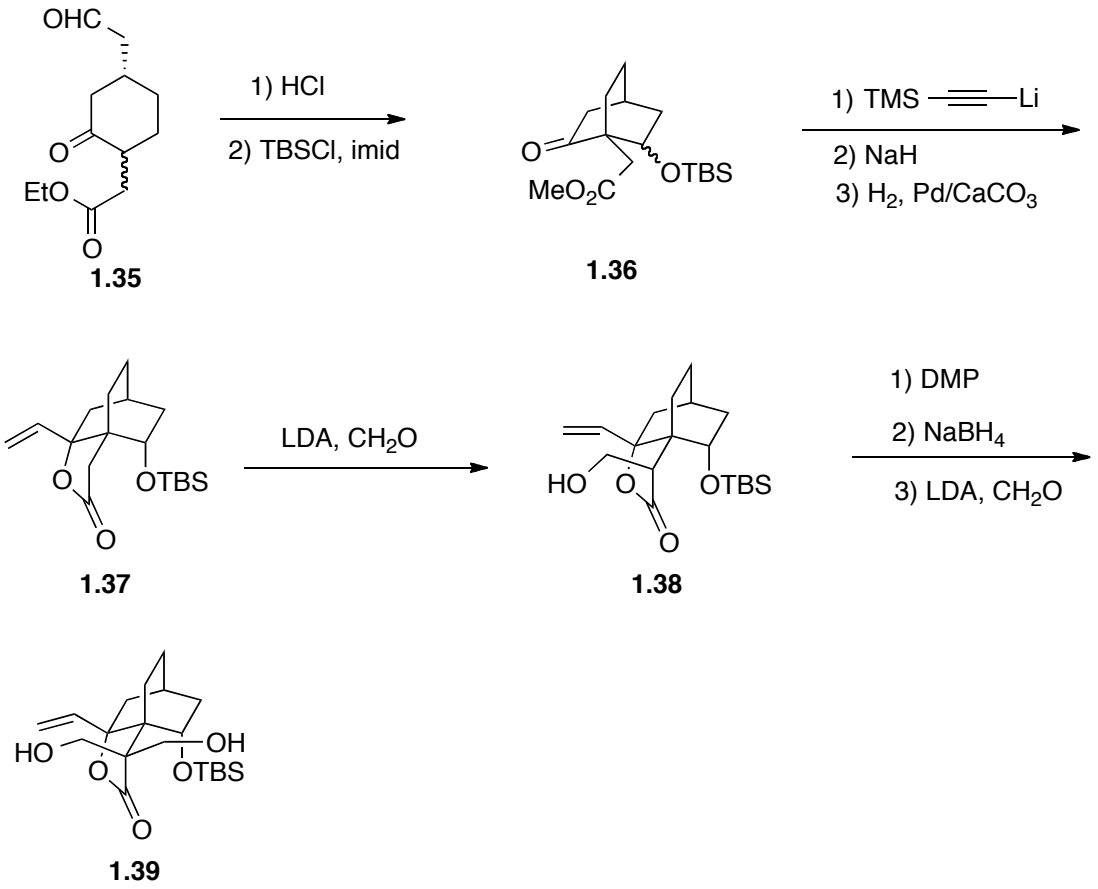
Scheme 1-4 Thomson's Approach toward Maoecrystal V

The resulting unsaturated Weinreb amide[15] was treated with **1.28** to furnish the desired intermediate **1.29**. An elegant Lewis-acid-catalyzed Nazarov cyclization[16] occurred on compound **1.29** and afforded intermediate **1.30** with the requisite quaternary carbon center. The ketone in compound **1.30** was reduced and the resulting diene was subjected to an intermolecular Diels-Alder reaction with nitroethylene to furnish the desired

cycloadduct **1.31**. Although the designed Nef reaction[17] with **1.31** did not afford the desired ketone, treatment of **1.31** with KOH resulted in complete epimerization of the nitro group, which provided a good chance to stereoselectively install the requisite C-8 hydroxyl group. Accordingly, the epimerized nitro compound was further subjected to a hydrogenation and a Jones oxidation to yield compound **1.32**. Rubottom oxidation of the ketone **1.32** afforded the desired C-8 hydroxyl compound **1.33**, which was poised for a creative oxygen-variant of the Hofmann-Loffler-Freytag reaction.[18] Toward this end, a remote C-H functionalization of **1.33** afforded a Grob fragmentation product **1.34**, presumably due to the ring strain.

1.3.4 Professor Trauner's Strategy toward Maoecrystal V[19]

Unlike the previous synthetic approaches, the Trauner group envisaged a non-DA approach toward Maoecrystal V. Their synthesis started with an intramolecular aldol condensation of substituted cyclohexenone **1.35**. The resulting secondary alcohol was protected as TBS ether **1.36**. This compound was followed by a acetylene anion addition to **1.36** and subsequent hydrogenation afforded the key intermediate (**1.37**), which contained one quaternary carbon center. At this stage, the plan was to install the second quaternary carbon center by a direct double aldol addition of **1.37** with formaldehyde; however, the second aldol addition proved to be very challenging, probably because it required a concave face addition. To circumvent this issue, the mono-alkylation product was epimerized by an oxidation/reduction sequence (**1.38** to **1.39**, condition 1 and 2). The resulting epimerized mono-alkylated product smoothly underwent a second alkylation reaction on the convex face and afforded the desired advanced intermediate **1.39** with



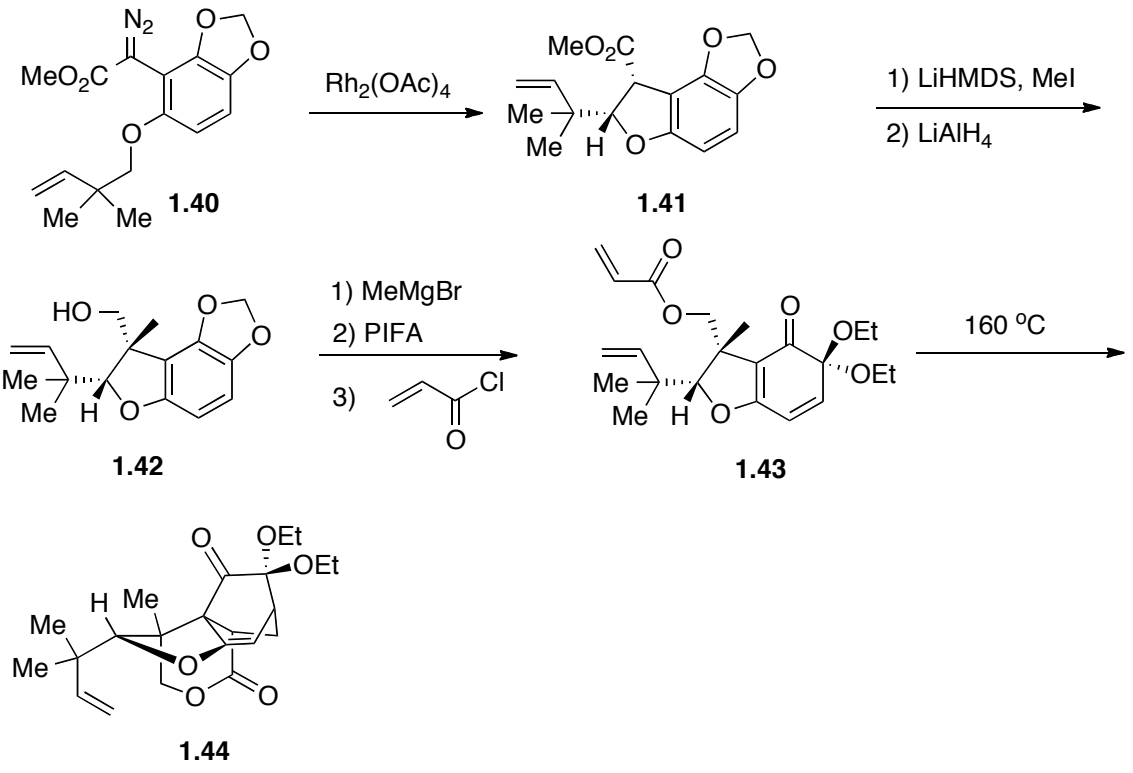
1.35 **1.36** **1.37** **1.38** **1.39**

Scheme 1-5 Trauner's Approach toward Maecrystal V

two continuous quaternary carbon centers. This strategy presented an efficient method to prepare the tetracyclic core with two quaternary centers. The remaining chemistry toward Maoecrystal V is to synthesize the enone A ring.

1.3.5 Professor Zakarian's Strategy toward Maoecrystal V[20]

The Zakarian group demonstrated an interesting IMDA approach toward Maoecrystal V.

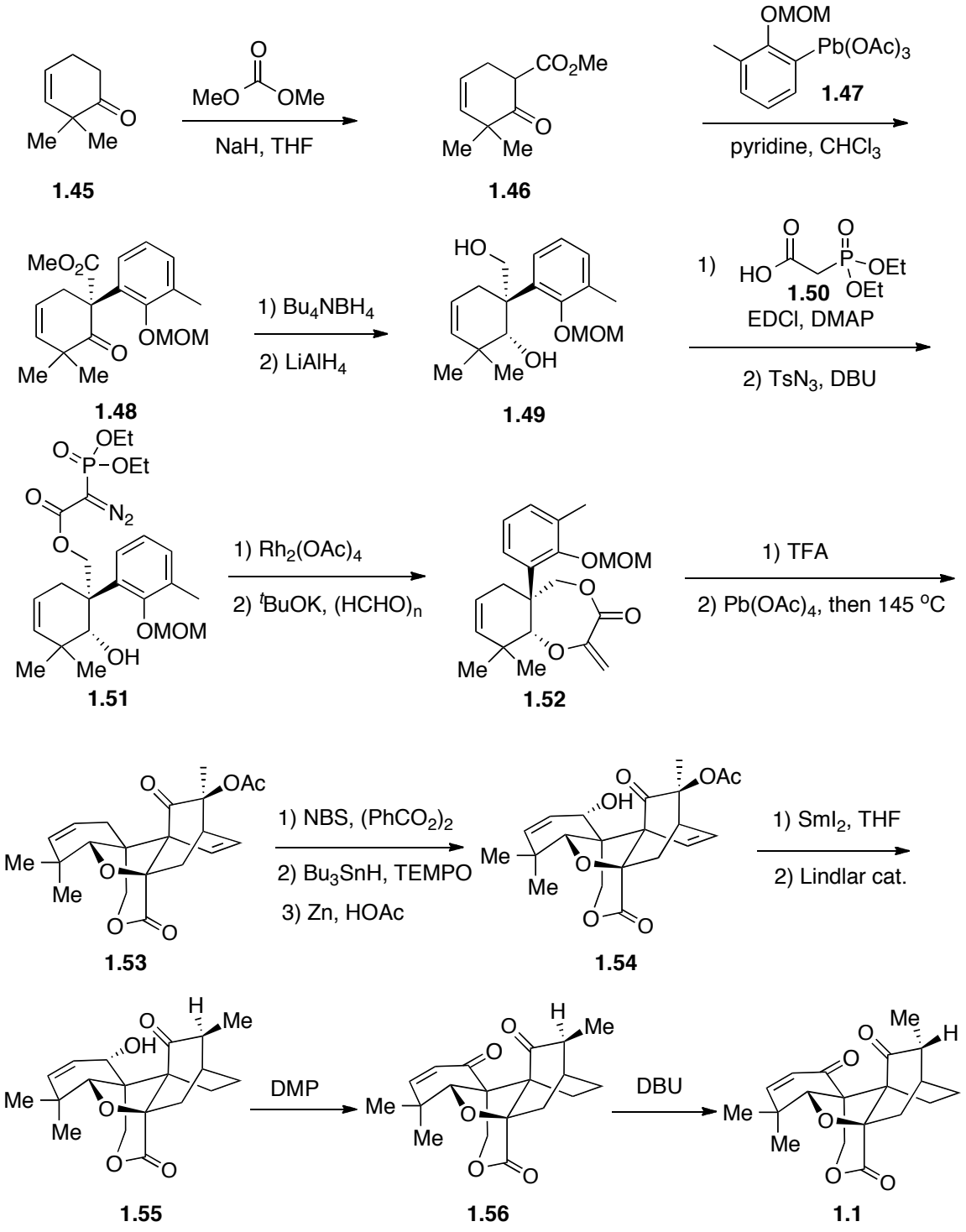


Scheme 1-6 Zakarian's Approach toward Maoecrystal V

Their strategy features an early installation of the THF ring. The synthesis commenced with an elegant C-H insertion reaction[21] (**1.40** to **141**) to provide a dihydrobenzofuran **1.41**. Alkylation of the ester and subsequent reduction of the ester gave alcohol **1.42**. Compound **1.42** was then subjected to MeMgBr to provide a mono ethyl-protected catechol derivative. Treatment with PIFA followed by acylation with acryloyl chloride gave the desired IMDA precursor **1.43**. The key IMDA occurred thermally to afford the desired cycloadduct **1.44** in excellent yield. What remains toward the total synthesis are the preparation of the desired lactone and the left A enone ring.

1.3.6 Professor Yang's Total Synthesis of Maoecrystal V in 2010 [22]

As the first research group published model study toward Maoecrystal V in 2009 [23], Prof. Zhen Yang's group achieved the first total synthesis of Maoecrystal V in 2010. Considering the concise strategy, their synthesis was really a milestone in this research field. Their synthesis started with the preparation of a β-ketoester **1.46** (**1.45** to **1.46**). A Barton arylation of this ketoester **1.46** with a lead reagent **1.47** provided the desired key intermediate (**1.48)**, with the requisite quaternary carbon center. The stereoselevtive reduction of the ketone proved to be challenging during their exploration; nevertheless, it was eventually found that Bu_4NBH_4 was the right hydride reagent to provide the desired C-5 β-hydroxyl compound exclusively. A subsequent $LiAlH_4$ reduction of the ester afforded the diol **1.49**. Esterification followed by a diazo transfer reaction furnished a diazo compound **1.51**. This diazo compound was then subjected to an elegant intramolecular C-H insertion[24] reaction and Horner-Wadsworth-Emmons reaction with paraformylaldehyde to furnish key intermediate **1.52**. At this stage the C-5 oxygen and lactone bis-tethered dienophile was ready. The MOM protecting group was removed with TFA and the free phenol was subjected to Wessely oxidation condition to provide the key IMDA precursor. Without isolation, the crude mixture was subjected to thermal-promoted DA condition to provide desired adduct **1.53** as a minor isomer (36% **1.53** and 42% undesired isomer). It would be a perfect solution to Maoecrystal V if a single diastereoisomer was obtained in this IMDA reaction. Actually, the diastereoselectivity is a challenging issue when IMDA strategy was employed to construct the bicyclo-[2.2.2] octane structure. Now the synthesis went to its endgame stage.



Scheme 1-7 Yang's Total Synthesis of Maoecrystal V

The C-1 oxygen functionality was introduced by an indirect allylic oxidation sequence (**1.53** to **1.54**) initiated by an allylic bromination reaction. The resulting allylic bromide was then treated with Bu_3SnH and TEMPO and subsequent Zn reduction furnished the desired alcohol **1.54**. SmI_2 reduction and hydrogenation provided a key intermediate **1.55**. This intermediate **1.55** was then subjected to DMP oxidation to furnish 16-*epi*-Maoecrystal V. A base-catalyzed epimerization reaction provided the natural Maoecrystal V. Yang's synthesis featured a concise strategy based on several elegant tranformations such as Barton arylation, Wessely oxidation, intramolecular OH insertion and subsequent Horner-Wadsworth-Emmons reaction.

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Chapter 2 First Generation Synthetic Approach

2.1 Introduction

Total synthesis and biological evaluation of structurally challenging natural products continue to be a main focus in our laboratory.[1] In this context, our attention was attracted by a recent isolated anti-cancer terpenoid, Maoecrystal V[2]. Maeocrystal V is a densely functionalized diterpene, which possesses a novel rearranged *ent*-kaurane skeleton with a bicyclo-[2.2.2] octane motif. There are three continuous quaternary carbon centers imbedded within a pentacyclic ring system, and, at the same time, these three quaternary centers are spiro centers.

2.2 Synthetic Plan: Intramolecular Diels-Alder Reaction

We started with a close pattern-analysis of the preparation of the bicyclo-[2.2.2] octane moiety.[3] Generally speaking, there are three known approaches to build a bicyclo-[2.2.2] octane structure. The first method is a Diels-Alder reaction using 1,3-cyclohexadiene **2.2** or its derivatives as dienes.[4] In this Diels-Alder reaction, two C-C bonds and a ring are formed at the same time, which is highly efficient. The second method is intramolecular C-C bond formation (eg: aldol, 1, 4-addition) from a substituted cyclohexane derivative **2.5**.[5] The stereochemistry of the final bicyclo-[2.2.2] structure is usually controlled by the precursor **2.5**. The third method is the ring-closing metathesis of

the 1,4-*syn*-di-vinyl substituted cylohexane derivatives **2.6**.[6] This approach requires preparation of a diene precursor **2.7**, which is not straightforward from simple starting materials.

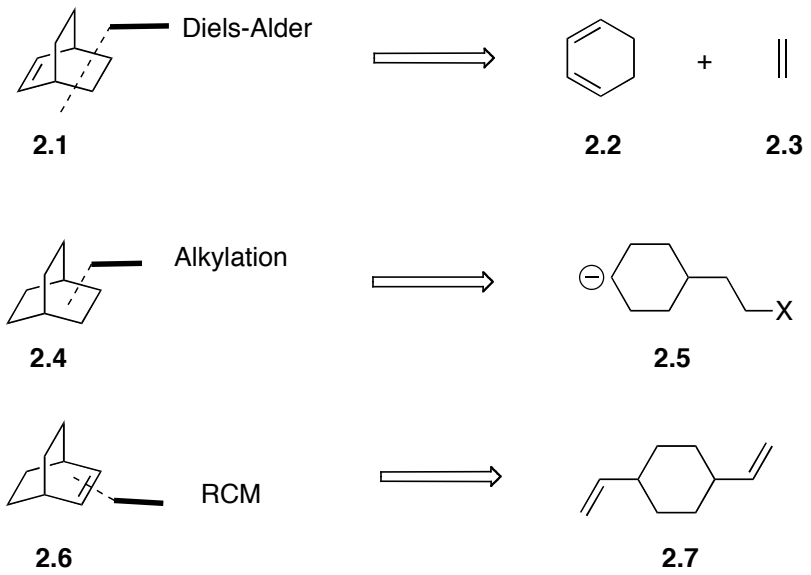
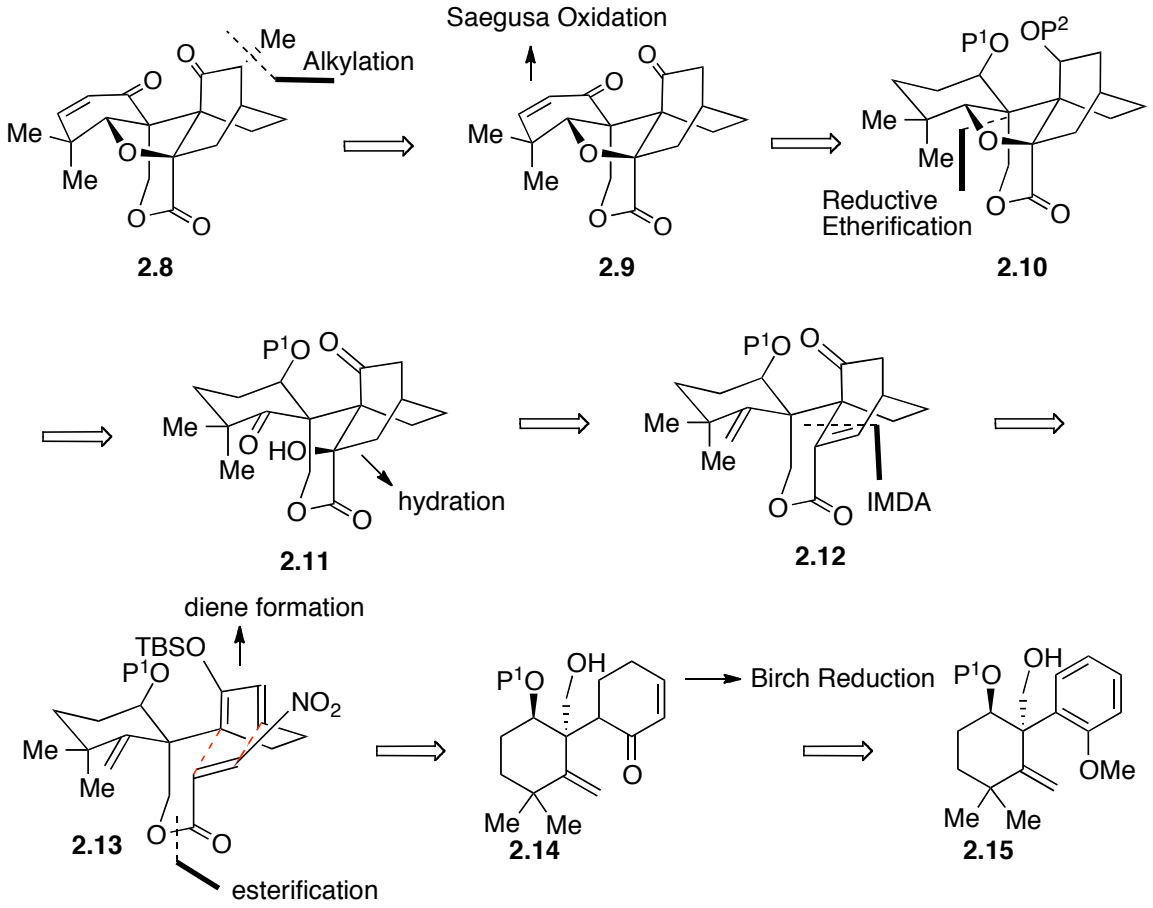


Figure 2-1 Methods to prepare bicyclic-[2.2.2] octane structure

Based on this pattern analysis and the structure evaluation of Maoecrystal V, we designed our first generation synthesis plan. The key design of this strategy is an intramolecular Diels-Alder reaction (IMDA)[7] of substrate **2.11**.



Scheme 2-1 Retrosynthesis of Maoecrystal V

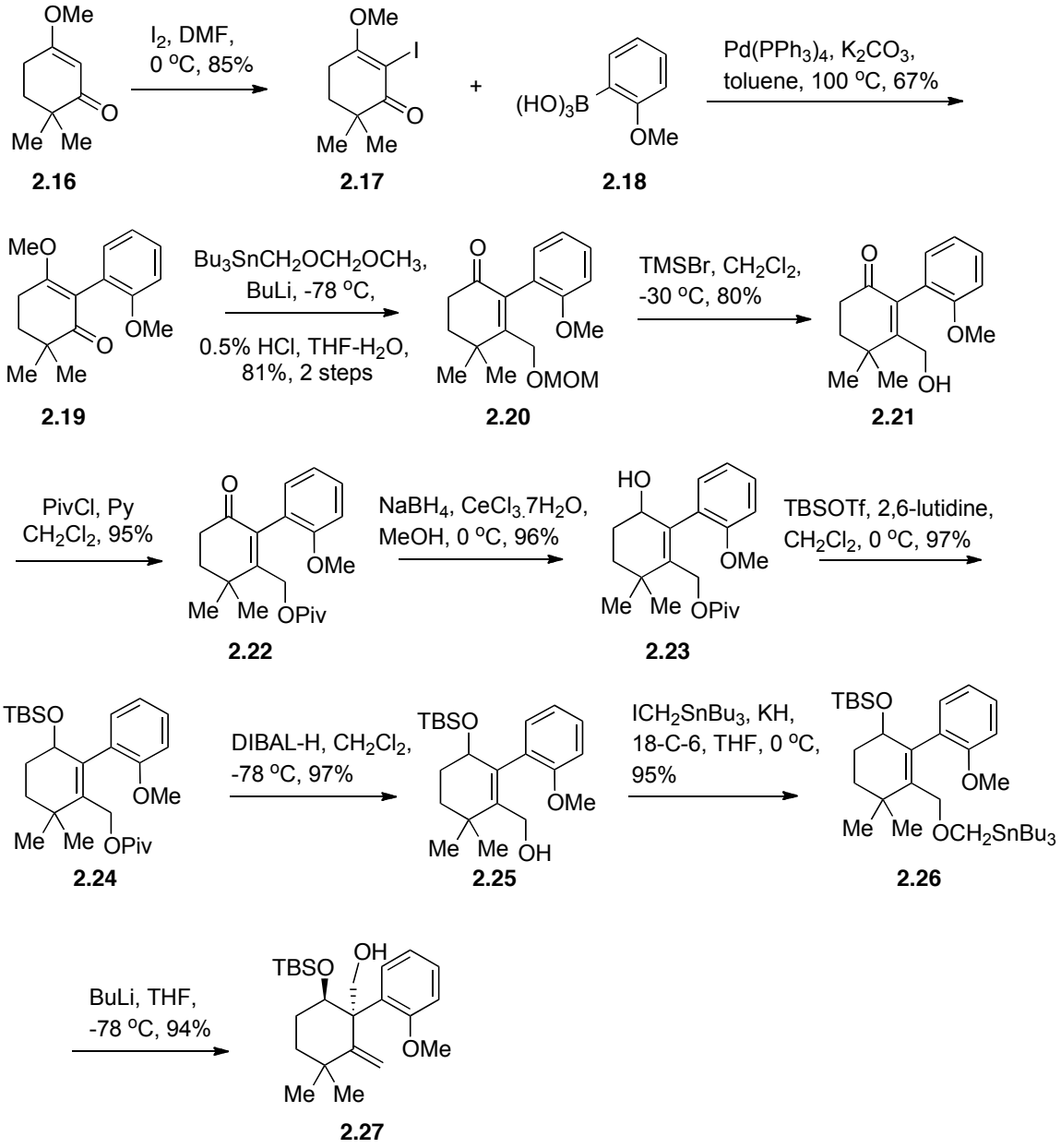
We envisioned that Maoecrystal V could be synthesized from a stereoselective alkylation of substrate **2.9**. The enone moiety could be prepared using Saegusa oxidation[8] from compound **2.10** in a forward sense. At this stage, we further envisioned that the core THF ring could be closed through a reductive etherification reaction from substrate **2.11**, in which C-5 is a ketone and C-8 is a tertiary alcohol. We hoped that the axial hydride attack to the corresponding oxonium would afford the desired stereochemistry. The requisite C-8 tertiary alcohol could be synthesized through a selective hydration of the corresponding enone alkene in compound **2.12** in the forward sense. The stereoselectivity

of this hydration process would be a potential problem since the spatial differences of the α and β faces in a bicyclo-[2.2.2] octane structure is subtle. We rationalized that the C-15 ketone function group would help to afford the desired β–hydroxyl group due to stereoelectronic effect (Cieplak effect[9]). Key intermediate **2.12** was anticipated to be synthesized from compound **2.13** through an intramolecular Diels-Alder reaction. The IMDA precursor **2.13** was anticipated to be prepared from compound **2.14** through an esterification reaction using β-nitro acrylate. We anticipated that the nitro group would increase the reactivity of the dienophile and would also serve as a leaving group after DA reaction to generate an alkene. The net result was a DA from propiolate; however, we concerned that a retro-DA would give an aromatic ring if propiolate was used directly here. The enone moiety in compound **2.14** was envisioned to be prepared from the corresponding functionalized aromatic ring from compound **2.15**. Our synthetic plan required the preparation of a substituted cyclohexane derivative **2.15**.

2.3 Results and Discussion

Our first objective was to synthesize of the key cyclohexane derivative **2.15**. This goal was eventually achieved by our previous postdoctoral researcher, Dr. Maolin Yu. Maolin developed an elegant route to stereoselectively synthesize compound **2.27** and his route is shown in Scheme 2-2.

As outlined in Scheme 2-2, the synthesis commenced with a Carl-Johnson iodination[10] of cycloalkenone **2.16**. The resultant α-iodo cyclohexenone was subjected to the Suzuki-Miyaura coupling, with boronic acid **2.18**, to afford α-arylcyclohexenone **2.19**

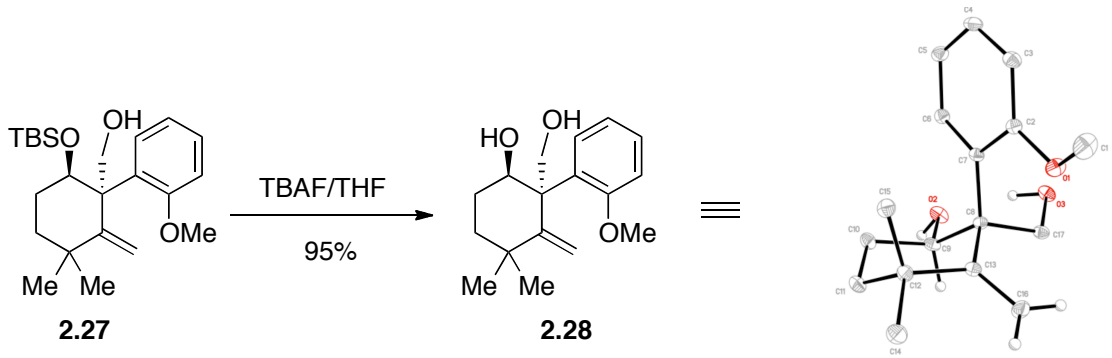


Scheme 2-2 Preparation of compound **2.27**

in 67% yield. This intermediate **2.19** was then transformed to the 1,2-disubstituted cyclohexenone **2.20** using Stork-Danheiser protocol.[11] Following replacement of MOM ether with a pivaloate ester, compound **2.22** was in hand. Luche reduction of **2.22**

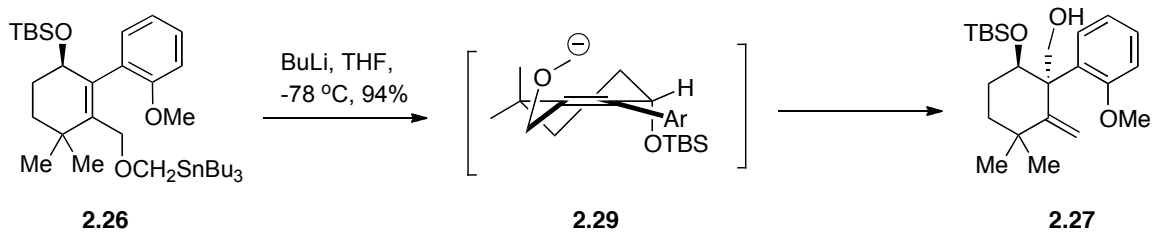
provided an allylic alcohol, which was protected as its TBS ether (**2.24)**. DIBAL-H reduction of **2.24** freed the pivaloate-protected hydroxyl group. The resulting allylic alcohol (**2.25)** was then alkylated with ICH_2SnBu_3, and Wittig-Still [2,3] rearrangement[12] did occur as planned and afforded the desired **2.27** in 94% yield as a single stereoisomer.

The relative chemistry of compound **2.17** was unambiguously assigned based on a derivative **2.28** by X-ray crystallography. X-ray crystallography clearly presented that the axial C-18 methyl resides above the phenyl ring, which makes the chemical shift of this methyl group in ^{1}H NMR to be 0.64 while that of the equatorial C-19 methyl group is 1.1.



Scheme 2-3 Preparation of **2.28**

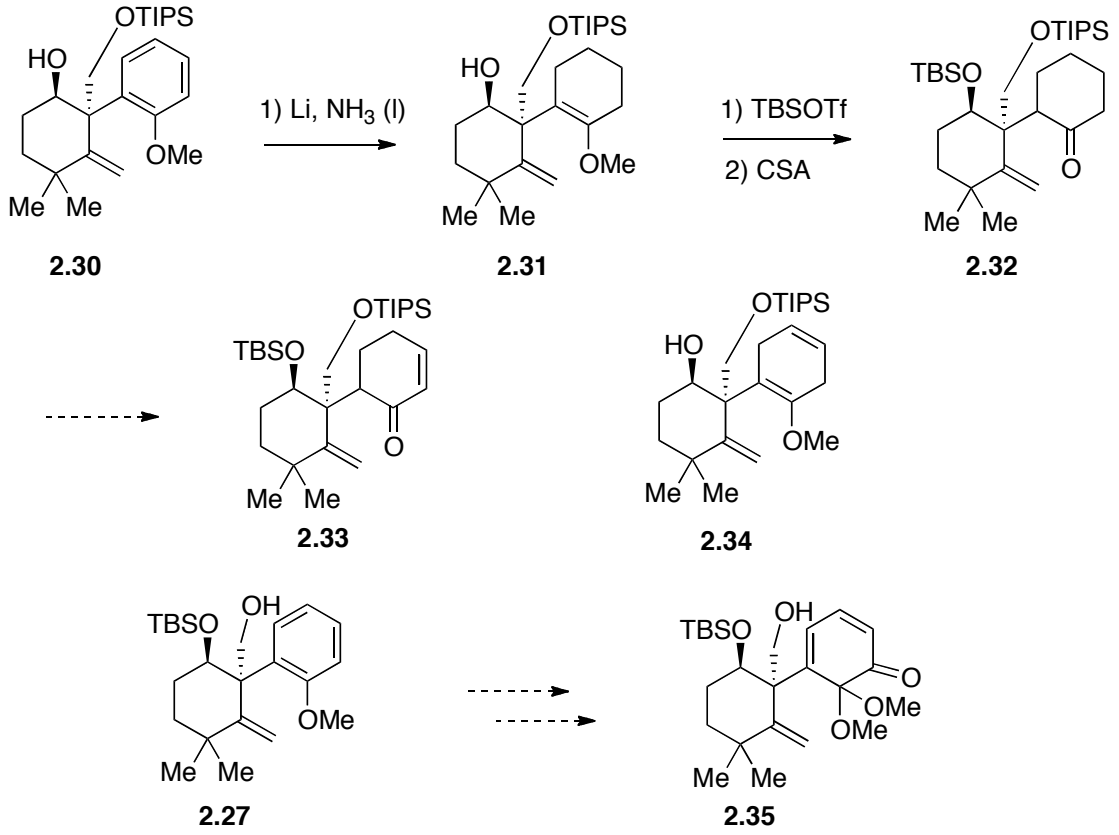
Based on the analysis above, we proposed that the Wittig-Still [2,3] rearrangement took the transition structure **2.29**, to afford our desired product. With compound **2.27** in hand, Maolin then explored the Birch reduction[13] on it and its derivatives. After extensive study, Maolin eventually found that the Birch reduction of compound **2.30** afforded mono alkene **2.3** instead of the desired para-diene **2.34**. Compound **2.32**, however, did not undergo dehydrogenation to provide the desired enone



2.26 **2.29** **2.27**

Scheme 2-4 Wittig-Still [2,3]-rearrangement

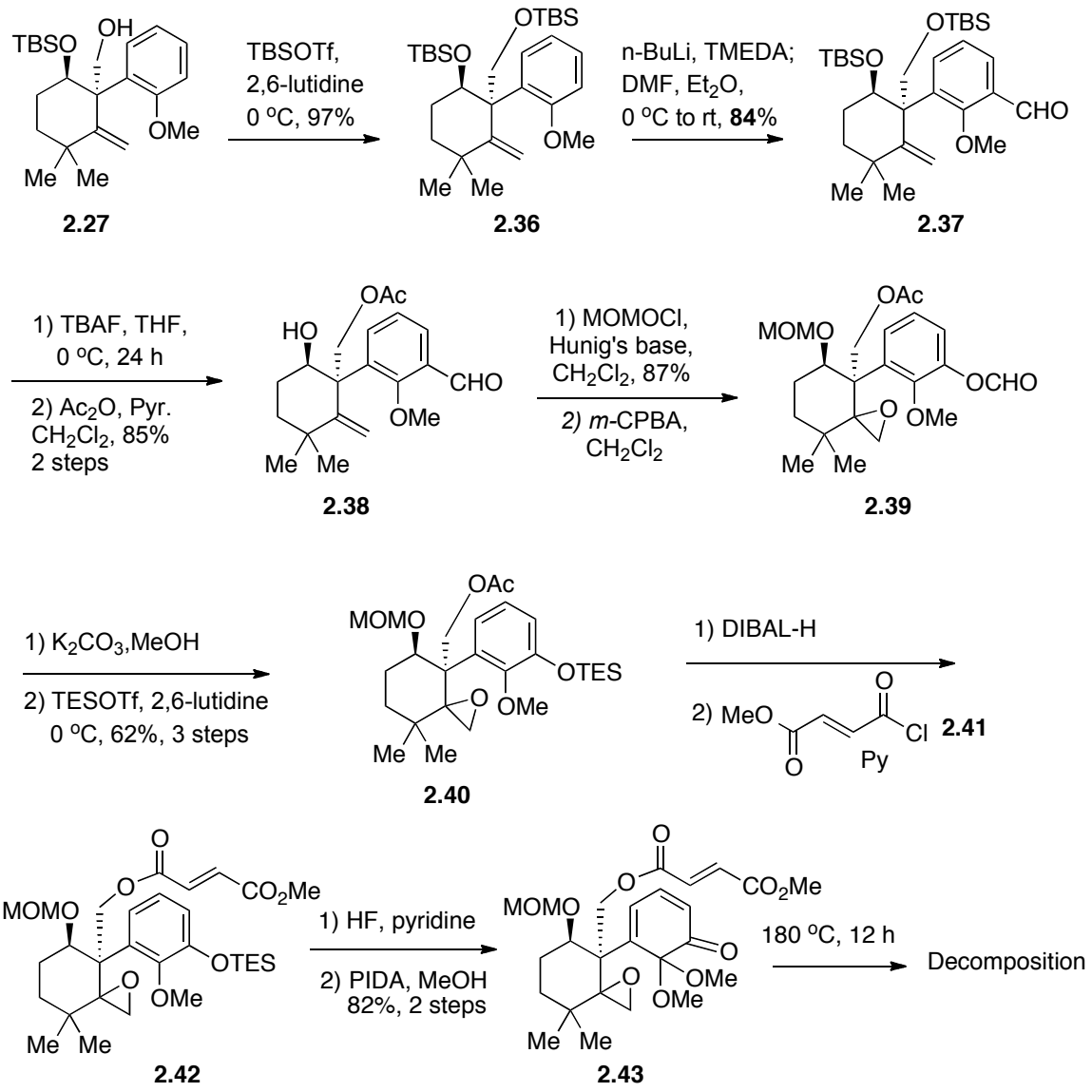
2.33. At this stage, Maolin then planned to use an alternative diene **2.35**, which could be prepared through an oxidative dearomatization reaction[14], to explore the IMDA reaction.



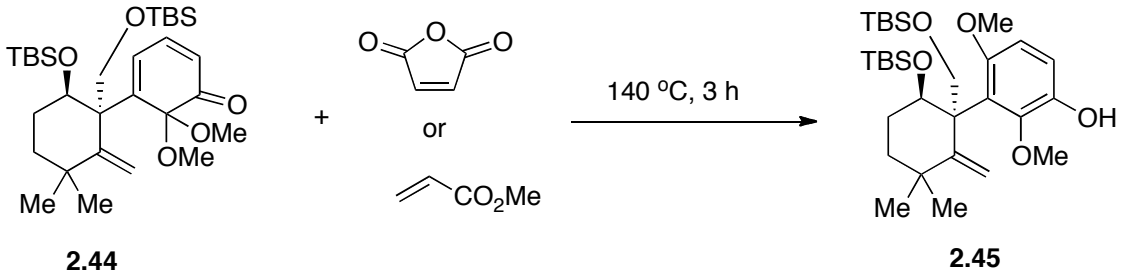
Scheme 2-5 Summary of Birch reduction

This goal was eventually achieved by Maolin and the successful route was outlined as the following scheme (Scheme 2-6). The synthesis started with a protection of the primary alcohol **2.27** as a TBS ether **2.36**. Direct lithiation followed by quenching with DMF furnished the aldehyde **2.37**. Global deprotection of the silyl protecting group and selective reprotection of the primary alcohol using acetic anhydride afforded a secondary alcohol **2.38**, which was further protected as a MOM ether. This protected aromatic aldehyde was subjected to a Dakin oxidation protocol, furnishing a formyl ester **2.39**. During this oxidation, the *exo*-methylene was also oxidized to an epoxide. The formyl ester **2.39** was then hydrolyzed, and the resultant free phenol was protected as a TES ether to provide intermediate **2.40**. DIBAL-H reduction served to free the primary alcohol and the resultant primary alcohol underwent an esterification with **2.41** to furnish compound **2.42**. At this stage, the TES protecting group was removed using HF and PIDA oxidation of the free phenol afforded our key IMDA precursor **2.43**. With this intermediate **2.43** in hand, Maolin tested the key IMDA reaction, but under the conditions tested, thermo and Lewis-acid-catalyzed conditions did not provide the DA adduct. Only decomposition of starting material was observed.

Then, Maolin was heading for his new place: Boehringer Ingelheim, and I took over this project. Since decomposition was observed during the exploration of IMDA of compound **2.43**, this result indicated that the diene **2.46** might be unstable during the IMDA condition. In order to further explore the stability of the diene, an intermolecular Diels-Alder reaction using **2.44** and maleic anhydride or methyl acrylate as dienophile was explored. The thermo-promoted DA reaction afforded a dienone-phenol rearrangement product **2.45**, and the desired DA adduct was not observed.



Scheme 2-6 Preparation of compound **2.43**



Scheme 3-7 Intermolecular DA reaction of **2.44**

We also thought about other dienes that could be used as an alternative in our forward synthesis, such as diene **2.48**. This is a Danishefsky-type diene and should be very reactive. It could be prepared from a *para*-methoxyl phenyl ring through a Birch reduction and thus I could use Maolin's route to prepare our designed compound **2.52**.

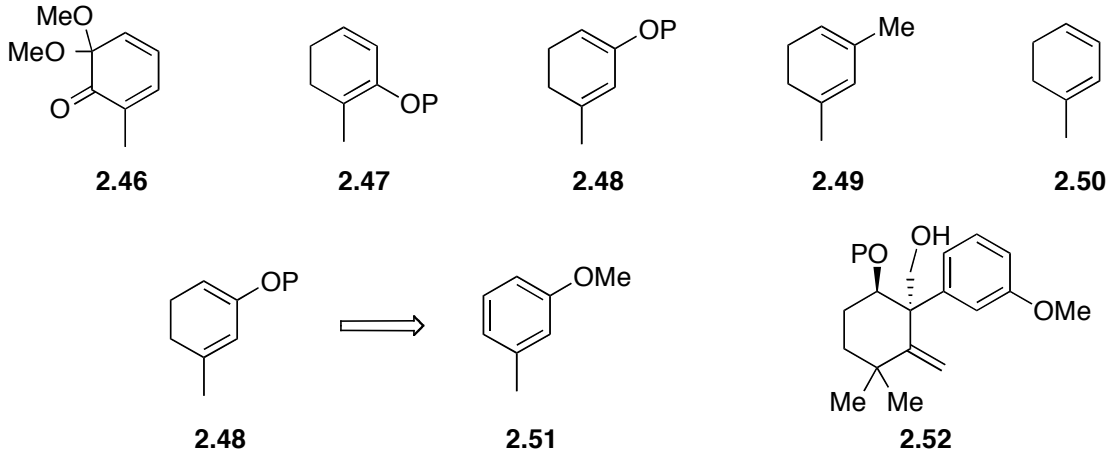
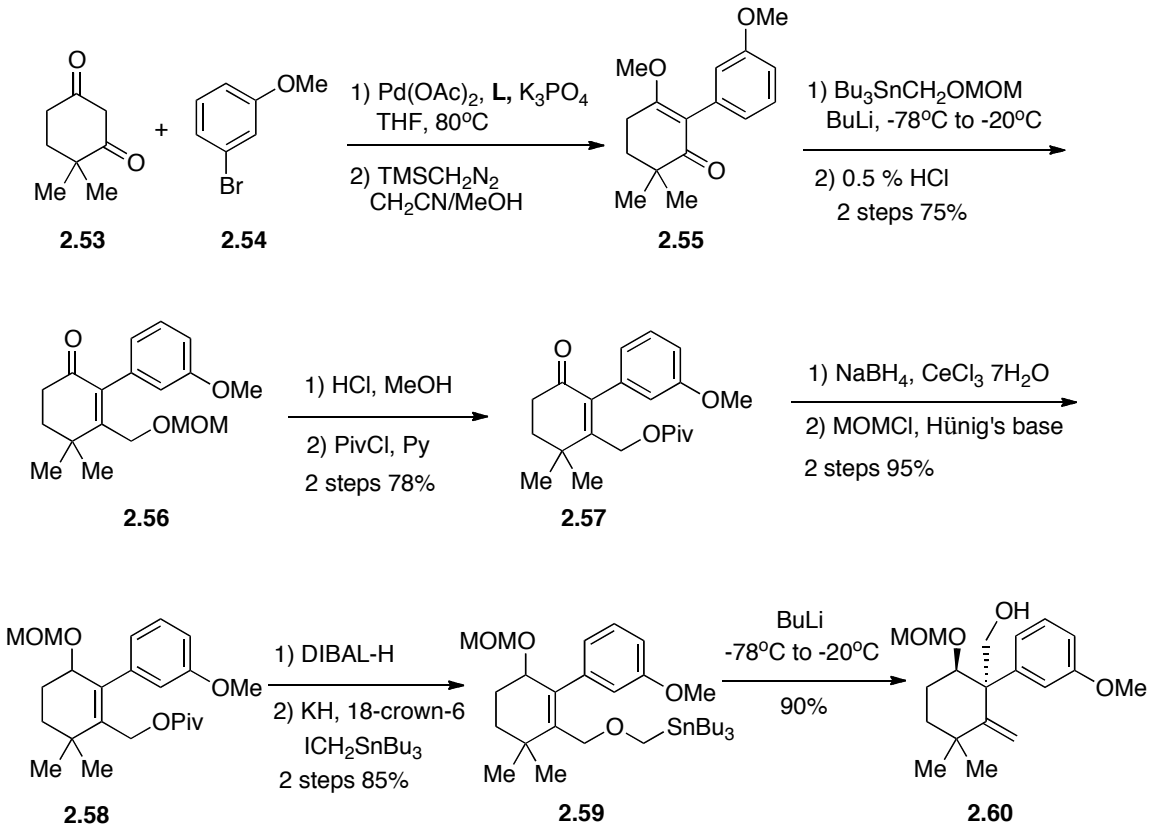


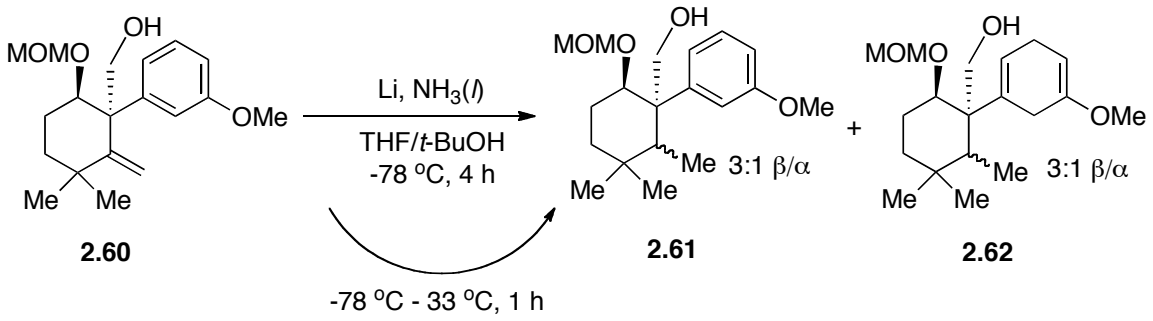
Figure 2-2 Summary of dienes

Similar to Maolin's route, the synthesis of compound **2.52** started with a palladium-catalyzed ketone α-arylation[15] reaction of **2.53**, and after etherification with $TMSCHN_2$, compound **2.55** was obtained in 90% overall yield. The β-methoxylenone was subjected to the Stork-Danheiser protocol using tributyl[(methoxymethoxy)methyl]stannane, to provide compound **2.56** in 75% yield. The MOM ether protecting group was cleaved under acidic conditions, and the resulting alcohol was protected as its pivaloate ester **2.57**. Luche reduction of **2.57** provided an allylic alcohol, which was immediately protected as the MOM ether **2.58**. Hydrolysis of **2.58** liberated a hydroxymethyl intermediate that was alkylated with α-iodomethyl tributylstannane to furnish the Wittig-Still [2,3]-rearrangement precursor **2.59**. By careful monitoring of the reaction temperature, we were pleased to find that the Wittig-Still [2,3] rearrangement proceeded smoothly to provide alcohol **2.60** in 88% yield. It is noteworthy that this transformation established the requisite quaternary carbon center in a highly stereo-controlled fashion. Enantiopure **2.60**, in principle, could be prepared from an enantiopure compound **2.58**, which could be accessed through an enantioselective reduction of ketone **2.57**.



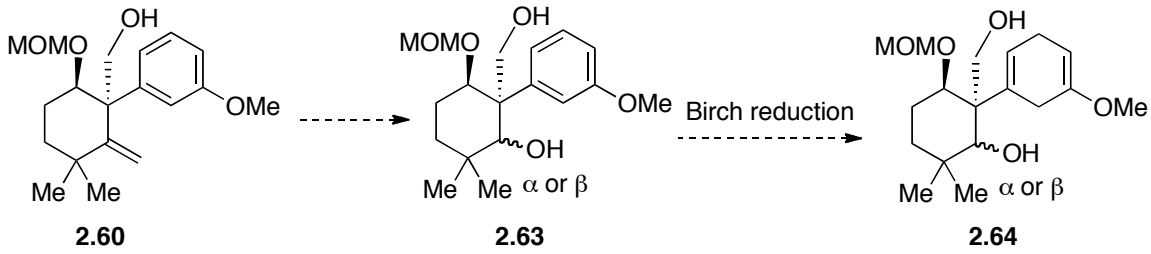
Scheme 2-8 Preparation of compound **2.60**

With compound **2.60** in hand, we then explored the Birch reduction reaction on this substrate. We found that when the reaction proceeded for 1 hour, the isolated product was **2.61**, as an 1:3 α/β mixture of methyl epimers, in which the *exo*-methylene was reduced instead of the phenyl ring. Continuation of the reaction time to 4 hour resulted the reduction of both *exo*-methylene and the phenyl ring. These results indicated that the *exo*-methylene was reduced faster than phenyl ring on compound **2.62**, which would cause problem for our forward synthesis since the *exo*-methylene group would be used as a ketone precursor.



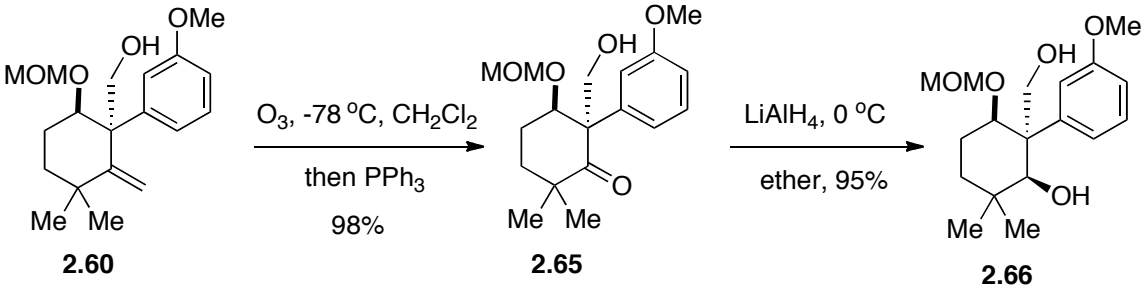
Scheme 2-9 Birch reduction of compound **3.60**

To circumvent this problem, we thought that we could transfer compound **2.60** to substrate **2.63** first and carry the Birch reduction on this substrate secondly.



Scheme 2-10 New plan for Birch reduction

Compound **2.60** was then subjected to ozonolysis reaction, and the intermediate was then treated with PPh_3 to afford the desire ketone **2.65** in excellent yield. Further reduction of the ketone **2.65** with $LiAlH_4$ gave a diol **2.66**. We noticed that the stereochemistry of the C-5 hydroxyl group is opposite as required by the natural product, presumably due to an axial hydride reduction directed by the primary alcohol (**Figure 2-3**).



Scheme 2-11 Preparation of compound **2.66**

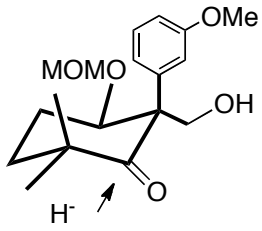
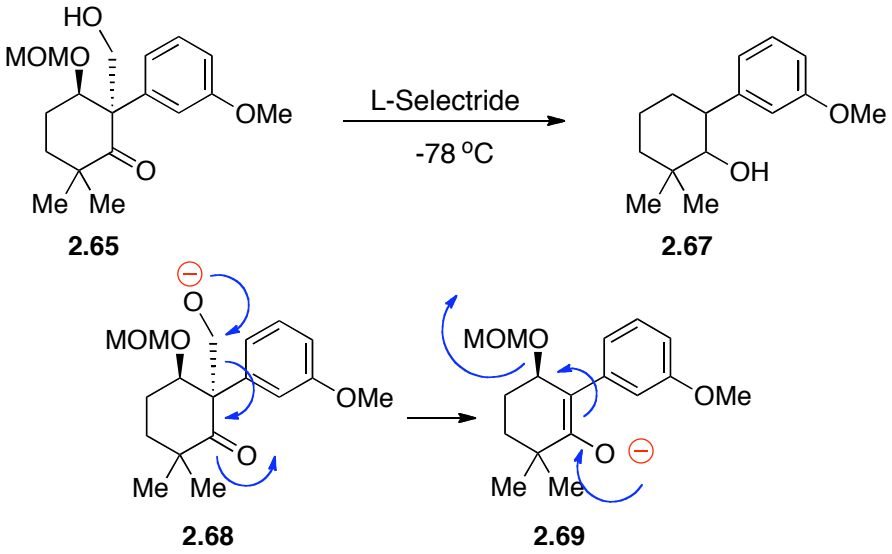
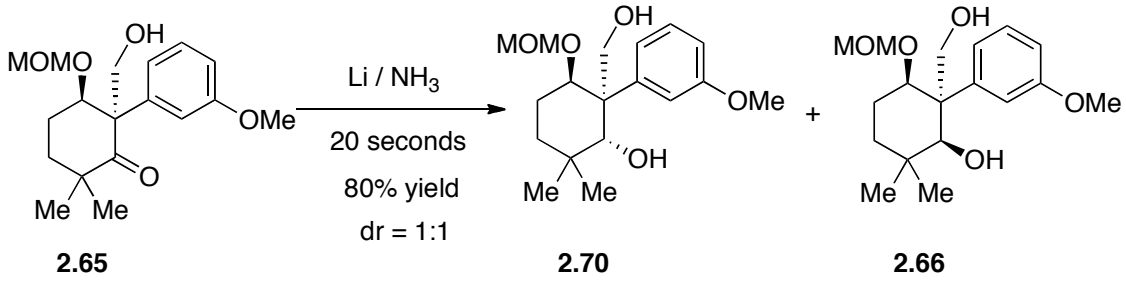


Figure 2-3 Axial Hydride attack of **2.65**

We then did further study on this ketone reduction, hoping to obtain a C-5 α-hydroxyl compound **2.63**. While DIBAL-H and $NaBH_4$ gave the same results as $LiAlH_4$, L-Selectride reduction gave a decomposed compound **2.67**. At this stage, we recalled the stereochemistry of the *exo*-methylene reduction of compound **2.60** during the Birch reduction, in which α-methyl epimer was obtained as a minor isomer. This result suggested that during the single electron transfer condition, a β-hydrogen delivery process would occur. To our delight, when ketone **2.65** was subjected to the $Li/NH_3(l)$ reduction protocol, the C-5 β-hydroxyl compound **2.70** was observed indeed.



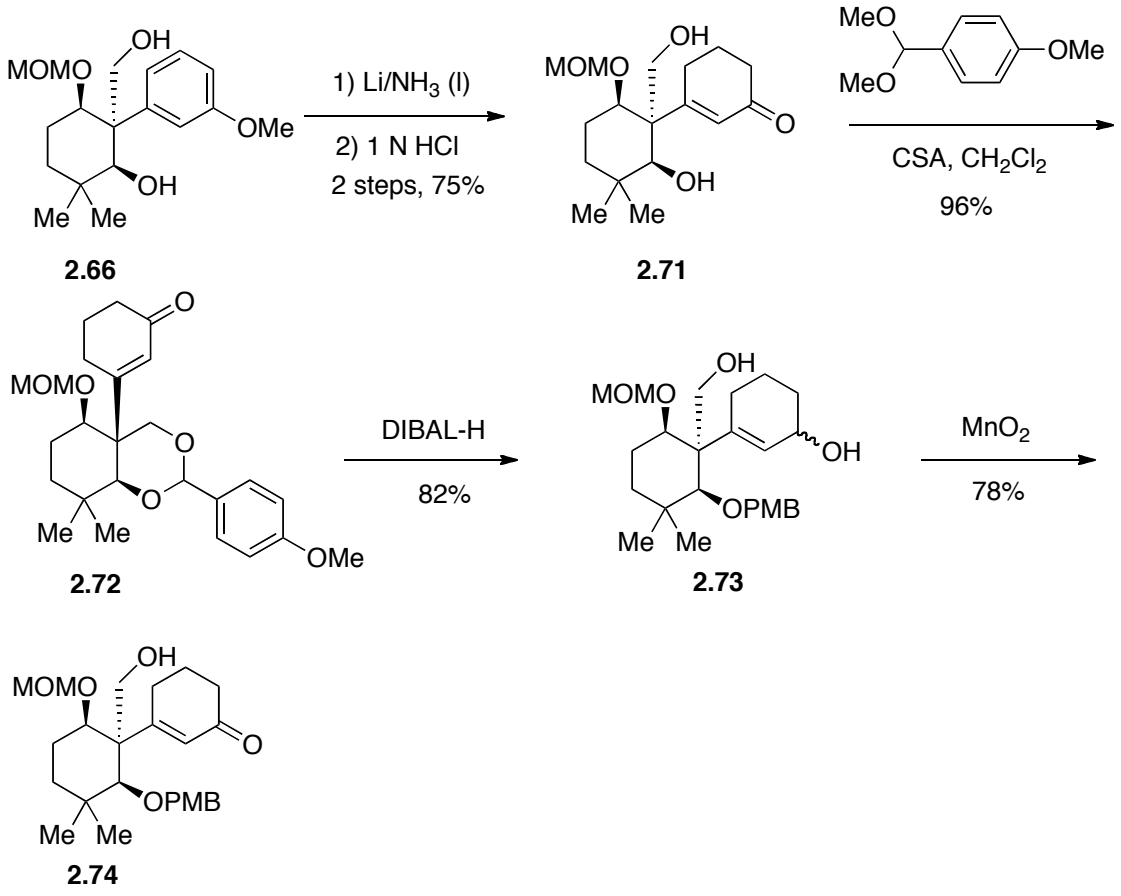
Scheme 2-12 L-Selectride reduction of **2.65**



Scheme 2-13 Preparation of **2.70**

With compound **2.66** in hand, we carried out Birch reduction on this compound **2.66**. Luckily, the Birch reduction went smoothly and afforded the desired diene. Upon treatment with dilute HCl, enone **2.71** was obtained in good yield. The protection of the C-5 secondary alcohol turned out to be problematic, since it is a bis-neopentyl secondary alcohol. At a highly congested situation, an intramolecular reaction would be more

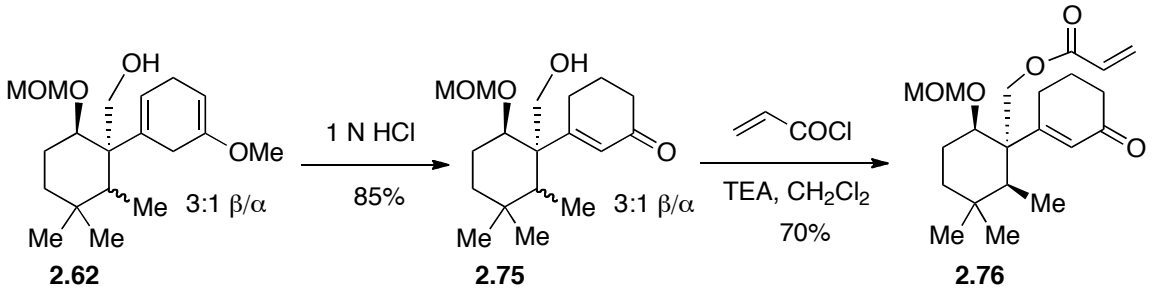
possible to occur than the corresponding intermolecular reaction. Based on this concept, we developed an "intramolecular protecting group delivery" method to achieve a selective protection of the C 5 secondary alcohol in the presence of the primary alcohol. As outlined in the **Scheme 2-14**, diol **2.71** was treated with anisaldehyde dimethyl acetal under acidic condition, which afforded acetal **2.72**. Upon treatment with DIBAL-H, the PMB protecting group was transferred to the C-5 hydroxyl group. The resulting allylic alcohol **2.72** was selectively re-oxidized to enone **2.74**.



2.66 **2.71** **2.72** **2.73** **2.74**

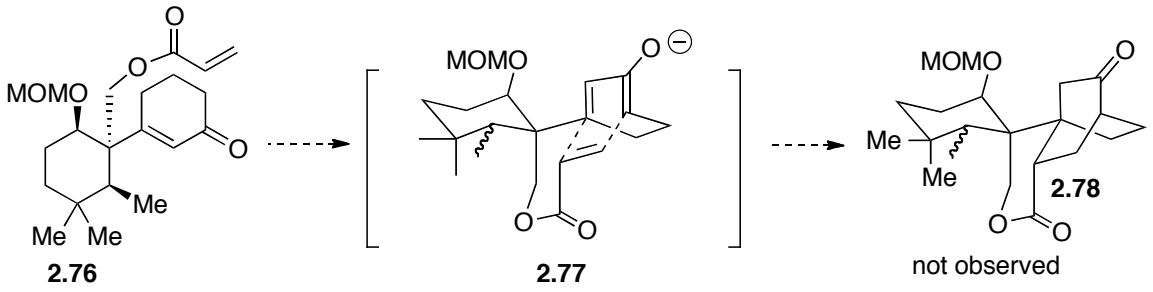
Scheme 2-14 Preparation of compound **2.74**

After solving the *exo*-methylene reduction on substrate **2.62**, we then focused on the exploration of the key intramolecular Diels-Alder reaction, hoping to find the right dienophiles and factors controlling the stereoselectivity. With plenty of compound **2.62** in hand, I felt that this compound could serve as a valuable model substrate to probe the viability of the proposed IMDA reaction. Accordingly, acidic hydrolysis of **2.62** furnished enone **2.75**, which was then subjected to esterification with acryloyl chloride, to provide acrylate **2.76**. Since there are several reported intermolecular Diels-Alder reaction using 2-siloxyl-1,3-cyclohexadiene as diene and acrylate as dienophile[16], we were confident that our intramolecular Diels-Alder would work.



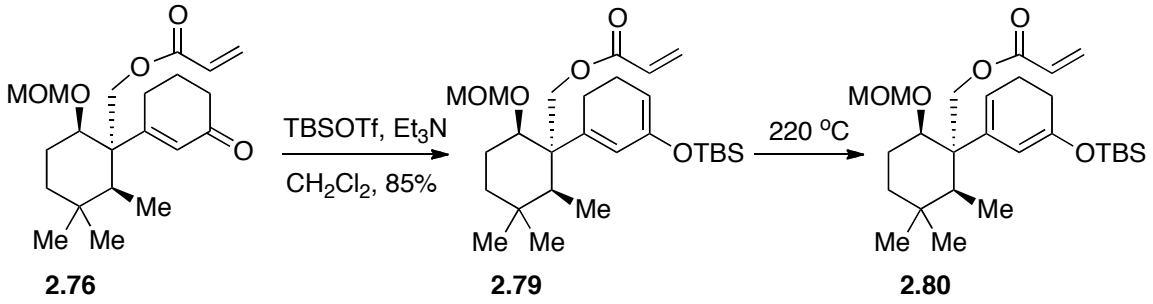
Scheme 2-15 Preparation of compound **2.76**

We first explored a double-Michael approach[17] (i.e, an anionic Diels-Alder reaction). Thus substrate **2.76** was treated with strong base such as LDA, LHMDS. To our disappointment, we only observed decomposition of **2.76** and no DA adduct was obtained. This suggested that our substrate **2.76** might be unstable toward basic condition and we need to carry on a neutral DA reaction.



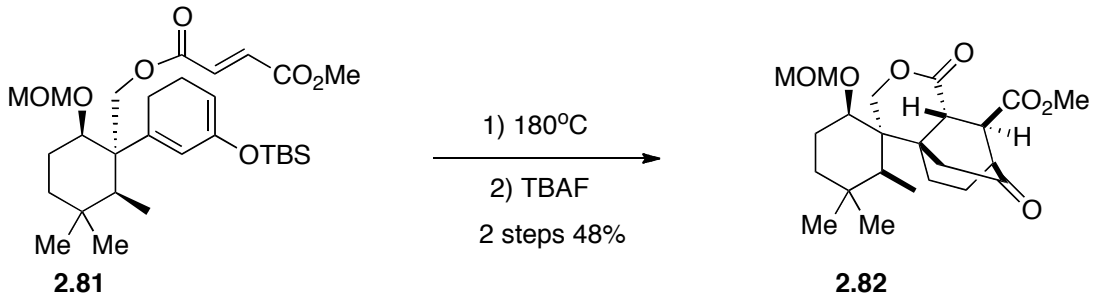
Scheme 2-16 Double-Michael approach

We then prepared the corresponding siloxyl diene **2.79** and were ready to explore the thermo DA reaction. After extensive study of different temperature factors, we did not observe any cycloadduct, but only isomerized diene **2.80**.



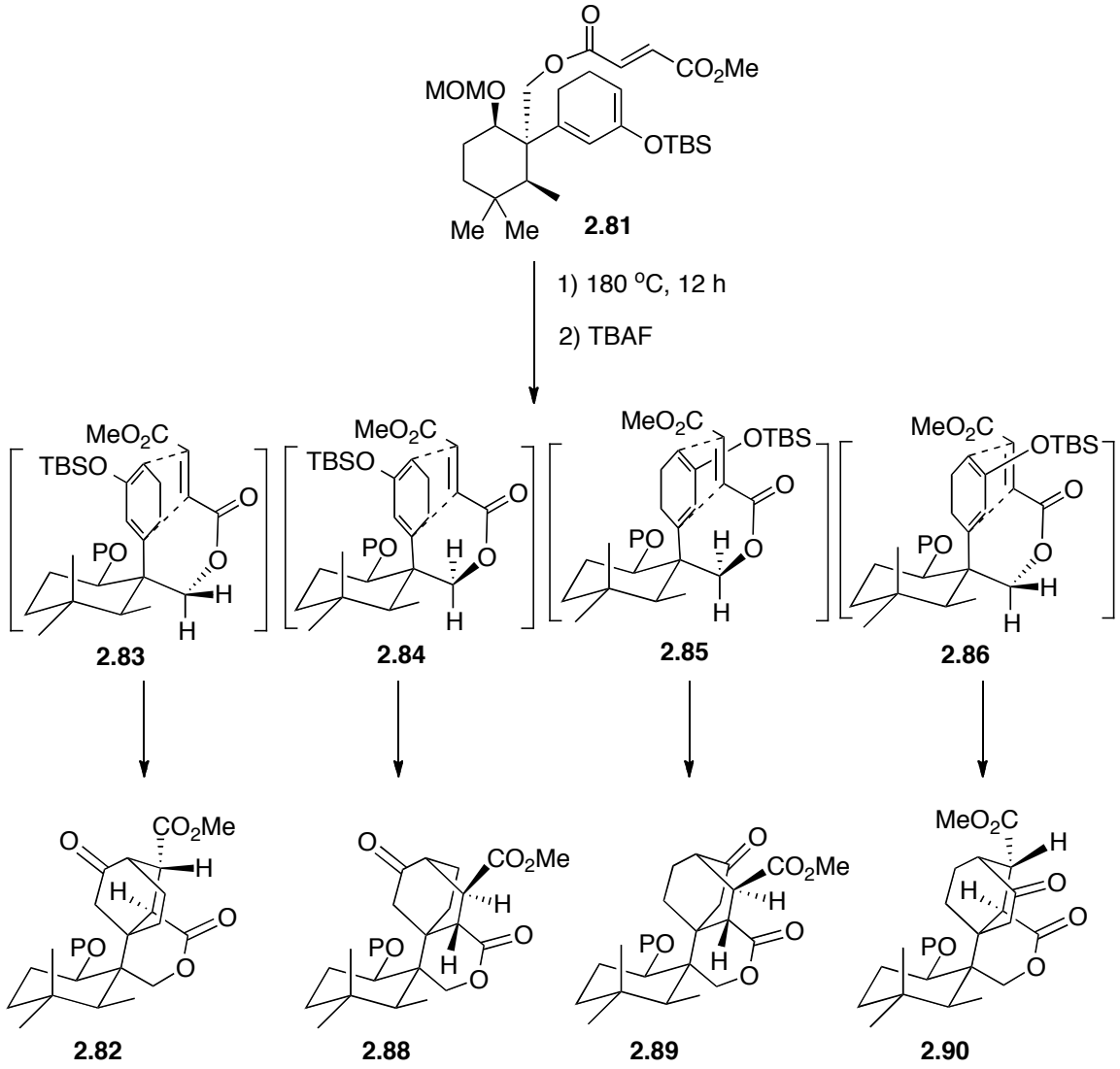
Scheme 2-17 Thermo Diels-Alder reaction of **2.79**

We then switched the dienophile to fumaric ester, which is a more reactive dienophile. After heating the reaction vessel at 180 ^{o}C for 12 hour, we obtained the desired cycloadduct. Upon treatment of TBAF, ketone **2.82** was obtained, in which the stereochemistry was tentatively assigned based on NMR techniques.



Scheme 2-18 IMDA of compound **2.81**

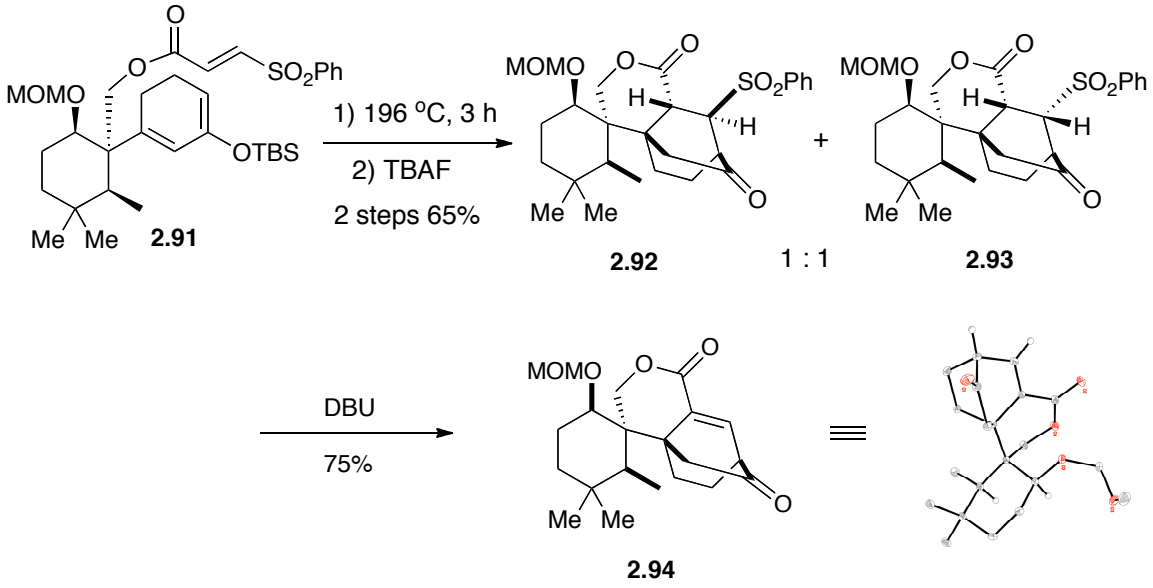
To our disappointment, a key NOESY experiment revealed that the IMDA cycloaddition afforded the opposite facial adduct than that required for the synthetic plan. To analyze the reason for this result, we first listed all the four possible cycloadducts in a non-stereoselective situation. These four diastereoisomers were formed due to the rotation of diene and *endo*-/*exo*-adducts of each diene rotamer. In our case, adduct **2.82** formed predominantly, which suggested the possible transition structure would be **2.83** A.



Scheme 2-19 Transition structure of IMDA of **2.81**

We also tried a *β*–sulfone acrylate **2.91** as an IMDA precursor. We used this dienophile for particular two reasons: (1) changing an IMDA precursor might provide us the desired facial product. (2) sulfone, still activated the dienophile but could serve also as a leaving group after DA reaction.[18] As predicted, this IMDA reaction proceeded smoothly and afforded us the desired adduct **2.92** and **2.93** as a diastereoisomer at

sulfone-substituted carbon center. Upon treatment with DBU, compound **2.94** was obtained as a single isomer, whose structure was confirmed by X-ray. Again, the IMDA proceeded with the opposite sense of facial selectivity than that required for our synthetic plan.



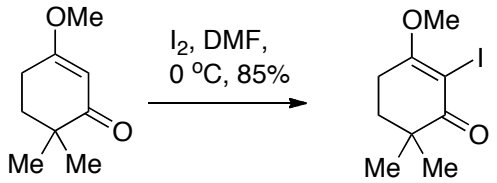
Scheme 2-20 Preparation of **2.94**

At this stage, the synthesis seemed to reach a dead end, because none of these cycloadducts could be used to elaborate to the natural product, Maoecrystal V.

2.4 Experimental

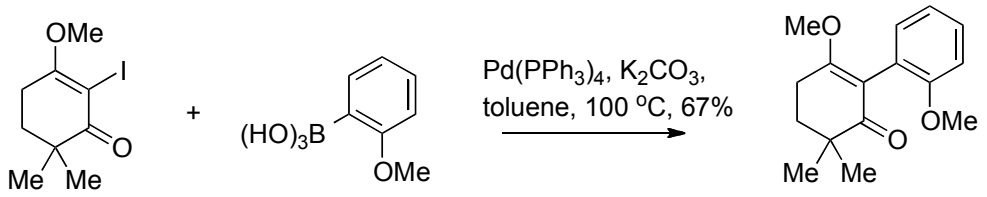
General information

Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. Toluene, hexanes and CH_2Cl_2 were distilled over CaH_2. THF and Et_2O were distilled over sodium/benzophenone ketyl. All reagents were commercially available and used without further purification unless indicated otherwise. Thin layer chromatography (TLC) was performed on Silica Gel 60 F254 plates and was visualized with UV light and $KMnO_4$ stain. Preparative thin layer chromatography was performed with Merck silica gel 60-F254 coated 0.50 mm plates. Flash chromatography was performed with Sorbent Tech. silica gel 60. Yields are for isolated, spectroscopically pure compounds. NMR spectra were recorded on 300, 400 or 500 MHz instruments. The residual solvent protons (^1H) or the solvent carbons (^{13}C) were used as internal standards. ^1H NMR data are presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, coupling constant, integration). The following abbreviations are used in reporting NMR data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; qt, quartet of triplets; dd, doublet of doublets; dt, doublet of triplets; AB, AB quartet; m, multiplet. High-resolution mass spectra were recorded by the Columbia University Mass Spectrometry Core facility on a JEOL HX110 spectrometer.



2.16 **2.17**

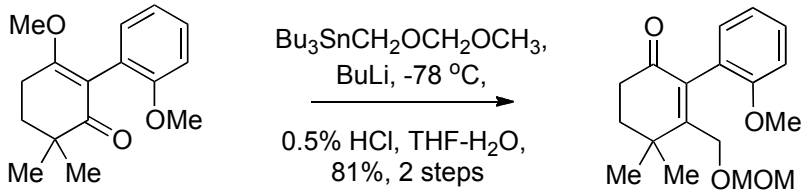
To a stirred and cooled (0 ^{o}C) solution of enone **2.16** (120 mg, 0.78 mmol) in DMF (4 mL) was added I_2 (396 mg, 1.56 mmol). The solution was stirred at this temperature for 30 min before quenched with $Na_2S_2O_3$ (2 mL) and $NaHCO_3$ (2 mL). The mixture was extracted with EtOAc (3 X 20 mL). The combined extracts were successively washed with H_2O (10 mL), brine (10 mL) and dried (Na_2SO_4). Flash chromatography of the residue over silica (3 X 18 cm), using 5:1 to 3:1 hexane: EtOAc, gave iodide (185 mg, 85%) as semi-solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 6 H), 1.84 (t, J = 6.0 Hz, 2 H), 2.70 (t, J = 6.0 Hz, 2 H), 3.92 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.3, 24.7, 34.2, 40.7, 56.2, 81.8, 174.9, 197.1; HRMS (FAB) *m/z* calcd for $C_9H_{14}O_2I$ $[M + H]^+$ 281.0039, found 281.0051.



2.17 **2.18** **2.19**

To a solution of iodide **2.17** (50.0 mg, 0.18 mmol) in toluene (2.5 mL) were added successively 2-methoxyphenylboronic acid **2.18** (54 mg, 0.36 mmol), K_2CO_3 (99.0 mg, 0.71 mmol) and $Pd(PPh_3)_4$ (21.0 mg, 0.018 mmol) under argon. The mixture was stirred at 100 ^{o}C for 18 h and then cooled to room temperature. Solvent was evaporated. Flash chromatography of the residue over silica (2.5 X 18 cm), using 4:1 to 2:1 hexane: EtOAc, gave enone **2.19** (31.0mg, 67%) as white solid: FTIR (CH_2Cl_2, cast) 2961, 1651, 1617, 1592, 1367, 1250 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (s, 3 H), 1.20 (s, 3 H), 1.94 (t, J = 6.0 Hz, 2 H), 2.61-2.76 (m, 2 H), 3.65 (s, 3 H), 3.72 (s, 3 H), 6.87-7.02 (m, 3 H),

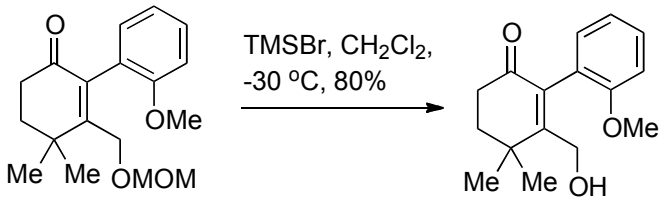
7.22-7.27 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1, 24.3, 24.7, 34.1, 39.8, 55.6, 55.7, 110.9, 115.2, 120.1, 123.7, 128.3, 132.0, 157.2, 169.8, 201.7; HRMS (FAB) *m/z* calcd for $C_{16}H_{21}O_3$ $[M + H]^+$ 261.1491, found 261.1482.



2.19 **2.20**

To a stirred and cooled (-78 ^{o}C) solution of stannane (3.9 g, 10.7 mmol) in THF (30 mL) was added dropwise BuLi (2.5 M, 4.3 mL, 10.7 mmol). After 5 min stirring at this temperature, a solution of enone **2.19** (1.63 g, 6.27 mmol) in THF (10 mL) was quickly introduced to the above anion solution and stirring was continued for 30 min. The reaction was quenched by successively adding MeOH (5 mL) and NH_4Cl (20 mL). The mixture was extracted with EtOAc (3 X 100 mL). The combined extracts were washed with brine (50 mL) and dried (Na_2SO_4). Flash chromatography of the residue over silica (3 X 18 cm), using 4:1 hexane:EtOAc, gave crude enone **2.20**, which was used directly in the next step without further purification. The above crude (ca. 2 g) was dissolved in THF (20 mL) and the resultant solution was cooled to (0 ^{o}C). To this solution were successively added H_2O (5 mL) and 0.5 N HCl (1.5 mL). After stirring at 0 ^{o}C for 2 h, the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (20 mL). The mixture was extracted with EtOAc (3 X 20 mL). The combined extracts were successively washed with H_2O (20 mL), brine (30 mL) and dried (Na_2SO_4). Flash chromatography of the residue over silica (3 X 20 cm), using 6:1 to 3:1 hexane:EtOAc, gave enone **2.20** (1.54 g, 81%, over two steps) as colorless oil: FTIR (CH_2Cl_2, cast) 2940,

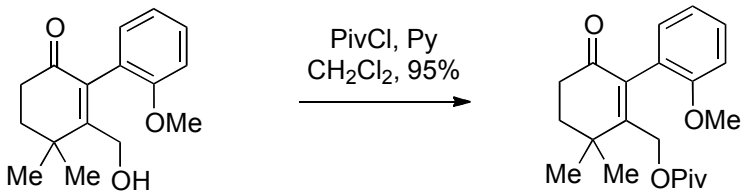
1678, 1492, 1247, 1150, 1035 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 6 H), 1.97-2.02 (m, 2 H), 2.55- 2.78 (m, 2 H), 3.20 (s, 3 H), 3.73 (s, 3 H), 3.87 (d, J = 10.5 Hz, 1 H), 4.06 (d, J = 10.5 Hz, 1 H), 4.43 (ABq, $\Delta\nu$ = 20.1, J = 6.6, 2 H), 6.89-6.97 (m, 2 H), 7.02 (dd, J = 7.5, 2.1 Hz, 1 H), 7.27-7.33 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.4, 27.5, 34.7, 35.3, 37.9, 55.3, 55.5, 66.0, 96.4, 110.6, 120.1, 125.0, 129.0, 131.0, 136.9, 156.8, 159.4, 198.0; HRMS (FAB) *m/z* calcd for $C_{18}H_{24}O_4$ $[M]^+$ 304.1675, found 304.1676.



2.20 **2.21**

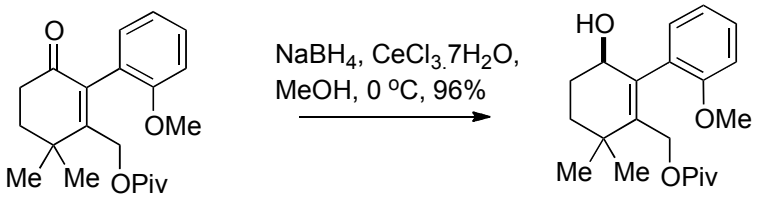
To a stirred and cooled (-30 ^oC) solution of MOM ether **2.20** (75.0 mg, 0.25 mmol) in CH_2Cl_2 (2 mL) was added TMSBr (0.33mL, 2.46 mmol) dropwise. After stirring at this temperature for 30 min, the reaction was quenched by the addition of saturated aqueous Na_2CO_3 (2 mL). The mixture was extracted with EtOAc (2 X 15 mL). The combined extracts were washed with brine (5 mL) and dried (Na_2SO_4). Flash chromatography of the residue over silica (2 X 20 cm), using 3:1 to 1:1, hexane:EtOAc, gave alcohol **2.21** (51.5 mg, 80%) as colorless oil: FTIR (CH_2Cl_2, cast) 3434, 2960, 1669, 1593, 1491, 1246 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 3 H), 1.39 (s, 3 H), 1.95-2.00 (m, 2 H), 2.26 (dd, J = 7.6, 5.6 Hz, 1 H), 2.60-2.66 (m, 2 H), 3.74 (s, 3 H), 3.98-4.00 (m, 2 H), 6.91-7.00 (m, 3 H), 7.29-7.33 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.0, 34.8, 35.3, 37.5, 55.9, 61.1,

111.6, 121.0, 124.8, 129.2, 131.1, 134.8, 156.3, 163.1, 198.5; HRMS (FAB) *m/z* calcd for $C_{16}H_{20}O_3$ $[M]^+$ 260.1412, found 260.1418.



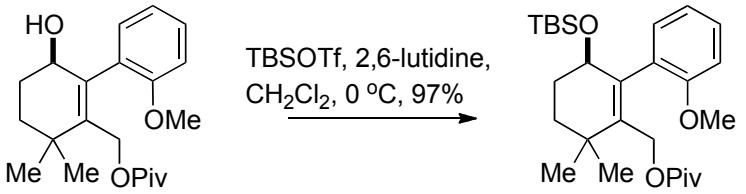
2.21 **2.22**

To a stirred and cooled (0 ^oC) solution of alcohol **2.21** (1.10 g, 4.2 mmol) in CH_2Cl_2 (10 mL) were added successively pyridine (2 mL) and PivCl (2.1 mL, 16.9 mmol). The stirring was continued at 0 ^oC for 5 h and room temperature for 3 h. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (20 mL). The mixture was extracted with EtOAc (3 X 50 mL). The combined extracts were washed with brine (20 mL) and dried (Na_2SO_4). Flash chromatography of the residue over silica (2.5 X 18 cm), using 4:1 hexane:EtOAc, gave Piv ester **2.22** (1.41 g, 97%) as white solid: FTIR (CH_2Cl_2, cast) 2968, 1729, 1681, 1276, 1248, 1149 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 9 H), 1.28 (s, 3 H), 1.34 (s, 3 H), 2.00-2.05 (m, 2 H), 2.59-2.65 (m, 1 H), 2.71-2.75 (m, 1 H), 3.72 (s, 3 H) 4.24 (d, J = 11.6 Hz, 1 H), 4.64 (d, J = 11.6 Hz, 1 H), 6.88-6.93 (m, 2 H), 6.97-7.00 (m, 1 H), 7.28-7.32 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.1, 27.0, 27.5, 34.6, 35.3, 37.7, 38.6, 55.4, 62.5, 110.6, 120.0, 124.3, 129.4, 131.0, 138.6, 156.6, 157.0, 177.7, 197.7; HRMS (FAB) *m/z* calcd for $C_{21}H_{28}O_3$ $[M]^+$ 344.1988, found 344.1971.



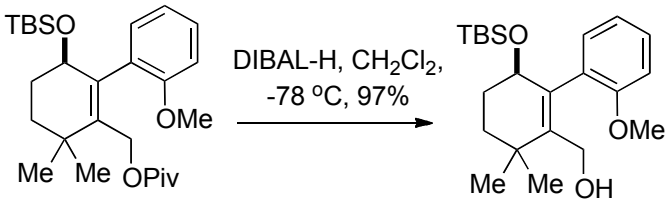
2.22 **2.23**

To a stirred and cooled (0 °C) solution of enone **2.22** (1.41 g, 4.10 mmol) in MeOH (30 mL) was added $CeCl_3$-$7H_2O$ (3.05 g, 8.20 mmol). After stirring for 10 min, $NaBH_4$ (465 mg, 12.3 mmol) was added piece by piece. Stirring was continued for 15 min and the reaction was quenched by the addition of saturated aqueous NH_4Cl (20 mL). The mixture was extracted with EtOAc (3 X 50 mL). The combined extracts were washed with brine (20 mL) and dried (Na_2SO_4). Flash chromatography of the residue over silica (3 X 18 cm), using 4:1 hexane:EtOAc, gave alcohols **2.23**(1.36 g, 96%) as a mixture of ca 1:1 two rotomers, which both are colorless oil: FTIR (CH_2Cl_2, cast) 3459, 2961, 1723, 1480, 1284, 1244, 1157 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(mixture of 1:1 two rotomers) δ 1.05- 1.21 (m, 30 H), 1.50-1.56 (m, 1 H), 1.79-1.91 (m, 2 H), 1.95-2.05 (m, 1 H), 3.76 (s, 3 H), 3.80 (s, 3 H), 3.99 (d, J = 11.6 Hz, 1 H), 4.09 (d, J = 11.6 Hz, 1 H), 4.16 (t, J = 4.8 Hz, 1 H), 4.37-4.40 (m, 2 H), 4.48 (d, J = 11.6 Hz, 1 H), 6.85-6.95 (m, 4 H), 7.01 (dd, J = 7.2, 1.6 Hz, 1 H), 7.10 (dd, J = 8.0, 1.6 Hz, 1 H), 7.23-7.28 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$)(mixture of 1:1 two rotomers) δ 27.0, 27.2, 27.5, 28.2, 28.3, 28.4, 31.3, 34.2, 34.41, 34.44, 34.7, 38.4, 55.2, 55.5, 62.0, 62.1, 66.9, 70.4, 110.5, 110.6, 119.8, 121.0, 127.6, 128.7, 128.9, 129.1, 130.5, 132.0, 138.3, 139.1, 139.9, 141.2, 156.0, 156.3, 178.05, 178.10; HRMS (FAB) *m/z* calcd for $C_{21}H_{30}O_4$ $[M]^+$ 346.2144, found 346.2159.



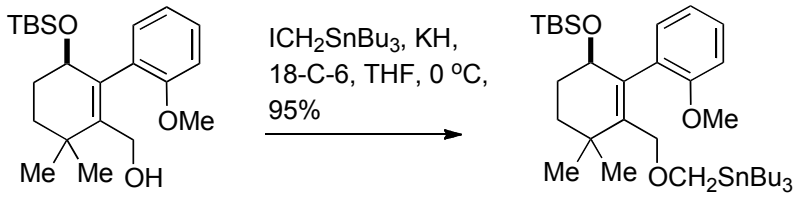
2.23 **2.24**

To a stirred and cooled (0 °C) solution of alcohol **2.23** (1.50 g, 4.3 mmol) in CH_2Cl_2 (20 mL) were added successively 2,6-lutidine (3.0 mL, 26.0 mmol) and TBSOTf (2.0 mL, 8.6 mmol). Stirring was continued at this temperature for 3 h. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (20 mL). The mixture was extracted with EtOAc (3 X 50 mL). The combined extracts were washed with brine (20 mL), dried (Na_2SO_4) and concentrated. Flash chromatography of the residue over silica (3 X 18 cm), using 10:1 hexane:EtOAc, gave silyl ethers **2.24** (1.93 g, 97%) as mixture of ca 10:1 two rotomers, which are colorless oil: FTIR (CH_2Cl_2, cast) 2957, 2857, 1725, 1474, 1249, 1156, 1048 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(major isomer) δ -0.55 (s, 3 H), -0.21 (s, 3 H), 0.72 (s, 9 H), 1.04-1.17 (m, 18 H), 1.42-1.46 (m, 1 H), 1.70-1.74 (m, 1 H), 1.82-1.88 (m, 1 H), 1.92-1.98 (m, 1 H), 3.73 (s, 3 H), 4.00 (d, J = 11.6 Hz, 1 H), 4.33 (t, J = 4.4 Hz, 1 H), 4.44 (d, J = 11.6 Hz, 1 H), 6.76-6.83 (m, 2 H), 7.00 (dd, J = 7.2, 1.6 Hz, 1 H), 7.15-7.19 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$)(major rotomer) δ -5.8, -5.2, 17.9, 25.7, 27.1, 28.5, 28.9, 34.3, 34.4, 38.4, 55.2, 62.4, 67.4, 110.1, 119.6, 128.2, 128.8, 133.1, 137.1, 142.1, 156.3, 178.2; HRMS (FAB) *m/z* calcd for $C_{27}H_{43}O_4Si$ $[M - H]^+$ 459.2931, found 459.2917.



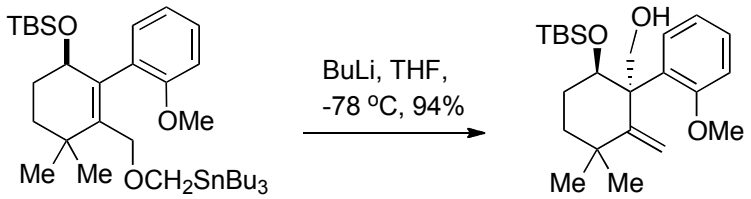
2.24 **2.25**

To a stirred and cooled (-78 °C) solution of ester (1.93 g, 4.20 mmol) in CH_2Cl_2 (30 mL) was added dropwise a solution of DIBAL-H (21.0 mL, 21.0 mmol). After stirring at this temperature for 30 min, the reaction was quenched by the addition of MeOH (5 mL) and then Na_2SO_4-$10H_2O$ (15 g). Stirring was continued at room temperature for 3 h. The mixture was filtered through a pad of celite (5 X 6 cm), rinsed with EtOAc (4 X 20 mL). Solvent was evaporated. Flash chromatography of the residue over silica (3 X 18 cm), using 10:1 hexane:EtOAc, gave alcohols **2.25** (1.50 g, 97%) as a mixture of ca. 2:1 two rotamers, which are colorless oil: FTIR (CH_2Cl_2, cast) 3469, 2932, 2856, 1598, 1580, 1490, 1463, 1435, 1249, 1048, 836 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)(mixture of 2:1 two rotomers) δ -0.53 (s, 1.5 H), -0.52 (s, 3 H), -0.20 (s, 3 H), -0.13 (s, 1.5 H), 0.71 (s, 4.5 H), 0.77 (s, 9 H), 1.09 (s, 1.5 H), 1.17 (s, 3 H), 1.20 (s, 3 H), 1.31 (s, 1.5 H), 1.47-1.56 (m, 1.5 H), 1.67 (dd, J = 8.4, 3.2 Hz, 1 H), 1.74-1.86 (m, 3 H), 1.91-1.94 (m, 1.5 H), 2.86 (dd, J = 10.4, 2.0 Hz, 0.5 H), 3.71-3.91 (m, 7.5 H), 4.19 (t, J = 5.2 Hz, 1 H), 4.24 (t, J = 5.2 Hz, 0.5 H), 6.89-6.95 (m, 2.5 H), 6.97-6.99 (m, 1 H), 7.06 (dd, J = 7.2, 1.6 Hz, 1 H), 7.21-7.29 (m, 1.5 H); ^{13}C NMR (100 MHz, $CDCl_3$)(mixture of 2:1 two rotomers) δ -5.82, -5.76, -5.3, -5.1, 17.7, 17.9, 25.5, 25.7, 27.56, 27.64, 28.4, 28.6, 29.3, 29.8, 34.27, 34.3, 34.96, 35.0, 55.4, 55.9, 60.3, 60.9, 68.6, 71.3, 110.4, 111.9, 120.3, 121.2, 127.9, 128.1, 129.0, 129.5, 131.2, 132.6, 135.8, 137.6, 143.3, 143.5, 155.9, 157.1; HRMS (FAB) *m/z* calcd for $C_{22}H_{35}O_3Si$ $[M - H]^+$ 375.2355, found 375.2339.



2.25 **2.26**

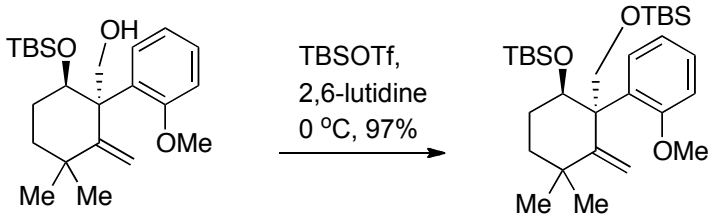
To a stirred and cooled (0 °C) solution of aocohol **2.25** (30 mg, 0.08 mmol) in THF (2 mL) were added successively 18-Crown-6 (10.0 mg, 0.04 mmol) and KH (10.0 mg, 0.24 mmol). After stirring at this temperature for 30 min, Bu_3SnCH_2I (105.0 mg, 0.24 mmol) was added. Stirring was continued for 12 h at 0 °C. The reaction was quenched by the addition of saturated aqueous NH_4Cl (1 mL). The mixture was extracted with EtOAc (3 X 5 mL). The combined extracts were dried (Na_2SO_4) and the solvent was evaporated. Flash chromatography of the residue over silica (1.5 X 18 cm), using hexane to 10:1 hexane:EtOAc, gave stannane **2.26** (52.0 mg, 95%) as colorless oil, which was used directly in the next step.



2.26 **2.27**

To a stirred and cooled (-78 °C) solution of stannane **2.26** (640.0 mg, 0.95 mmol) in THF (10 mL) was added dropwise a solution of BuLi (1.6 M, 2.4 mL, 3.81 mmol). The resultant solution was slowly warmed to –20 °C over 6 h and the reaction was quenched by the addition of MeOH (2 mL) and then NH_4Cl (3 mL). The mixture was extracted

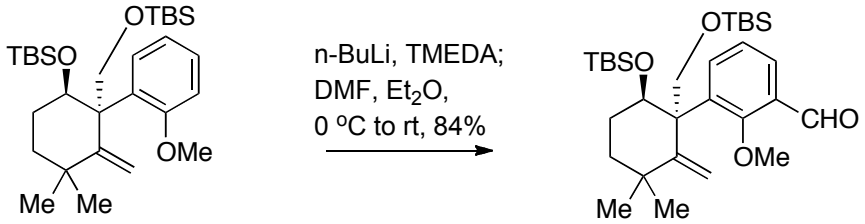
with EtOAc (2 X 15 mL). The combined extracts were dried (Na_2SO_4) and the solvent was evaporated. Flash chromatography of the residue over silica (2.5 X 18 cm), using 10:1 hexane:EtOAc, gave olefin (350.0 mg, 94%) as colorless oil: : FTIR (CH_2Cl_2, cast) 3512, 2954, 1626, 1594, 1462, 1249, 1100, 1036 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.043 (s, 3 H), 0.12 (s, 3 H), 0.59 (s, 3 H), 0.87 (s, 9 H), 1.08 (s, 3 H), 1.24-1.34 (m, 1 H), 1.48 (dt, J = 4.0, 13.6 Hz, 1 H), 1.73-1.80 (m, 1 H), 2.33-2.43 (m, 1 H), 2.65 (dd, J = 8.0, 3.6 Hz, 1 H), 3.66 (s, 3 H), 3.88 (dd, J = 4.0, 11.2 Hz, 1 H), 4.03 (dd, J = 10.4, 8.4 Hz, 1 H), 4.16 (dd, J = 11.2, 4.0 Hz, 1 H), 4.96 (s, 1 H), 5.17 (s, 1 H), 6.76 (d, J = 8.0 Hz, 1 H), 6.88 (t, J = 7.6 Hz, 1 H), 7.17 (t, J = 7.2 Hz, 1 H), 8.07 (d, J = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.7, -3.8, 18.4, 26.3, 29.0, 32.5, 37.5, 39.1, 54.9, 55.1, 67.4, 79.3, 110.2, 112.1, 120.3, 127.8, 130.9, 131.4, 155.8, 159.4; HRMS (FAB) *m/z* calcd for $C_{23}H_{39}O_3Si$ $[M + H]^+$ 491.2668, found 491.2668.



2.27 **2.36**

To a stirred and cooled (0 °C) solution of alcohol **2.27** (135.0 mg, 0.35 mmol) in CH_2Cl_2 (5 mL) were added successively 2,6-lutidine (0.16 mL, 1.38 mmol) and TBSOTf (0.16 mL, 0.69 mmol). Stirring was continued at this temperature for 10 h. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (3 mL). The mixture was extracted with EtOAc (3 X 15 mL). The combined extracts were washed with brine (10

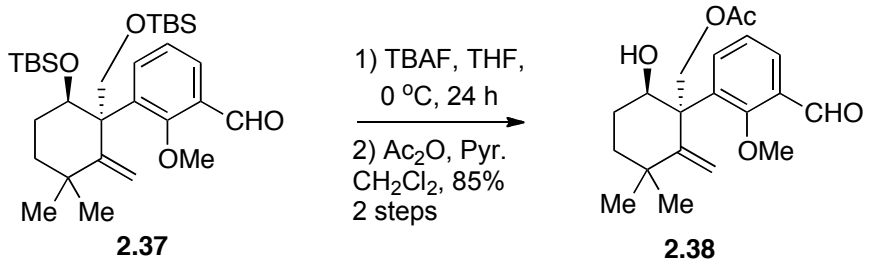
mL), dried (Na_2SO_4) and concentrated. Flash chromatography of the residue over silica (2.5 X 16 cm), using 5% EtOAc in hexane, gave silyl ethers **2.36** (169 mg, 97%) as colorless oil: FTIR (CH_2Cl_2, cast) 2954, 2859, 1465, 1251, 1084 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ -0.24 (s, 3 H), -0.010 (s, 3 H), 0.082 (s, 3 H), 0.12 (s, 3 H), 0.75 (s, 9 H), 0.94 (s, 12 H), 1.13 (s, 3 H), 1.32-1.38 (m, 1 H), 1.61-1.67 (m, 1 H), 1.77-1.81 (m, 1 H), 2.04-2.12 (m, 1 H), 3.66 (s, 3 H), 3.88 (d, J = 10.0 Hz, 1 H), 4.00 (d, J = 10.0 Hz, 1 H), 4.21-4.24 (m, 1 H), 4.74 (s, 3 H), 4.99 (s, 1 H), 6.74 (d, J = 8.0 Hz, 1 H), 6.84 (t, J = 7.6 Hz, 1 H), 7.13 (t, J = 8.0 Hz, 1 H), 7.85 (d, J = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.5, -5.07, -5.03, -4.54, 17.9, 18.4, 25.8, 26.1, 28.6, 30.9, 33.4, 35.9, 36.0, 54.4, 55.1, 68.4, 72.3, 110.9, 111.6, 119.4, 126.8, 129.6, 134.1, 156.9, 158.8; HRMS (FAB) *m/z* calcd for $C_{29}H_{51}O_3Si_2[M - H]^+$ 503.3377, found 503.3377.



2.36 **2.37**

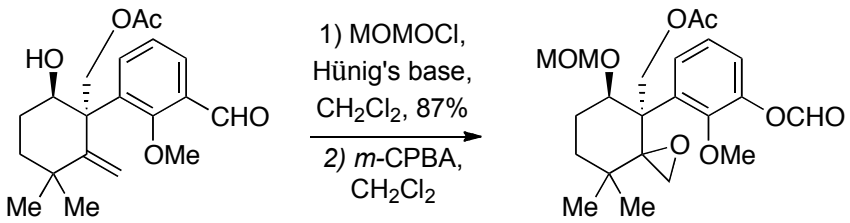
To a stirred and cooled (0 °C) solution of methyl aryl ether **2.36** (600.0 mg, 1.19 mmol) in Et_2O (10 mL) were added successively TMEDA (0.54 mL, 3.57 mmol) and a solution of BuLi (2.5 M, 1.43 mL, 3.57 mmol). The resultant solution was stirred at 0 °C for 2 h and then DMF (0.92 mL, 11.9 mmol) was added in one portion. Stirring was continued at this temperature for another 3 h and the reaction was quenched by the addition of saturated aqueous NH_4Cl (3 mL). The mixture was extracted with EtOAc (3 X 20 mL).

The combined extracts were dried (Na_2SO_4) and the solvent was evaporated. Flash chromatography of the residue over silica (2.5 X 18 cm), using 1% to 2% EtOAc in hexane, gave aldehyde **2.37** (76.0 mg, 84% based on recovered starting material) as colorless oil: FTIR (CH_2Cl_2, cast) 2955, 2857, 1689, 1581, 1471, 1256, 1094 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ -0.21 (s, 3 H), 0.014 (s, 3 H), 0.049 (s, 3 H), 0.085 (s, 3 H), 0.78 (s, 9 H), 0.89 (s, 9 H), 1.00 (s, 3 H), 1.15 (s, 3 H), 1.28-1.33 (m, 1 H), 1.63-1.69 (m, 1 H), 1.82-1.87 (m, 1 H), 1.95-2.00 (m, 1 H), 3.79 (s, 3 H), 3.82 (d, J = 10.4 Hz, 1 H), 4.10 (d, J = 10.4 Hz, 1 H), 4.18 (dd, J = 9.6, 4.8 Hz, 1 H), 4.95 (s, 1 H), 5.15 (s, 1 H), 7.07 (t, J = 8.0 Hz, 1 H), 7.68 (t, J = 7.6 Hz, 1 H), 8.29 (d, J = 8.0 Hz, 1 H), 10.28 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.5, -5.1, -5.0, -4.5, 18.0, 18.3, 25.8, 26.0, 28.3, 30.6, 33.6, 35.7, 36.2, 55.5, 65.6, 67.9, 72.3, 111.8, 122.6, 127.8, 129.3, 136.9, 138.8, 156.0, 164.4, 190.8; HRMS (FAB) *m/z* calcd for $C_{30}H_{51}O_4Si_2[M - H]^+$ 531.3326, found 531.3307.



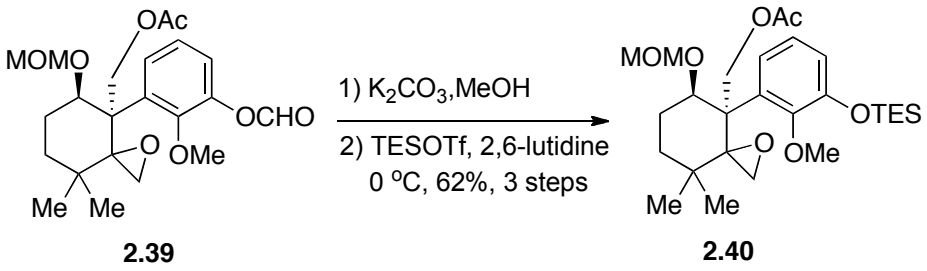
To a stirred and cooled (0 °C) solution of silyl ether **2.37** (201.0 mg, 0.38 mmol) in THF (3 mL) was added dropwise a solution of TBAF (1.0 M, 1.13 mL, 1.13 mmol). The resultant solution was stirred at 0 °C for 24 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl (2 mL). The mixture was extracted with EtOAc (3 X 10 mL).

The combined extracts were dried (Na_2SO_4) and concentrated. The residue was purified by a short silica column (1.5 x 16 cm), using 5:1 hexane/EtOAc, gave diol (ca. 120 mg), which was used directly in the next step. To a stirred and cooled (0 ^oC) solution of the above diol (ca. 120 mg) in CH_2Cl_2 (3 mL) were added successively pyridine (0.193 mL, 2.39 mmol) and Ac_2O (0.12 mL, 1.19 mmol). The resulting solution was stirred at 0 ^oC for 5 days and the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (3 mL). The mixture was extracted with EtOAc (3 X 10 mL). The combined extracts were dried (Na_2SO_4) and the solvent was evaporated. Flash chromatography of the residue over silica (2 X 18 cm), using 4:1 to 1:1 hexane/EtOAc, gave monoacetate **2.38** (117.0 mg, 85%) as colorless oil: FTIR (CH_2Cl_2, cast) 3476, 2959, 1738, 1685, 1581, 1466, 1381, 1240, 1044 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.72 (s, 3 H), 1.15 (s, 3 H), 1.30-1.38 (m, 1 H), 1.46-1.52 (m, 1 H), 1.96-2.03 (m, including a singlet at 2.03, 4 H in all), 2.14-2.20 (m, 1 H), 3.76 (d, J = 6.0 Hz, 1 H), 3.82-3.88 (m, including a singlet at 3.88, 4 H in all), 4.69 (ABq, $\Delta\nu$ = 13.3 Hz, J = 12.0 Hz, 2 H), 5.15 (s, 1 H), 5.32 (s, 1 H), 7.16 (t, J = 8.0 Hz, 1 H), 7.73 (d, J = 7.6 Hz, 1 H), 8.27 (d, J = 8.0 Hz, 1 H), 10.25 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 27.3, 29.2, 32.3, 37.0, 37.7, 54.3, 65.8, 67.0, 74.1, 112.4, 123.6, 129.7, 134.6, 137.6, 153.8, 162.7, 171.3, 189.9; HRMS (FAB) *m/z* calcd for $C_{20}H_{27}O_5$ $[M + H]^+$ 347.1858, found 347.1861.



2.38 **2.39**

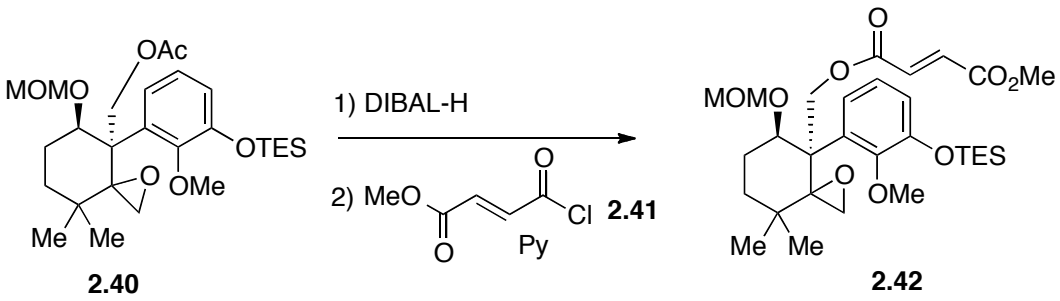
To a stirred and cooled (0 ^{o}C) solution of alcohol **2.38** (117.0 mg, 0.338 mmol) in CH_2Cl_2 (5 mL) were added successively Hunig's base (1.18 mL, 6.76 mmol) and MOMCl (0.26 mL, 3.38 mmol). The resulting solution was stirred at room temperature for 3 days and the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (2 mL). The mixture was extracted with EtOAc (3 X 10 mL). The combined extracts were dried (Na_2SO_4) and the solvent was evaporated. Flash chromatography of the residue over silica (1.5 X 18 cm), using 3:1 hexane/EtOAc, gave MOM ether **2.39** (115.0 mg, 87%) as colorless oil: FTIR (CH_2Cl_2, cast) 2959, 1738, 1685, 1580, 1472, 1240 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.68 (s, 3 H), 1.15 (s, 3 H), 1.37-1.45 (m, 1 H), 1.51-1.56 (m, 1 H), 2.02-2.09 (m, including a singlet at 2.07, 4 H in all), 2.26-2.37 (m, 1 H), 3.34 (s, 3 H), 3.84 (s, 3 H), 3.92 (dd, J = 11.6, 4.4 Hz, 1 H), 4.18 (d, J = 11.2 Hz, 1 H), 4.63 (ABq, $\Delta\nu$ = 18.0 Hz, J = 6.8 Hz, 2 H), 5.01 (d, J = 11.6 Hz, 1 H), 5.04 (s, 1 H), 5.27 (s, 1 H), 7.15 (t, J = 8.0 Hz, 1 H), 7.73 (d, J = 7.6 Hz, 1 H), 8.29 (d, J = 8.0 Hz, 1 H), 10.27 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 25.7, 28.6, 32.2, 37.1, 38.5, 54.0, 55.7, 65.3, 65.9, 80.4, 97.0, 111.9, 123.3, 129.1, 129.8, 135.4, 137.1, 152.7, 164.1, 170.8, 190.2; HRMS (FAB) *m/z* calcd for $C_{22}H_{31}O_6$ $[M + H]^+$ 391.2121, found 391.2139. To a stirred and cooled (0 ^{o}C) solution of aldehyde (115.0 mg, 0.29 mmol) in CH_2Cl_2 (8 mL) was added *m*-CPBA (264.0 mg, 1.18 mmol). The resulting solution was stirred at room temperature for 12 h and the reaction mixture was diluted by the addition of CH_2Cl_2 (100 mL). The mixture was washed with saturated $NaHCO_3$ (4 X 30 mL). The CH_2Cl_2 solution was dried (Na_2SO_4) and concentrated. The residue was used directly in the next step without further purification.



2.39 **2.40**

The above residue **2.39** was dissolved in MeOH (5 mL). The solution was then cooled to 0 °C. A 5% aqueous K_2CO_3 solution (0.5 mL) was added. Stirring was continued at this temperature for 30 min and the reaction mixture was acidified by the addition of PH = 6 buffer (2 mL). The mixture was extracted with EtOAc (3 X 10 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated. The residue was filtered through a pad of silica (1 X 4 cm), using EtOAc (10 mL), giving crude phenol, which was dried under high vacuum oil pump and used directly in the next step without further purification. To a stirred and cooled (0 °C) solution of the above crude phenol in CH_2Cl_2 (5 mL) were added successively 2,6-lutidine (0.15 mL, 1.27 mmol) and TBSOTf (0.17 mL, 0.76 mmol). Stirring was continued at this temperature for 30 min. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (3 mL). The mixture was extracted with EtOAc (3 X 15 mL). The combined extracts were washed with brine (10 mL), dried (Na_2SO_4) and concentrated. Flash chromatography of the residue over silica (2 X 18 cm), using 6:1 hexane/EtOAc, gave silyl ethers **2.40** (105.0 mg, 62% over 3 steps) as colorless oil: FTIR (CH_2Cl_2, cast) 2956, 1740, 1465, 1284, 1237, 1050 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.49 (s, 3 H), 0.68 (s, 3 H), 0.74 (q, J = 8.0 Hz, 6 H), 0.98 (t, J = 8.0 Hz, 9 H), 1.23-1.28 (m, 1 H), 1.68-1.76 (m, 1 H), 2.02 (s, 3 H), 2.04-2.09 (m, 1 H), 2.42-2.53 (m, 1 H), 2.97 (d, J = 3.6 Hz, 1 H), 3.40 (d, J = 3.6 Hz, 1 H), 3.45 (s, 3 H), 3.72 (d, J

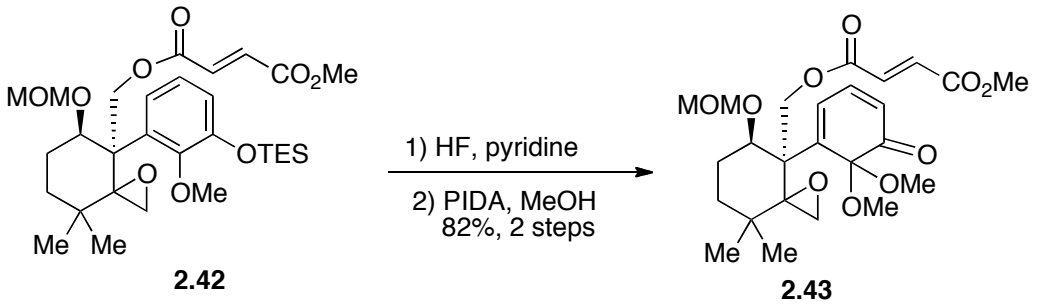
= 12.0 Hz, 1 H), 3.87 (s, 3 H), 4.28 (dd, *J* = 12.8, 4.0 Hz, 1 H), 4.80 (ABq, Δν = 18.7 Hz, *J* = 6.8 Hz, 2 H), 4.88 (d, *J* = 12.0 Hz, 1 H), 6.76 (dd, *J* = 8.0, 1.6 Hz, 1 H), 6.87 (t, *J* = 8.0 Hz, 1 H), 7.76 (dd, *J* = 8.0, 1.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.1, 6.6, 21.3, 24.6, 25.8, 26.2, 36.0, 37.1, 50.9, 52.5, 55.7, 59.8, 63.1, 65.2, 81.3, 97.9, 119.7, 122.6, 123.9, 132.9, 148.9, 151.4, 170.5; HRMS (FAB) *m/z* calcd for $C_{27}H_{44}O_7Si$ $[M]^+$ 508.2856, found 508.2865.



To a stirred and cooled (-78 ^{o}C) solution of actetate **2.40** (80.0 mg, 0.16 mmol) in CH_2Cl_2 (5 mL) was added DIBAL-H (1.0 M, 0.63mL, 0.63 mmol). Stirring was continued at this temperature for 30 min. The reaction was quenched by the addition of MeOH (1 mL) and Na_2SO_4•$10H_2O$ (1 g). After warmed up to room temperature, the mixture was stirred for 1 h and filtered through a pad of celite (2 X 4 cm), using EtOAc (30 mL) as rinse. After concentration of the filtrate, the residue was purified by flash chromatography over silica (2 X 16 cm), using 4:1 hexane/EtOAc, gave alcohol (67.0 mg, 90%) as colorless oil: FTIR (CH_2Cl_2, cast) 3468, 2956, 1464, 1424, 1284, 1049 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.51 (s, 3 H), 0.69 (s, 3 H), 0.74 (q, *J* = 8.0 Hz, 6 H), 0.98 (t, *J* = 8.0 Hz, 9 H), 1.26-1.31 (m, 1 H), 1.71-1.79 (m, 1 H), 2.04-2.09 (m, 1 H), 2.43-2.54 (m, 1 H), 3.19 (d, *J* = 2.8 Hz, 1 H), 3.47 (s, 3 H), 3.52 (d, *J* = 10.8 Hz, 1 H), 3.62 (d, *J* = 2.8 Hz, 1 H), 3.84 (s,

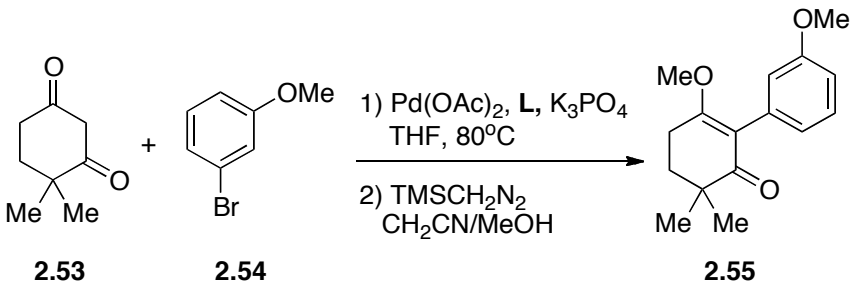
3 H), 3.84-3.92 (m, including a singlet at 3.84, 4 H in all), 3.94 (d, *J* = 11.6 Hz, 1 H), 4.37 (dd, *J* = 12.8, 4.0 Hz, 1 H), 4.77 (d, *J* = 6.8 Hz, 1 H), 5.00 (d, *J* = 6.8 Hz, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 6.87 (t, *J* = 8.0 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.1, 6.6, 24.2, 25.4, 26.3, 35.9, 37.3, 51.3, 52.6, 55.6, 59.8, 64.2, 68.6, 79.5, 98.1, 119.6, 122.7, 123.9, 133.1, 148.8, 151.2; HRMS (FAB) *m/z* calcd for $C_{25}H_{42}O_6Si$ $[M]^+$ 466.2751, found 466.2732.

The resulting alcohol was then under esterification with **2.41** to afford **2.42.** FTIR (CH_2Cl_2, cast) 2956, 1727, 1650, 1466, 1296, 1154, 1047 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.51 (s, 3 H), 0.68 (s, 3 H), 0.75 (q, *J* = 8.0 Hz, 6 H), 0.98 (t, *J* = 8.0 Hz, 9 H), 1.26-1.30 (m, 1 H), 1.70-1.77 (m, 1 H), 2.05-2.11 (m, 1 H), 2.45-2.54 (m, 1 H), 2.99 (d, *J* = 2.8 Hz, 1 H), 3.40 (d, *J* = 2.8 Hz, 1 H), 3.42 (s, 3 H), 3.38 (s, 3 H), 3.79 (s, 3 H), 3.88 (s, 3 H), 3.94 (d, *J* = 12.0 Hz, 1 H), 4.30 (dd, *J* = 12.4, 3.6 Hz, 1 H), 4.80 (ABq, Δν = 11.7 Hz, *J* = 6.4 Hz, 2 H), 4.93 (d, *J* = 12.0 Hz, 1 H), 6.78 (d, *J* = 7.6 Hz, 1 H), 6.89 (t, *J* = 8.0 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.1, 6.6, 24.6, 25.8, 25.9, 36.0, 37.0, 50.8, 52.2, 52.4, 55.7, 59.8, 64.0, 65.3, 81.4, 97.7, 119.9, 122.7, 124.0, 132.4, 133.1, 134.2, 148.8, 151.3, 164.4, 165.6; HRMS (FAB) *m/z* calcd for $C_{30}H_{46}O_9Si$ $[M]^+$ 578.2911, found 578.2900.



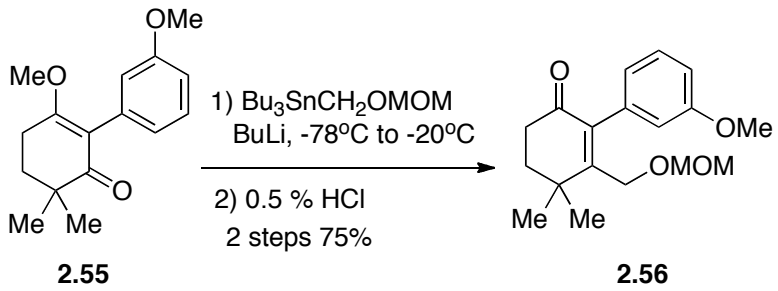
2.42 **2.43**

To a stirred and cooled (0 ^{o}C) solution of TES silyl ether **2.42** (10.0 mg, 0.017 mmol) in THF (1.5 mL) was added pyridine (0.05 mL) and HF.pyr. (0.02mL). Stirring was continued at this temperature for 15 min. The reaction mixture was concentrated and the residue was filtered through a pad of silica (1 X 5 cm), using EtOAc (5 mL) as rinse. After concentration of the filtrate, the residue was dried under oil pump and used directly in the next step without further purification. The above residue was dissolved in MeOH (1.5 mL) and the solution was cooled to 0 ^{o}C. A solution of PIDA (14.0 mg, 0.043 mmol) in MeOH (0.5 mL) was added dropwise. After 10 min at 0 ^{o}C, the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (1 mL). The mixture was extracted with EtOAc (3 X 3 mL). The combined extracts were dried (Na_2SO_4) and concentrated. The residue was purified by preparative TLC (500 μm, 20 X 20 cm), using 2:1 hexane/EtOAc, gave *o*-quinoneketal **2.43** (7.0 mg, 82% over 2 steps) as colorless oil: FTIR (CH_2Cl_2, cast) 2950, 1724, 1675, 1439, 1302, 1257, 1156, 1030 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.73 (s, 3 H), 0.99 (s, 3 H), 1.38-1.44 (m, 1 H), 1.64-1.72 (m, 1 H), 2.07-2.13 (m, 1 H), 2.24-2.35 (m, 1 H), 2.77 (d, *J* = 3.2 Hz, 1 H), 3.10 (s, 3 H), 3.17 (d, *J* = 3.2 Hz, 1 H), 3.38 (s, 3 H), 3.45 (s, 3 H), 3.80 (s, 3 H), 3.90 (d, *J* = 12.0 Hz, 1 H), 4.28 (dd, *J* = 12.4, 4.8 Hz, 1 H), 4.72 (ABq, Δν = 11.8 Hz, *J* = 6.8 Hz, 2 H), 5.03 (d, *J* = 12.0 Hz, 1 H), 6.03 (d, *J* = 9.2 Hz, 1 H), 6.86 (s, 2 H), 6.98 (dd, *J* = 10.0, 7.2 Hz, 1 H), 7.28 (d, *J* = 6.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.5, 25.9, 26.3, 35.7, 37.3, 49.0, 49.4, 52.2, 53.1, 54.2, 55.8, 64.2, 64.6, 81.2, 95.7, 97.6, 125.3, 128.2, 133.0, 134.2, 141.2, 147.0, 164.3, 165.5, 196.8; HRMS (FAB) *m/z* calcd for $C_{25}H_{35}O_{10}$ $[M + H]^{+}$ 495.2230, found 495.2235.



Compound 2.55: An oven-dried, 250 mL round bottom high-pressure flask containing a stirbar was capped with a rubber septum. This flask was then charged with 1,3-diketone **2.53** (5.1 g, 36 mmol), $Pd(OAc)_2$ (67 mg, 0.3 mmol), 2-di-t-butylphosphino-2'-methylbiphenyl (206 mg, 0.6 mmol), and K_3PO4 (14.6 g, 69 mmol). The flask was evacuated and backfilled with argon. 100 mL of THF and aryl bromide **2.54** (3.8 mL, 30 mmol) were sequentially injected, and the septum was replaced with a Teflon screw cap. The flask was sealed and heated at 80 °C for 12 hours. The reaction mixture was then diluted with MeOH and filtered. The filtrate was concentrated and dissolved in 27 mL of CH_3CN and 3 ml of MeOH under argon. To this mixture, Hunig's base (7.5 mL, 43 mmol) and a solution of $TMSCHN_2$ (21 mL, 2M) in hexane were added sequentially at 0 °C. The reaction mixture was stirred at room temperature for additional 12 hours. Solvents were removed under reduced pressure using rotavap. The residues were purified by flash chromatography to give a colourless oil **2.55**. (7.1g, 91% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.24 (dd, J = 7.8, 7.8 Hz, 1H), 6.81-6.70 (m, 3H), 3.79 (s, 3H), 3.70 (s, 3H), 2.70 (dd, J = 6.3, 6.3 Hz, 2H), 1.93 (dd, J = 6.3, 6.3 Hz, 2H), 1.18 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 201.7, 170.0, 158.9, 135.3, 128.4, 123.2, 118.4, 116.3, 112.3, 55.5, 55.1, 39.6, 34.0, 24.5, 22.7; HRMS (FAB, *m/z*) calcd for $C_{16}H_{21}O_3$ $[M+H]^+$

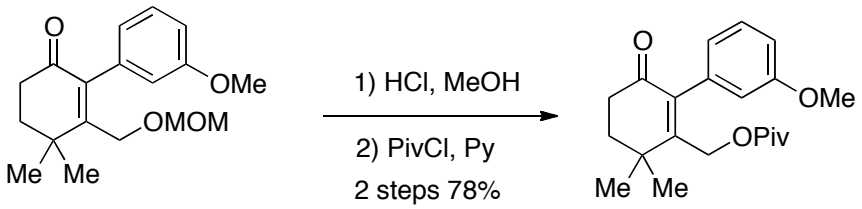
261.1491, found 261.1485.



2.55 **2.56**

compound 2.56: A solution of Bu_3SnCH_2OMOM (5.9 g, 16 mmol) in 40 mL of anhydrous THF was cooled to -78 ^oC under argon. BuLi in hexane (6.45 ml, 2.5 M) was added dropwise in 5 mins. The reaction mixture was stirred at this temperature for additional 10 min and a solution of **2.55** (2.6 g, 10 mmol) in 10 mL of THF was injected quickly. The reaction mixture was slowly warmed up to -40 ^oC in 30 min and stirred for additional 1 hour at this temperature. Then the reaction mixture was warmed up to 0 ^oC and acidified with 0.5% HCl solution until pH = 3. 30 min later, the reaction mixture was neutralized with saturated $NaHCO_3$ solution, extracted with ethyl acetate (3 x 20 mL) , and dried over $MgSO_4$. The extract was filtered over cotton and the solvent was removed under reduced pressure. The residue was put on a short silica gel column. The nonpolar impurity was removed by hexane and the polar part was collected using ethyl acetate as eluent. The ethyl acetate was removed under reduced pressure and the residue was dissolved in 50 mL of MeOH. 8 drops of concentrated HCl (37%) was added dropwise and the reaction mixture was stirred at 50 ^oC for 3 hours. Then the mixture was cooled to room temperature, neutralized with saturated $NaHCO_3$ solution, and extracted with ethyl acetate (3 x 30 mL). The extract was dried over $MgSO_4$, filtered and the solvent was

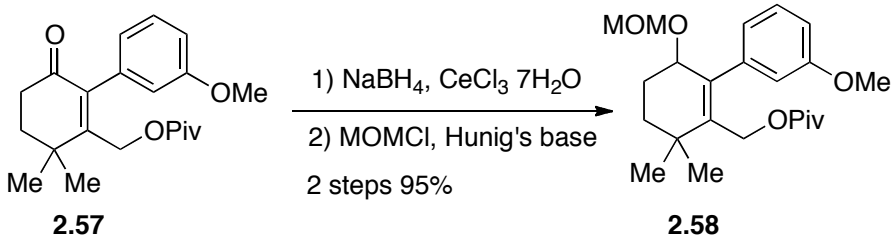
removed using rotovap. The residue was purified using flash chromatography to give a colorless oil **2.56** (1.5 g, 56% for two steps). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26 (dd, J = 7.6, 7.6 Hz, 2H), 6.84 (dd, J = 8.0, 2.4 Hz, 1H), 6.63 (d, J = 7.6 Hz, 1H), 6.60 (s, 1H), 4.08 (d, J = 5.6 Hz, 2H), 3.77 (s, 3H), 2.61 (dd, J = 6.4, 6.4 Hz, 2H), 1.95 (dd, J = 6.3, 6.3 Hz, 2H), 1.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.5, 162.7, 159.4, 138.5, 136.9, 129.3, 121.7, 115.1, 113.1, 60.4, 55.1, 37.6, 35.3, 34.6, 26.8; IR (neat): cm^{-1} 3441, 2960, 2926, 1701, 1670, 1596, 1484, 1466, 1287, 1256, 1047; HRMS (FAB, *m/z*) calcd for $C_{16}H_{20}O_3$ $[M+H]^+$ 261.1412, found 261.1417.



2.56 **2.57**

Compound 2.57: compound **2.56** (1.3 g, 5 mmol) was dissolved in 20 mL of anhydrous DCM under argon at 0 ^{o}C. Pyridine (2.4 mL, 30 mmol) was injected into this solution and 5 min later pivaloyl chloride (2.4 mL, 20 mmol) was injected into the mixture. The reaction mixture was stirred at this temperature for 12 hours, quenched with water, extracted with ether (3 x 20 mL) and dried over $MgSO_4$. After filtration of the drying agent, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (1.65 g, 96%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22 (dd, J = 8.0, 8.0 Hz, 1H), 6.82 (dd, J = 8.4, 2.0 Hz, 1H), 6.61 (d, J = 7.6 Hz, 1H), 6.58 (br s, 1H), 4.43 (s, 2H), 3.76 (s, 3H), 2.66 (dd, J = 6.4, 6.4 Hz, 2H), 2.13 (dd, J = 6.8, 6.8 Hz, 2H), 1.28

(s, 6H), 1.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.9, 177.6, 159.1, 157.3, 141.4, 136.2, 128.8, 122.0, 115.6, 113.1, 62.3, 55.1, 38.6, 37 .5, 35.3, 34.7, 27.1; IR (neat): cm^{-1} 2952, 1724, 1667, 1453, 1437, 1301, 1259, 1156, 1034; HRMS (FAB, *m/z*) calcd for $C_{21}H_{28}O_4$ $[M]^+$ 344.1988, found 344.2001.

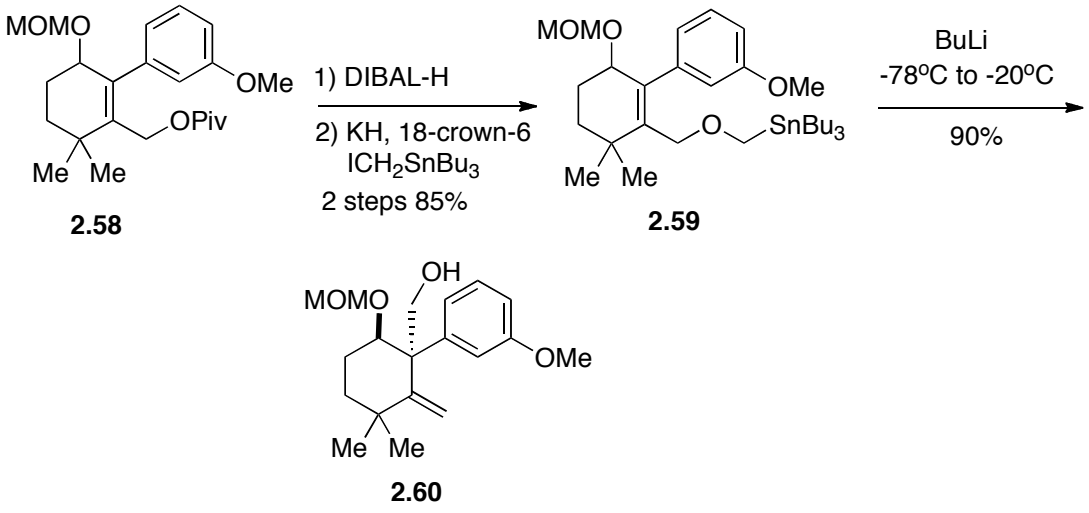


2.57 **2.58**

Compound 2.58: compound **2.57** (3.4g, 10 mmol) and cerium chloride heptahydrate (5g, 13 mmol) were dissolved in 20 mL of methanol at 0 ^oC. 5 min later $NaBH_4$ (600 mg, 15 mmol) was added carefully in three portions. The reaction mixture was stirred at 0 ^oC for two hours and quenched with water. The product was extracted with ethyl acetate (3 x 30 mL) and dried over $MgSO_4$. After filtration of the drying agent, the solvent was removed under reduced pressure and the residue was purified using flash chromatography (3.22 g, 93%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.20 (dd, J = 7.6, 7.6 Hz, 2H), 6.79 (dd, J = 7.6 Hz, 1H), 6.75 (d, J = 7.6 Hz, 1H), 6.71 (s, 1H), 4.42 (d, J = 11.2 Hz, 1H), 4.32 (s, 1H), 4.11 (d, J = 11.2 Hz, 1H), 3.77 (s, 3H), 2.02-1.74 (m, 4H), 1.16 (s, 9H), 1.14 (s, 3H), 1.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.1, 159.4, 143.1, 140.7, 138.3, 129.2, 121.4, 114.8, 112.6, 69.1, 62.0, 55.1, 38.5, 34.7, 34.4, 28.3, 27.5, 27.2, 27.1; IR (neat): cm^{-1} 3435, 2960, 2936, 2870, 1724, 1597, 1577, 1480, 1285; HRMS (FAB, *m/z*) calcd for $C_{21}H_{30}O_4$ $[M]^+$ 346.2144, found 346.2158. The above alcohol (1.8 g, 5.2 mmol) and

Hunig's base (2.72 mL, 15.6 mmol) were dissolved in anhydrous DCM under argon at room temperature. MOMCl (775 mL, 11 mmol) was injected into the solution and the reaction mixture was stirred at room temperature for 12 hours. Then the reaction was quenched with 2 drops of water. The solvent was removed under reduced pressure and the residue was purified using flash chromatography (1.93 g, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.16 (dd, J = 7.6, 7.6 Hz, 1H), 6.79-6.74 (m, 3H), 4.53 (d, J = 7.2 Hz, 1H), 4.46 (d, J = 11.6 Hz, 1H), 4.27-4.25 (m, 1H), 4.24 (d, J = 7.2 Hz, 1H), 4.10 (d, J = 11.6 Hz, 1H), 3.76 (s, 3H), 2.85 (s, 3H), 1.94-1.77 (m, 3H), 1.49-1.44 (m, 1H), 1.16 (s, 9H), 1.13 (s, 3H), 1.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.1, 159.1, 143.8, 141.6, 139.4, 128.6, 121.7, 114.8, 112.3, 94.9,

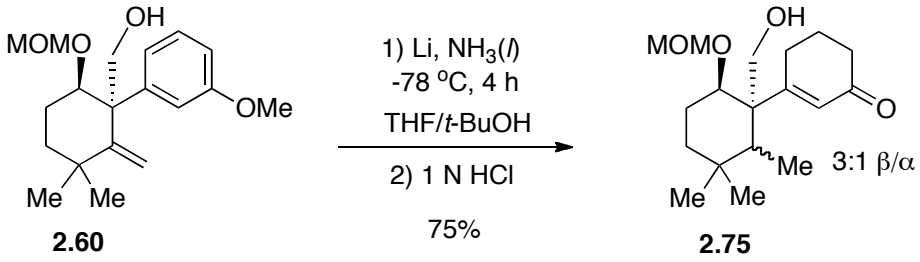
73.4, 62.0, 55.2, 54.8, 38.5, 34.4, 34.3, 28.4, 27.1, 26.7, 25.1; IR (neat): cm^{-1} 2959, 2935, 1724, 1577, 1480, 1284, 1152, 1032; HRMS (FAB, *m/z*) calcd for $C_{23}H_{34}O_5$ $[M]^+$ 390.2406, found 390.2418.



Compound 2.59 : compound **2.58** (1.95 g, 5 mmol) was dissolved in anhydrous DCM under argon and cooled to -78 ^{o}C. 7.5 mL of DIBAL-H in hexane (2 M) was injected into the reaction mixture slowly and the reaction mixture was stirred for 30 min at this temperature. Then the reaction was quenched with 0.5 mL of methanol and 5 g of sodium sulfate decahydrate. After warming up to room temperature, the mixture was stirred for additional 1 hour and filtered. The solvent was removed using rotovap and the residue was purified with flash chromatography (1.45, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22 (dd, J = 7.6, 7.6 Hz, 1H), 6.82-6.79 (m, 3H), 4.53 (d, J = 7.2 Hz, 1H), 4.25 (d, J = 7.2 Hz, 1H), 4.21 (dd, J = 4.0, 4.0 Hz, 1H), 4.05 (dd, J = 12.0, 4.4 Hz, 1H), 3.86 (dd, J = 12.0, 5.6 Hz, 1H), 3.80 (s, 3H), 2.88 (s, 3H), 1.93-1.76 (m, 3H), 1.48-1.43 (m, 1H), 1.22 (s, 3H), 1.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.5, 144.7, 142.5, 138.3, 129.2, 121.3, 114.4, 112.6, 94.9, 73.8, 59.7, 55.2, 54.9, 34.5, 34.4, 28.4, 26.8, 25.2; IR (neat): cm^{-1} 3458, 2936, 1597, 1577, 1483, 1149, 1027; HRMS (FAB, *m/z*) calcd for $C_{18}H_{26}O_4$ $[M]^+$ 306.1831, found 306.1836. an oven-dried round-bottomed flask was charged with KH (360 mg, 9 mmol) and 20 mL of THF under argon at 0 ^{o}C. A solution of compound **2.59** (920 mg, 3 mmol) in 5 mL of THF was injected slowly into the flask. 30 mins later, 18-crown-6 (780 mg, 3 mmol) was added. The reaction mixture was stirred for additional 5 min and then α-iodomethyl tributylstanne (3.9 g, 9 mmol) was injected and the reaction mixture was stirred at this temperature for 6 hours. After quenched with water carefully, the product was extracted with ether (3 x 20 mL) and dried over $MgSO_4$. The drying agent was removed by filtration and the solvent was concentrated using rotovap. The residue was purified by flash chromatograph. And the desired product was dissolved in THF under argon. The mixture was cooled to -78 ^{o}C and BuLi in hexane (3.6 mL, 9

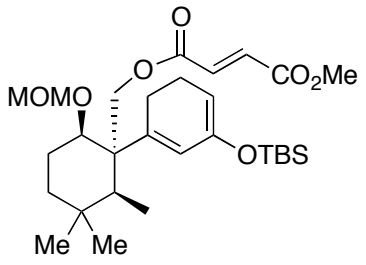
mmol) was injected dropwise. The temperature was slowly warmed up to -20 ^{o}C in 6 hours and the reaction was quenched with saturated NH_4Cl solution, extracted with ether (3 x 30 mL), and dried over $MgSO_4$. After filtration, the extract was concentrated and the residue was purified by chromatography (0.78g, 80% for 2 steps).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25-7.14 (m, 3H), 6.75-6.71 (m, 1H), 5.37 (s, 1H), 5.34 (s, 1H), 4.78 (d, J = 10.4 Hz, 2H), 3.96 (dd, J = 16.0, 6.4 Hz, 1H), 3.84-3.79 (m, 2H), 3.78 (s, 3H), 3.45 (s, 3H), 3.26 (dd, J = 9.6, 9.6 Hz, 1H), 2.27 (dddd, J = 16.4, 16.4, 16.4, 6.8 Hz, 1H), 1.96 (dddd, J = 17.6, 6.0, 6.0, 6.0 Hz, 1H), 1.46-1.31 (m, 2H), 1.10 (s, 3H), 0.52 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.0, 154.6, 143.0, 128.5, 121.4, 115.4, 110.8, 110.7, 96.8, 80.5, 66.5, 56.3, 55.9, 55.0, 38.5, 36.9, 31.3, 30.1, 24.9; IR (neat): cm^{-1} 3485, 2953, 1606, 1579, 1485, 1464, 1053, 1027; HRMS (FAB, *m/z*) calcd for $C_{19}H_{28}O_4$ $[M+Na]^+$ 343.1885, found 343.1868.



Compound 2.75: an oven-dried three-neck flash equipped with a dry ice acetone condenser was charged with 30 mg of compound **2.60**, 1 mL of THF, 1 mL of *tert*-butanol, and 2 mL of liquid ammonia. Then 20 mg of lithium was added and the reaction mixture was stirred at -78 ^{o}C for 20 mins and -33 ^{o}C for 40 mins. Then ammonium chloride solid was added to quench the reaction until the blue color disappeared. The

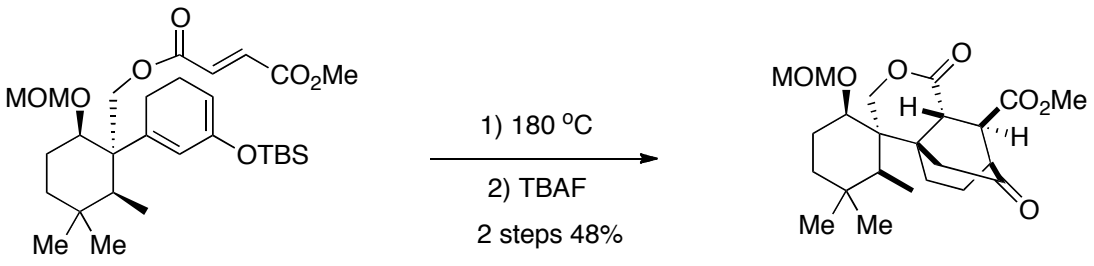
reaction mixture was then slowly warmed up to room temperature to vaporize the ammonia. The residue was extracted with ethyl acetate (3 x 20 mL) and dried over magnesium sulfate. After filtration of the drying agent, the solvent was removed under the reduced pressure and the residue was dissolved in THF/MeOH mixed solvent (THF/MeOH = 10: 1). The mixture was cooled to 0 ^{o}C and 2 drop of 1N HCl solution was added. The reaction mixture was stirred at 0 ^{o}C for 12 hours and quenched with saturated $NaHCO_3$. The extract was dried over $MgSO_4$. After filtration, the solvent was removed using rotovap and the residue was used without purification in the next step.



2.81

Compound 2.81: **2.75** (28 mg) and pyridine (73 υL, 0.9 mmol) was dissolved in DCM under argon at 0 ^{o}C. Acyl chloride (65 mg, 0.4 mmol) in 1 mL of DCM was injected slowly. After addition of acyl chloride solution, the reaction mixture was stirred at this temperature for 12 hours. The reaction was then quenched with methanol and the solvent was removed under the reduced pressure. The residue was purified using preparation TLC. **2.81**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.88 (d, J =15.6 Hz, 2H), 6.52 (s, 1H), 4.68 (d, J = 6.8 Hz, 1H), 4.52 (d, J = 7.2 Hz, 1H), 4.45 (d, J = 11.2 Hz, 1H), 4.22 (d, J = 11.2 Hz, 1H), 3.82 (s, 3H), 3.74 (dd, J = 12, 4 Hz, 1H), 3.29 (s, 3H), 2.63-2.56 (m, 1H), 2.52-2.29 (m, 3H), 2.13 (dddd, J = 13.2, 13.2, 13.2, 4 Hz, 1H), 2.00-1.97 (m, 1H), 1.92-1.84 (m, 2H), 1.67 (ddd, J = 7.2, 7.2, 7.2 Hz, 1H), 1.53 (ddd, J = 13.6, 3.6, 3.6 Hz, 1H), 1.37 (ddd, J = 13.2, 13.2, 4 Hz, 1H), 1.04 (d, J = 7.6 Hz, 3H), 0.89 (s, 3H), 0.84 (s, 3H); ^{13}C

NMR ($CDCl_3$, 100 MHz): δ 199.8, 165.3, 164.5, 163.7, 133.7, 133.3, 131.4, 96.2, 80.1, 65.2, 55.9, 52.4, 52.1, 45.2, 40.1, 37.6, 34.4, 32.0, 29.1, 25.0, 23.7, 21.2, 12.4 ; IR (neat): cm^{-1} 2967, 1728, 1680, 1579, 1480, 1280, 1256, 1147; HRMS (FAB, *m/z*) calcd for $C_{23}H_{35}O_7$ $[M + H]^+$ 423.2383, found 423.2400. an oven-dried flask was charged with starting material (22 mg, 0.05 mmol), TEA (22 μL, 0.15 mmol), and 5 mL of DCM under argon at 0 ^oC. TBSOTf (27 μL, 0.1 mmol) was added and the reaction mixture was stirred at this temperature for 12 hours. The product was purified using preparation TLC. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.88 (d, J =15.6 Hz, 2H), 6.18 (s, 1H), 4.91-4.89 (m, 1H), 4.69 (d, J = 6.8 Hz, 1H), 4.52 (d, J = 6.8 Hz, 1H), 4.45 (d, J = 11.6 Hz, 1H), 4.7 (d, J = 11.2 Hz, 1H), 3.82 (s, 3H), 3.74 (dd, J = 12.4, 4 Hz, 1H), 3.30 (s, 3H), 2.25-2.01 (m, 5H), 1.89-1.84 (m, 1H), 1.56 (ddd, J = 7.2, 7.2, 7.2 Hz, 1H), 1.49 (ddd, J = 13.6, 3.6, 3.6 Hz, 1H), 1.35 (ddd, J = 13.2, 13.2, 4 Hz, 1H), 1.01 (d, J = 7.6 Hz, 3H), 0.92 (s, 9H), 0.89 (s, 3H), 0.86 (s, 3H), 0.12 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.4, 164.8, 148.9, 138.7, 133.8, 133.2, 127.4, 102.5, 96.5, 81.0, 65.5, 55.6, 52.3, 50.8, 44.8, 40.9, 34.3, 32.3, 26.4, 25.7, 25.3, 22.7, 20.6, 18.1, 12.1; IR (neat): cm^{-1} 2952, 2360, 1725, 1721, 1667, 1455, 1300, 1258, 1155, 1035; HRMS (FAB, *m/z*) calcd for $C_{29}H_{49}O_7Si$ $[M + H]^+$ 537.3248, found 537.3237.



2.81 **2.82**

Compound 2.83: compound **2.81** (37 mg, 0.07 mmol) was dissolved in 5 mL of anhydrous toluene in a high-pressure tube. The reactor was wash with BSA first and dried in oven for 12 hours. The reaction mixture was degassed with argon and then stirred at 180 ^{o}C for 16 hours. After cooling to room temperature and the mixture was transfer to a round bottom flask. The mixture was further cooled to 0 ^{o}C and TBAF in THF (70 μL, 0.07 mmol) was added. 5 mins later the reaction was quenched with saturated ammonium chloride solution. After extracting with ethyl acetate (3 x 10 mL), the solution was dried over $MgSO_4$. The drying agent was removed by filtration and the solvent was removed under reduced pressure. The residue was purified using flash chromatography (14 mg, 48%) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.76 (d, J = 7.2 Hz, 1H), 4.68 (d, J = 12.0 Hz, 1H), 4.62 (d, J = 6.8 Hz, 1H), 4.12 (br s, 1H), 3.94 (dd, J = 3.2, 3.2 Hz, 1H), 3.88 (d, J = 12.0 Hz, 1H), 3.67 (s, 3H), 3.48 (dd, J = 18.8, 3.2 Hz, 1H), 3.44 (s, 3H), 3.11 (dd, J = 12.4, 4.8 Hz, 1H), 2.93 (d, J = 18.4 Hz, 1H), 2.74 (br s, 1H), 2.04-1.72 (m, 5H), 1.60-1.55 (m, 2H), 1.40-1.29 (m, 2H), 1.19 (d, J = 7.6 Hz, 3H), 0.97 (s, 3H), 0,88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.5, 175.7, 173.5, 96.0, 84.1, 78.0, 56.8, 56.6, 52.5, 48.7, 47.0, 44.7, 43.9, 43.3, 41.6, 40.7, 34.1, 32.7, 27.2, 25.9, 23.1, 21.9, 13.9; IR (neat): cm^{-1} 2952, 2850, 1740, 1665, 1461, 1311, 1184, 1023; HRMS (FAB, *m/z*) calcd for $C_{23}H_{35}O_7$ $[M + H]^+$ 423.2383, found 423.2396.

2.5 Reference

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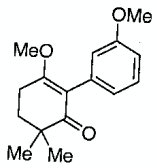

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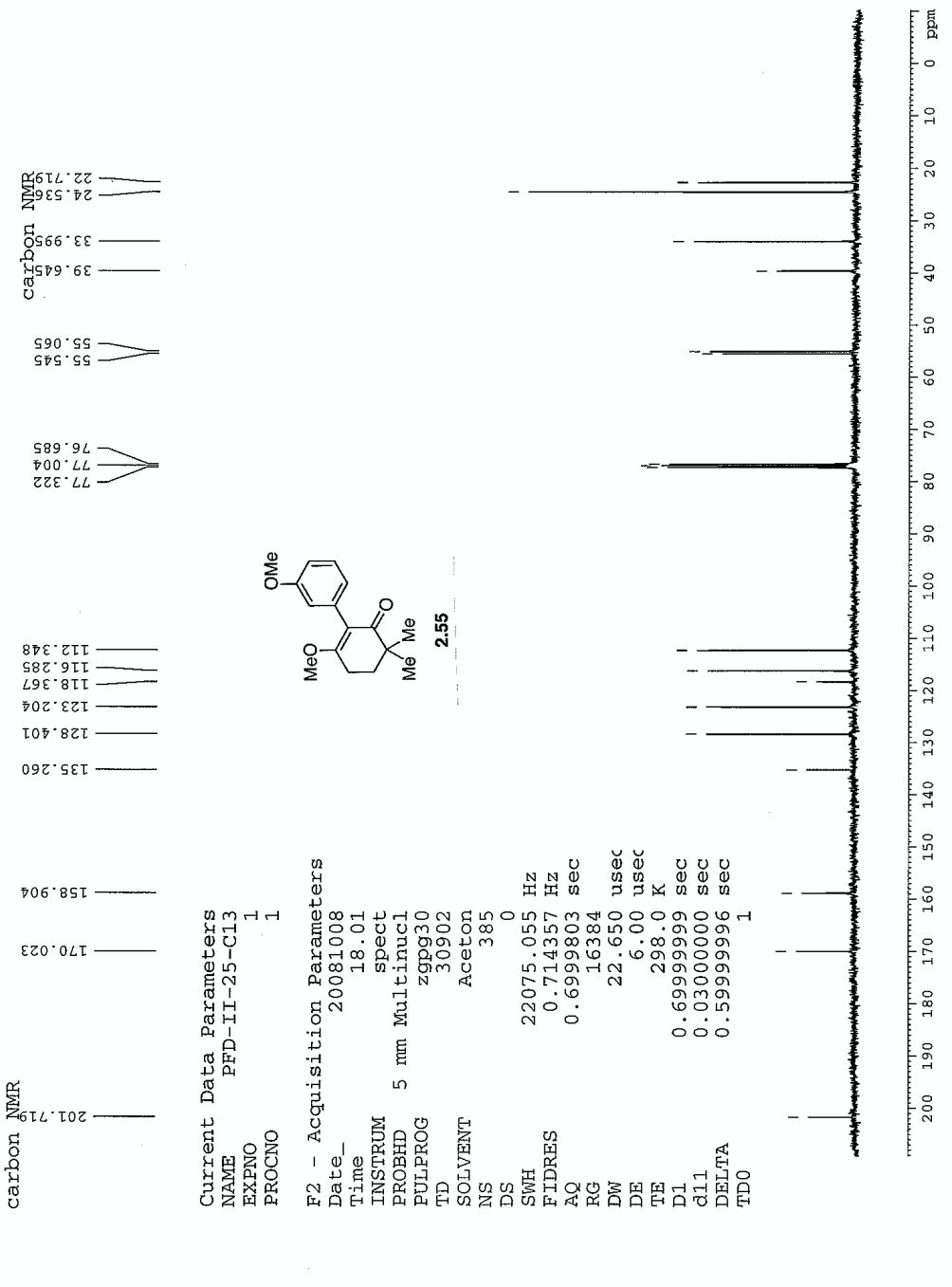
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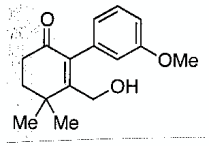
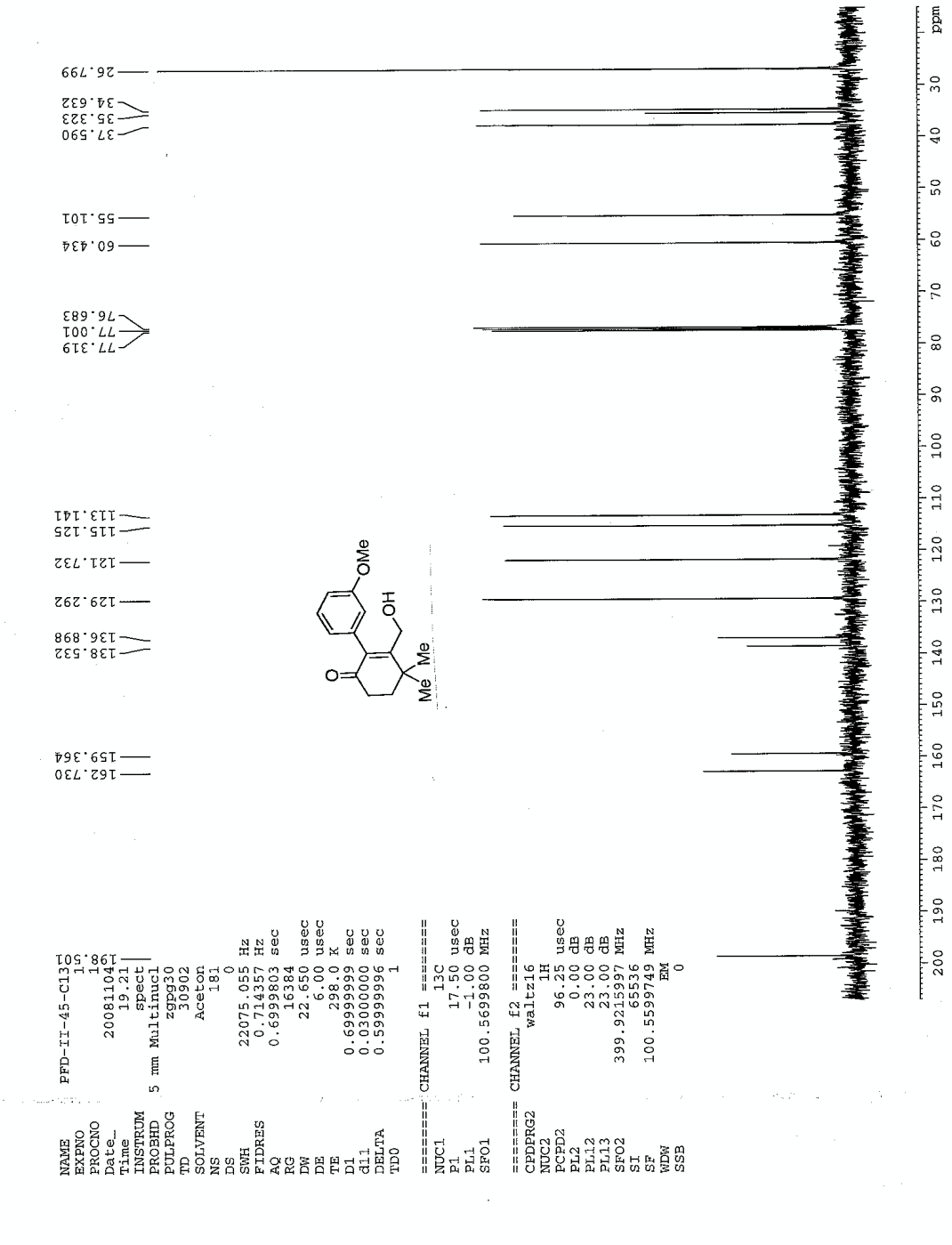
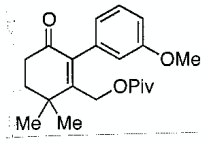
201.719
170.023
158.904
135.260
128.401
123.204
118.367
116.285
112.348
77.322
77.004
76.685
55.545
55.065
39.645
33.995
24.536
22.719
carbon NMR
OMe
MeO
O
Me
Me
2.55
Current Data Parameters
NAME PFD-II-25-C13
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20081008
Time 18.01
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 385
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.6999803 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 298.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

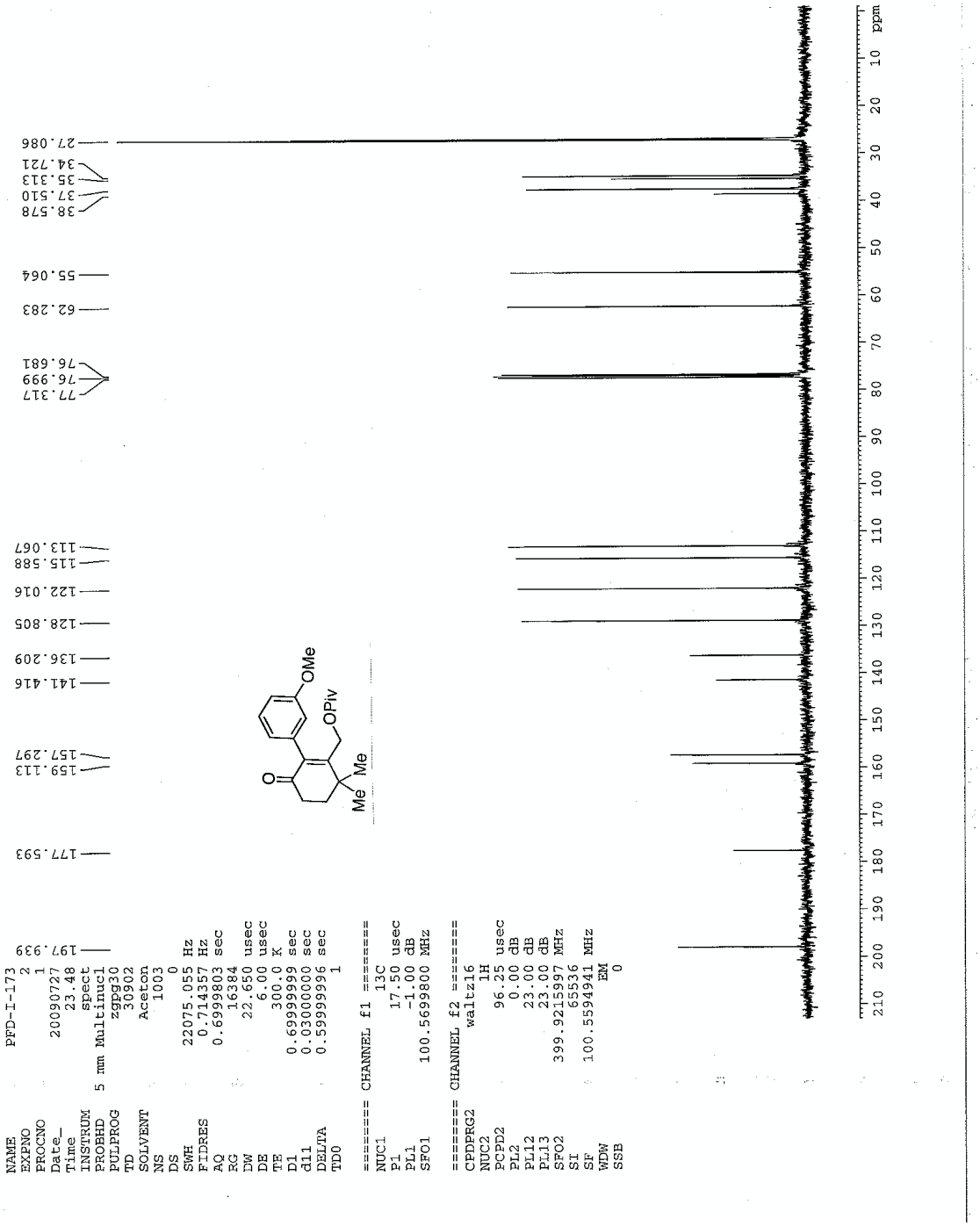
NAME	PFD-II-45
EXPNO	1
PROCNO	1
Date_	20081104
Time	19.18
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	D2O
NS	32
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200095 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00

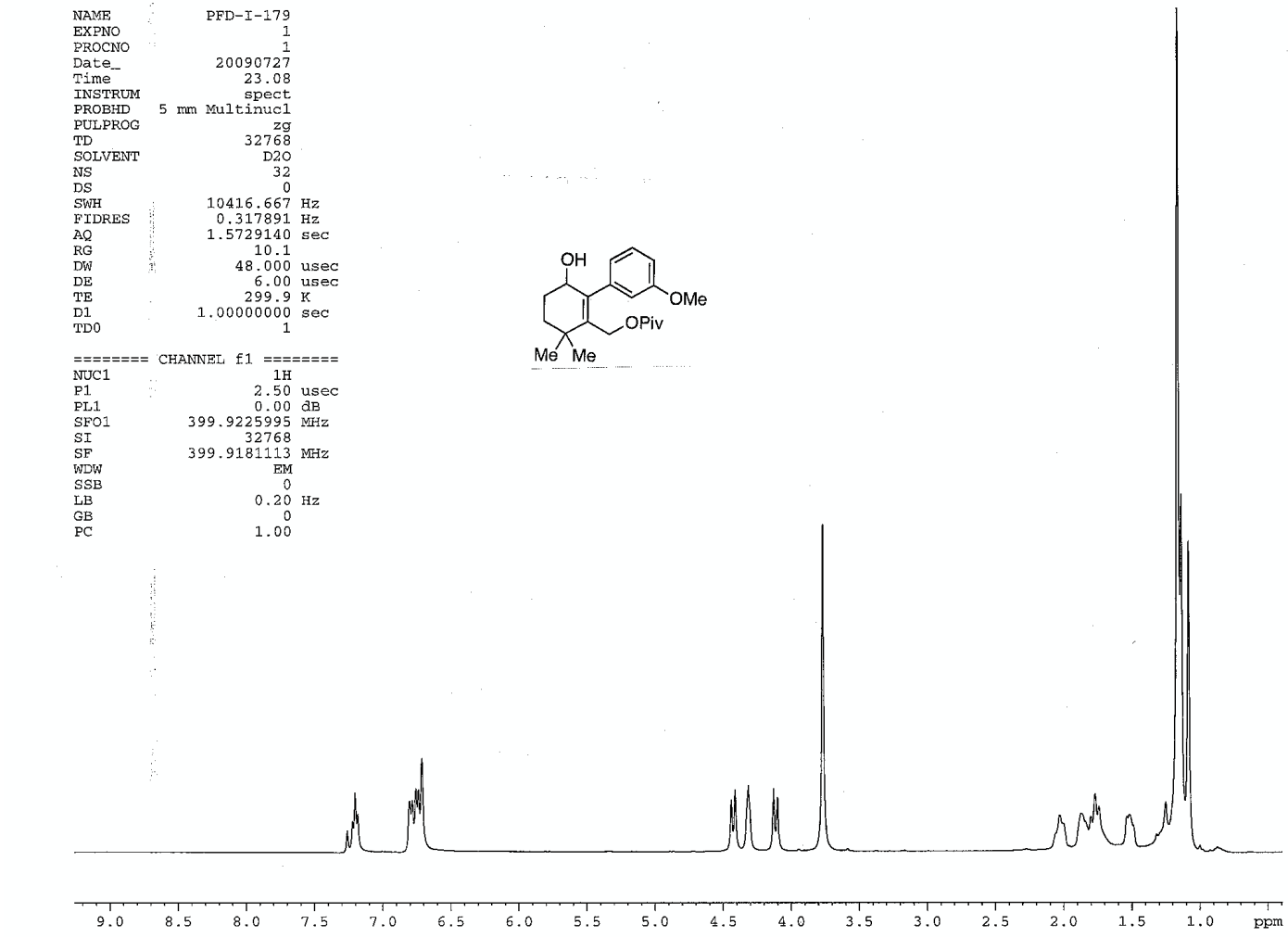


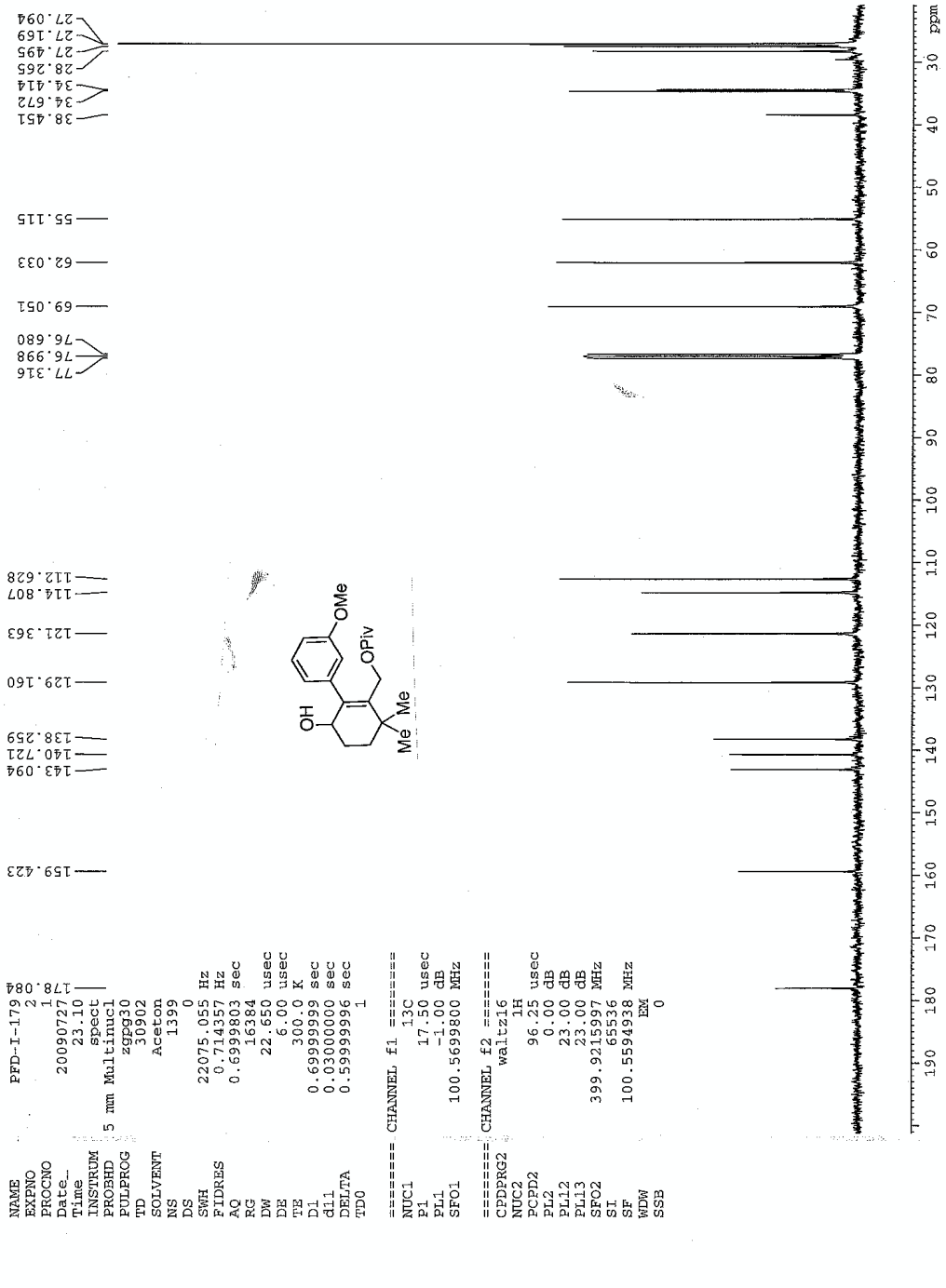

NAME PFD-IT-45-C13
EXPNO 15
PROCNO 1
Date_ 20081104
Time 19.21
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 181
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.6999803 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 298.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 96.25 usec
PL2 0.00 dB
PL12 23.00 dB
PL13 23.00 dB
SFO2 399.9215997 MHz
SI 65536
SF 100.5599749 MHz
WDW EM
SSB 0
198.501
162.730
159.364
138.532
136.898
129.292
121.732
115.125
113.141
77.319
77.001
76.683
60.434
55.101
37.590
35.323
34.632
26.799
OMe
OH
Me
Me
ppm

NAME	PFD-I-173
EXPNO	1
PROCNO	1
Date_	20090727
Time	23.46
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	26
DS	0
SWH	10416.667 Hz
FIDRES	0.317891 Hz
AQ	1.5729140 sec
RG	10.1
DW	48.000 usec
DE	6.00 usec
TE	300.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9181115 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00

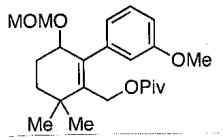


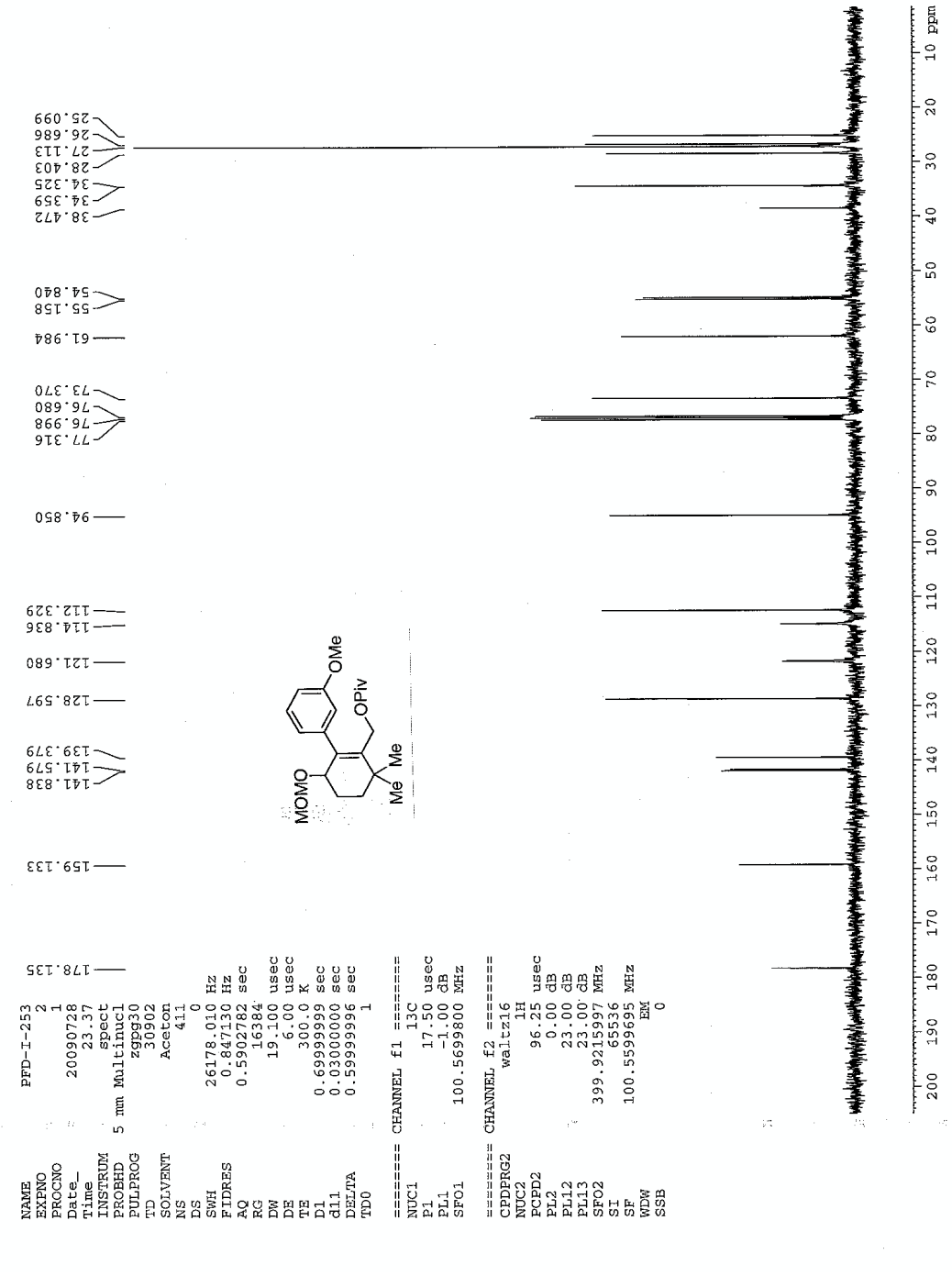

NAME PFD-I-173
EXPNO 2
PROCNO 1
Date_ 20090727
Time 23.48
INSTRUM spect
PROBHD 5 mm Multinuc1
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 1003
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.6999803 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 96.25 usec
PL2 0.00 dB
PL12 23.00 dB
PL13 23.00 dB
SFO2 399.9215997 MHz
SI 65536
SF 100.5594941 MHz
WDW EM
SSB 0
177.593
159.113
157.297
141.416
136.209
128.805
122.016
115.588
113.067
77.317
76.999
76.681
62.283
55.064
38.578
37.510
35.313
34.721
27.086
OMe
OPiv
Me
Me
O
ppm


NAME PFD-I-179
EXPNO 1
PROCNO 1
Date_ 20090727
Time 23.08
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT D2O
NS 32
DS 0
SWH 10416.667 Hz
FIDRES 0.317891 Hz
AQ 1.5729140 sec
RG 10.1
DW 48.000 usec
DE 6.00 usec
TE 299.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 2.50 usec
PL1 0.00 dB
SFO1 399.9225995 MHz
SI 32768
SF 399.9181113 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
OH
OMe
OPiv
Me Me
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 ppm

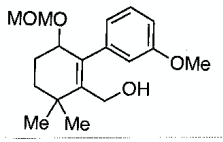

NAME PFD-I-179
EXPNO 2
PROCNO 1
Date_ 20090727
Time 23.10
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 1399
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.6999803 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 96.25 usec
PL2 0.00 dB
PL12 23.00 dB
PL13 23.00 dB
SFO2 399.9215997 MHz
SI 65536
SF 100.5594938 MHz
WDW EM
SSB 0
OMe
OPiv
OH
Me Me
178.084
159.423
143.094
140.721
138.259
129.160
121.363
114.807
112.628
77.316
76.998
76.680
69.051
62.033
55.115
38.451
34.672
34.414
28.265
27.495
27.169
27.094
ppm

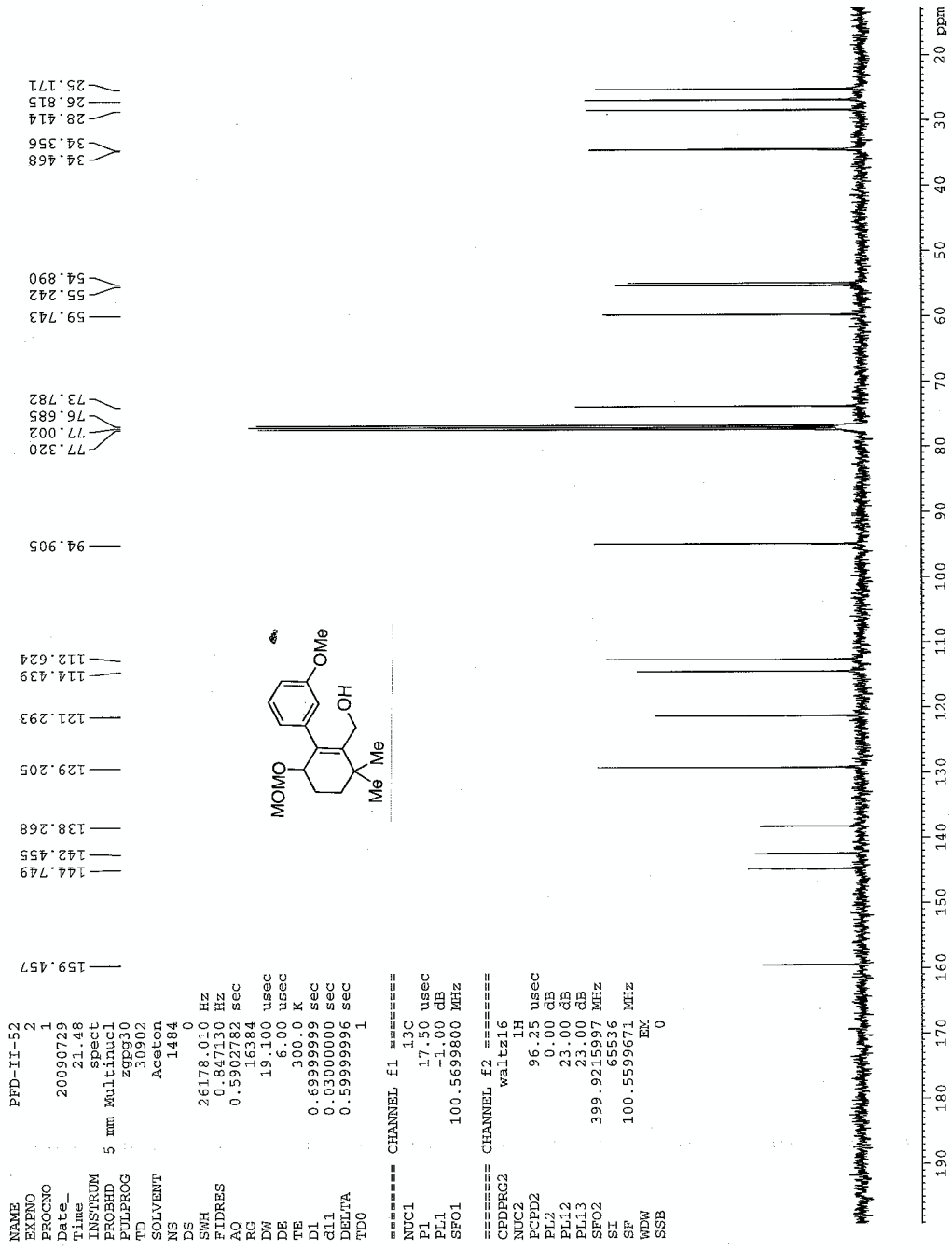
NAME	PFD-I-253	
EXPNO	1	
PROCNO	1	
Date_	20090728	
Time	23.34	
INSTRUM	spect	
PROBHD	5 mm Multinucl	
PULPROG	zg	
TD	32768	
SOLVENT	CDCl3	
NS	26	
DS	0	
SWH	5995.204	Hz
FIDRES	0.182959	Hz
AQ	2.7329011	sec
RG	10.1	
DW	83.400	usec
DE	6.00	usec
TE	300.0	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	1H	
P1	2.50	usec
PL1	0.00	dB
SFO1	399.9225995	MHz
SI	32768	
SF	399.9200111	MHz
WDW	EM	
SSB	0	
LB	0.20	Hz
GB	0	
PC	1.00	

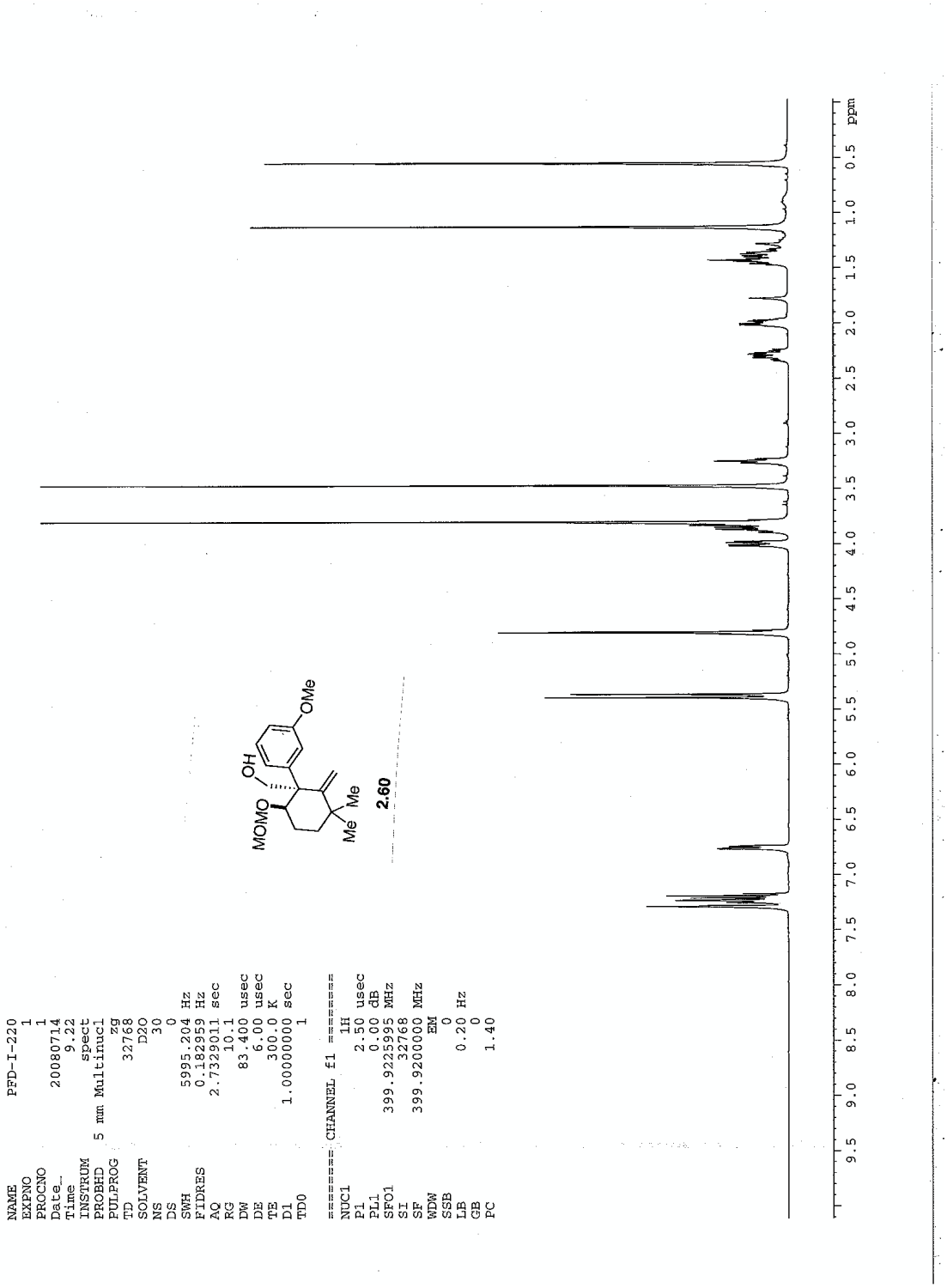


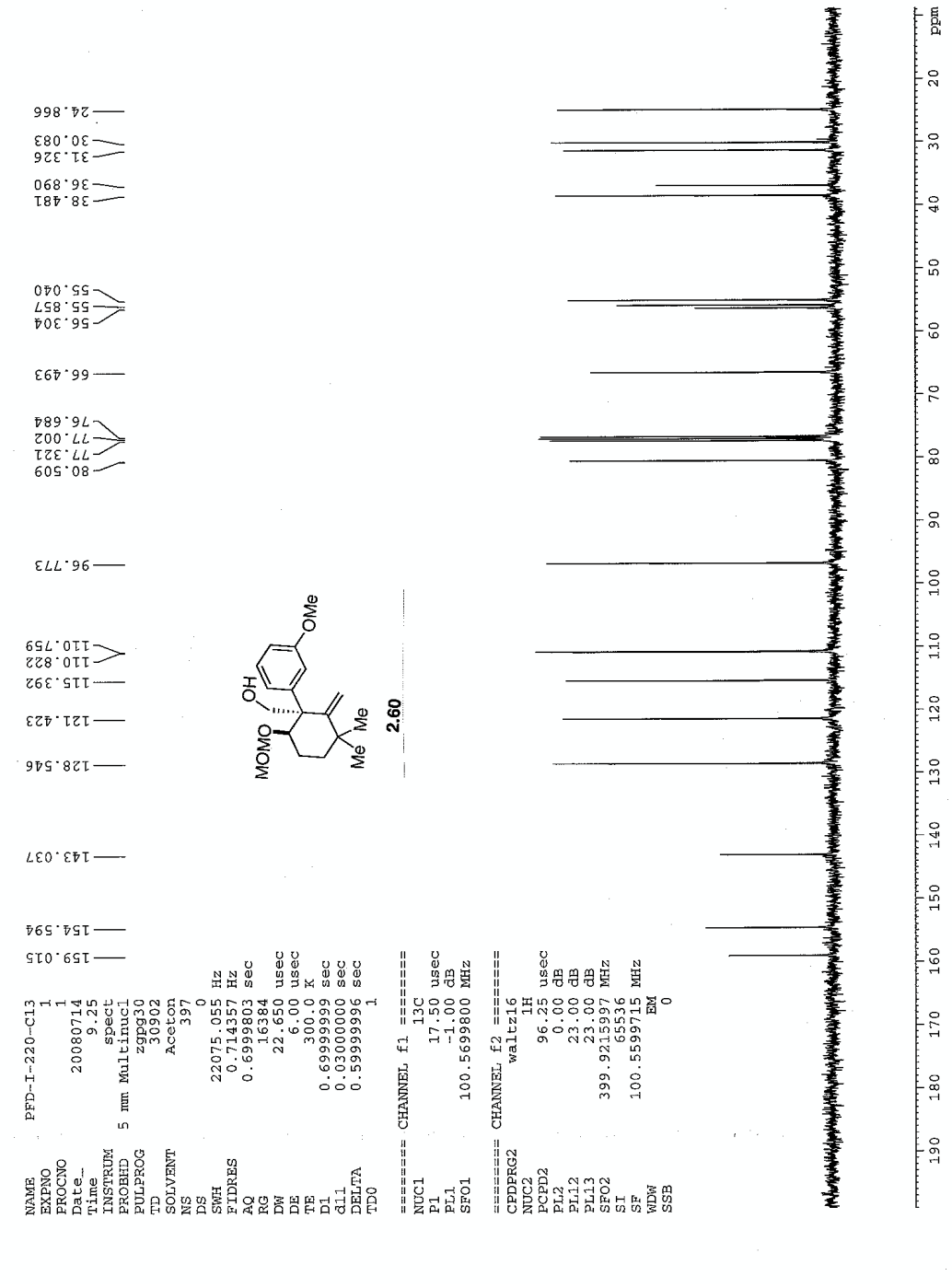

NAME PFD-I-253
EXPNO 2
PROCNO 1
Date_ 20090728
Time 23.37
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 411
DS 0
SWH 26178.010 Hz
FIDRES 0.847130 Hz
AQ 0.5902782 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 96.25 usec
PL2 0.00 dB
PL12 23.00 dB
PL13 23.00 dB
SFO2 399.9215997 MHz
SI 65536
SF 100.5599695 MHz
WDW EM
SSB 0
MOMO
OMe
OPiv
Me Me
178.135
159.133
141.838
141.579
139.379
128.597
121.680
114.836
112.329
94.850
77.316
76.998
76.680
73.370
61.984
55.158
54.840
38.472
34.359
34.325
28.403
27.113
26.686
25.099
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

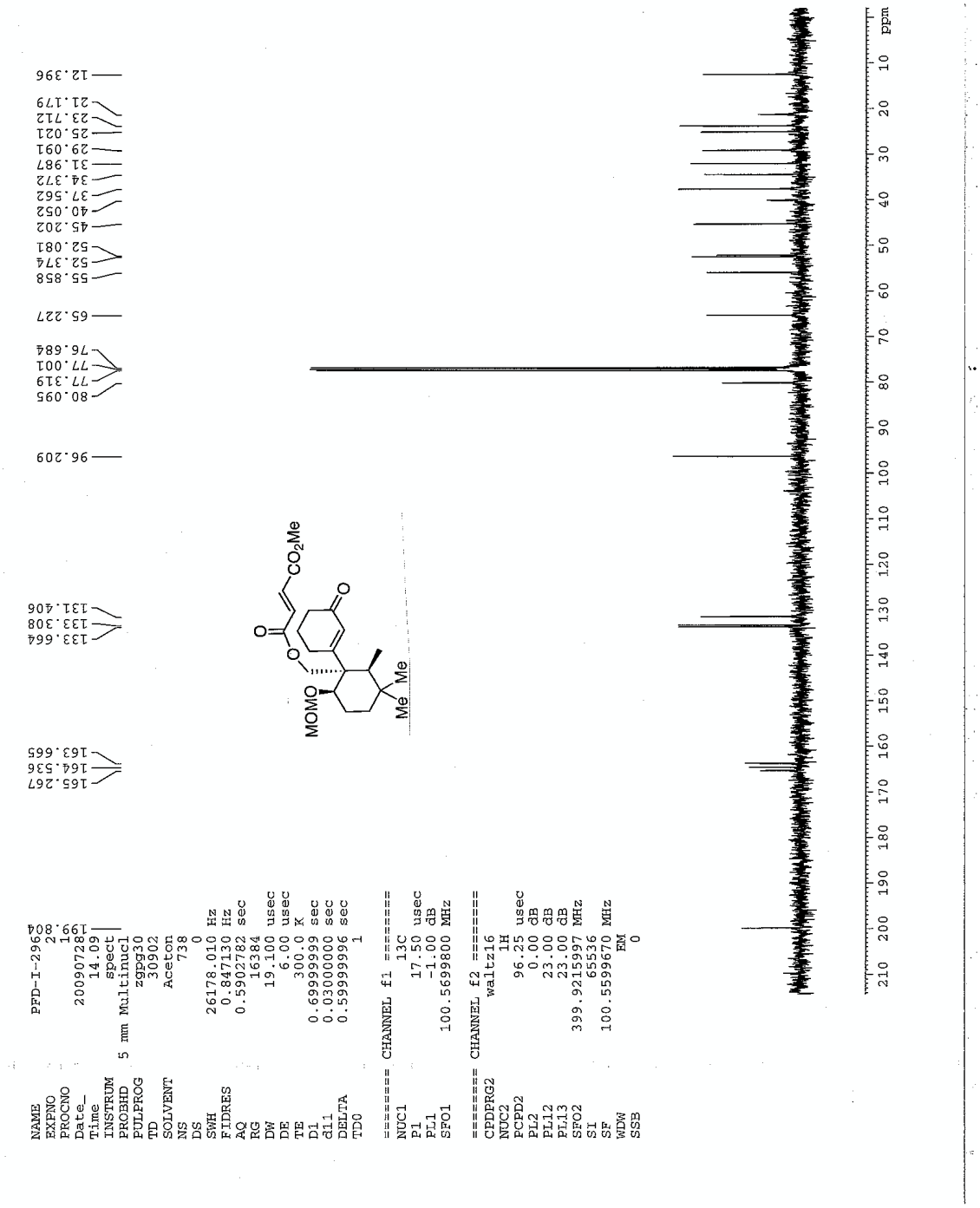
NAME	PFD-II-52
EXPNO	1
PROCNO	1
Date_	20090729
Time	21.44
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	D2O
NS	32
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	299.9 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200110 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00

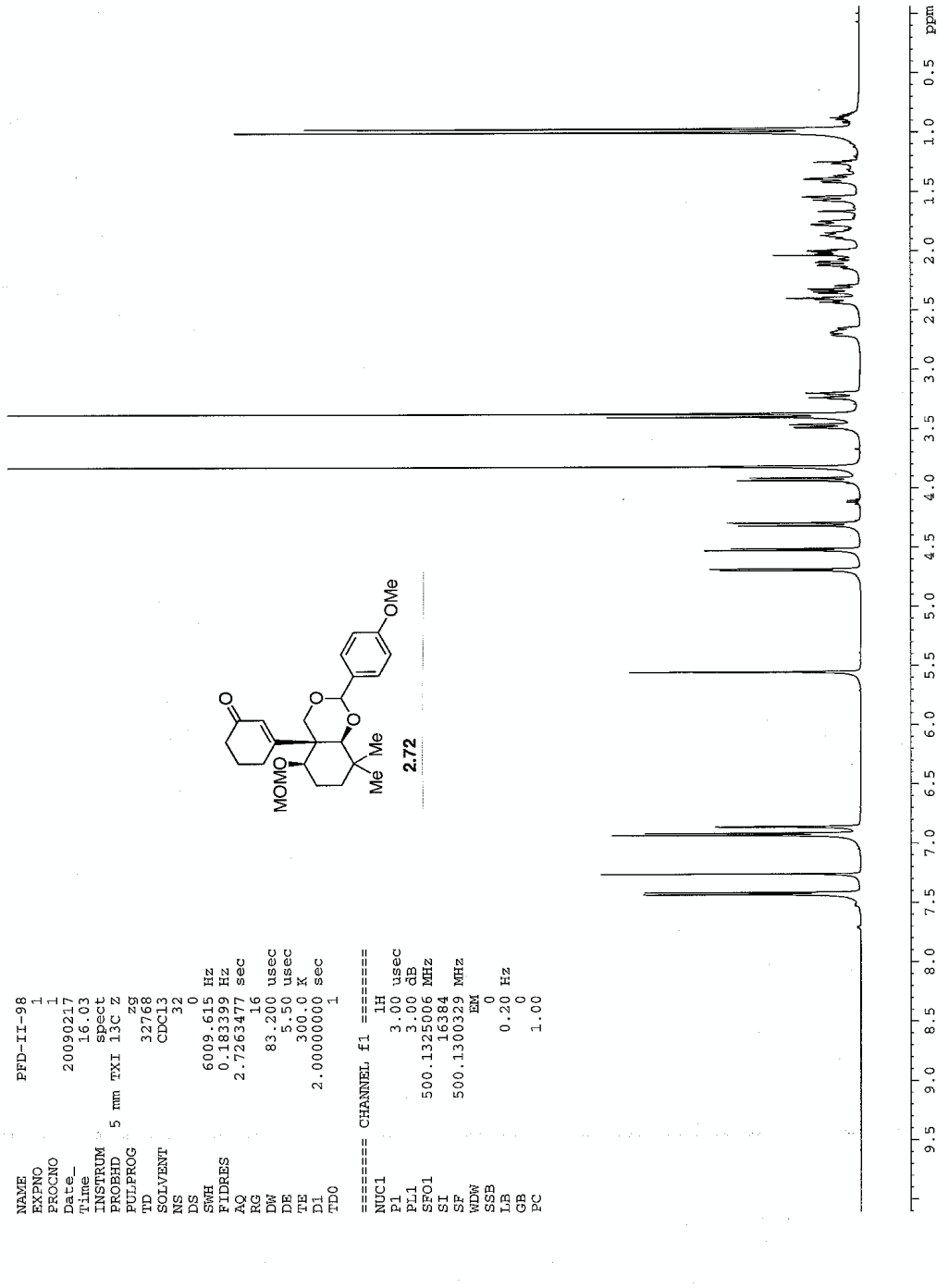


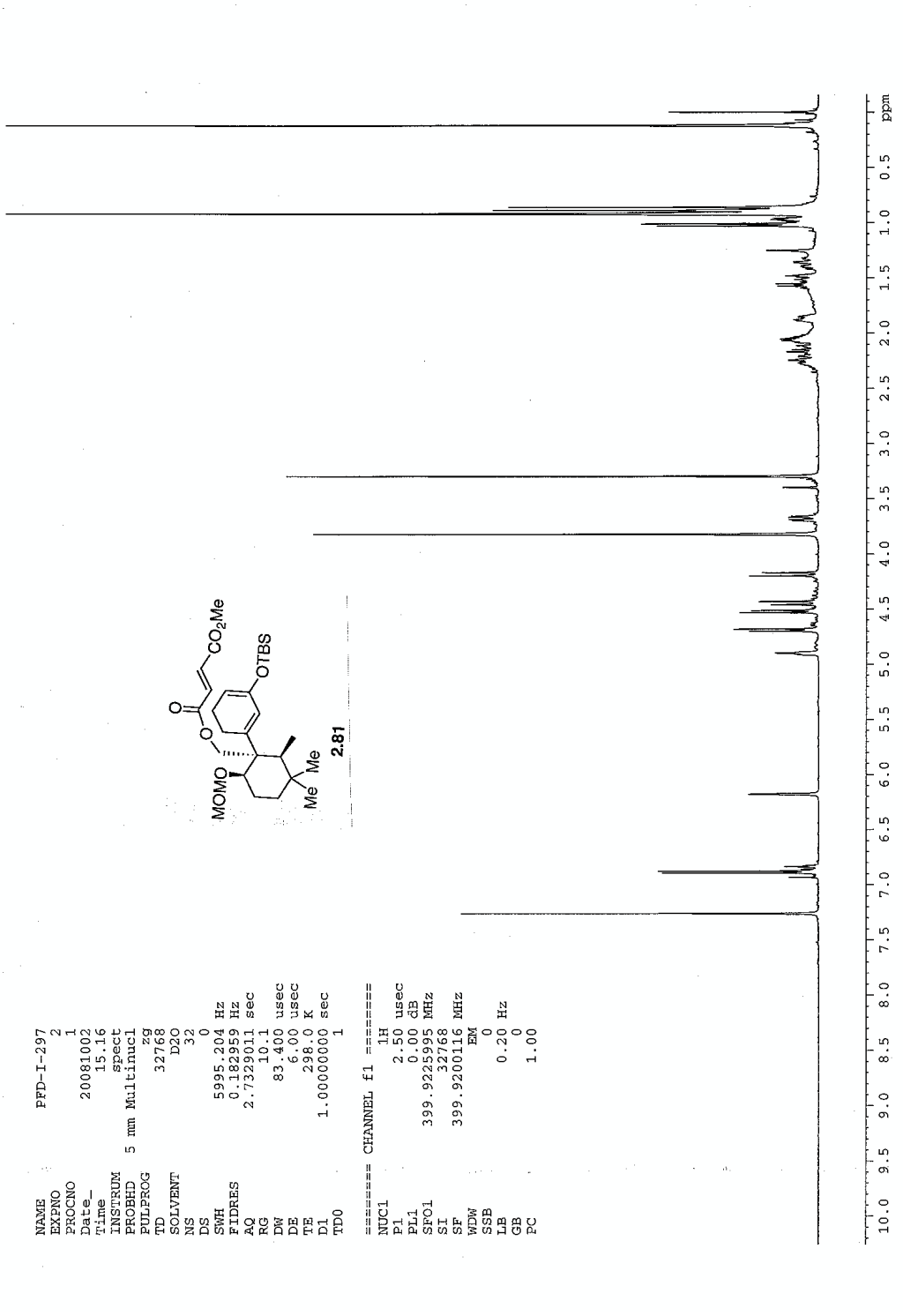

NAME PFD-II-52
EXPNO 2
PROCNO 1
Date_ 20090729
Time_ 21.48
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 1484
DS 0
SWH 26178.010 Hz
FIDRES 0.847130 Hz
AQ 0.5902782 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 96.25 usec
PL2 0.00 dB
PL12 23.00 dB
PL13 23.00 dB
SFO2 399.9215997 MHz
SI 65536
SF 100.5599671 MHz
WDW EM
SSB 0
159.457
144.749
142.455
138.268
129.205
121.293
114.439
112.624
94.905
77.320
77.002
76.685
73.782
59.743
55.242
54.890
34.468
34.356
28.414
26.815
25.171
MOMO
OMe
OH
Me
Me
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

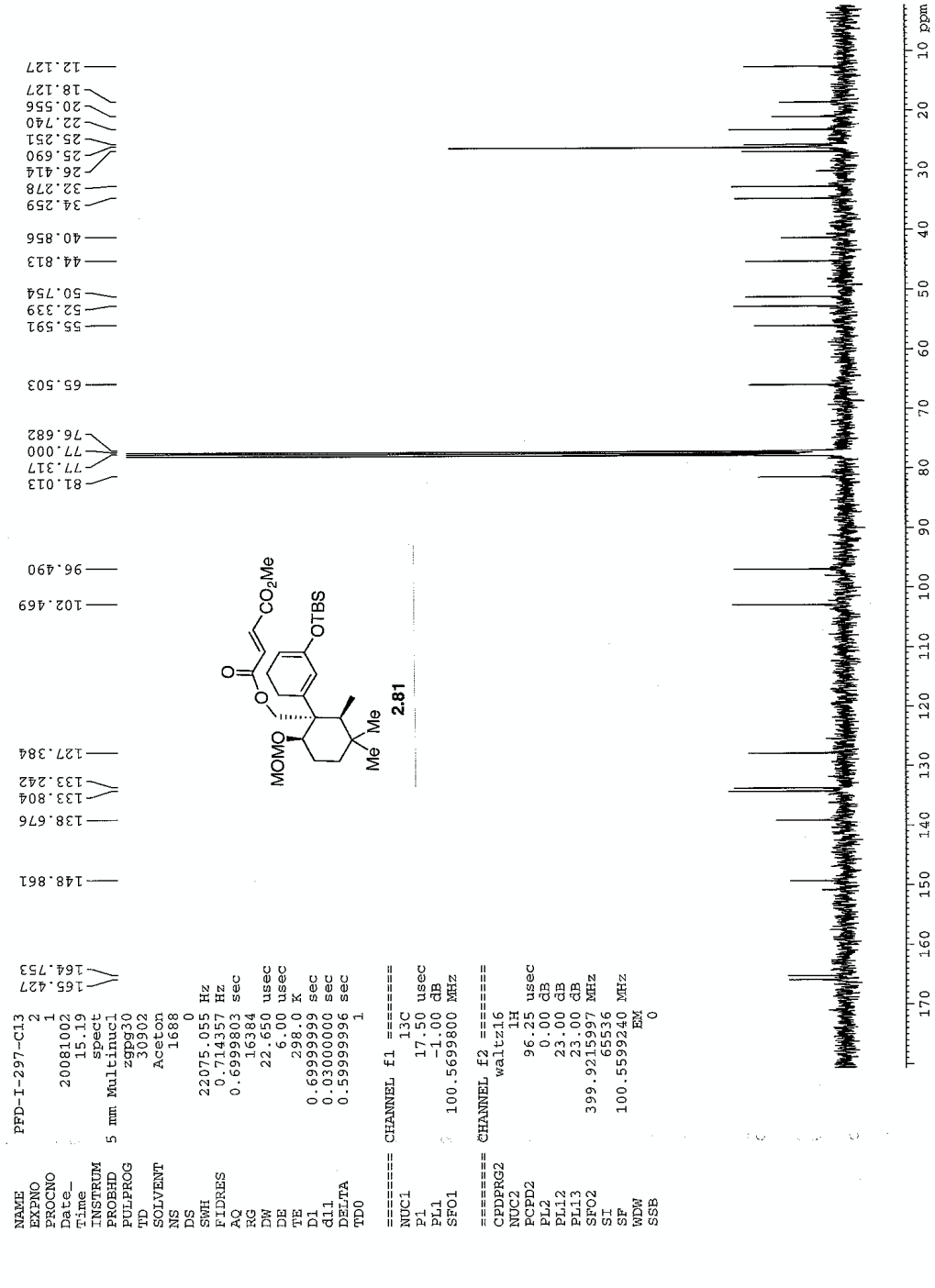

NAME PFD-I-220
EXPNO 1
PROCNO 1
Date_ 20080714
Time_ 9.22
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT D2O
NS 30
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 10.1
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 2.50 usec
PL1 0.00 dB
SFO1 399.9225995 MHz
SI 32768
SF 399.9200000 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40
OH
MOMO
Me
Me
OMe
2.60
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 0.5 ppm


NAME PFD-I-220-C13
EXPNO 1
PROCNO 1
Date_ 20080714
Time 9.25
INSTRUM spect
PROBHD 5 mm Multinuc1
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 397
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.6999803 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 96.25 usec
PL2 0.00 dB
PL12 23.00 dB
PL13 23.00 dB
SFO2 399.9215997 MHz
SI 65536
SF 100.5599715 MHz
WDW EM
SSB 0
2.60
MOMO
OH
Me
Me
OMe
24.866
30.083
31.326
36.890
38.481
55.040
55.857
56.304
66.493
76.684
77.002
77.321
80.509
96.773
110.759
110.822
115.392
121.423
128.546
143.037
154.594
159.015
ppm


NAME PFD-I-296
EXPNO 2
PROCNO 1
Date_ 20090728
Time_ 14.09
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 738
DS 0
SWH 26178.010 Hz
FIDRES 0.847130 Hz
AQ 0.5902782 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 96.25 usec
PL2 0.00 dB
PL12 23.00 dB
PL13 23.00 dB
SFO2 399.9215997 MHz
SI 65536
SF 100.5599670 MHz
WDW EM
SSB 0
MOMO
Me Me
CO2Me
165.267
164.536
163.665
133.664
133.308
131.406
96.209
80.095
77.319
77.001
76.684
65.227
55.858
52.374
52.081
45.202
40.052
37.562
34.372
31.987
29.091
25.021
23.712
21.179
12.396
ppm

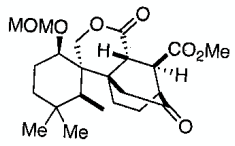

NAME PFD-II-98
EXPNO 1
PROCNO 1
Date_ 20090217
Time 16.03
INSTRUM spect
PROBHD 5 mm TXI 13C z
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 16
DW 83.200 usec
DE 5.50 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 3.00 dB
SFO1 500.1325006 MHz
SI 16384
SF 500.1300329 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
MOMO
Me
Me
OMe
2.72
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 0.5 ppm


NAME PFD-I-297
EXPNO 2
PROCNO 1
Date_ 20081002
Time 15.16
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT D2O
NS 32
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 10.1
DW 83.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 2.50 usec
PL1 0.00 dB
SFO1 399.9225995 MHz
SI 32768
SF 399.9200116 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
CO2Me
OTBS
MOMO
Me
Me
2.81
10.0 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 0.5 ppm


NAME PFD-I-297-C13
EXPNO 2
PROCNO 1
Date_ 20081002
Time 15.19
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 1688
DS 0
SWH 22075.055 Hz
FIDRES 0.714357 Hz
AQ 0.6999803 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 298.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 96.25 usec
PL2 0.00 dB
PL12 23.00 dB
PL13 23.00 dB
SFO2 399.9215997 MHz
SI 65536
SF 100.5599240 MHz
WDW EM
SSB 0
MOMO
OTBS
CO2Me
Me
Me
2.81
165.427
164.753
148.861
138.676
133.804
133.242
127.384
102.469
96.490
81.013
77.317
77.000
76.682
65.503
55.591
52.339
50.754
44.813
40.856
34.259
32.278
26.414
25.690
25.251
22.740
20.556
18.127
12.127
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

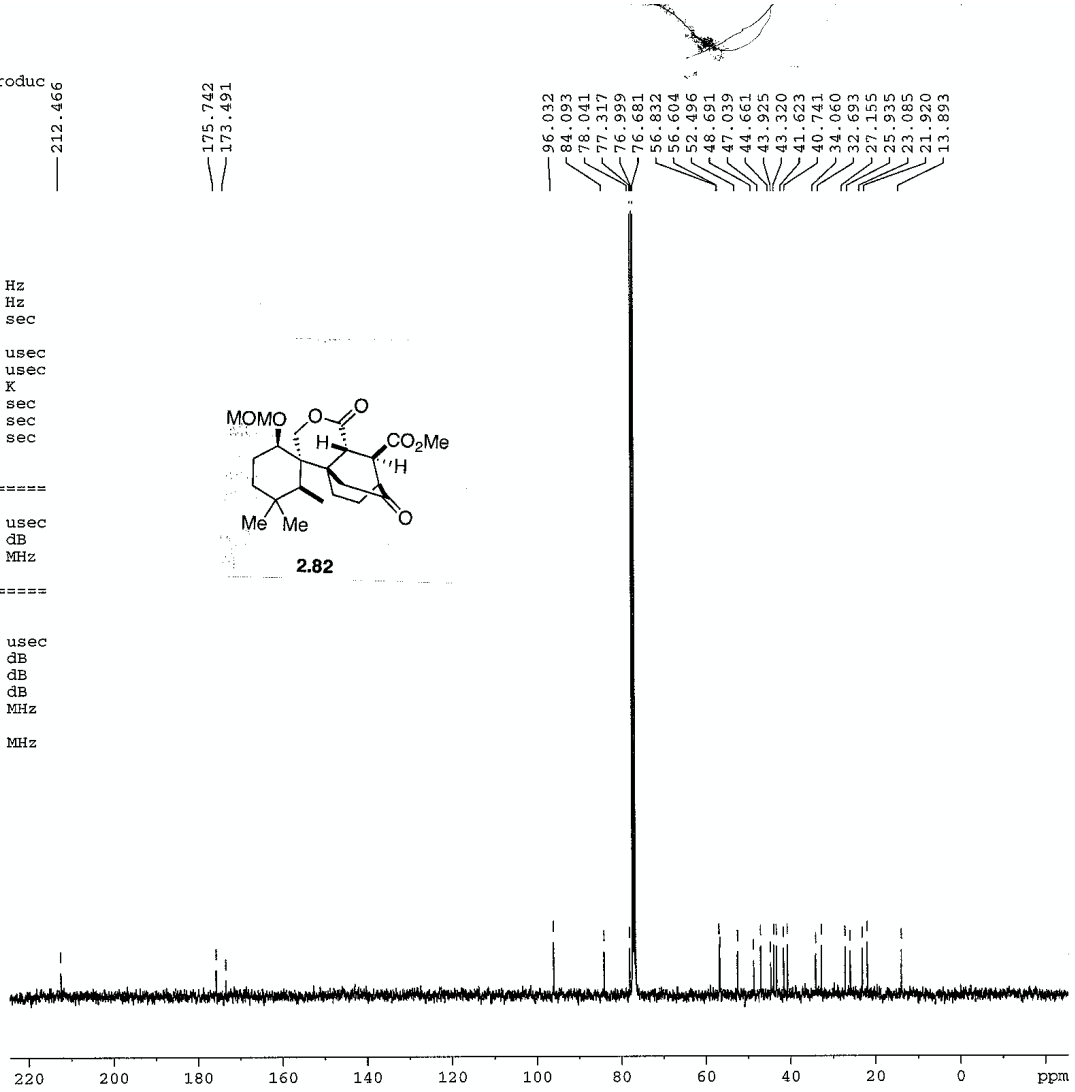
proton 400Mhz

```
Current Data Parameters
NAME      PFD-I-298-r2-product
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20081006
Time              21.00
INSTRUM           spect
PROBHD   5 mm Multinucl
PULPROG             zg
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH             5995.204 Hz
FIDRES          0.182959 Hz
AQ             2.7329011 sec
RG                 10.1
DW                83.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                2.50 usec
PL1               0.00 dB
SFO1        399.9225995 MHz

F2 - Processing parameters
SI                32768
SF          399.9200000 MHz
```



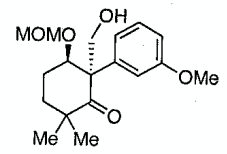
2.82

NAME	PFD-I-298-r2-produc	
EXPNO	1	
PROCNO	1	
Date_	20081006	212.466
Time	21.15	
INSTRUM	spect	
PROBHD	5 mm Multinucl	
PULPROG	zgpg30	
TD	30902	
SOLVENT	Aceton	
NS	4614	
DS	0	
SWH	25125.629	Hz
FIDRES	0.813074	Hz
AQ	0.6149998	sec
RG	16384	
DW	19.900	usec
DE	6.00	usec
TE	298.0	K
D1	0.69999999	sec
d11	0.03000000	sec
DELTA	0.59999996	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	17.50	usec
PL1	-1.00	dB
SFO1	100.5699800	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	96.25	usec
PL2	0.00	dB
PL12	23.00	dB
PL13	23.00	dB
SFO2	399.9215997	MHz
SI	65536	
SF	100.5599669	MHz
WDW	EM	
SSB	0	

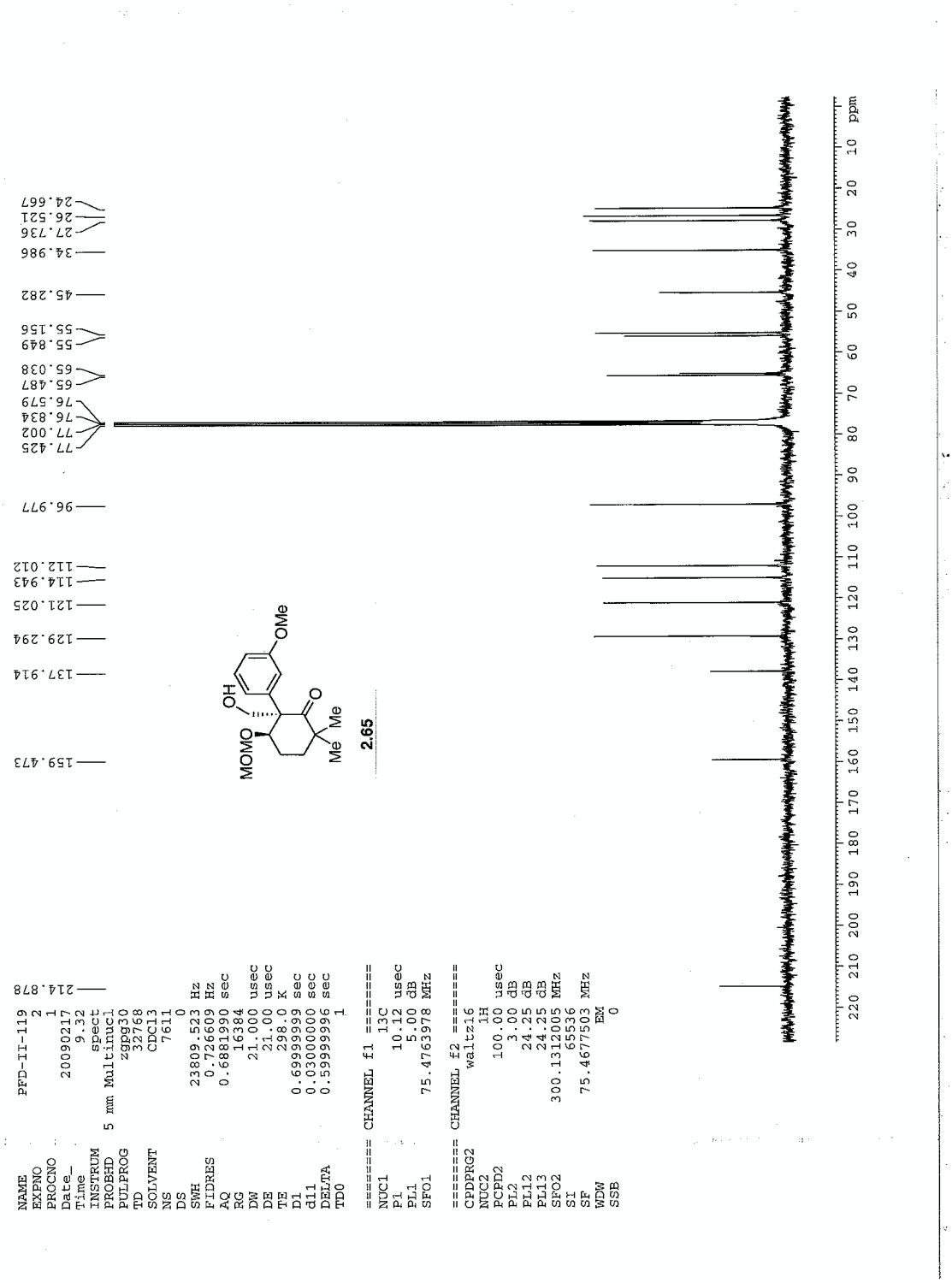


2.82

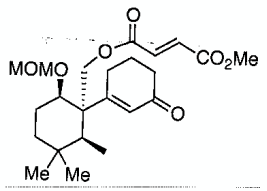
NAME	PFD-II-119
EXPNO	1
PROCNO	1
Date_	20090217
Time	9.30
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	22522
SOLVENT	CDCl3
NS	13
DS	0
SWH	4496.403 Hz
FIDRES	0.199645 Hz
AQ	2.5046077 sec
RG	256
DW	111.200 usec
DE	6.00 usec
TE	298.0 K
D1	0.10000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	3.00 dB
SFO1	300.1321009 MHz
SI	32768
SF	300.1300063 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00

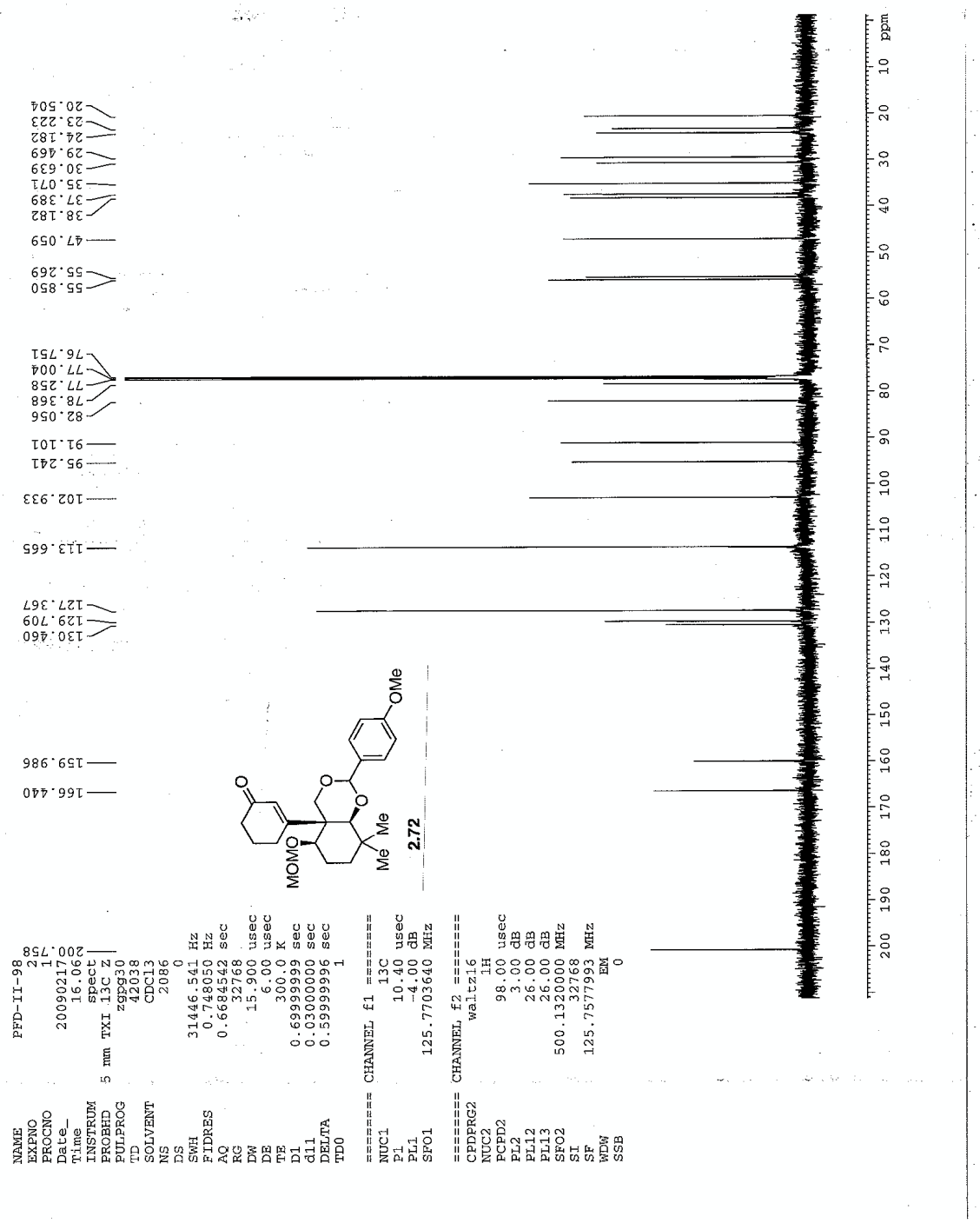


2.65

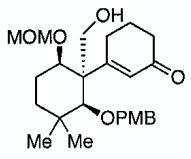

NAME PFD-II-119
EXPNO 2
PROCNO 1
Date_ 20090217
Time 9.32
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 7611
DS 0
SWH 23809.523 Hz
FIDRES 0.726609 Hz
AQ 0.68811990 sec
RG 16384
DW 21.000 usec
DE 21.00 usec
TE 298.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.12 usec
PL1 5.00 dB
SFO1 75.4763978 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 24.25 dB
PL13 24.25 dB
SFO2 300.1312005 MHz
SI 65536
SF 75.4677503 MHz
WDW EM
SSB 0
214.878
159.473
137.914
129.294
121.025
114.943
112.012
96.977
77.425
77.002
76.834
76.579
65.487
65.038
55.849
55.156
45.282
34.986
27.736
26.521
24.667
OMe
OH
O
MOM
Me Me
2.65
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

NAME	PFD-I-296
EXPNO	1
PROCNO	1
Date_	20090728
Time	14.06
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	30
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	10.1
DW	83.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	2.50 usec
PL1	0.00 dB
SFO1	399.9225995 MHz
SI	32768
SF	399.9200111 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00

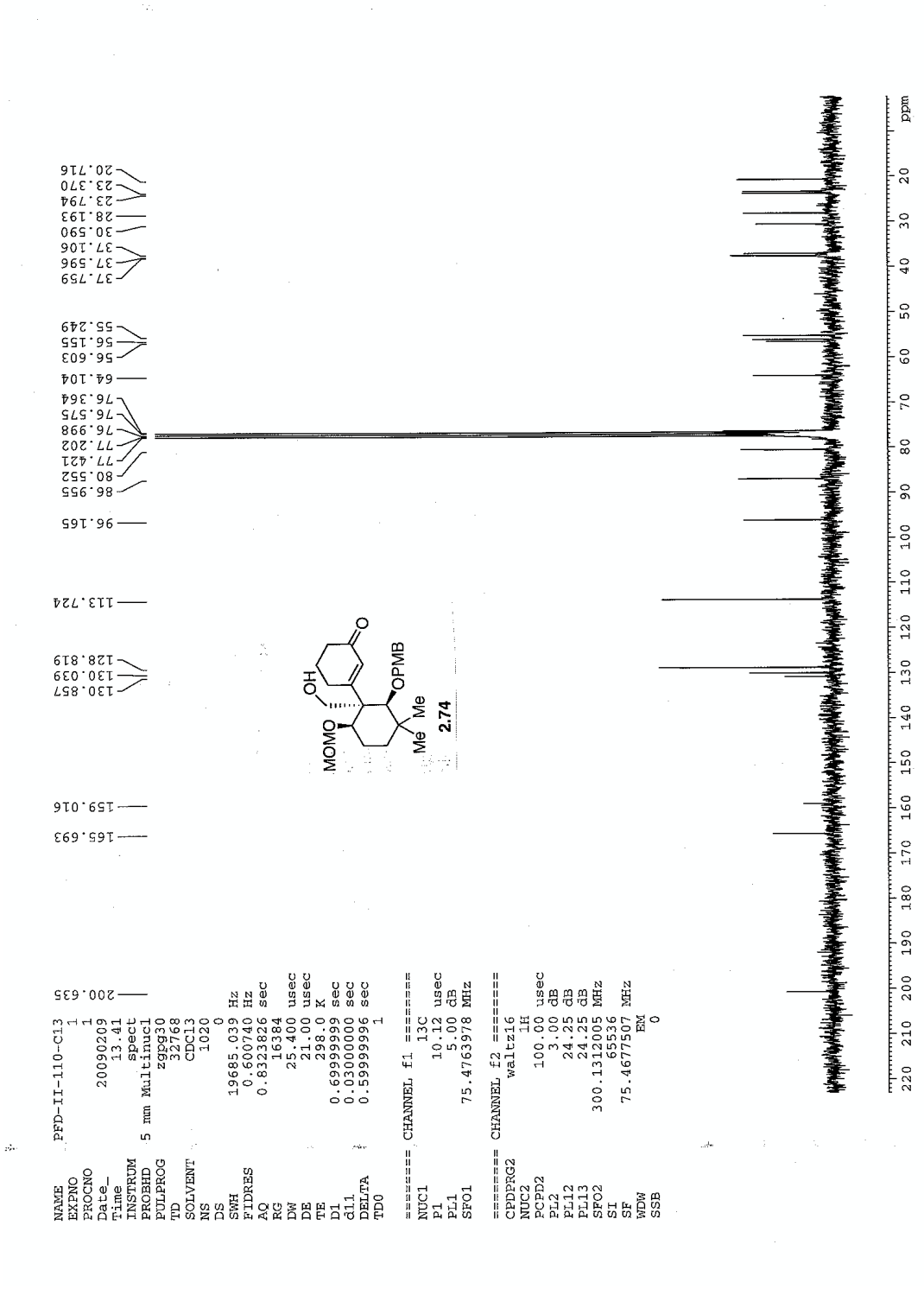



NAME PFD-II-98
EXPNO 2
PROCNO 1
Date_ 20090217
Time 16.06
INSTRUM spect
PROBHD 5 mm TXI 13C z
PULPROG zgpg30
TD 42038
SOLVENT CDCl3
NS 2086
DS 0
SWH 31446.541 Hz
FIDRES 0.748050 Hz
AQ 0.6684542 sec
RG 32768
DW 15.900 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.40 usec
PL1 4.00 dB
SFO1 125.7703640 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 98.00 usec
PL2 3.00 dB
PL12 26.00 dB
PL13 26.00 dB
SFO2 500.1320000 MHz
SI 32768
SF 125.7577993 MHz
WDW EM
SSB 0
MOMO
Me Me
Me
OMe
2.72
166.440
159.986
130.460
129.709
127.367
113.665
102.933
95.241
91.101
82.056
78.368
77.258
77.004
76.751
55.850
55.269
47.059
38.182
37.389
35.071
30.639
29.469
24.182
23.223
20.504
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

NAME	PDF-II-110
EXPNO	1
PROCNO	1
Date_	20090209
Time	13.06
INSTRUM	spect
PROBHD	5 mm QNP 1H/1
PULPROG	zg
TD	28900
SOLVENT	Aceton
NS	25
DS	0
SWH	4816.956 Hz
FIDRES	0.166677 Hz
AQ	2.9998701 sec
RG	32
DW	103.800 usec
DE	6.00 usec
TE	1664.2 K
D1	0.10000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	3.00 usec
PL1	-2.00 dB
SFO1	300.1321009 MHz
SI	16384
SF	300.1300062 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



2.74


NAME PFD-II-110-C13
EXPNO 1
PROCNO 1
Date_ 20090209
Time 13.41
INSTRUM spect
PROBHD 5 mm Multinuc1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1020
DS 0
SWH 19685.039 Hz
FIDRES 0.600740 Hz
AQ 0.8323826 sec
RG 16384
DW 25.400 usec
DE 21.00 usec
TE 298.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.12 usec
PL1 5.00 dB
SFO1 75.4763978 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 24.25 dB
PL13 24.25 dB
SFO2 300.1312005 MHz
SI 65536
SF 75.4677507 MHz
WDW EM
SSB 0
200.635
165.693
159.016
130.857
130.039
128.819
113.724
96.165
86.955
80.552
77.421
77.202
76.998
76.575
76.364
64.104
56.603
56.155
55.249
37.759
37.596
37.106
30.590
28.193
23.794
23.370
20.716
OH
MOMO
OPMB
Me
Me
2.74
ppm

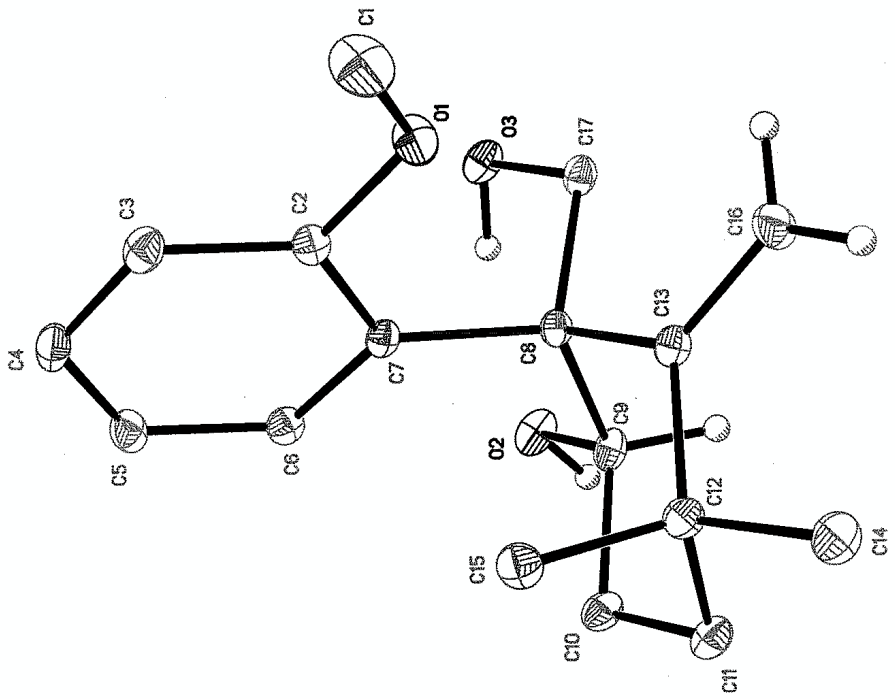

C1
O1
O3
C17
C3
C2
C16
C4
C7
C8
C13
C9
O2
C12
C14
C15
C10
C11
C5
C6

Table 1. Crystal data and structure refinement for fps10.

Identification code	fps10
Empirical formula	$C_{17}H_{24}O_3$
Formula weight	276.36
Temperature	125(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.2406(19) Å alpha = 90° b = 14.273(2) Å beta = 100.285(3)° c = 9.6195(16) Å gamma = 90°
Volume, Z	1518.5(4) $Å^3$, 4
Density (calculated)	1.209 Mg/m^3
Absorption coefficient	0.081 mm^{-1}
F(000)	600
Crystal size	0.37 x 0.10 x 0.02 mm
Θ range for data collection	1.84 to 28.28°
Limiting indices	$-14 \le h \le 14$, $-19 \le k \le 18$, $-12 \le l \le 12$
Reflections collected	20394
Independent reflections	3753 (R_{int} = 0.0761)
Completeness to Θ = 28.28°	99.9 %
Absorption correction	EMPIRICAL
Max. and min. transmission	0.9984 and 0.9706
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3753 / 0 / 192
Goodness-of-fit on F^2	1.024
Final R indices [I>2σ(I)]	R1 = 0.0444, wR2 = 0.0958
R indices (all data)	R1 = 0.0927, wR2 = 0.1165
Largest diff. peak and hole	0.276 and -0.216 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for fps10. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	-2253(1)	143(1)	-671(1)	25(1)
O(2)	-1604(1)	2196(1)	-4756(1)	25(1)
O(3)	-686(1)	2274(1)	-2047(1)	23(1)
C(1)	-2629(2)	-462(2)	321(2)	37(1)
C(2)	-3057(1)	798(1)	-1327(2)	18(1)
C(3)	-4057(2)	1081(1)	-776(2)	22(1)
C(4)	-4813(2)	1771(1)	-1446(2)	23(1)
C(5)	-4561(2)	2177(1)	-2658(2)	22(1)
C(6)	-3569(2)	1880(1)	-3218(2)	19(1)
C(7)	-2803(1)	1174(1)	-2589(2)	16(1)
C(8)	-1677(1)	854(1)	-3172(2)	15(1)
C(9)	-1638(2)	1193(1)	-4702(2)	19(1)
C(10)	-2643(2)	786(1)	-5799(2)	22(1)
C(11)	-2527(2)	-278(1)	-5822(2)	23(1)
C(12)	-2472(2)	-742(1)	-4367(2)	20(1)
C(13)	-1538(2)	-225(1)	-3274(2)	18(1)
C(14)	-2131(2)	-1773(1)	-4525(2)	28(1)
C(15)	-3732(2)	-734(1)	-3952(2)	22(1)
C(16)	-601(2)	-669(1)	-2534(2)	26(1)
C(17)	-571(1)	1284(1)	-2195(2)	19(1)

Table 3. Bond lengths [Å] and angles [°] for fps10.

O(1)-C(2)	1.373(2)	O(1)-C(1)	1.407(2)
O(2)-C(9)	1.435(2)	O(3)-C(17)	1.429(2)
C(2)-C(3)	1.386(2)	C(2)-C(7)	1.402(2)
C(3)-C(4)	1.383(2)	C(4)-C(5)	1.377(2)
C(5)-C(6)	1.389(2)	C(6)-C(7)	1.392(2)
C(7)-C(8)	1.542(2)	C(8)-C(17)	1.546(2)
C(8)-C(13)	1.553(2)	C(8)-C(9)	1.556(2)
C(9)-C(10)	1.517(2)	C(10)-C(11)	1.525(2)
C(11)-C(12)	1.540(2)	C(12)-C(14)	1.535(2)
C(12)-C(13)	1.536(2)	C(12)-C(15)	1.539(2)
C(13)-C(16)	1.322(2)		

C(2)-O(1)-C(1)	118.47(14)	O(1)-C(2)-C(3)	122.33(15)
O(1)-C(2)-C(7)	116.07(14)	C(3)-C(2)-C(7)	121.60(15)
C(4)-C(3)-C(2)	120.16(16)	C(5)-C(4)-C(3)	119.49(16)
C(4)-C(5)-C(6)	120.12(16)	C(5)-C(6)-C(7)	121.91(16)
C(6)-C(7)-C(2)	116.65(15)	C(6)-C(7)-C(8)	122.63(14)
C(2)-C(7)-C(8)	120.60(14)	C(7)-C(8)-C(17)	106.56(12)
C(7)-C(8)-C(13)	114.50(13)	C(17)-C(8)-C(13)	110.62(13)
C(7)-C(8)-C(9)	114.56(13)	C(17)-C(8)-C(9)	107.23(13)
C(13)-C(8)-C(9)	103.21(12)	O(2)-C(9)-C(10)	112.25(14)
O(2)-C(9)-C(8)	110.51(13)	C(10)-C(9)-C(8)	113.32(13)
C(9)-C(10)-C(11)	109.66(14)	C(10)-C(11)-C(12)	113.87(14)
C(14)-C(12)-C(13)	112.13(14)	C(14)-C(12)-C(15)	106.90(14)
C(13)-C(12)-C(15)	111.53(13)	C(14)-C(12)-C(11)	106.99(14)
C(13)-C(12)-C(11)	109.10(13)	C(15)-C(12)-C(11)	110.07(14)
C(16)-C(13)-C(12)	121.29(15)	C(16)-C(13)-C(8)	121.39(15)
C(12)-C(13)-C(8)	117.09(14)	O(3)-C(17)-C(8)	112.08(13)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for fps10.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^*b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	24(1)	27(1)	25(1)	11(1)	9(1)	4(1)
O(2)	38(1)	16(1)	23(1)	2(1)	13(1)	-3(1)
O(3)	28(1)	16(1)	25(1)	-5(1)	9(1)	-6(1)
C(1)	36(1)	42(1)	35(1)	22(1)	10(1)	2(1)
C(2)	17(1)	15(1)	21(1)	-1(1)	3(1)	-1(1)
C(3)	23(1)	23(1)	22(1)	-1(1)	9(1)	-5(1)
C(4)	20(1)	24(1)	29(1)	-8(1)	10(1)	-1(1)
C(5)	21(1)	18(1)	28(1)	-3(1)	3(1)	4(1)
C(6)	21(1)	15(1)	19(1)	-1(1)	3(1)	0(1)
C(7)	17(1)	13(1)	18(1)	-3(1)	5(1)	-2(1)
C(8)	16(1)	13(1)	18(1)	0(1)	5(1)	1(1)
C(9)	24(1)	14(1)	21(1)	0(1)	10(1)	0(1)
C(10)	29(1)	22(1)	16(1)	1(1)	6(1)	0(1)
C(11)	26(1)	21(1)	22(1)	-5(1)	6(1)	-2(1)
C(12)	21(1)	15(1)	23(1)	-3(1)	2(1)	-1(1)
C(13)	19(1)	15(1)	20(1)	-1(1)	6(1)	-1(1)
C(14)	30(1)	18(1)	35(1)	-7(1)	2(1)	-1(1)
C(15)	20(1)	19(1)	26(1)	-2(1)	3(1)	-4(1)
C(16)	27(1)	18(1)	32(1)	-4(1)	-2(1)	5(1)
C(17)	18(1)	17(1)	23(1)	-3(1)	7(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for fps10.

	x	y	z	U(eq)
H(1A)	-2028	-959	572	56
H(1B)	-3410	-741	-87	56
H(1C)	-2713	-107	1171	56
H(3B)	-4224	800	64	27
H(4A)	-5502	1963	-1072	28
H(5A)	-5066	2662	-3111	27
H(6A)	-3407	2168	-4056	22
H(9A)	-859	963	-4940	23
H(10A)	-2592	1044	-6742	26
H(10B)	-3438	961	-5569	26
H(11A)	-1785	-443	-6189	27
H(11B)	-3225	-538	-6484	27
H(14A)	-2124	-2101	-3629	43
H(14B)	-1327	-1809	-4781	43
H(14C)	-2725	-2067	-5267	43
H(15A)	-3680	-1003	-3005	33
H(15B)	-4292	-1107	-4633	33
H(15C)	-4027	-88	-3953	33
H(16A)	-495	-1320	-2675	31
H(16B)	-33	-336	-1863	31
H(17A)	-478	986	-1252	23
H(17B)	167	1148	-2588	23
H(2A)	-1330(20)	2354(15)	-5560(20)	44(6)
H(3A)	-950(20)	2470(17)	-2930(30)	51(7)

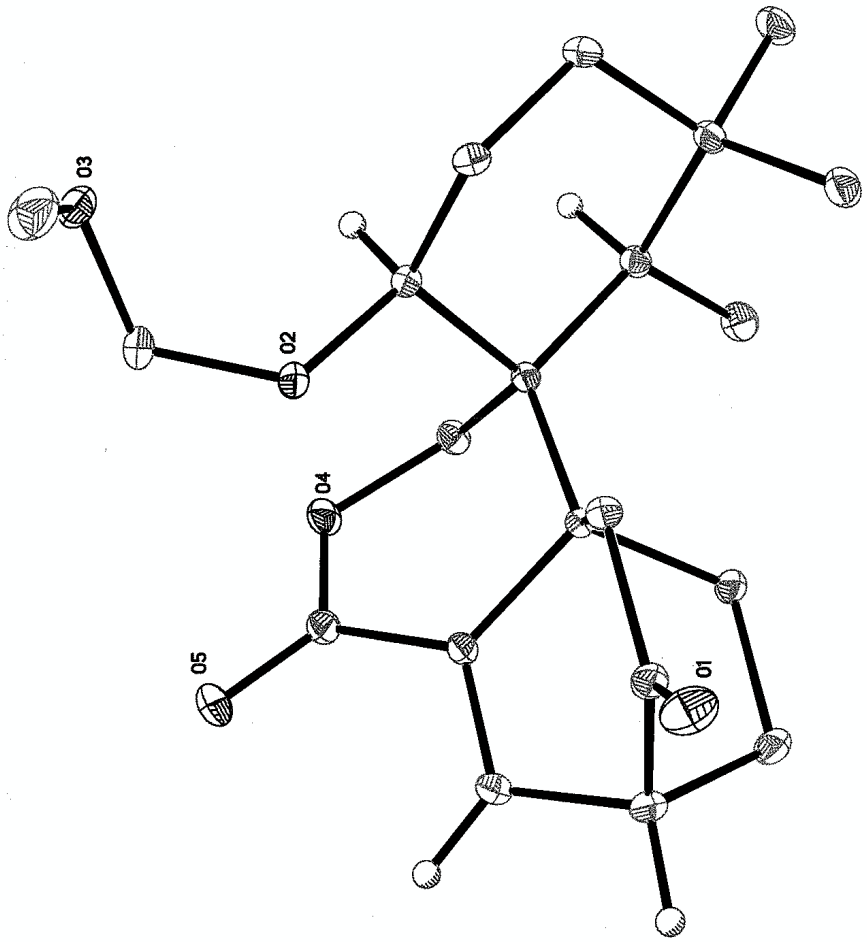

O3
O2
O4
O5
O1

Table 1. Crystal data and structure refinement for FENGWS10.

Identification code	fengws10
Empirical formula	$C_{21.50}H_{31}ClO_5$
Formula weight	404.91
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 27.8193(10) Å alpha = 90° b = 12.7116(5) Å beta = 97.0270(10)° c = 11.3549(4) Å gamma = 90°
Volume, Z	3985.2(3) Å^3, 8
Density (calculated)	1.350 Mg/m^3
Absorption coefficient	0.222 mm^{-1}
F(000)	1736
Crystal size	0.32 x 0.29 x 0.27 mm
Θ range for data collection	1.48 to 30.51°
Limiting indices	$-39 \le h \le 39$, $-18 \le k \le 18$, $-16 \le l \le 16$
Reflections collected	31578
Independent reflections	6088 (R_{int} = 0.0215)
Completeness to Θ = 30.51°	100.0 %
Absorption correction	EMPIRICAL
Max. and min. transmission	0.9424 and 0.9323
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6088 / 0 / 253
Goodness-of-fit on F^2	1.032
Final R indices [I>2σ(I)]	R1 = 0.0373, wR2 = 0.1031
R indices (all data)	R1 = 0.0428, wR2 = 0.1077
Largest diff. peak and hole	0.389 and -0.312 eÅ^{-3}

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for FENGWS10. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	3930(1)	5945(1)	3184(1)	38(1)
O(2)	3493(1)	2331(1)	1920(1)	25(1)
O(3)	3666(1)	1158(1)	432(1)	34(1)
O(4)	2656(1)	1938(1)	2967(1)	29(1)
O(5)	2351(1)	3148(1)	1695(1)	37(1)
C(1)	3665(1)	5268(1)	3492(1)	24(1)
C(2)	3170(1)	5475(1)	3878(1)	26(1)
C(3)	3217(1)	5111(1)	5194(1)	29(1)
C(4)	3358(1)	3933(1)	5301(1)	23(1)
C(5)	3412(1)	3442(1)	4063(1)	18(1)
C(6)	3487(1)	2209(1)	4085(1)	19(1)
C(7)	3775(1)	1609(1)	5185(1)	22(1)
C(8)	3579(1)	1737(1)	6391(1)	32(1)
C(9)	4339(1)	1620(1)	5322(1)	25(1)
C(10)	4576(1)	2666(1)	5742(1)	31(1)
C(11)	4524(1)	786(1)	6253(1)	36(1)
C(12)	4500(1)	1267(1)	4138(1)	29(1)
C(13)	4258(1)	1866(1)	3065(1)	25(1)
C(14)	3707(1)	1794(1)	2975(1)	21(1)
C(15)	3304(1)	1667(1)	976(1)	30(1)
C(16)	3913(1)	1852(1)	-265(1)	45(1)
C(17)	2971(1)	1747(1)	4052(1)	25(1)
C(18)	2630(1)	2941(1)	2569(1)	26(1)
C(19)	2944(1)	3715(1)	3260(1)	22(1)
C(20)	2829(1)	4739(1)	3173(1)	26(1)
C(21)	3804(1)	4114(1)	3556(1)	21(1)
C(22)	0	-106(1)	7500	44(1)
Cl	282(1)	672(1)	8673(1)	55(1)

Table 3. Bond lengths [Å] and angles [°] for FENGWS10.

O(1)-C(1)	1.2140(13)	O(2)-C(15)	1.4145(12)
O(2)-C(14)	1.4417(11)	O(3)-C(15)	1.4015(13)
O(3)-C(16)	1.4181(16)	O(4)-C(18)	1.3511(13)
O(4)-C(17)	1.4431(12)	O(5)-C(18)	1.2107(12)
C(1)-C(21)	1.5163(12)	C(1)-C(2)	1.5163(14)
C(2)-C(20)	1.4931(14)	C(2)-C(3)	1.5553(14)
C(3)-C(4)	1.5483(14)	C(4)-C(5)	1.5627(12)
C(5)-C(19)	1.5348(12)	C(5)-C(21)	1.5521(12)
C(5)-C(6)	1.5814(12)	C(6)-C(17)	1.5465(12)
C(6)-C(14)	1.5591(12)	C(6)-C(7)	1.5929(12)
C(7)-C(8)	1.5421(14)	C(7)-C(9)	1.5586(13)
C(9)-C(10)	1.5340(14)	C(9)-C(12)	1.5347(14)
C(9)-C(11)	1.5409(14)	C(12)-C(13)	1.5220(14)
C(13)-C(14)	1.5289(13)	C(18)-C(19)	1.4767(13)
C(19)-C(20)	1.3405(13)	C(22)-Cl#1	1.7639(11)
C(22)-Cl	1.7639(11)		

C(15)-O(2)-C(14)	115.07(7)	C(15)-O(3)-C(16)	112.44(9)
C(18)-O(4)-C(17)	116.56(7)	O(1)-C(1)-C(21)	122.54(9)
O(1)-C(1)-C(2)	124.46(9)	C(21)-C(1)-C(2)	112.98(8)
C(20)-C(2)-C(1)	106.02(8)	C(20)-C(2)-C(3)	107.57(8)
C(1)-C(2)-C(3)	104.69(8)	C(4)-C(3)-C(2)	110.69(7)
C(3)-C(4)-C(5)	111.52(7)	C(19)-C(5)-C(21)	103.91(7)
C(19)-C(5)-C(4)	106.05(7)	C(21)-C(5)-C(4)	105.24(7)
C(19)-C(5)-C(6)	109.57(7)	C(21)-C(5)-C(6)	116.97(7)
C(4)-C(5)-C(6)	114.10(7)	C(17)-C(6)-C(14)	107.78(7)
C(17)-C(6)-C(5)	104.79(7)	C(14)-C(6)-C(5)	112.76(7)
C(17)-C(6)-C(7)	102.27(7)	C(14)-C(6)-C(7)	105.27(7)
C(5)-C(6)-C(7)	122.73(7)	C(8)-C(7)-C(9)	111.78(8)
C(8)-C(7)-C(6)	116.60(8)	C(9)-C(7)-C(6)	118.46(7)
C(10)-C(9)-C(12)	111.46(9)	C(10)-C(9)-C(11)	106.74(8)
C(12)-C(9)-C(11)	106.93(8)	C(10)-C(9)-C(7)	115.36(8)
C(12)-C(9)-C(7)	107.96(7)	C(11)-C(9)-C(7)	108.01(8)
C(13)-C(12)-C(9)	114.04(8)	C(12)-C(13)-C(14)	111.36(8)
O(2)-C(14)-C(13)	109.57(8)	O(2)-C(14)-C(6)	110.43(7)
C(13)-C(14)-C(6)	114.51(7)	O(3)-C(15)-O(2)	112.92(9)
O(4)-C(17)-C(6)	114.97(8)	O(5)-C(18)-O(4)	118.84(9)
O(5)-C(18)-C(19)	124.64(10)	O(4)-C(18)-C(19)	116.52(8)
C(20)-C(19)-C(18)	119.24(8)	C(20)-C(19)-C(5)	116.06(8)
C(18)-C(19)-C(5)	124.67(8)	C(19)-C(20)-C(2)	116.07(8)
C(1)-C(21)-C(5)	111.21(7)	Cl#1-C(22)-Cl	111.77(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+3/2

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for FENGWS10.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2$ [$(ha^*)^2U_{11}$ + ... + $2hka^*b^*U_{12}$]

	U11	U22	U33	U23	U13	U12
O(1)	47(1)	23(1)	46(1)	4(1)	14(1)	-2(1)
O(2)	30(1)	24(1)	18(1)	-3(1)	-2(1)	4(1)
O(3)	51(1)	27(1)	24(1)	-4(1)	4(1)	8(1)
O(4)	22(1)	29(1)	32(1)	-2(1)	-5(1)	-4(1)
O(5)	30(1)	44(1)	32(1)	-2(1)	-11(1)	2(1)
C(1)	31(1)	20(1)	21(1)	1(1)	2(1)	2(1)
C(2)	31(1)	21(1)	26(1)	-2(1)	2(1)	8(1)
C(3)	37(1)	26(1)	24(1)	-5(1)	5(1)	6(1)
C(4)	28(1)	23(1)	18(1)	-2(1)	3(1)	2(1)
C(5)	18(1)	18(1)	17(1)	0(1)	1(1)	2(1)
C(6)	18(1)	18(1)	19(1)	0(1)	1(1)	0(1)
C(7)	24(1)	19(1)	21(1)	2(1)	0(1)	1(1)
C(8)	39(1)	34(1)	22(1)	8(1)	4(1)	3(1)
C(9)	24(1)	22(1)	26(1)	0(1)	-5(1)	3(1)
C(10)	28(1)	27(1)	36(1)	-2(1)	-7(1)	-1(1)
C(11)	38(1)	29(1)	37(1)	5(1)	-11(1)	7(1)
C(12)	24(1)	28(1)	34(1)	-3(1)	-1(1)	8(1)
C(13)	23(1)	27(1)	27(1)	-3(1)	5(1)	5(1)
C(14)	24(1)	20(1)	19(1)	-2(1)	0(1)	2(1)
C(15)	34(1)	34(1)	22(1)	-7(1)	-2(1)	0(1)
C(16)	62(1)	45(1)	32(1)	2(1)	17(1)	9(1)
C(17)	21(1)	26(1)	27(1)	1(1)	1(1)	-3(1)
C(18)	20(1)	31(1)	26(1)	-4(1)	-1(1)	2(1)
C(19)	19(1)	26(1)	19(1)	-1(1)	0(1)	3(1)
C(20)	24(1)	28(1)	26(1)	0(1)	-1(1)	8(1)
C(21)	22(1)	18(1)	23(1)	1(1)	4(1)	2(1)
C(22)	39(1)	31(1)	64(1)	0	17(1)	0
Cl	59(1)	50(1)	61(1)	-7(1)	20(1)	-8(1)

Chapter 3 Synthesis of Maoecrystal V Pentacyclic Core Structure

The undesired facial selectivity of the IMDA reaction is a serious problem to our first approach toward Maoecrystal V, since cycloadduct **2.82** or **2.84** could not be used to elaborate to the final natural product with the right relative stereochemistry. We were at a cross point whether to kill this project or to explore a new route to solve this problem. We decided to take this great challenge and develop a modified route to achieve a diastereoselective synthesis of the Maoecrystal V core structure.

3.1 IMDA Using a Symmetric Precursor

Although the IMDA reaction proceeded with the undesired sense of facial selectivity, it indeed afforded the bicyclo-[2.2.2] octane core substructure of Maoecrystal V. Since it was not quite clear what is the exact factor controlling the facial selectivity in our previous key IMDA reaction due to the rotamer character of the IMDA precursor, we envisioned that it would be very difficult to redesign a new IMDA precursor which would only afford us the desired facial adduct.[1] We then turned our attention to the comparison of the stereochemistry of desired and undesired adducts, hoping to find some clues to solve this problem.

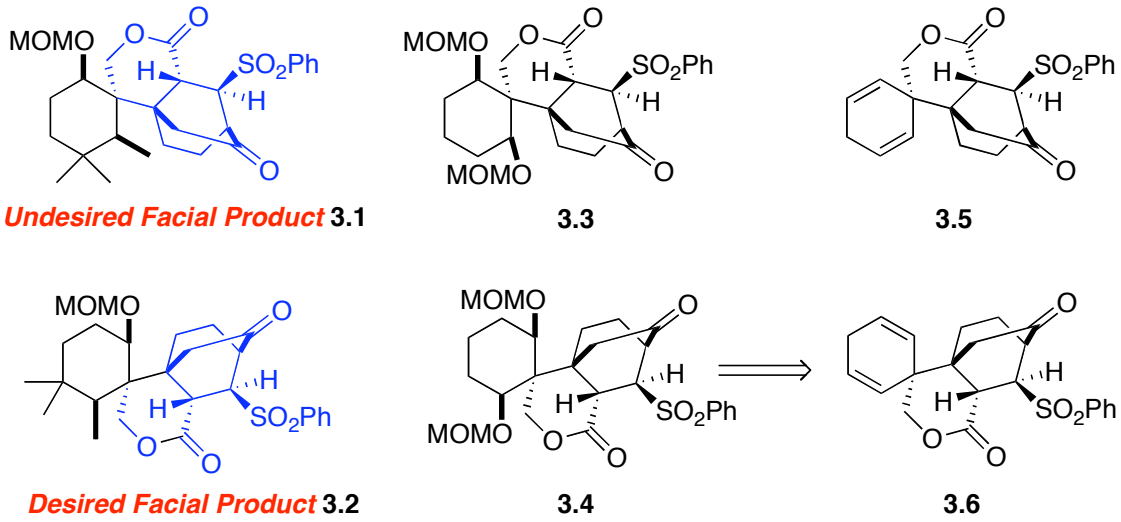
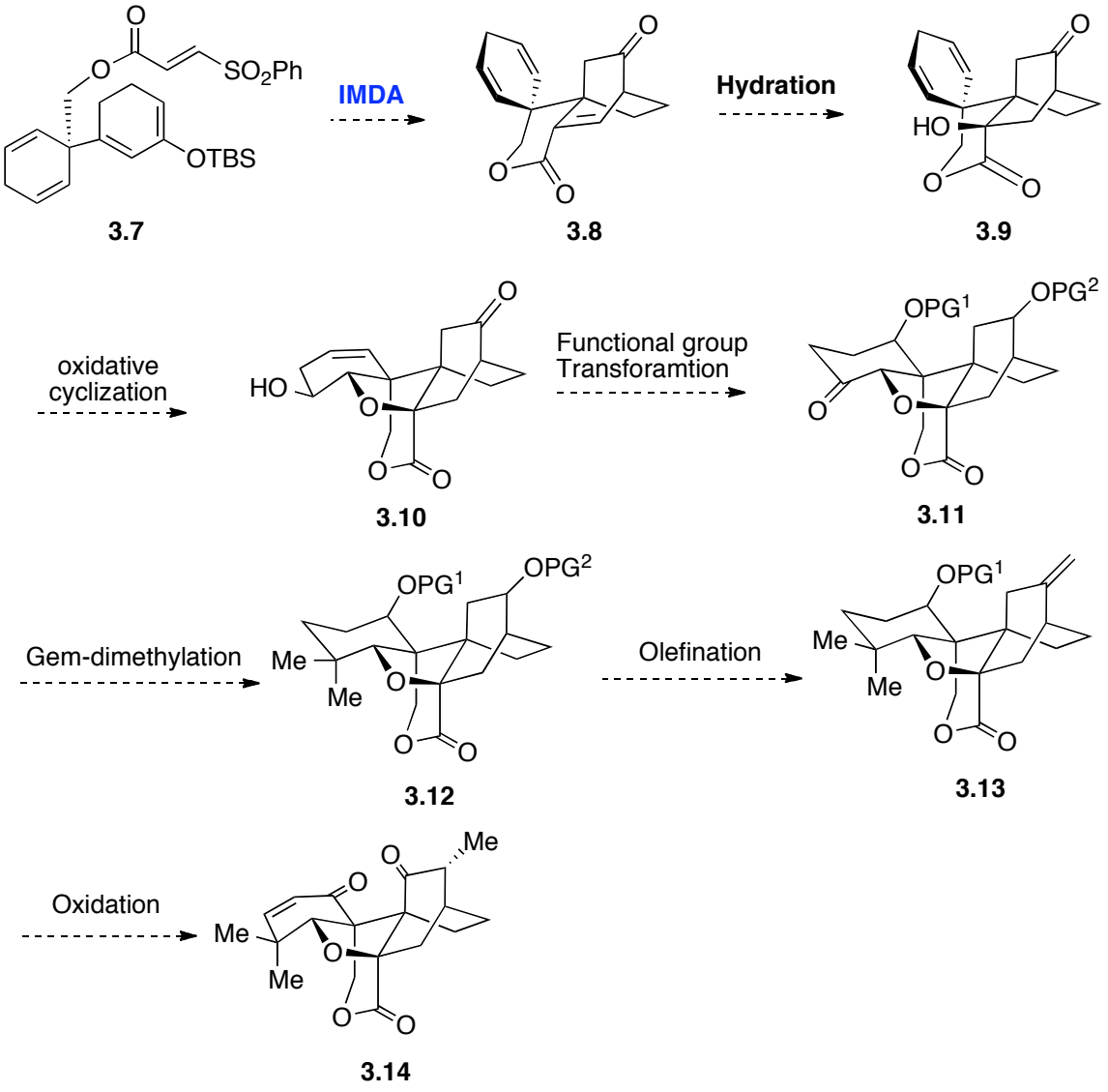


Figure 3-1 Symmetry logic to solve IMDA facial problem

As shown in the **Figure 3-1**, we soon noticed the right part substructure from both undesired facial product and the desired facial product, which has a lactone ring and a bicyclo-[2.2.2] octane motif (in blue color), shared mirror symmetry character. If the left A-ring was also a symmetric structure such as **3.3** and **3.4**, then the cycloadducts would share a mirror symmetry character totally and they were enantiomers.[2] We further envisioned that compounds **3.3** and **3.4** could be prepared from compounds **3.5** and **3.6** respectively by sequential oxidation of the alkenes.

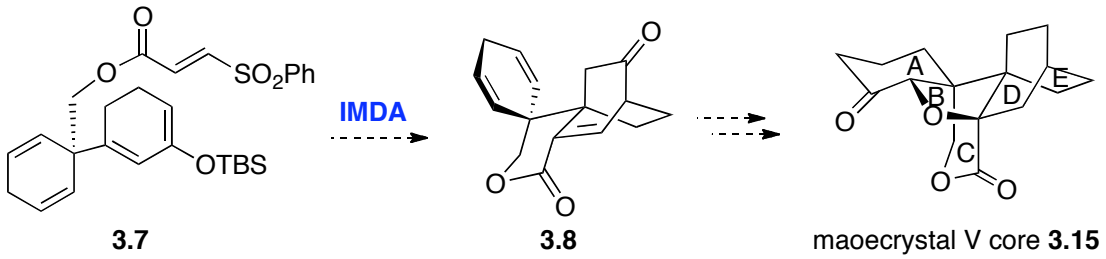
From this analysis, we then designed a new route (Scheme 3-1), featuring using an IMDA reaction with a symmetric precursor **3.7**. After IMDA reaction, a tetracyclic core **3.8** would be obtained. Selective hydration of the enone alkene would provide tertiary alcohol **3.9**, in which the stereochemistry may be directed by C-16 ketone function group.

At this stage, a key oxidative cyclization reaction through a 5-*exo* ring closure would afford compound **3.10**,[3] which upon functional group transformation would provide **3.11**. The C-4 ketone in **3.11** then would be used to prepare gem-dimethyl group, a concept was introduced by Oppolzer in his longifolene synthesis.[4] With **3.12** in hand, an olefination reaction and the following oxidation state tuning would eventually afford Maoecrystal V.



Scheme 3-1 Second generation synthetic plan toward Maoecrystal V

In order to prove our new design, we began to explore the possibility to prepare a pentacyclic core model structure **3.15** with the appropriate relative stereochemistry (Scheme 3-2), which we envisioned it would be a big challenge in the Maoecrystal V synthesis.

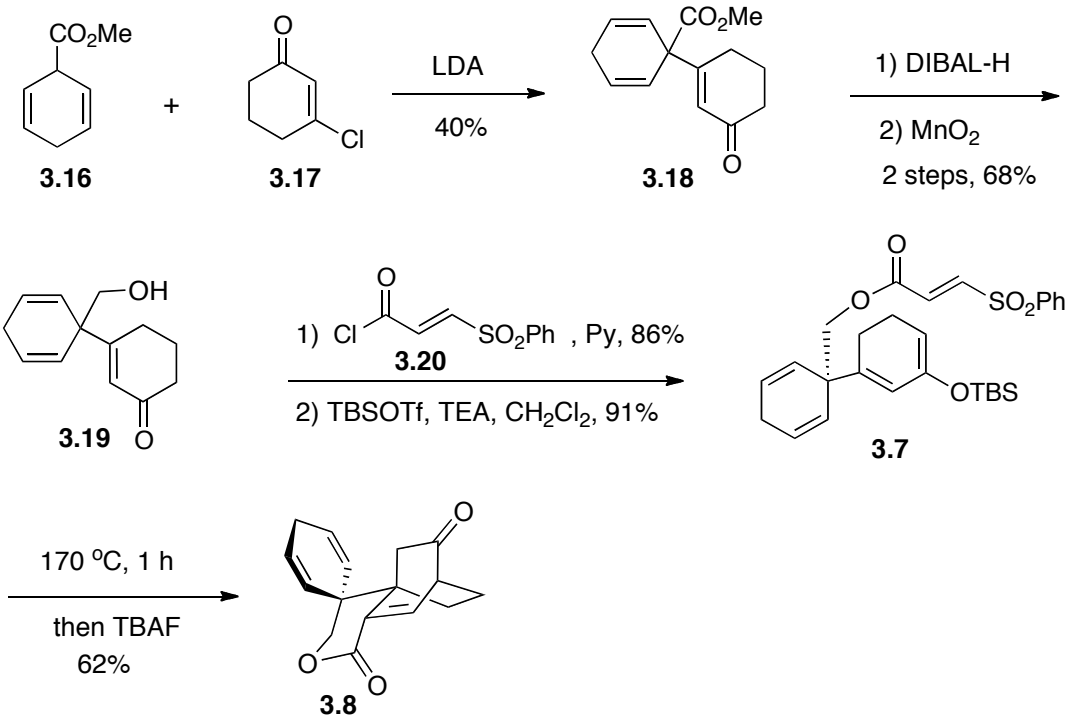


3.7 **3.8** maoecrystal V core **3.15**

Scheme 3-2 Plan to synthesize Maoecrystal V core structure

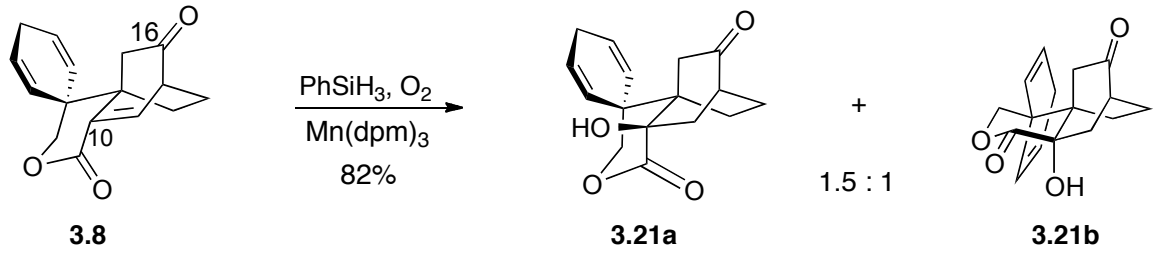
3.2 Results and Discussions

Our new route to the IMDA precursor **3.7** started with a Birch-type vinylogous acylation between substrate **3.16** and **3.17**,[5] which afforded compound **3.18**, possessing one of the requisite quaternary carbon centers. Intermediate **3.18** was subjected to global DIBAL-H reduction, followed by selective MnO_2-mediated reoxidation of the resultant allylic alcohol, to provided **3.19**. Esterification of compound **3.19** with acyl chloride **3.20** [6] followed by formation of the TBS enol ether, furnished our IMDA precursor **3.7**. The thermo-promoted Diels-Alder reaction of compound **3.7** went on smoothly and without isolation, the cycloadduct was treated with TBAF, which furnished key intermediate **3.8** in 62% yield.



Scheme 3-3 Preparation of **3.8**

We then turned to the emplacement of the requisite C-10 tertiary alcohol. We first tested our proposed hydration reaction, which took place through a cascade 1,4-reduction/oxidation sequence,[7] and we obtained the desired tertiary alcohol **3.21** as a 1.5:1 diastereomeric mixture of compound **3.21a** and **3.21b**.



Scheme 3-4 Hydration of alkene **3.8**

The poor diastereoselectivity probably arose from the enol oxidation step, in which the stereo-bias caused by C-11 and C-15 were not significant (Figure 3-2).[8] Thus a larger difference between C-11 and C-15 might improve the diastereoselectivity of this hydration process. Based this hypothesis, we prepared compound **3.23** and subjected it to the hydration process.

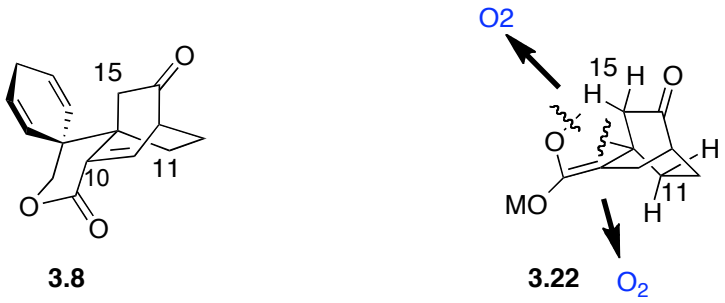
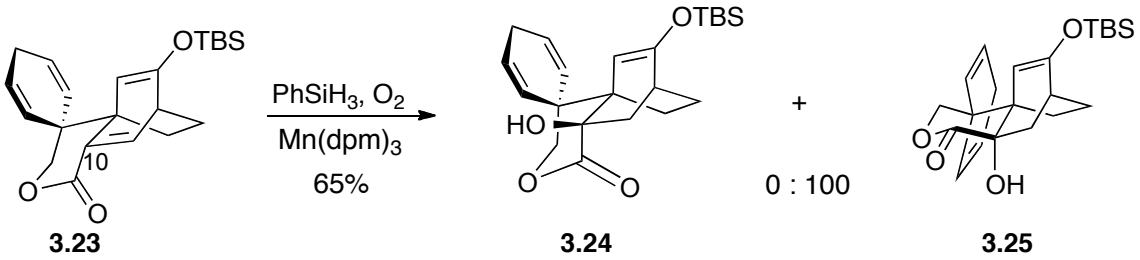


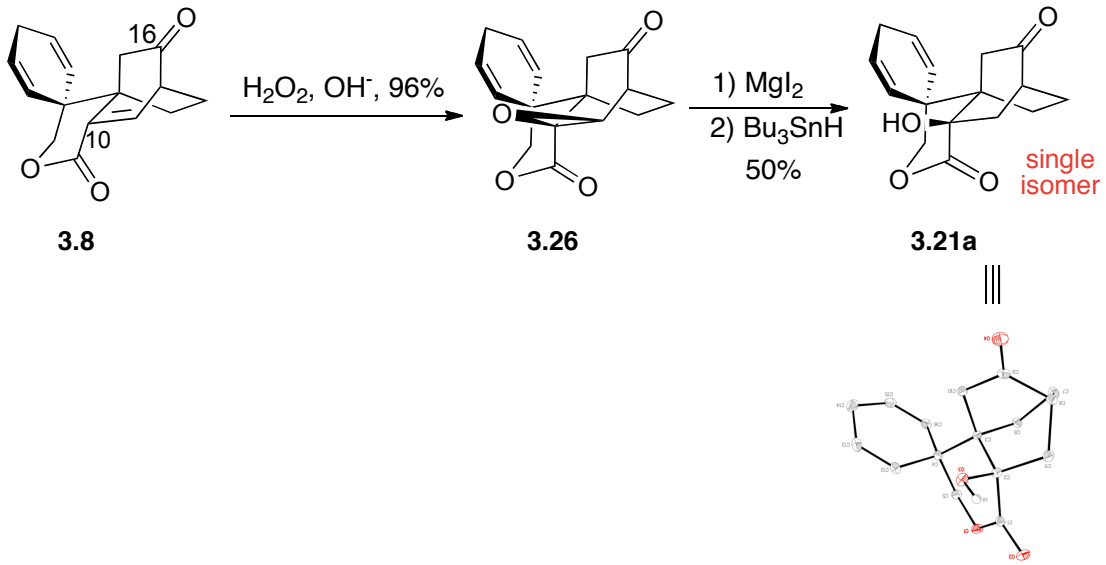
Figure 3-2 Explanation of stereoselectivity of hydration

In this case, we did obtain a single diastereomer, however, it was the undesired isomer (**3.25**).



Scheme 3-5 Hydration reaction of **3.23**

While the direct hydration process met with difficulty to afford **3.21a** as a single isomer, it was soon found that epoxidation of **3.8** with H_2O_2 provided epoxide **3.26** as a single isomer. Upon exposure to sequential epoxide opening and reduction of the resultant iodohydrin, epoxide **3.26** was converted to **3.21a** as a single diastereoisomer.[9]



Scheme 3-6 Preparation **3.21a**

We thought there might be two reasons to account for the stereoselective epoxidation of compound **3.8** (Figure 3-3). First, the stereo-bias between the C-12 and C-16 now was significant and obvious the C-12 β–hydrogen atom probably blocked the β-facial nucleophilic attack. Second, σ bond between C-12 and C-13 had more donating effect to the σ^* of the new formed C-O bond than σ bond between C-16 and C-13, which is called Cieplak effect.[10]

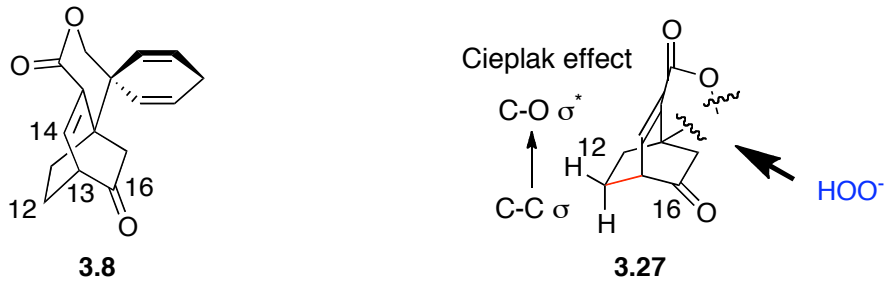
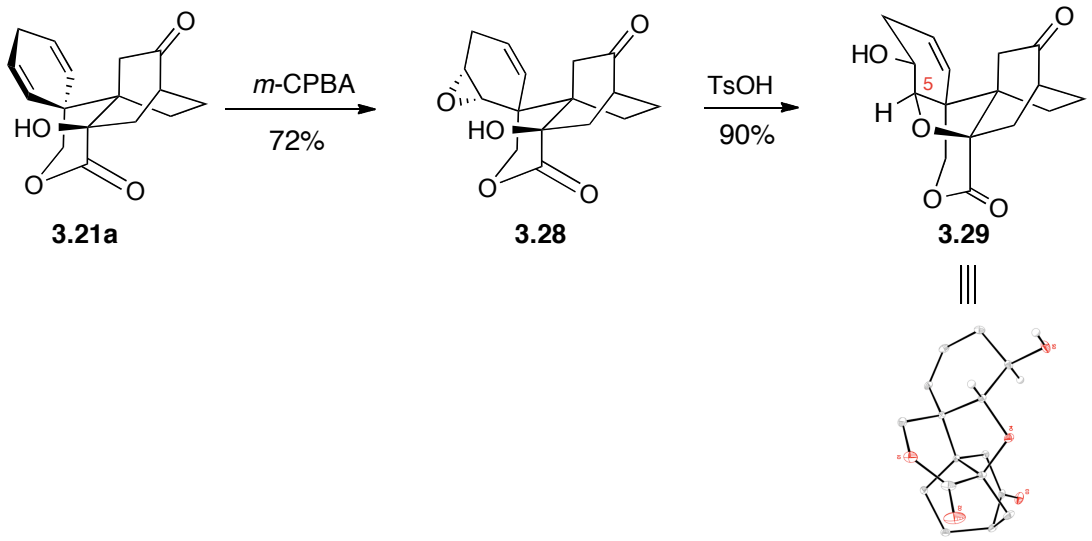


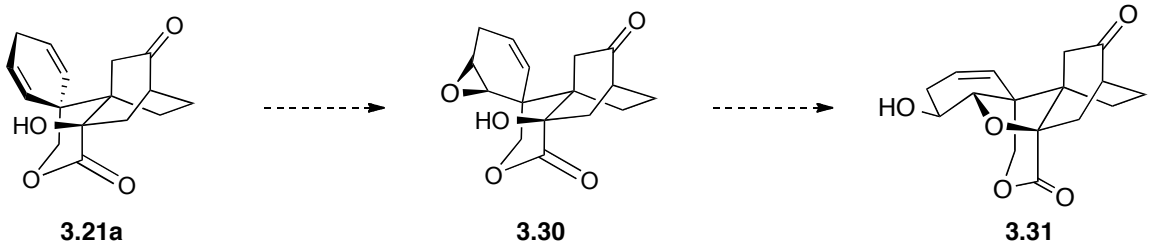
Figure 3-3 Explanation of stereoselectivity of epoxidation of **3.8**

With compound **3.21a** in hand, our effort now was focused on ring closure of the THF ring. Initially we screened a lot of electrophiles such as I_2, NIS, PhSeCl, NBS, Br_2, Hg(TFA), $Pb(OAc)_4$, and $Pd(OAc)_2$, hoping to achieve a ring closure through the activation of the A-ring-5-*exo* alkene moiety. To our disappointment, none of these conditions afforded a desired ring closure product, either starting material was recovered (eg: I_2, NIS, $Pd(OAc)_2$,), or decomposition of material was observed (eg: $Hg(TFA)_2$, $Pb(OAc)_4$, PhSeBr). Further screening revealed that *m*-CPBA reacted with **3.21a** and provided epoxide **3.28** as a single isomer. Following treatment with *p*-TsOH•H_2O,[11] a cyclized product (**3.29)** was obtained as a single diastereomer. X-ray analysis indicated that the stereochemistry at C 5 was opposite as that required for Maeocrystal V.



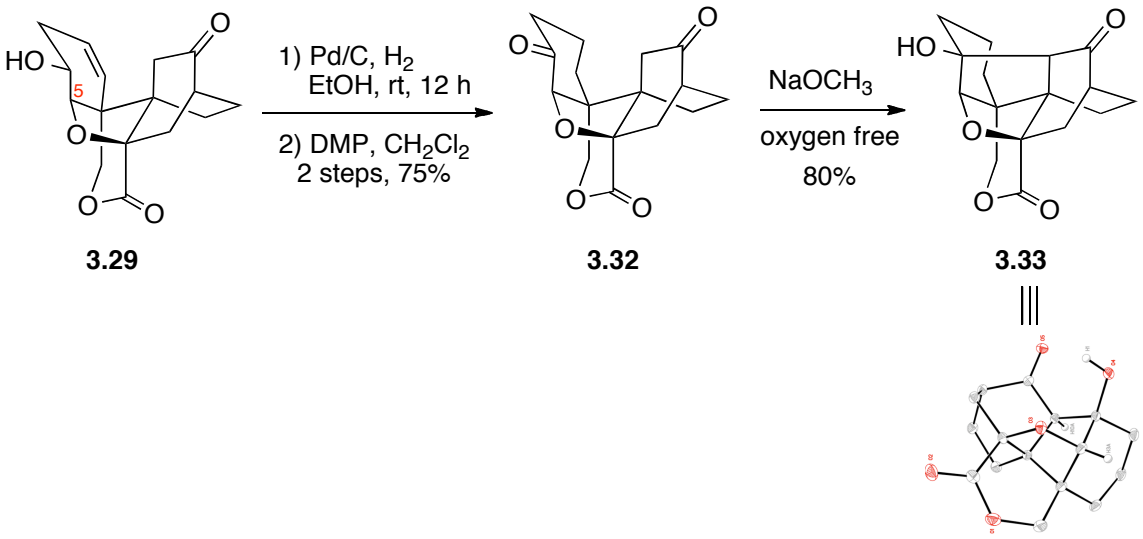
Scheme 3-7 Preparation of **3.29**

To correct the C-5 stereocenter, our initial plan was to prepare *β*-epoxide **3.30**, which a trans diaxial opening of epoxide would provide desired compound **3.31**. We then screened several epoxidation conditions such as Payne epoxidation[12] and hydroxyl-directed epoxidation[13]; unfortunately, we only recovered our starting material. These results indicated that the *β*-face of the A-ring was very congested and reagents could not reach it.



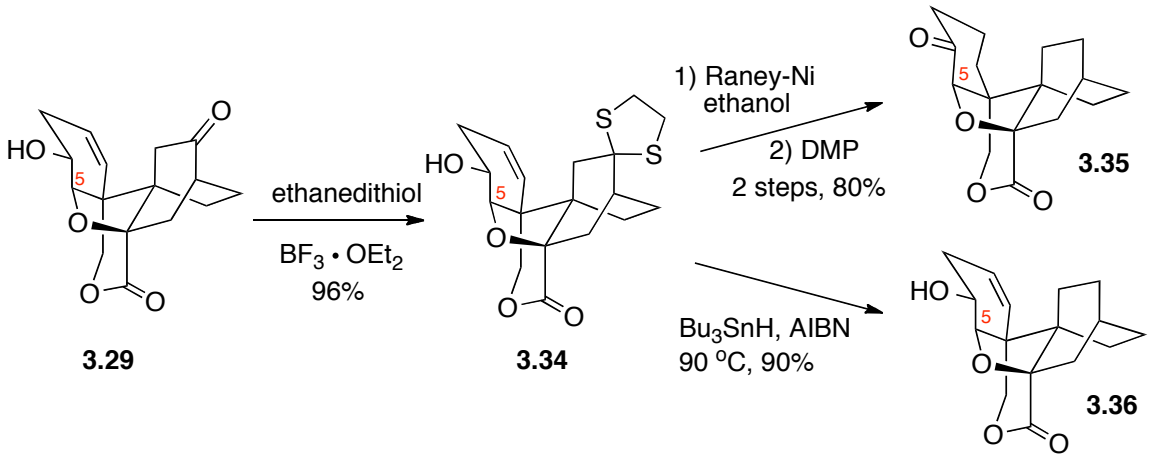
Scheme 3-8 *β*-Epoxide to form *trans* ring junction

We then turned our efforts to correct the C-5 center on compound **3.29**, hoping to achieve an epimerization reaction on C-5. We first prepared compound **3.32** through a hydrogenation and oxidation sequence on which we planed to test a base-promoted epimerization reaction.[14] After careful degassing oxygen (with trace oxygen, hydroxylation of ketone α position was observed.), compound **3.32** was subjected to NaOMe condition and to our delight, a new compound **3.33** was isolated in about 80% yield. However, X-ray crystallography results revealed structure **3.33** as shown. Instead of epimerization, a transannular aldol reaction occurred.



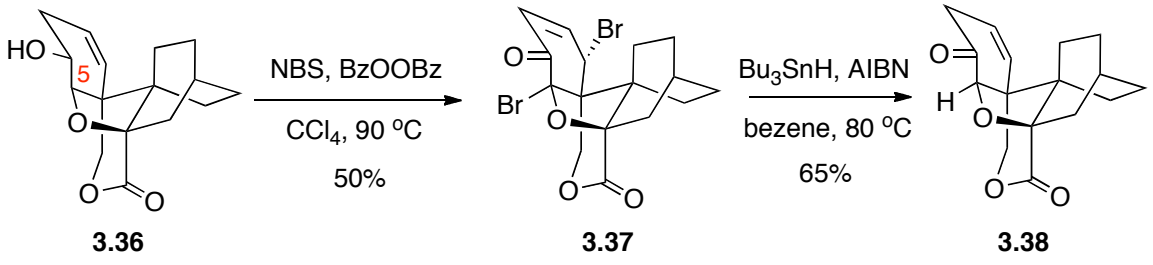
Scheme 3-9 Epimerization of **3.32**

In order to circumvent the undesired aldol reaction, we then reduced the C-16 ketone functional group to a methylene through a dithioketal intermediate **3.34**. Compound **3.35** and compound **3.36** then would serve as model compounds to explore the epimerization of C-5 center. In our real synthetic plan, the C-16 ketone functional group would be masked as a protected secondary alcohol.



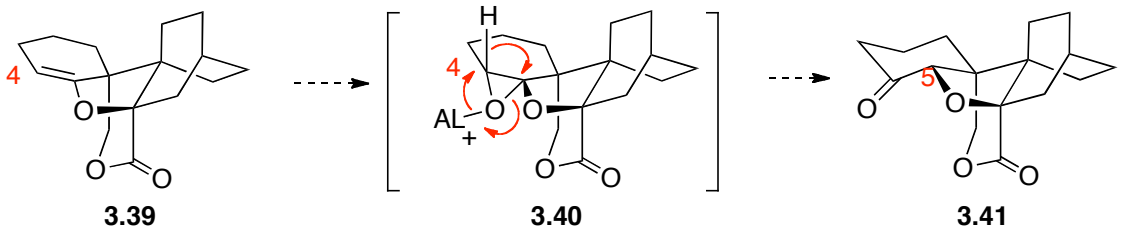
Scheme 3-10 Functionalization of C-16 ketone

We then subjected compound **3.35** to NaOMe condition and to our disappointment we only recovered starting material **3.35**. During the time I was working on this problem, our group developed a trans-de-nitro-hydrogenation protocol to synthesis trans-fused hydro indane motifs.[15] I wondered if I could use this method to solve the junction problem. We first prepared the bromo compound **3.37** and the following de-bromo-hydrogenation reaction again provided us with a *cis*-fused compound **3.38**. This result indicated hydrogenation process happened on α–face of A-ring.



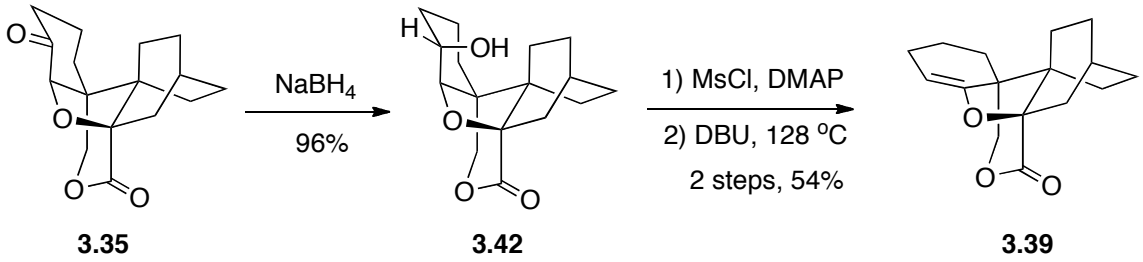
Scheme 3-11 Radical reduction approach to synthesis **3.38**

It seemed that we needed to answer a key question: how to deliver a hydrogen atom to a more congested *β*-face in order to solve this junction problem. We soon realized that a possible solution was to design an intramolecular hydrogen transfer process, which allowed for delivery of a hydrogen atom from more congested *β*–face of A-ring. As such, we designed a reaction termed "*exo*-glycal epoxide rearrangement".[16] We envisioned that the *β*-epoxidation reaction of **3.39** would provide *exo*-glycal epoxide **3.40** and our strategically important C-4 hydrogen was pushed into the *β*–face of A-ring. Subsequent rearrangement would provide the desired trans-fused structure **3.41**. Since glycal epoxide **3.40** was not a stable species, we would take great care when handling it.



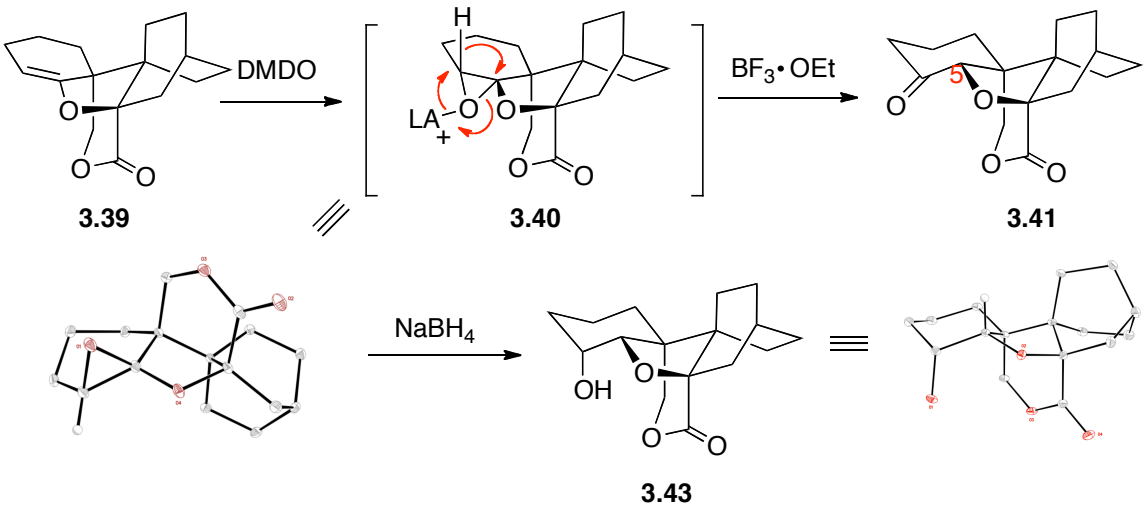
Scheme 3-12 *Exo*-glycal epoxide rearrangement design

Our initially approach to prepare junction enol ether **3.39**, which involved dehydration of alcohol **3.29**, didn't work well and only starting material was recovered with several conditions such as Burgess dehydration and Martin dehydration. This is probably due to the equatorial configuration of the hydroxyl group, which disfavored an E2 elimination. We then reduced compound **3.35** with $NaBH_4$ and the resultant axial alcohol was subjected to the dehydration conditions, which provided the desire compound **3.39** in good yield.



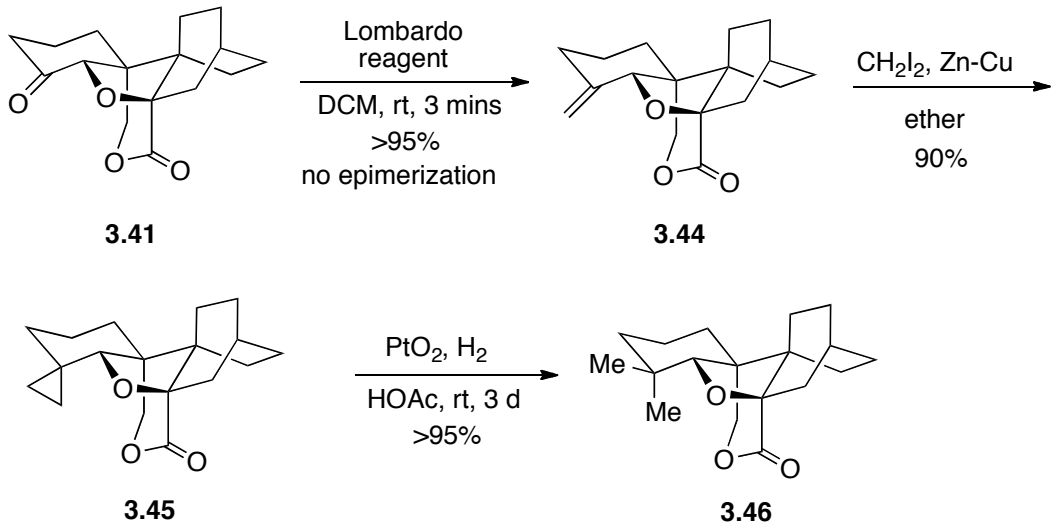
Scheme 3-13 Preparation of enol ether **3.39**

With the key intermediate **3.39** in hand, we treated it first with DMDO, which furnished the *exo*-glycal expoxide **3.40**. Without isolation, in situ treatment of BF_3•OEt_2[17] generated the target compound **3.41** as a single isomer, whose structure was verified by X-ray analysis of the reduced compound **3.43**.



Scheme 3-14 Preparation of compound **3.43**

We then further installed the gem-dimethyl group using Oppolzer's sequence[4] to compound **3.41**. As such, olefination of compound **3.41** afforded *exo*-methylene **3.44** without epimerization of the junction proton. Cyclopropanation and the following hydrogenation furnished gem-dimethyl compound **3.46**.



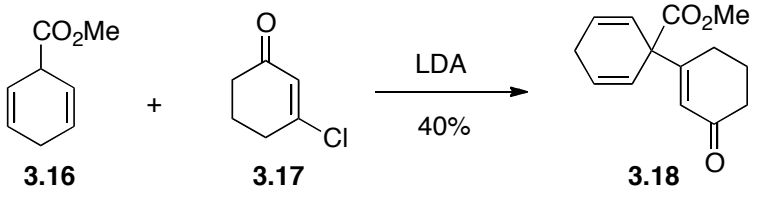
Scheme 3-15 Preparation of compound **3.46**

3. 3 Experimental

General information

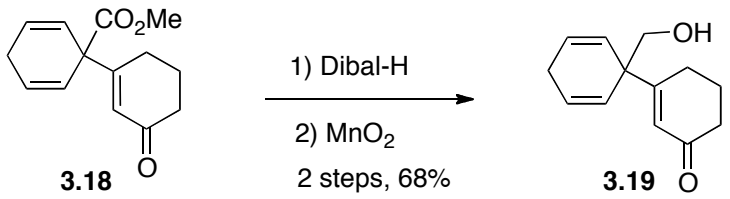
Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. CH_2Cl_2 (DCM) was distilled over CaH_2 under argon atmosphere. THF was distilled over sodium/benzophenone ketyl under argon atmosphere. Anhydrous toluene, hexane, ether were purchased and used without further purification. All reagents

were commercially available and used without further purification unless indicated otherwise. Thin layer chromatography (TLC) was performed on Silica Gel 60 F254 plates and was visualized with UV light and $KMnO_4$ stain. Preparative thin layer chromatography was performed with Merck silica gel 60-F254 coated 0.50 mm plates. Flash chromatography was performed with Sorbent Tech. silica gel 60. Yields reported are for isolated, spectroscopically pure compounds. NMR spectra were recorded on 300, 400 or 500 MHz instruments. The residual solvent protons (^1H) or the solvent carbons (^{13}C) were used as internal standards. ^1H NMR data are presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, coupling constant, integration). The following abbreviations are used in reporting NMR data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; qt, quartet of triplets; dd, doublet of doublets; dt, doublet of triplets; AB, AB quartet; m, multiplet. High-resolution mass spectra were recorded by the Columbia University Mass Spectrometry Core facility on a JEOL HX110 spectrometer.



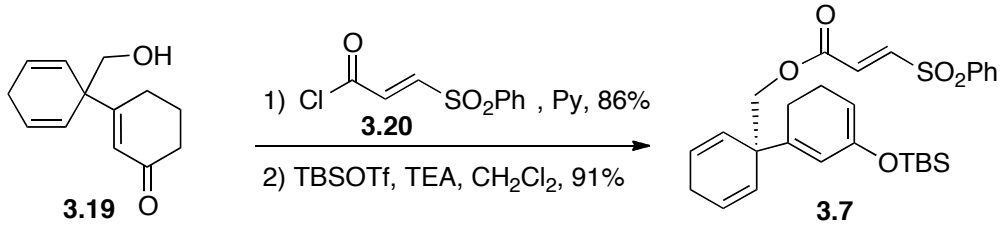
Compound 3.18: An oven-dried, 250 mL round bottom flask containing a stir bar was capped with a rubber septum. This flask was then charged with diisopropylamine (5.6 mL, 40 mmol) and 100 mL of anhydrous THF under argon. At 0 ^oC, n-BuLi (16 mL, 40 mmol) was injected dropwise in 10 mins. The reaction mixture was stirred at this temperature for additional 10 mins before cooled down to -78 ^oC. After stirring at -78 ^oC

for 20 mins, a solution of **7** (5.2 g, 38 mmol) in 10 mL of THF was injected slowly to the flask in 15 mins. After addition of compound **7**, the reaction mixture was stirred at -78 ^{o}C for additional 40 mins. Then a solution of 8 (7.3 g, 57 mmol) in 15 mL of THF was injected in 5 mins. 30 mins later, the reaction was quenched by addition of 30 mL of water, extracted with ethyl acetate and dried over anhydrous $MgSO_4$. The drying agent was filtered and solvents were removed under reduced pressure using rotavap. The residues were purified by flash chromatography to give a colourless oil. (3.5g, 40% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.03-5.97 (m, 2H), 5.90 (s, 1H), 5.87-5.82 (m, 2H), 3.73 (s, 3H), 2.69-2.67 (m, 2H), 2.38-2.34 (m, 2H), 2.30-2.26 (m, 2H), 2.00-1.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 199.7, 172.3, 164.6, 127.3, 126.2, 124.3, 54.3, 52.6, 37.4, 26.4, 25.9, 22.9; IR (neat): cm^{-1} 2951, 2869, 1734, 1671, 1250, 1225, 1040; HRMS (FAB, *m/z*) calcd for $C_{14}H_{17}O_3$ $[M+H]^+$ 233.113, found 233.118.



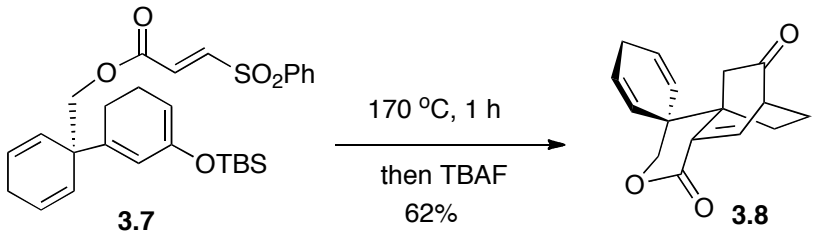
Compound 3.19: compound **3.18** (1.5 g, 6.4 mmol) was dissolved in anhydrous DCM under argon and cooled to -78 ^{o}C. 25.8 mL of DIBAL-H in hexane (1 M) was injected into the solution slowly and the reaction mixture was stirred for 50 mins at this temperature. Then the reaction was quenched with 0.5 mL of ethyl acetate and 5 g of sodium sulfate decahydrate. After warming up to room temperature, the mixture was stirred for additional 1 hour, dried over $MgSO_4$ and filtered. The solvent was removed

using rotovap and the residue was used directly in the next step. The residue was dissolved in DCM in a round bottom flask and 30 g of MnO_2 was added. The reaction mixture was stirred for 40 min and the solid was filtered (The reaction process was monitored carefully under TLC). After removing of the solvent with rotavap, the residues were purified with flash chromatography to give a colourless oil. (890 mg, 68% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.03 (ddd, J = 10.4, 3.2, 3.2 Hz, 2H), 5.91 (s, 1H), 5.51 (ddd, J = 10.4, 2.0, 2.0 Hz, 2H), 3.65 (d, J = 5.6 Hz, 2H), 2.70 (dd, J = 3.2, 3.2 Hz, 2H), 2.35-2.30 (m, 4H), 1.95-1.85 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 200.2, 167.1, 128.2, 126.7, 125.2, 67.1, 48.6, 37.4, 26.7, 26.2, 22.9; IR (neat): cm^{-1} 3416, 2944, 2869, 1652, 1348, 1033; HRMS (FAB, *m/z*) calcd for $C_{13}H_{17}O_2$ $[M+H]^+$ 205.123, found 205.122.



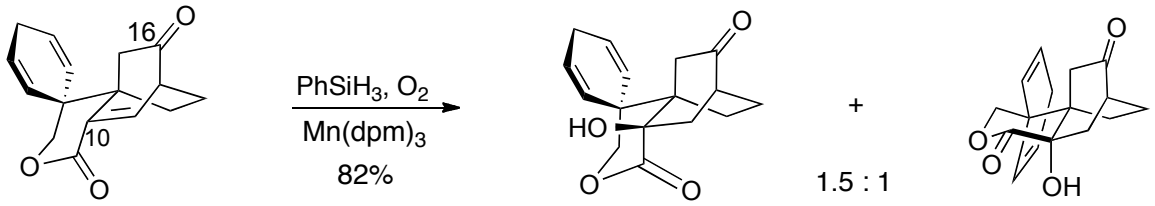
Compound 3.7: compound **3.19** (1.35 g, 6.6 mmol) and pyridine (10.4 mL, 12 mmol) was dissolved in DCM under argon at 0 ^{o}C. Acyl chloride **3.20** (1.67 g, 7.2 mmol) in 5 mL of DCM was injected slowly. After addition of acyl chloride solution, the reaction mixture was stirred at this temperature for 1 hour. The reaction was then quenched by addition of methanol and the solvent was removed under the reduced pressure. The residue was purified using flash chromatography. The pure product and TEA (1.6 mL, 12 mmol) was dissolved in anhydrous DCM under argon at -78 ^{o}C, TBSOTf (2.3 mL, 10

mmol) was injected dropwise and the reaction mixture was stirred at this temperature for 12 hours. The reaction mixture was quenched with water, extracted with ether and dried over $MgSO_4$. The solid was filtered and the solvent was removed with rotavap. Then the residues were purified by flash chromatography using TEA deactivated silica gel and afforded a colourless oil. (2,4 g, 72% yield for two steps). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.92 (d, J = 7.6 Hz, 2H), 7.71-7.67 (m, 1H), 7.61-7.57 (m, 2H), 7.29 (d, J = 15.2 Hz, 1H), 6.82 (d, J = 15.2 Hz, 1H), 5.92-5.89 (m, 2H), 5.49-5.46 (m, 3H), 4.80-4.78 (m, 1H), 4.27 (s, 2H), 2.62 (br s, 2H), 2.12-1.99 (m, 4H), 0.91 (s, 9H), 0.11 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.4, 148.7, 143.3, 143.0, 138.5, 134.4, 130.9, 129.6, 128.3, 127.4, 126.7, 121.1, 101.1, 69.5, 45.1, 26.2, 25.7, 24.1, 22.4, 18.1, –4.5; IR (neat): cm^{-1} 2951, 2858, 1729, 1670, 1448, 1294; HRMS (FAB, *m/z*) calcd for $C_{28}H_{37}O_5SiS$ $[M+H]^+$ 513.2131, found 513.2131.



Compound 3.8: compound **3.7** (513 mg, 1 mmol) was dissolved in 50 mL of anhydrous toluene in a high-pressure tube. The reaction mixture was degassed with argon and then stirred at 166 °C for 1 hour. After cooling to room temperature and the mixture was transferred to a round bottom flask and the solvent was removed with rotavap. The residue was dissolved in THF and cooled to 0 °C. Then TBAF in THF (1.5 mL, 1.5 mmol) was added. 2 hours later the reaction was quenched with saturated ammonium chloride solution, extracted with ethyl acetate (3 x 10 mL) and dried over $MgSO_4$. The

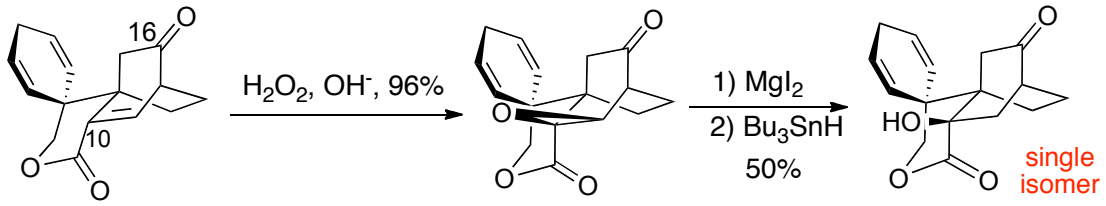
drying agent was removed by filtration and the solvent was removed under reduced pressure. The residue was purified using flash chromatography (156 mg, 62%) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (d, J = 6.8 Hz, 1H), 6.12-6.07 (m, 2H), 5.68-5.60 (m, 2H), 4.30 (d, J = 10.0 Hz, 1H), 4.15 (d, J = 10.0 Hz, 1H), 3.49-3.47 (m, 1H), 2.78-2.76 (m, 2H), 2.15 (d, J = 18 Hz, 1H), 2.08-1,99 (m, 2H), 1.88-1.60 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.5, 163.5, 143.1, 135.7, 129.3, 128.6, 124.4, 123.3, 71.7, 50.1, 46.5, 41.3, 38.9, 26.9, 25.9, 23.1; IR (neat): cm^{-1} 2946, 1720, 1616, 1242, 1075; HRMS (FAB, *m/z*) calcd for $C_{16}H_{17}O_3$ $[M + H]^+$ 257.1178, found 257.1178.



3.8 **3.21a** **3.21b**

Compound 3.21: An oven-dried, 50 mL round bottom flask containing a stir bar was capped with a rubber septum. This flask was then charged with **3.8** (125 mg, 0.5 mmol), $Mn(dpm)_3$ (6 mg, 0.01 mmol), 8 mL of anhydrous DMC and 8 mL of anhydrous IPA under argon. This mixture was stirred until a homogenous solution formed. Then $PhSiH_3$ (150 μL, 1.25 mmol) was injected and the reaction mixture was stirred under a balloon pressure of oxygen. 40 mins later, the ice-bath was removed and the reaction mixture was stirred at room temperature for 10 min. Then the oxygen balloon was removed and the reaction mixture was stirred at 0 ^{o}C. 5 mL of saturated $Na_2S_2O_3$ solution was added to the reaction mixture and the mixture was stirred at 0 ^{o}C for 1 hour. The mixture was extracted with Ethyl Acetate and the extract was dried over MgSO4. The drying agent

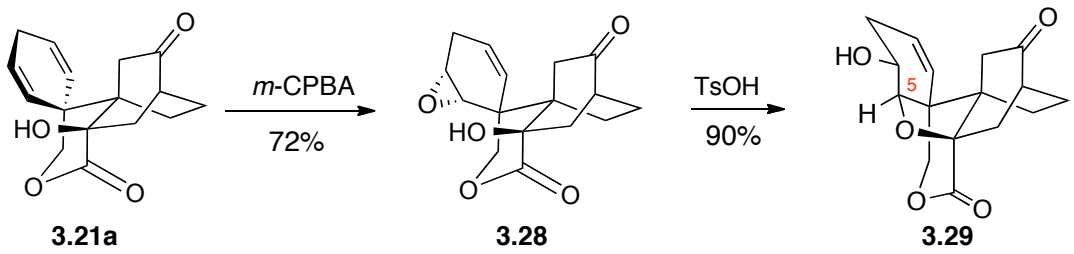
was filtered and the solvent was removed with rotavap. The residue was purified with flash chromatography to afford a diastereomer mixture 13a and 13b. (110 mg, 21a:21b = 1.5:1, 80%) **21a**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.06-6.02 (m, 2H), 5.96-5.92 (m, 1H), 5.60 (dd, J = 10.4, 2 Hz, 1H), 4.45 (d, J = 11.6 Hz, 1H), 4.28 (d, J = 11.6 Hz, 1H), 2.77 (dd, J = 14.8, 2.4 Hz, 1H), 2.70 (dd, J = 18.8, 3.2 Hz, 1H), 2.62 (br s, 2H), 2.45 (br s, 1H), 2.29 (br s, 1H), 2.00 (d, J = 18.4 Hz, 1H), 1.95-1.60 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.6, 172.9, 128.9, 128.3, 126.3, 125.7, 76.1, 73.9, 45.8, 41.9, 39.8, 39.7, 39.4, 26.2, 23.0, 22.1; IR (neat): cm^{-1} 3401, 2916, 2849,1728, 1075; HRMS (FAB, *m/z*) calcd for $C_{16}H_{19}O_4$ $[M + H]^+$ 275.1283, found 275.1278.



3.8 **3.26** **3.21a**

Compound 3.21a: Compound **3.8** (64 mg, 0.25 mmol) was dissolved in 5 mL of methanol at 0 ^{o}C under argon. 30% H_2O_2 (32 μL, 0.28 mmol) was injected into the reaction flask followed by an addition of 3 N NaOH aqueous solution (20 μL, 0.06 mmol). 3 hours later, 3 N NaOH solution (20 μL, 0.06 mmol) was added again to the reaction mixture and the reaction was stirred at 0 ^{o}C for additional 3 hours. The reaction was quenched with 200 μL of 1N HCl solution, extracted with ethyl acetate and the extract was dried over $MgSO_4$. After filtration of the drying agent and removing of the solvent, the residue was purified with flash chromatography to afford **3.26** (65 mg, 95%). Compound **3.26** (14 mg, 0.05 mmol) was dissolved in 5 mL of anhydrous DCM and

magnesium diiodide (42 mg, 0.15 mmol) was added to this solution. The reaction mixture was stirred at 45 ^{o}C for about 40 mins (Monitored under TLC). After cooling down to room temperature, the reaction mixture was filtered and the solvent was removed using rotavap. The residue and Bu_3SnH (43 μL, 0.15 mmol) were dissolved in anhydrous toluene and the solution was degassed three times with argon. After addition of 5 mg of AIBN, the reaction mixture was heated under reflux for 1 hour. Then the reaction mixture cooled down to room temperature and the toluene was removed with rotavap. The residue was purified with flash chromatography to afford **21a** (7 mg, 50%).

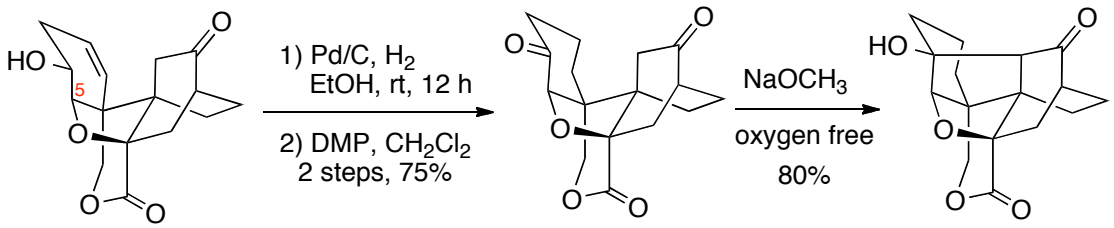


3.21a **3.28** **3.29**

Compound 3.29: *m*-CPBA (42 mg, 0.18 mmol) was added to a solution of **21a** (33 mg, 0.12 mmol) in 5 mL of anhydrous DCM at 0 ^{o}C. 12 hour later, the ice-bath was removed and the reaction mixture was stirred at room temperature for additional 12 hours. The reaction process was monitored under TLC until the disappearance of starting material. Then the reaction was quenched with $Na_2S_2O_3$ solution, extracted with ethyl acetate and the extract was dried over $MgSO_4$. The drying agent was filtered and the solvent was removed under reduced pressure. The residue was purified using flash chromatography to afford **3.28** (25 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.72-5.67 (m, 1H), 5.22 (d, J = 10.8 Hz 1H), 4.72 (d, J = 11.6 Hz, 1H), 4.30 (d, J = 11.6 Hz, 1H), 4.15-4.13 (m, 1H), 3.40-3.39 (m, 1H), 2.82-2.72 (m, 2H), 2.62 (dd J = 18.4, 5.6 Hz, 1H), 2.51-2.41 (m, 3H),

2.10 (d, *J* = 18 Hz, 1H), 2.00-1.65 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 212.5, 172.5, 125.8, 124.5, 73.5, 65.8, 60.4, 54.5, 51.9, 45.0, 41.6, 40.0, 38.9, 25.1, 23.5, 21.7; HRMS (FAB, *m/z*) calcd for $C_{16}H_{19}O_5$ $[M + H]^+$ 291.1219, found 291.1232.

Compound 3.29: compound **3.28** (12 mg, 0.04 mmol) dissolved in anhydrous DCM at room temperature and p-TSA monohydrate (2 mg, 0.01 mmol) was added to this solution. The reaction mixture was stirred at this temperature for about 12 hours. The solvent was removed under reduced pressure and the residue was purified using flash chromatography to afford compound **3.29** (11 mg, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 5.99-5,95 (m, 1H), 5.37 (dd, *J* = 9.6, 2.8 Hz, 1H), 4.37 (d, *J* = 11.2 Hz, 1H), 4.17 (d, *J* = 9.2 Hz, 1H), 4.00-3.97 (m, 2H), 3.09 (dd, *J* = 15.2, 4 Hz, 1H), 2.48 (ddd, *J* = 17.2, 6.0, 6.0 Hz, 1H), 2.45-2.30 (m, 2H), 2.12-2.04 (m, 1H), 1.96-1.67 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 211.4, 169.1, 131.1, 121.1, 88.3, 83.4, 76.1, 69.8, 49.2, 46.5, 42.9, 41.6, 30.7, 29.2, 21.4 , 20.2; IR (neat): cm^{-1} 3401, 2916, 2849,1728, 1075; HRMS (FAB, *m/z*) calcd for $C_{16}H_{19}O_5$ $[M + H]^+$ 291.1219, found 291.1232.



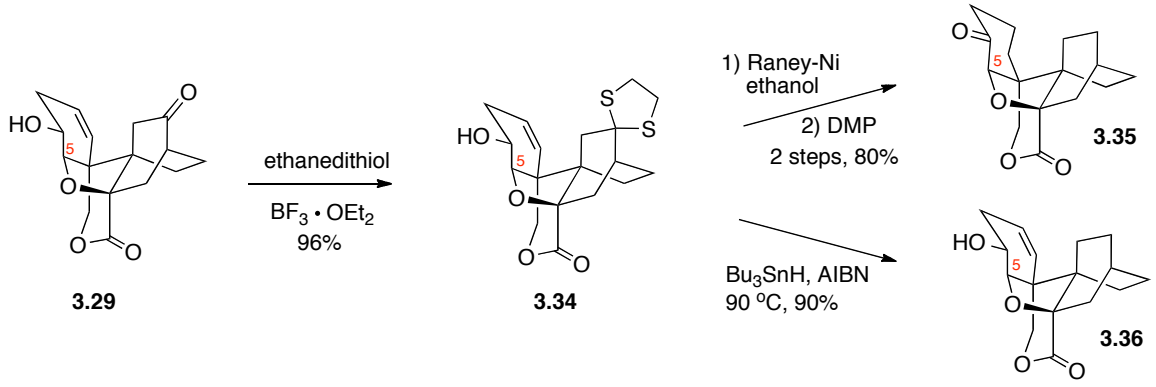
3.29 **3.32** **3.33**

Compound 3.33: compound **3.29** (30 mg, 0.1 mmol) was dissolved in anhydrous ethanol at room temperature and palladium on charcoal (3 mg) was added to this solution. The

reaction mixture was degassed with hydrogen for three times before stirred under a balloon pressure of hydrogen for 8 hours at room temperature. The reaction mixture was then filtered with a short column of silica gel . The solvent was removed under reduced pressure and the residue was dissolved in 5 mL of anhydrous DCM. To this solution, Dess-Marin reagent (130 mg, 0.3 mmol) was added and the reaction was stirred at room temperature for 8 hours. Then the reaction was quenched with $Na_2S_2O_3$, extracted with ethyl acetate and the extract was dried over $MgSO_4$. The drying agent was filtered and the solvent was removed under reduced pressure. The residue was purified using flash chromatography to afford compound **3.32** (23 mg, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.53 (s, 1H), 4.40 (d, J = 11.2 Hz, 1H), 4.32 (d, J = 11.2Hz, 1H), 3.13 (dd, J = 15.2, 4.0 Hz, 1H), 2.47-2.42 (m, 2H), 2.22 (d, J = 18.0 Hz, 1H), 2.10 (d, J = 15.2, 1H), 2.08-1.57 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 210.1, 206.6, 168.7, 86.7, 83.4, 76.1, 48.9, 47.4, 41.5, 41.1, 37.9, 28.9, 24.1, 21.2, 20.1; IR (neat): cm^{-1} 2956, 1730, 1133; HRMS (FAB, *m/z*) calcd for $C_{16}H_{19}O_5$ $[M + H]^+$ 291.1232, found 291.1246.

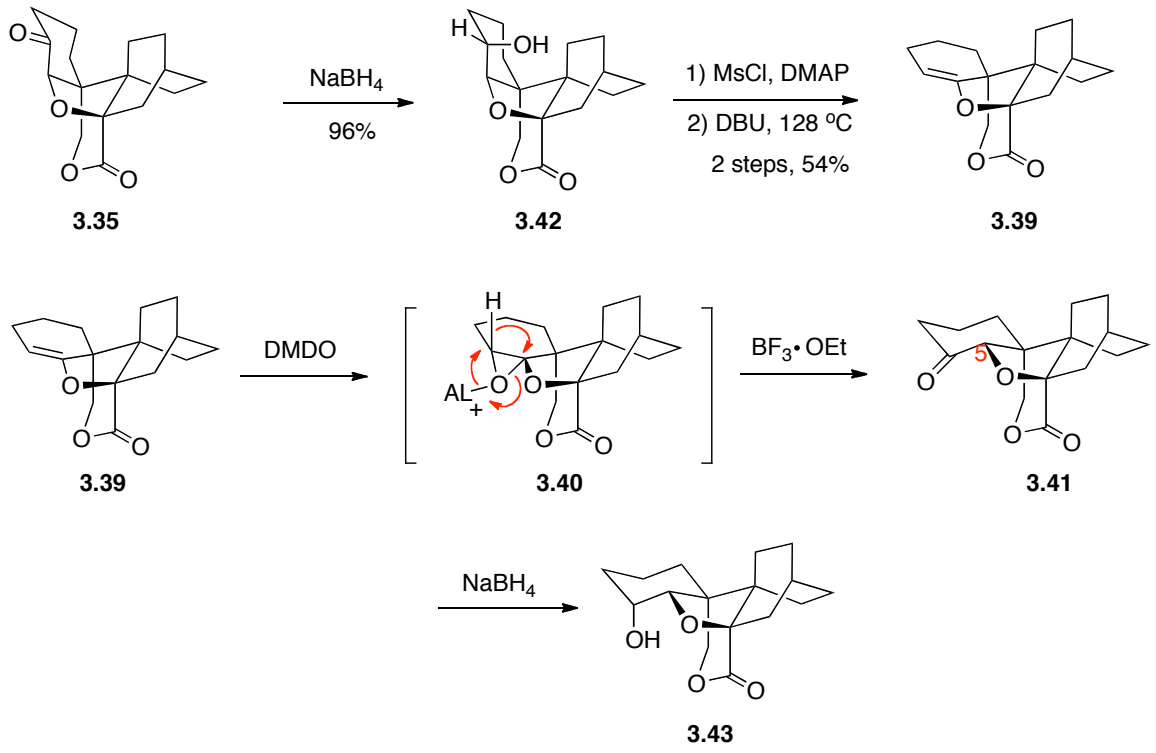
Compound 3.33: compound **3.22** (5 mg, 17 μmol) was dissolved in anhydrous methanol at room temperature and sodium methoxide (0.9 mg, 17 μmol) was added to this solution. The reaction mixture was degassed using the freeze-pump-thaw technique and then stirred at 40 ^{o}C for 36 hours. After quenching with 1 N HCl, the mixture was extracted with ethyl acetate and the extract was dried over $MgSO_4$. The drying agent was filtered and the solvent was removed under reduced pressure. The residue was purified using flash chromatography. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.50 (d, J = 12.4 Hz, 1H), 4.10 (d,

J = 12 Hz, 1H), 3.79 (s, 1H), 3.22 (s, 1H), 3.17(dd, *J* = 16, 3.2 Hz, 1H), 2.57-2.54 (m, 2H), 2.20-2.16 (m, 1H), 1.95-1.65 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 214.0, 169.2, 91.8, 81.1, 78.3, 72.0, 53.0, 52.9, 47.4, 43.4, 35.9, 33.1, 25.0, 21.5, 19.0, 17.4; HRMS (FAB, *m/z*) calcd for $C_{16}H_{19}O_5$ $[M + H]^+$ 291.1232, found 291.1247.



Compound 3.35: compound **3.29** (29 mg, 0.1 mmol) and ethanedithiol (27 μL, 0.3 mmol) dissolved in anhydrous DCM at 0 ^{o}C. To this solution, boron trifluoride etherate (5 μL, 50 μmol) was injected and the reaction mixture was stirred at 0 ^{o}C for 6 hours. After quenching with $NaHCO_3$ solution, the mixture was extracted with ethyl acetate and the extract was dried over MgSO4. The drying agent was filtered and the solvent was removed under reduced pressure. The residue was purified using flash chromatography. The pure thioketal dissolved in anhydrous ethanol. To this solution, 150 mg of Raney-Ni was added and the reaction mixture was stirred at 75 ^{o}C for 4 hours. Then the mixture was filtered through a short silica gel column using ethyl acetate as eluent. The solvent was removed under reduced pressure and the residue dissolved in anhydrous DCM. Dess Martin periodinane (120 mg, 0.28 mmol) was added and the reaction mixture was stirred at room temperature for 8 hours. Quenched with $Na_2S_2O_3$, the mixture was extracted with

ethyl acetate, dried over anhydrous $MgSO_4$. After filtration of the drying agent, the solvent was removed under reduced pressure and the residue was purified using flash chromatography. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.39 (s, 1H), 4.26 (s, 2H), 2.80 (ddd, J = 14.4, 4.8, 2.4 Hz, 1H), 2.45-2.34 (m, 2H), 2.04-1.75 (m, 4H), 1.75-1.45-1.60 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.4, 169.9, 86.9, 84.5, 76.4, 49.2, 42.4, 38.1, 31.1, 25.0, 24.4, 24.1, 23.9, 22.5, 21.5, 21.0; IR (neat): cm^{-1} 2940, 2868, 1742, 1270, 1203, 1158; HRMS (EI, *m/z*) calcd for $C_{16}H_{20}O_4$ [M]$^+$ 276.1362, found 276.1356.



Compound 3.42: compound **3.35** (27 mg, 100 μmol) dissolved in a solution of anhydrous DCM and anhydrous methanol (1:1) at room temperature. The reaction was cooled down to -78 °C and $NaBH_4$ (11 mg, 300 μmol) was added to this solution. The temperature was slowly warmed up to -50 °C in 2 hour. The reaction was then quenched with saturated NH_4Cl solution, extracted with ethyl acetate and dried over $MgSO_4$. After

filtration of the drying agent, the solvent was removed under reduced pressure and the residue was purified using flash chromatography. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.19 (ddd, J = 6.0, 3.2, 3.2 Hz, 1H), 4.13 (d, J = 10.8 Hz, 1H), 4.06 (d, J = 6.0 Hz, 1H), 3.77 (d, J = 10.4 Hz, 1H), 2.79 (ddd, J = 14.0, 4.8, 2.4 Hz, 1H), 2.49-2.46 (m, 2H), 2.10-1.95 (m, 1H), 1.83-1.79 (m, 1H), 1.76-1.71 (m, 1H), 1.64-1.38 (m, 9H), 1.32-1.23 (m, 2H), 0.94 (ddd, J = 14.0, 14.0, 5.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.6, 84.1, 83.4, 79.2, 63.7, 42.3, 41.4, 31.7, 27.7, 25.4, 24.4, 24.1, 22.2, 21.6, 15.5; IR (neat): cm^{-1} 3477, 2923, 2868, 1742, 1456, 1155; HRMS (EI, *m/z*) calcd for $C_{16}H_{23}O_4$ $[M+H]^+$ 279.1596, found 279.1592.

Compound 3.39: At room temperature, compound **3.42** (28 mg, 0.1 mmol) and DMAP (30 mg, 0.3 mmol) dissolved in anhydrous DCM. To this solution, methanesulfonyl chloride (24 μL, 0.3 mmol) was injected and the reaction mixture was heated to 55 ^{o}C and stirred at this temperature for 12 hours. Then the mixture was directly purified using flash chromatography. The pure product dissolved in anhydrous toluene in a sealed tube and 50 μL of DBU was injected into the solution. The reaction mixture was stirred at 130 ^{o}C for 2 hours. The reaction mixture was directly purified using flash chromatography. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.96 (dd, J = 3.6, 3.6 Hz, 1H), 4.39 (d, J = 10.4 Hz, 1H), 4.21 (d, J = 11.8 Hz, 1H), 2.85 (dd, J = 14.0, 3.2 Hz, 1H), 2.11-2.09 (m, 2H), 1.85 (br s, 1H) 1.72-1.43 (m, 13H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.9, 157.5, 95.3, 83.5, 75.4, 43.2, 41.9, 30.7, 25.1, 24.5, 24.1, 23.6, 22.6, 21.5, 20.6, 18.6; IR (neat): cm^{-1} 2947, 2867, 1745, 1702, 1210, 1147; HRMS (EI, *m/z*) calcd for $C_{16}H_{20}O_3$ $[M]^+$ 260.1412, found 260.1418.

Compound 3.41: At 0 ^{o}C, compound **3.39** (26 mg,100 μmol) dissolved in anhydrous DCM under argon. 50 mg of 4 A molecular sieve was added to the solution and the mixture was stirred for 1 hour. Then fresh dimethyldioxirane in acetone (120 μmol, 1.2 eq) was injected dropwise to the reaction mixture. 30 mins later, the solvent was blowed out using argon flow and 2 mL of anhydrous ether was injected to the residue. Boron trifluoride etherate (30 μL, 3 eq) was added sequentially to the reaction mixture slowly and the temperature was slowly warmed up to room temperature in 3 hours. Then the reaction was quenched with saturated $NaHCO_3$ when TLC indicated completion of the reaction, extracted with ethyl acetate and dried over $MgSO_4$. After filtration of the drying agent, the solvent was removed under reduced pressure and the residue was purified using flash chromatography to afford a white solid (19 mg, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.48 (d, J = 10.8 Hz, 1H), 4.45 (br s, 1H), 4.09 (br s, 1H), 4.23 (d, J = 12.0 Hz, 1H), 4.12 (dd J = 12, 2 Hz, 1H), 2.86 (ddd, J = 14.0, 3.2, 2 Hz, 1H), 2.43-2.39 (m, 2H), 2.13-1.59 (m, 14 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 204.9, 169.6, 88.2, 85.3, 70.3, 50.6, 42.8, 38.5, 30.7, 25.4, 24.8, 24.5, 23.7, 21.9, 21.4, 21.3; IR (neat): cm^{-1} 2925, 2869, 1743, 1269, 1150; HRMS (FAB, *m/z*) calcd for $C_{16}H_{21}O_4$ $[M+H]^+$ 277.1440, found 277.1446.

Compound 3.43: compound **3.41** (19 mg) dissolved in a solution of anhydrous DCM and anhydrous methanol (1:1) at room temperature. The reaction was cooled down to -78 ^{o}C and $NaBH_4$ (11 mg, 300 μmol) was added to this solution. The temperature was slowly warmed up to -50 ^{o}C in 2 hour. The reaction was then quenched with saturated NH_4Cl solution, extracted with ethyl acetate and dried over $MgSO_4$. After filtration of the drying

agent, the solvent was removed under reduced pressure and the residue was purified using flash chromatography to afford a white solid (19 mg, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.48 (d, J = 10.8 Hz, 1H), 4.45 (br s, 1H), 4.09 (br s, 1H), 4.07 (d, J = 10.8 Hz, 1H), 2.86 (dd, J = 14.0, 5.2 Hz, 1H), 2.70 (dd, J = 18.8, 3.2 Hz, 1H), 2.62 (br s, 2H), 2.45 (br s, 1H), 2.29 (br s, 1H), 2.00 (d, J = 18.4 Hz, 1H), 1.95-1.60 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.8, 85.7, 84.2, 72.3, 67.7, 43.6, 42.6, 31.0, 30.0, 26.0, 24.9, 24.7, 24.1, 21.3, 20.8, 16.9; HRMS (FAB, *m/z*) calcd for $C_{16}H_{22}O_4$ $[M]^+$ 278.1518, found 278.1512.

3.4 References

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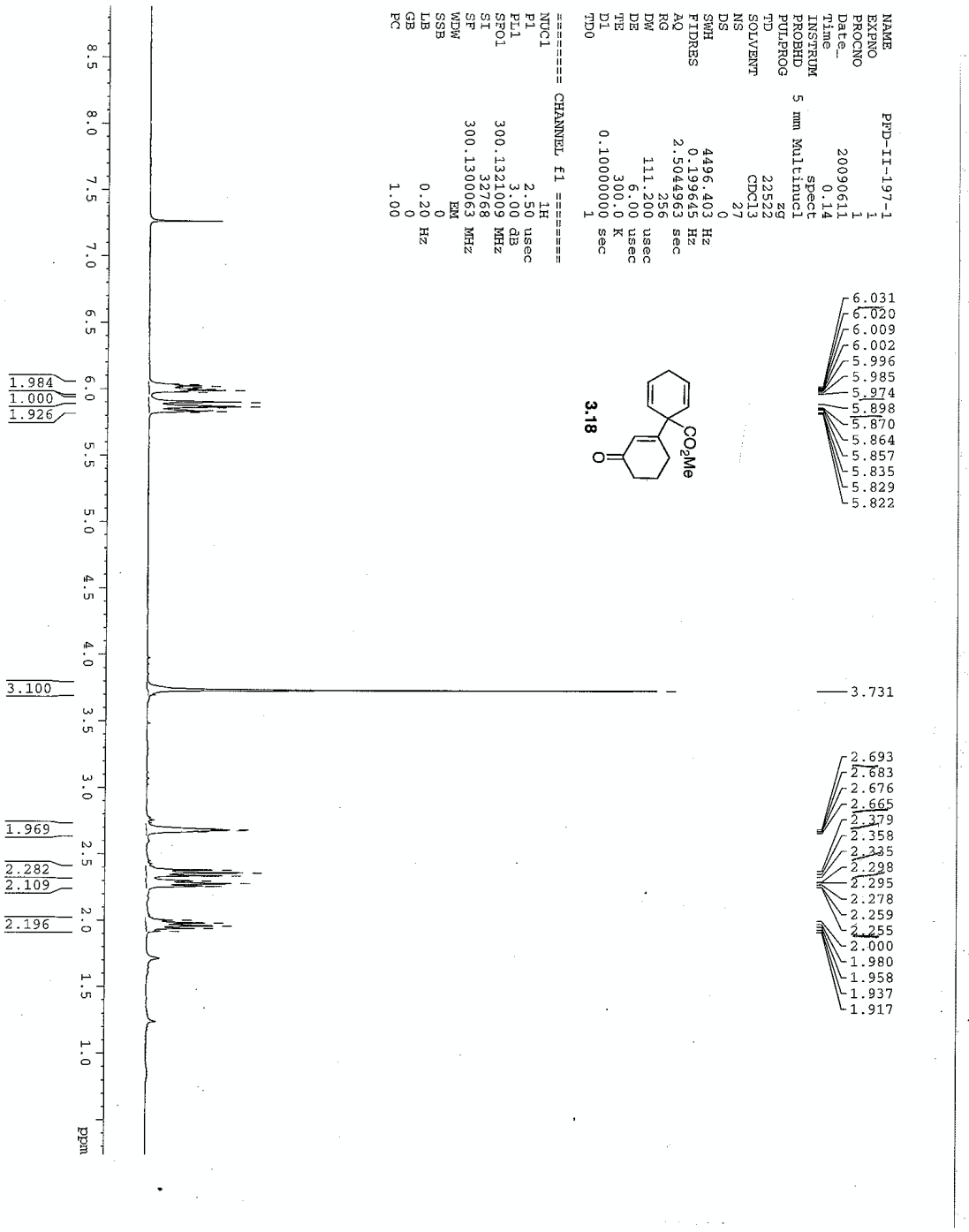
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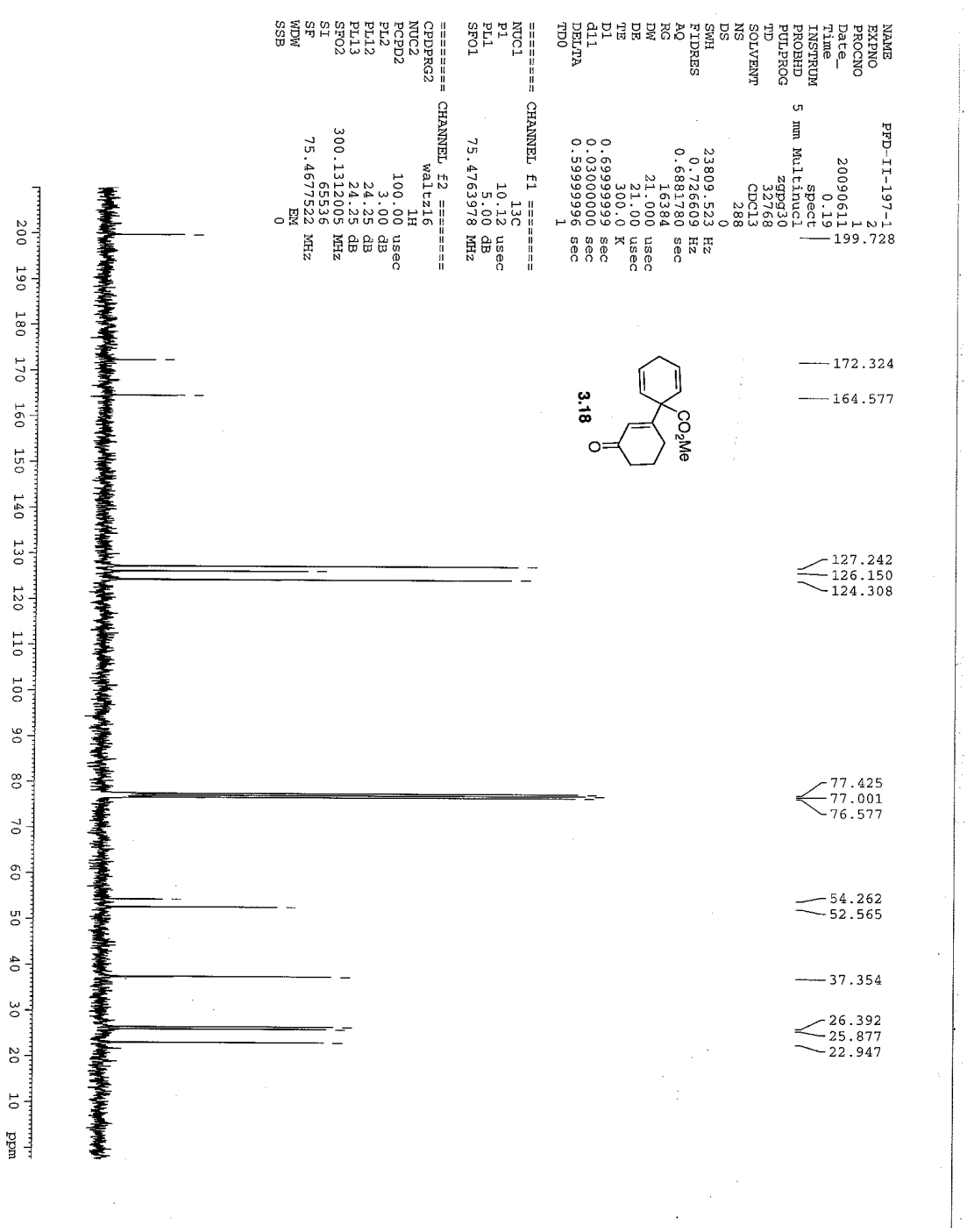
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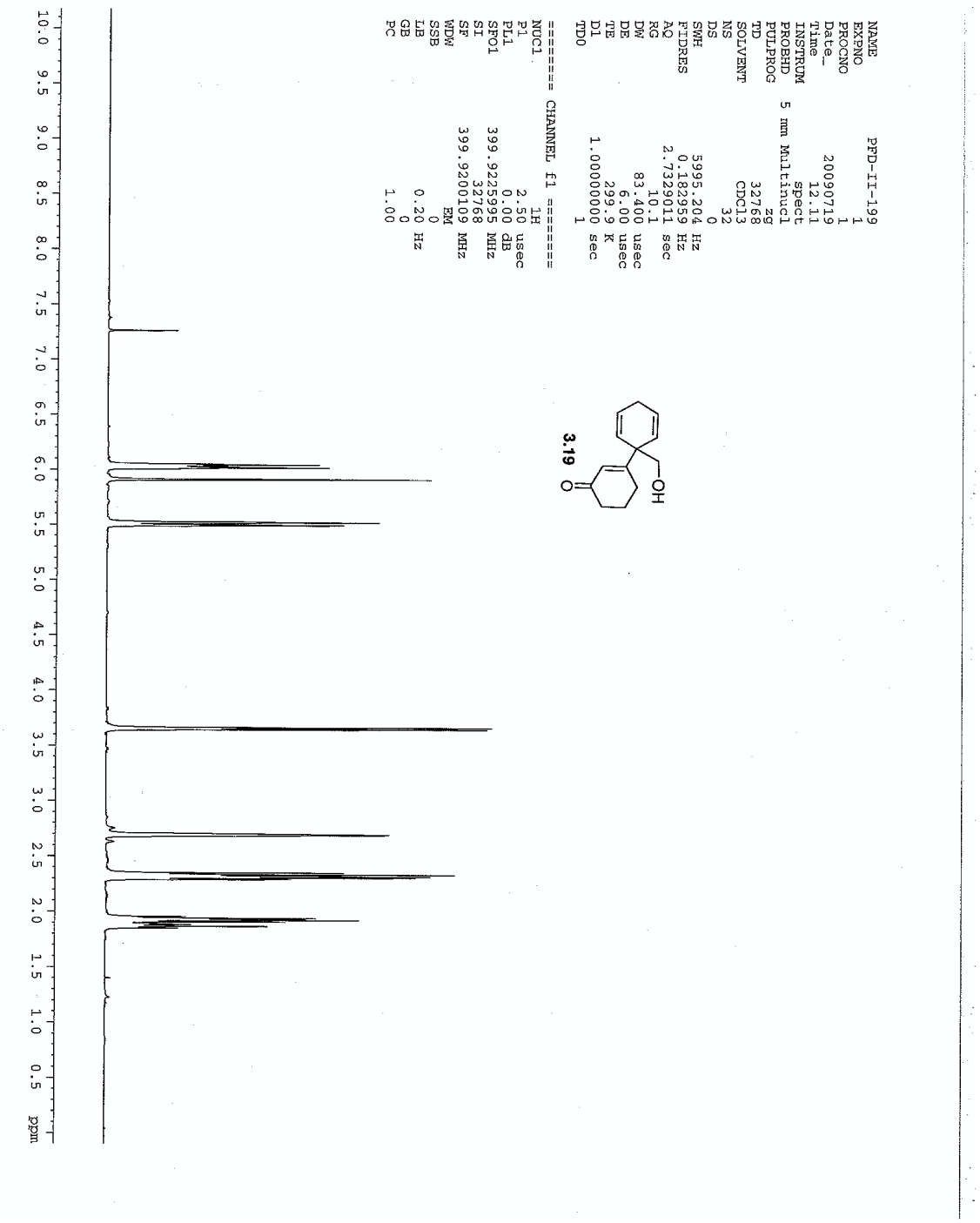
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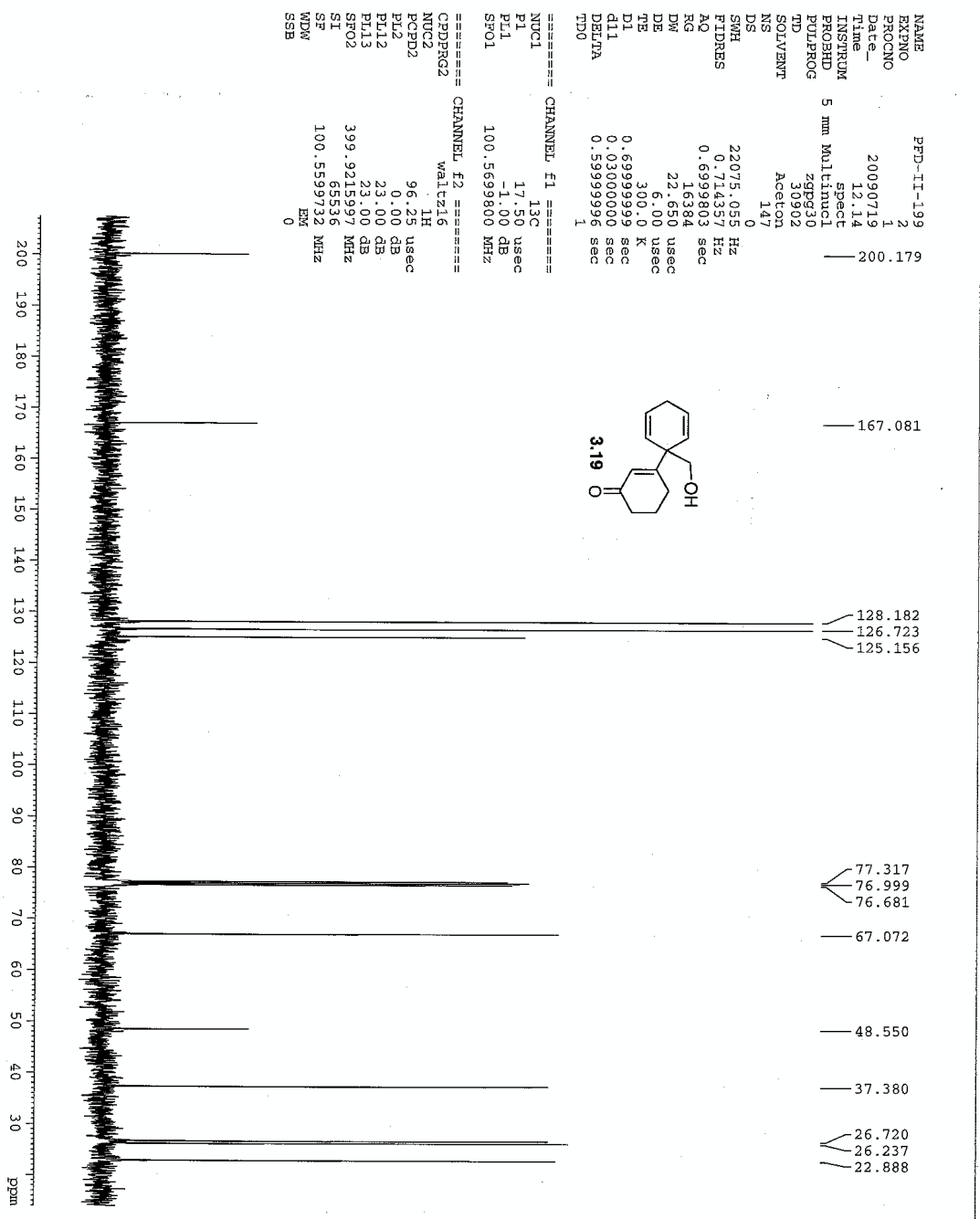
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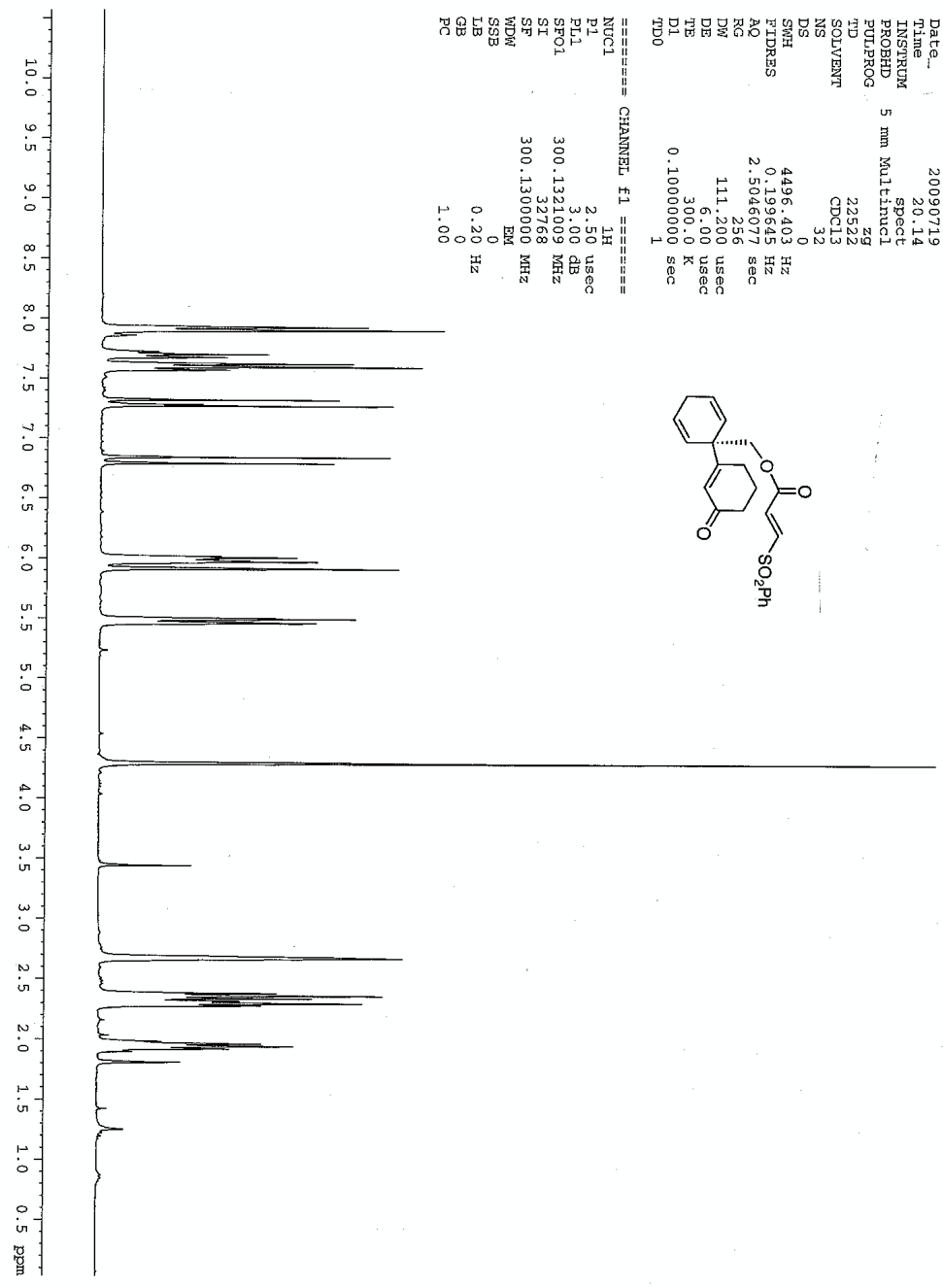
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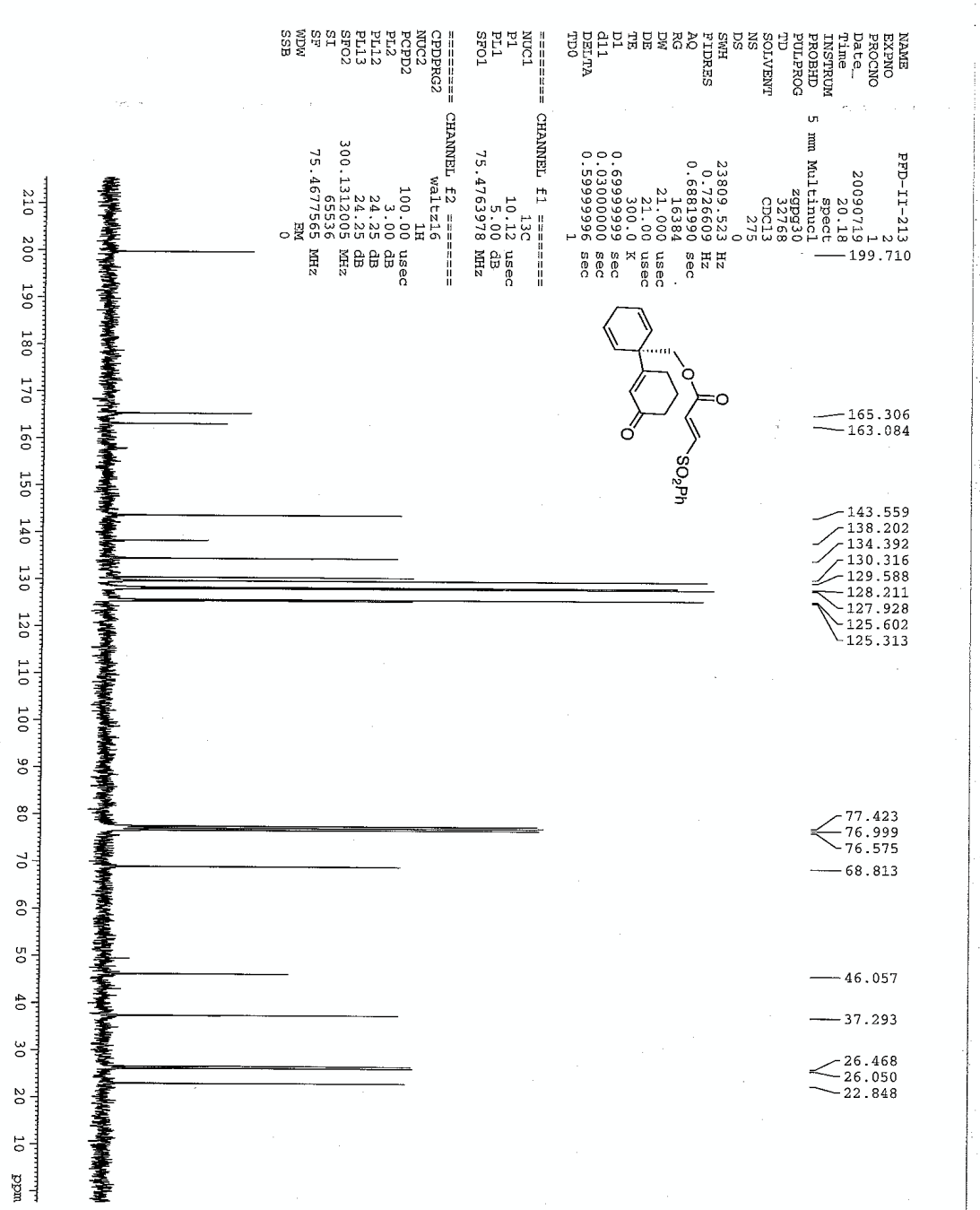
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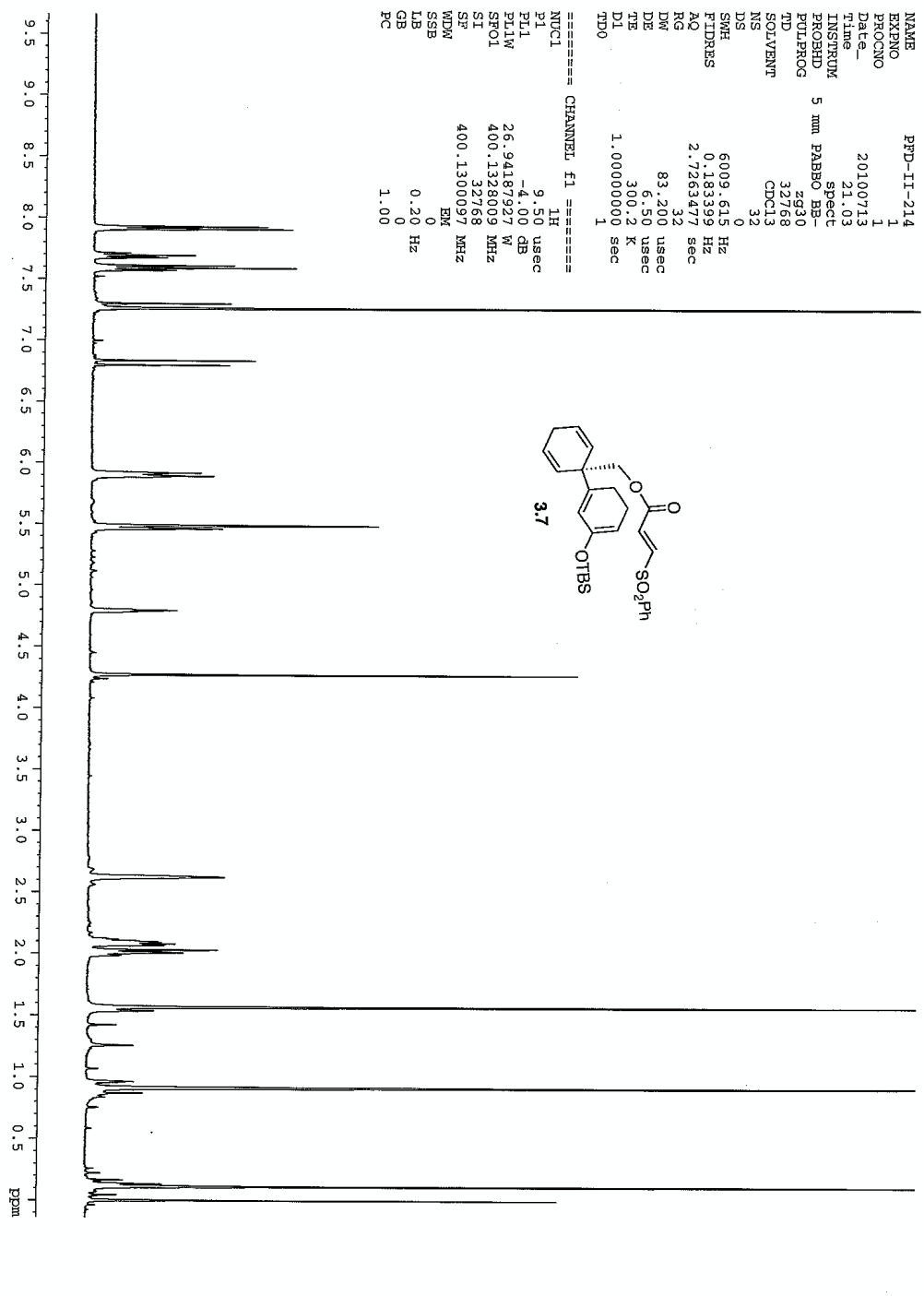
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Time 21.03
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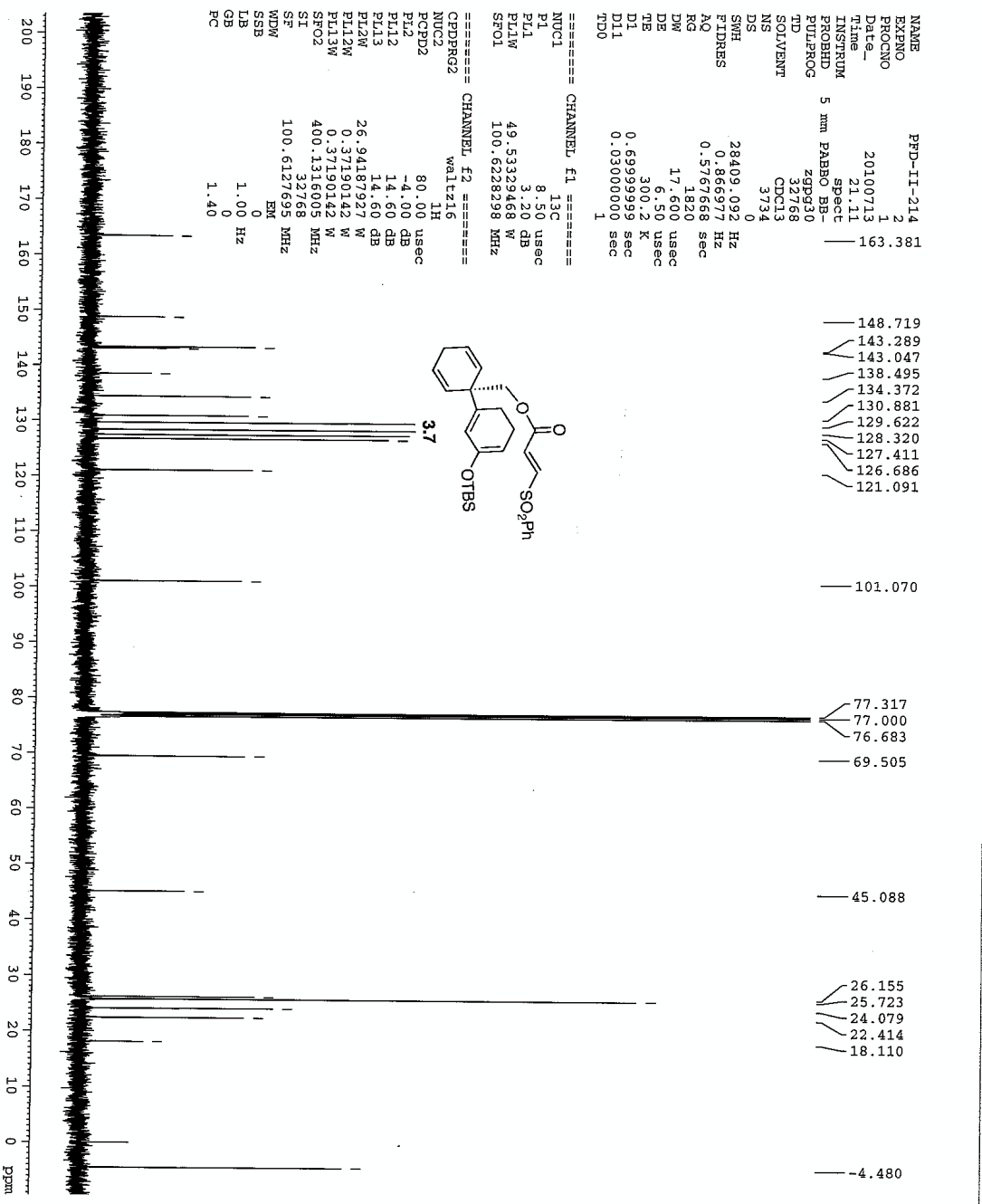
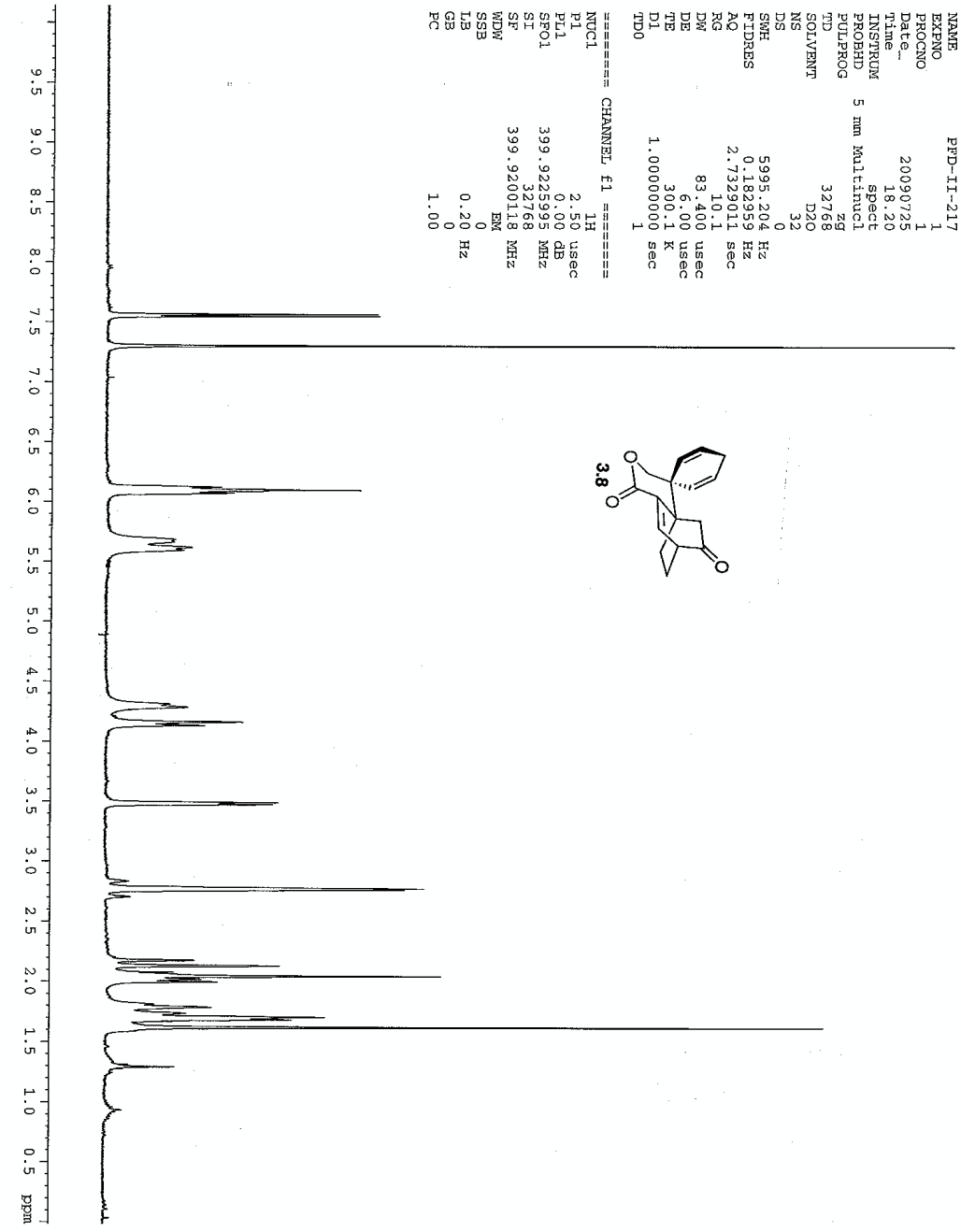
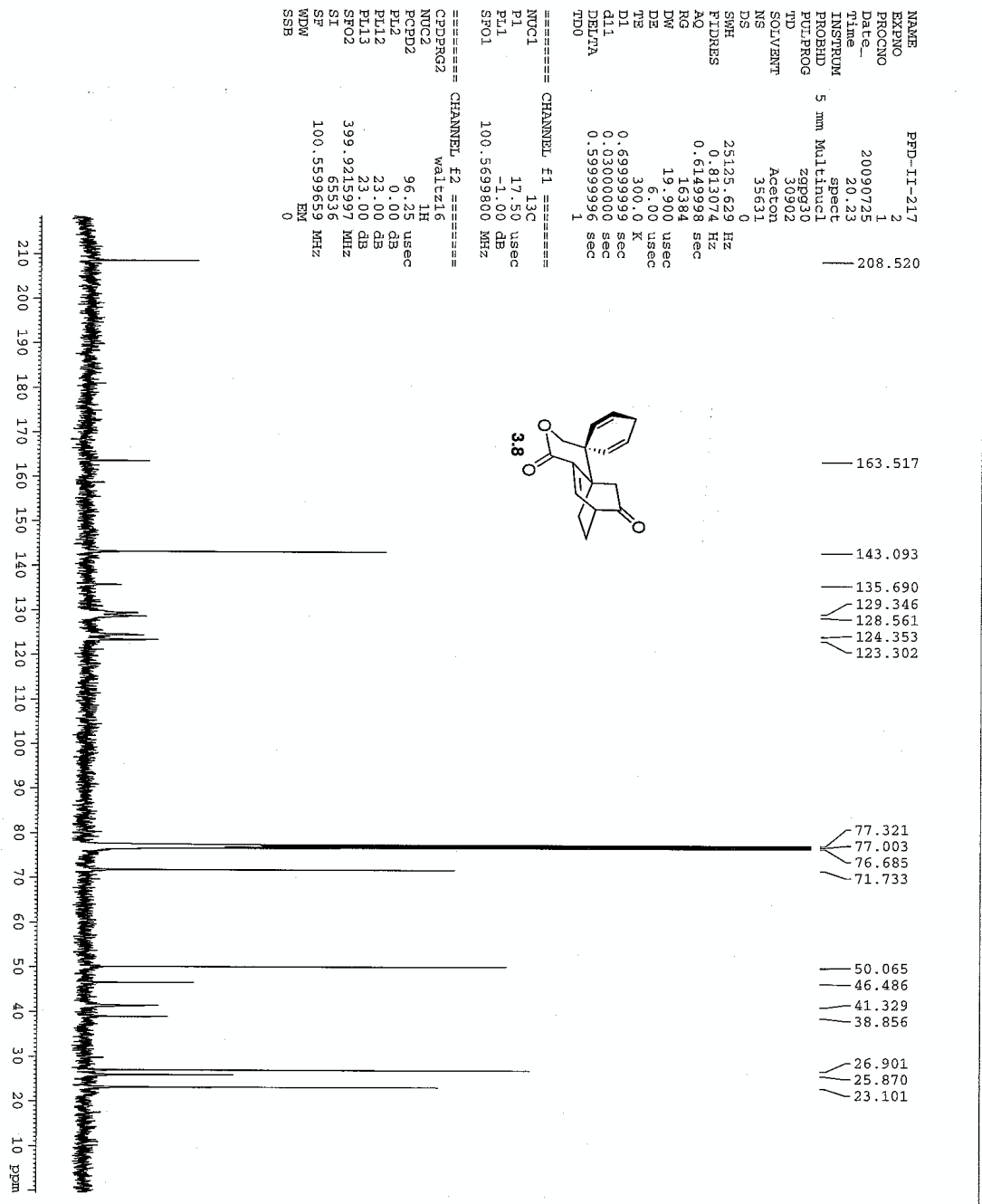
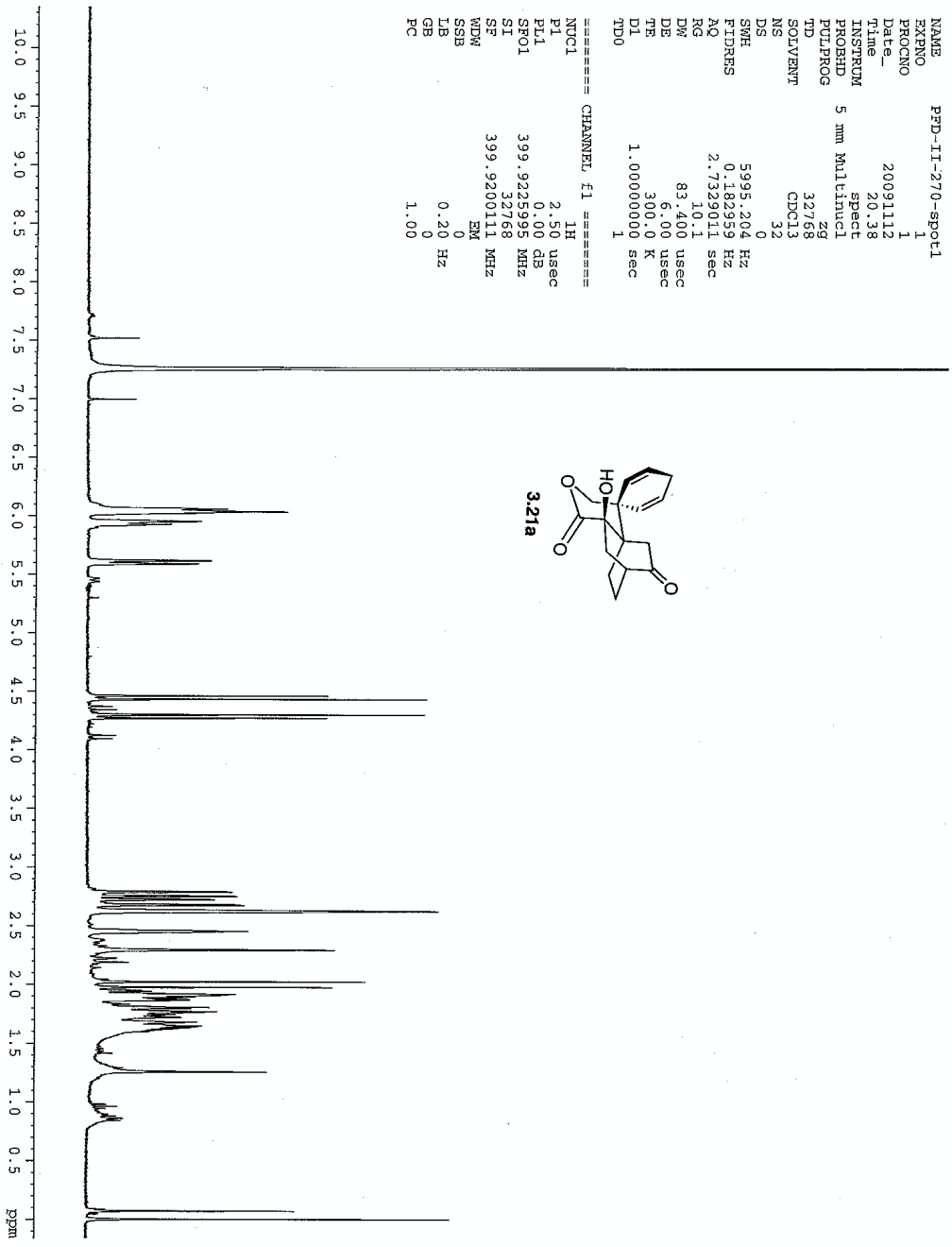
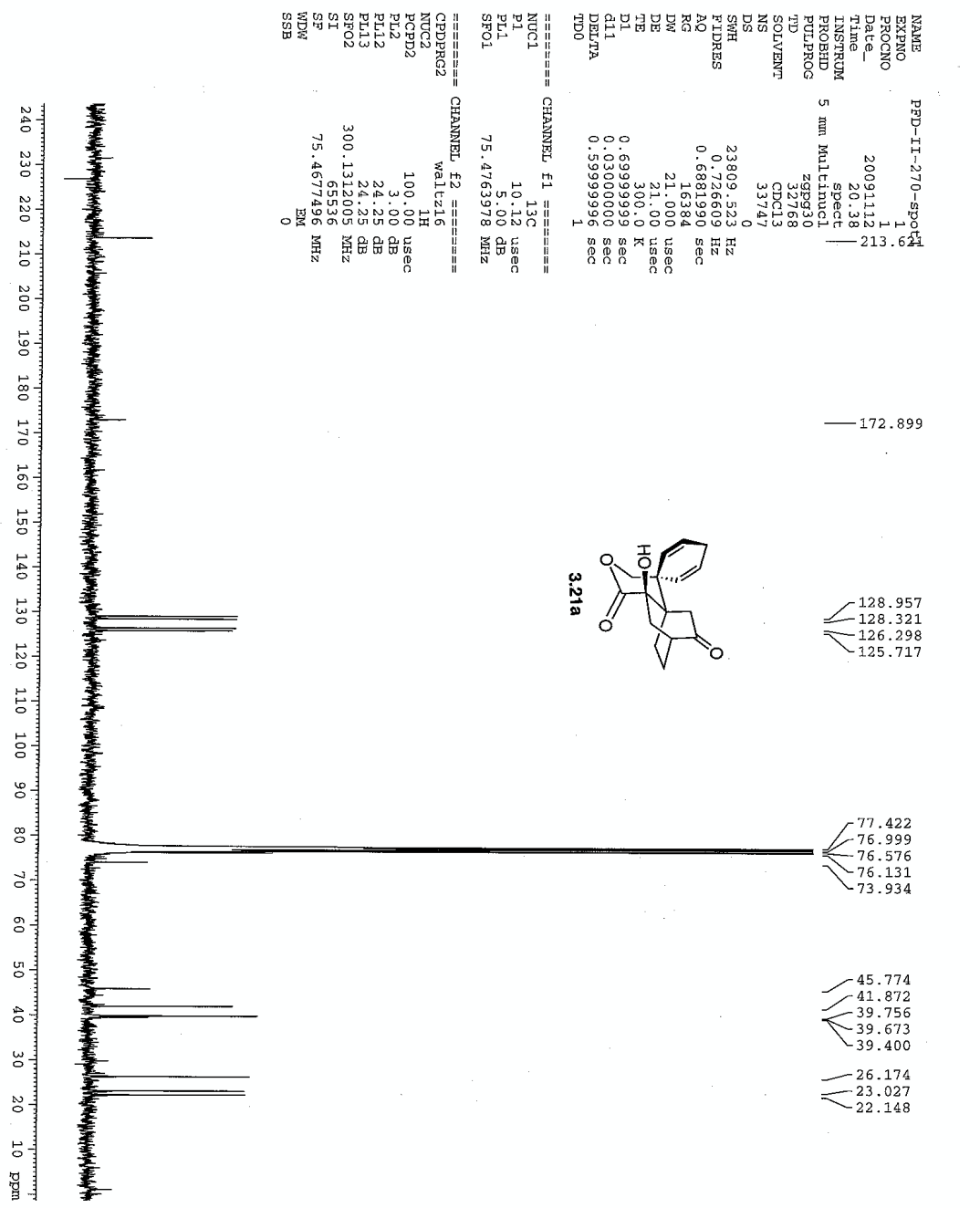
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1
========== CHANNEL f1 ==========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
SI 32768
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
OTBS
O
O
SO2Ph
3.7
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 0.5 ppm

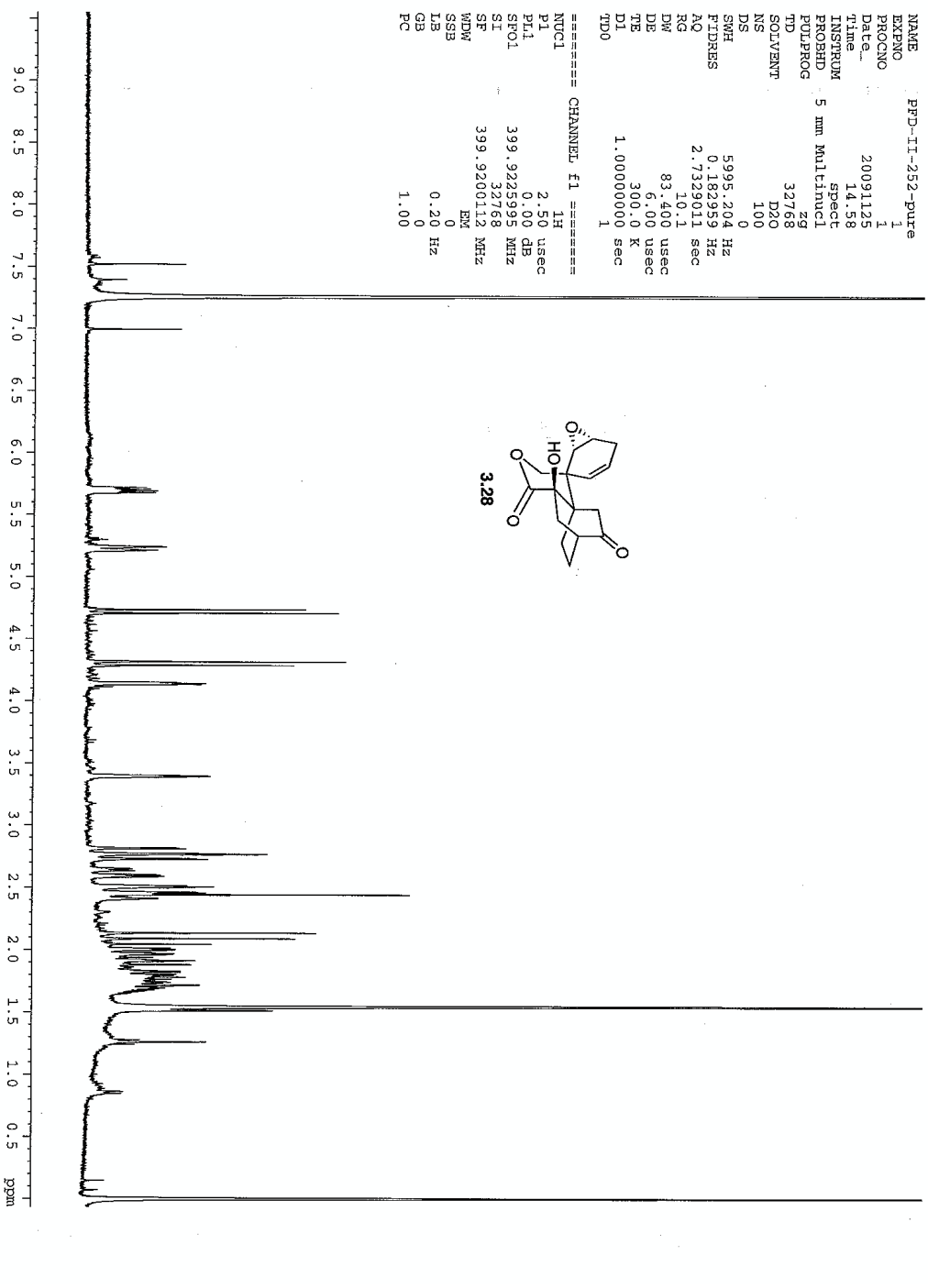

NAME PFD-II-214
EXPNO 2
PROCNO 2
Date_ 20100713
Time 21.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 3734
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 300.2 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127695 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
3.7
OTBS
O
O
SO2Ph
163.381
148.719
143.289
143.047
138.495
134.372
130.881
129.622
128.320
127.411
126.686
121.091
101.070
77.317
77.000
76.683
69.505
45.088
26.155
25.723
24.079
22.414
18.110
-4.480
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

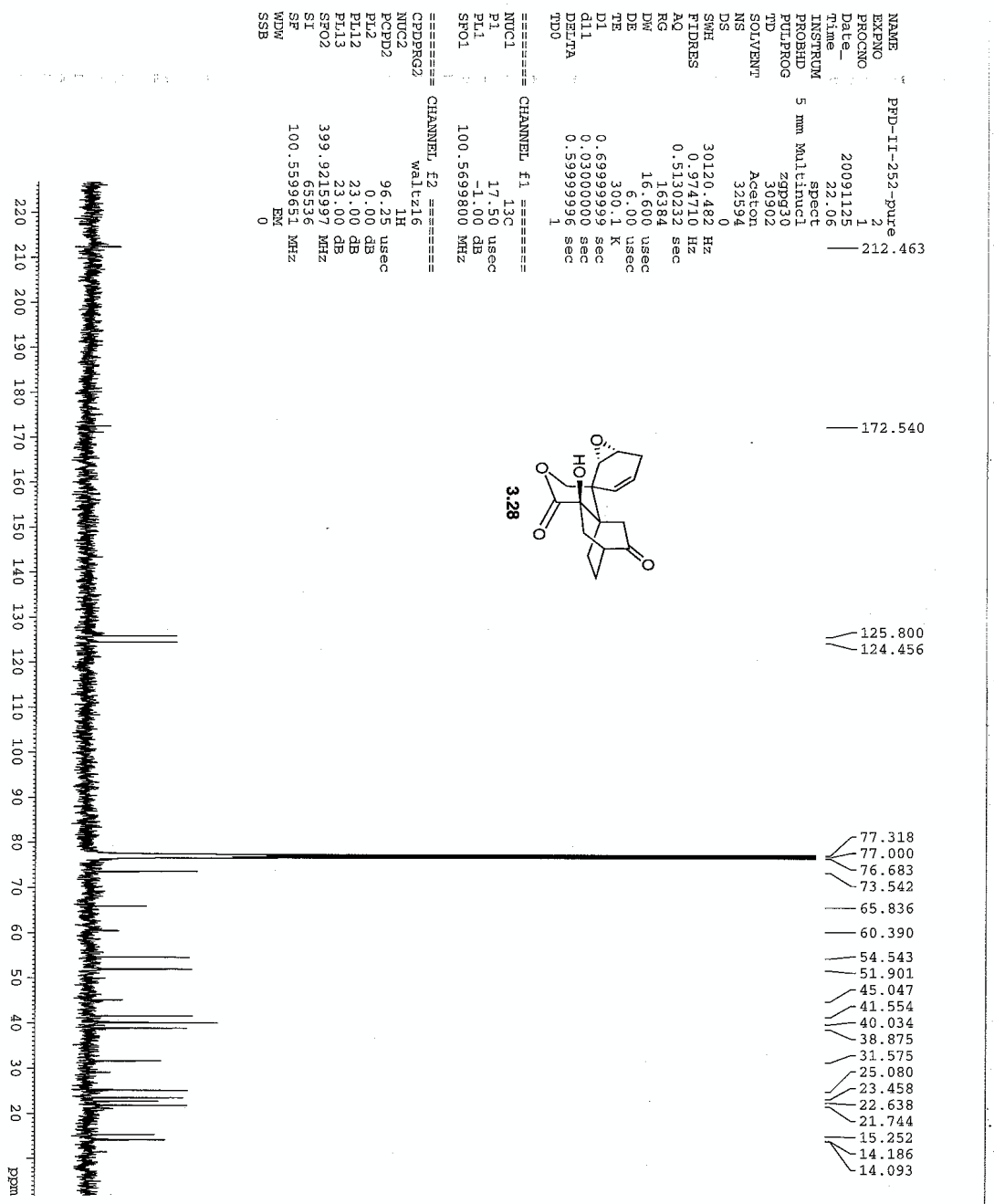

NAME PFD-II-217
EXPNO 1
PROCNO 1
Date_ 20090725
Time 18.20
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT D2O
NS 32
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 10.1
DW 83.400 usec
DE 6.00 usec
TE 300.1 K
D1 1.00000000 sec
TD0 1
========== CHANNEL f1 ==========
NUC1 1H
P1 2.50 usec
PL1 0.00 dB
SFO1 399.9225995 MHz
SI 32768
SF 399.9200118 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
3.8
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 0.5 ppm

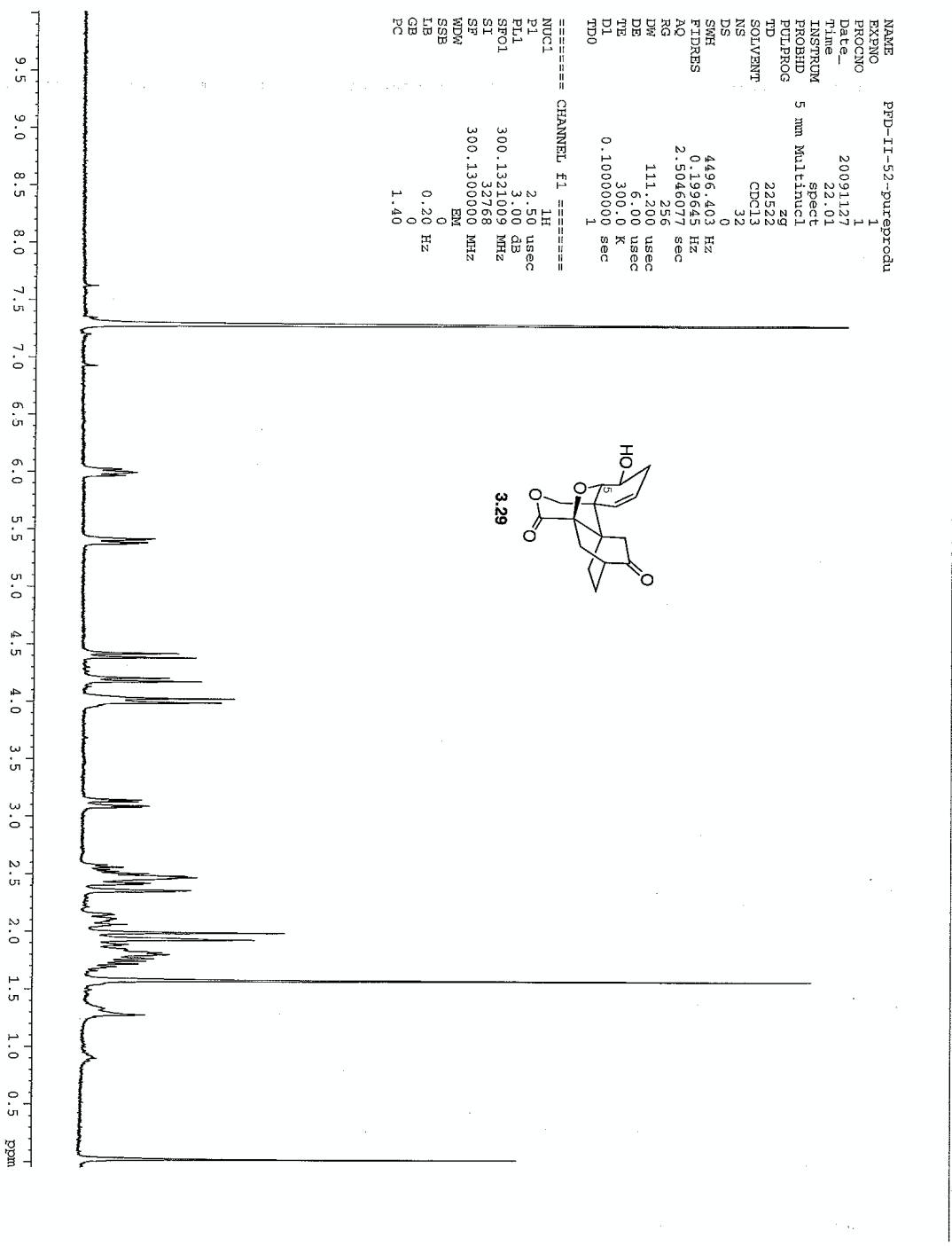

NAME PFD-II-217
EXPNO 2
PROCNO 1
Date_ 20090725
Time 20.23
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 35631
DS 0
SWH 25125.629 Hz
FIDRES 0.813074 Hz
AQ 0.6149998 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 96.25 usec
PL2 0.00 dB
PL12 23.00 dB
PL13 23.00 dB
SFO2 399.9215997 MHz
SI 65536
SF 100.5599659 MHz
WDW EM
SSB 0
3.8
208.520
163.517
143.093
135.690
129.346
128.561
124.353
123.302
77.321
77.003
76.685
71.733
50.065
46.486
41.329
38.856
26.901
25.870
23.101
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

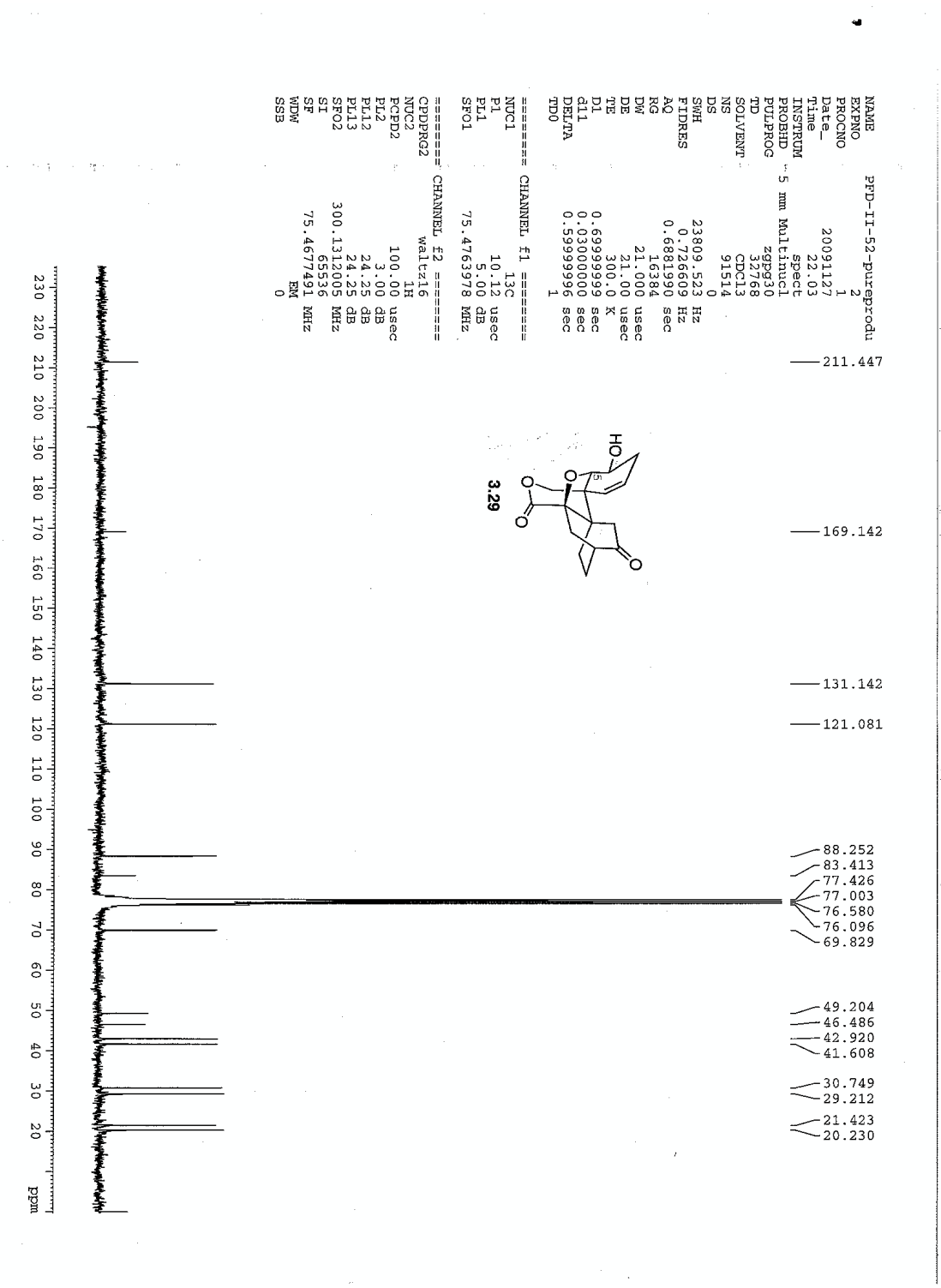

NAME PFD-II-270-spot1
EXPNO 1
PROCNO 1
Date_ 20091112
Time 20.38
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 10.1
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 2.50 usec
PL1 0.00 dB
SFO1 399.9225995 MHz
SI 32768
SF 399.9200111 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
HO
O
O
O
3.21a
10.0 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 0.5 ppm

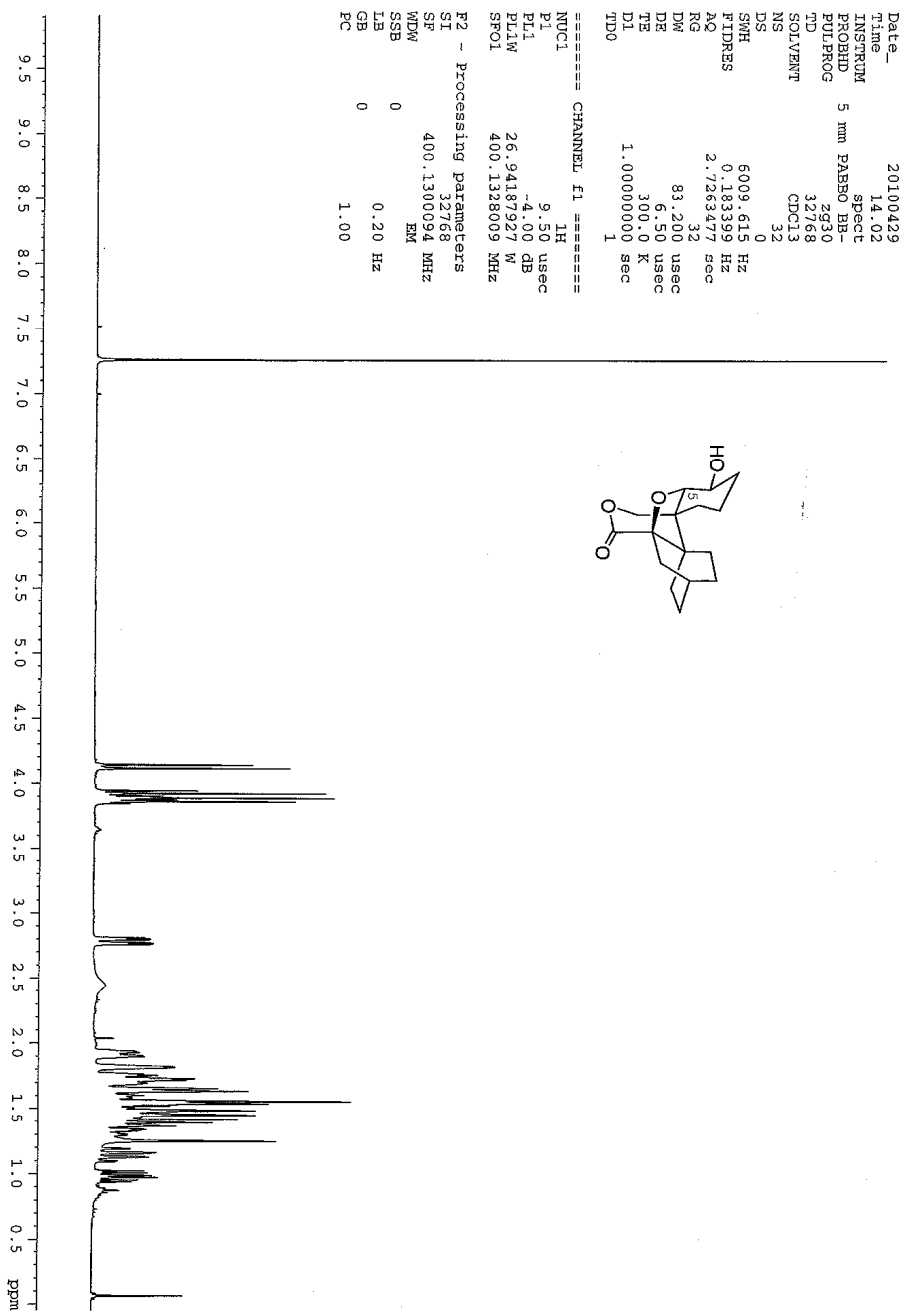

NAME PFD-II-270-sport
EXPNO 1
PROCNO 1
Date_ 20091112
Time 20.38
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 337
DS 0
SWH 23809.523 Hz
FIDRES 0.726609 Hz
AQ 0.6881990 sec
RG 16384
DW 21.000 usec
DE 21.000 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.12 usec
PL1 5.00 dB
SFO1 75.4763978 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 24.25 dB
PL13 24.25 dB
SFO2 300.1312005 MHz
SI 65536
SF 75.4677496 MHz
WDW EM
SSB 0
3.21a
172.899
128.957
128.321
126.298
125.717
77.422
76.999
76.576
76.131
73.934
45.774
41.872
39.756
39.673
39.400
26.174
23.027
22.148
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

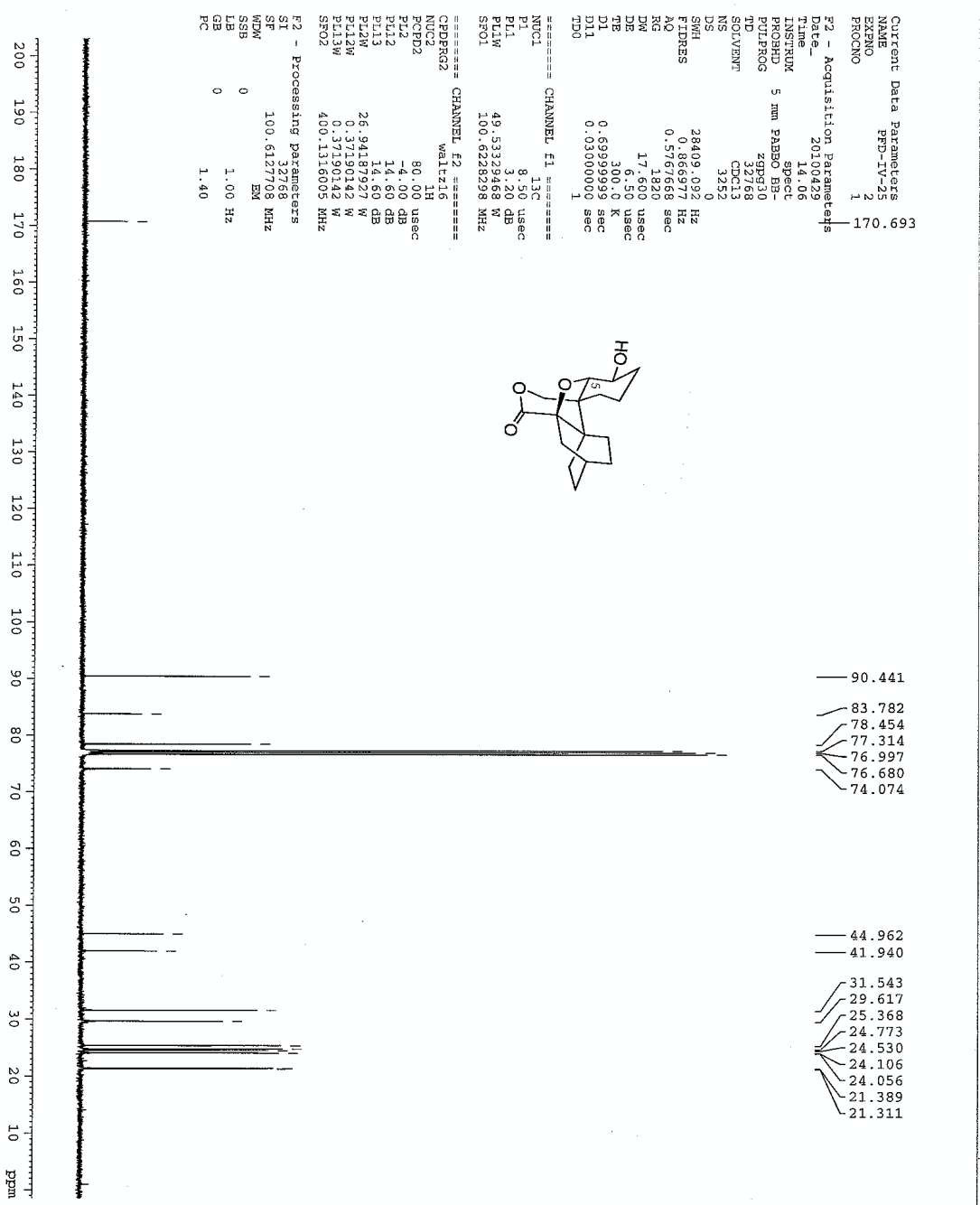

NAME PFD-II-252-pure
EXPNO 1
PROCNO 1
Date_ 20091125
Time 14.58
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT D2O
NS 100
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 10.1
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 2.50 usec
PL1 0.00 dB
SFO1 399.9225995 MHz
SI 32768
SF 399.9200112 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
HO
O
O
O
O
3.28
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 0.5 ppm

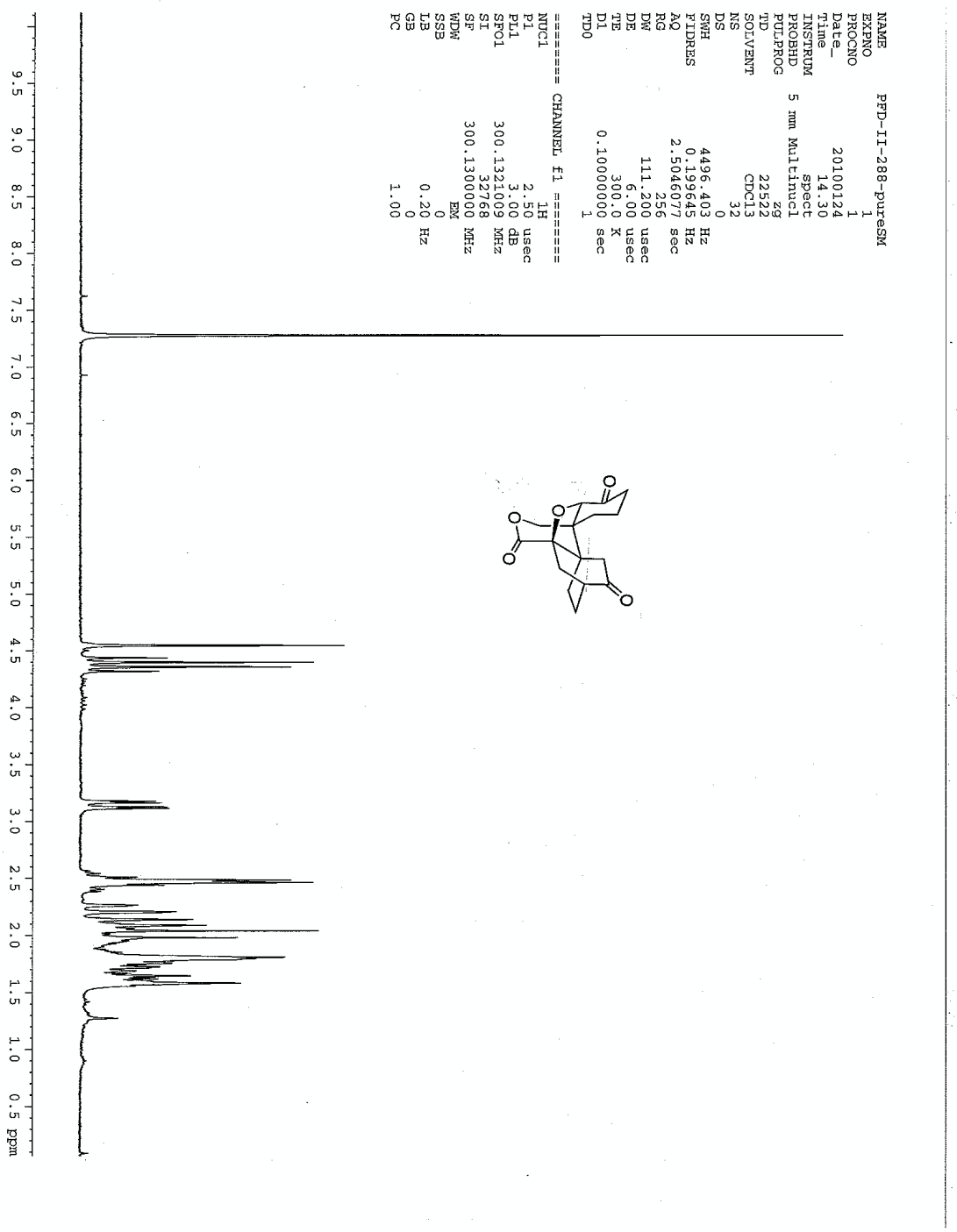

NAME PFD-II-252-pure
EXPNO 2
PROCNO 1
Date_ 20091125
Time 22.06
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 30902
SOLVENT Aceton
NS 32594
DS 0
SWH 30120.482 Hz
FIDRES 0.974710 Hz
AQ 0.5130232 sec
RG 16384
DW 16.600 usec
DE 6.00 usec
TE 300.1 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 96.25 usec
PL2 0.00 dB
PL12 23.00 dB
PL13 23.00 dB
SFO2 399.9215997 MHz
SI 65536
SF 100.5599651 MHz
WDW EM
SSB 0
3.28
212.463
172.540
125.800
124.456
77.318
77.000
76.683
73.542
65.836
60.390
54.543
51.901
45.047
41.554
40.034
38.875
31.575
25.080
23.458
22.638
21.744
15.252
14.186
14.093
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

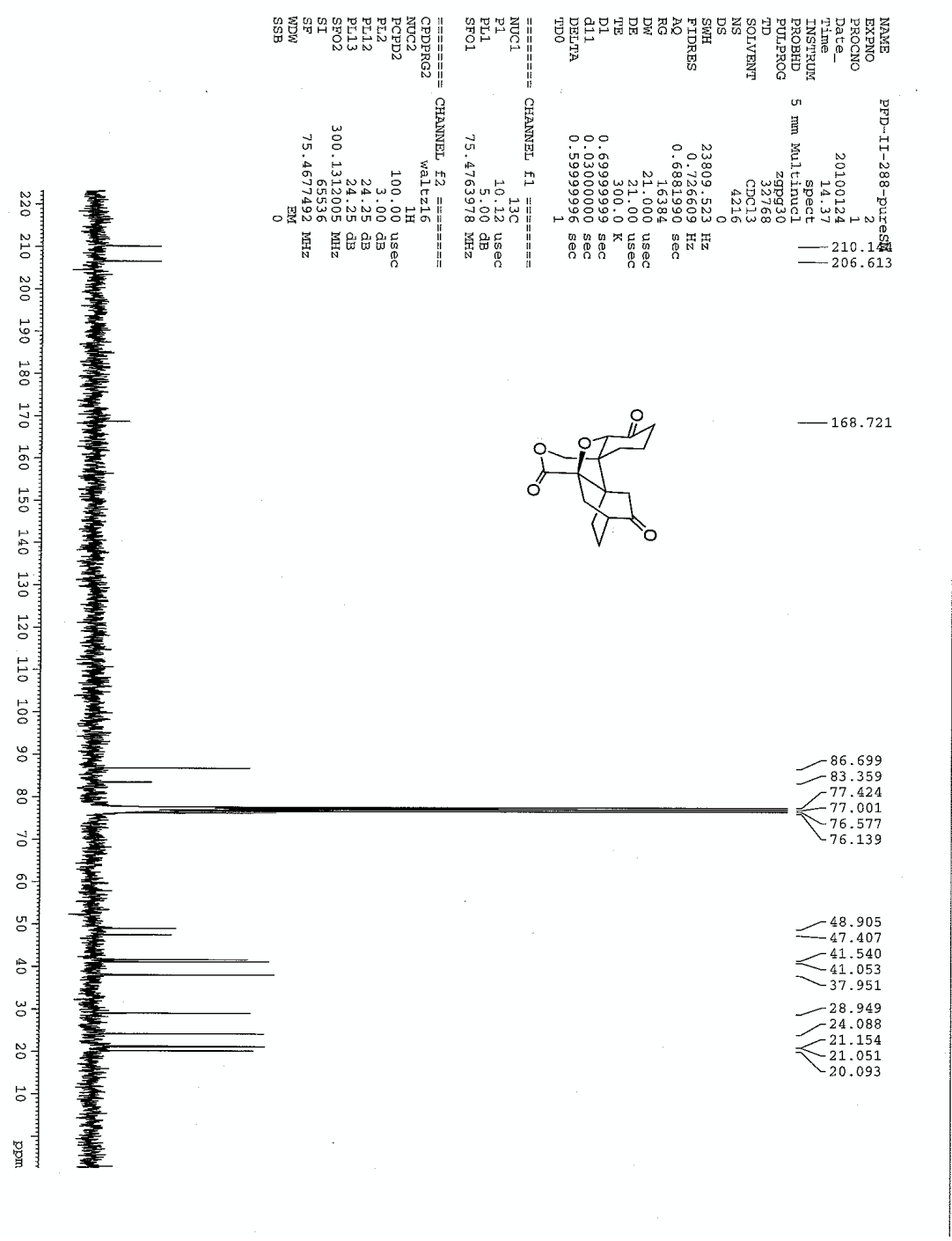

NAME PFD-II-52-pureprodu
EXPNO 1
PROCNO 1
Date_ 20091127
Time 22.01
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 22522
SOLVENT CDCl3
NS 32
DS 0
SWH 4496.403 Hz
FIDRES 0.199645 Hz
AQ 2.5046077 sec
RG 256
DW 111.200 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 2.50 usec
PL1 3.00 dB
SFO1 300.1321009 MHz
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40
HO
O
O
O
O
3.29
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 0.5 ppm


NAME PFD-II-52-pureprodu
EXPNO 2
PROCNO 1
Date_ 20091127
Time_ 22.03
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 91514
DS 0
SWH 23809.523 Hz
FIDRES 0.726609 Hz
AQ 0.6881990 sec
RG 16384
DW 21.000 usec
DE 21.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.12 usec
PL1 5.00 dB
SFO1 75.4763978 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 24.25 dB
PL13 24.25 dB
SFO2 300.1312005 MHz
SI 65536
SF 75.4677491 MHz
WDW EM
SSB 0
3.29
211.447
169.142
131.142
121.081
88.252
83.413
77.426
77.003
76.580
76.096
69.829
49.204
46.486
42.920
41.608
30.749
29.212
21.423
20.230
ppm

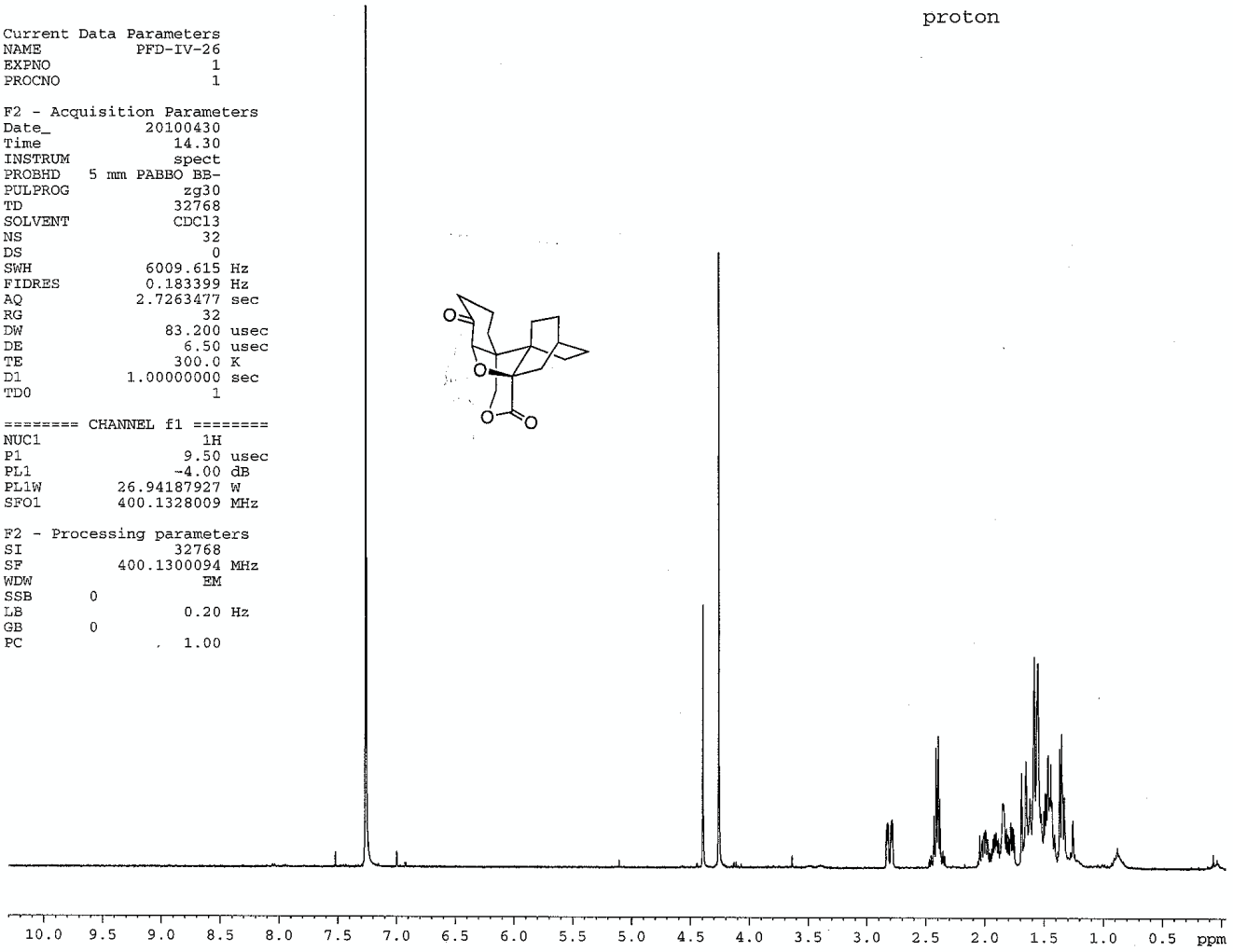

Current Data Parameters
NAME PFD-IV-25
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100429
Time_ 14.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
========== CHANNEL f1 ==========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PLIW 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
HO
O
O
O
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 0.5 ppm

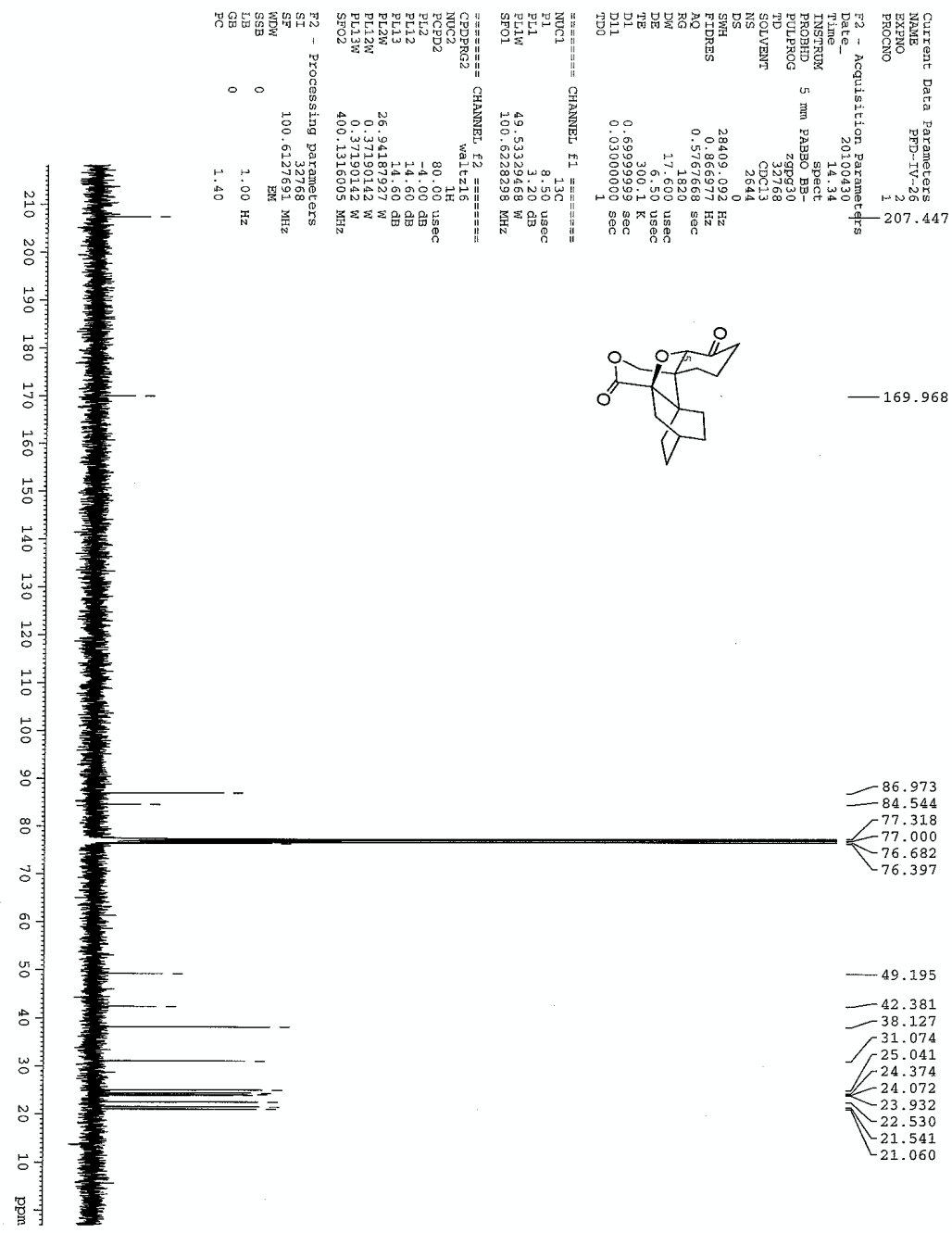

Current Data Parameters
NAME PFD-IV-25
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100429
Time 14.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 3252
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767658 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 300.0 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
========== CHANNEL f1 ==========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 14.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127708 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170.693
90.441
83.782
78.454
77.314
76.997
76.680
74.074
44.962
41.940
31.543
29.617
25.368
24.773
24.530
24.106
24.056
21.389
21.311
OH
O
O
O
S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

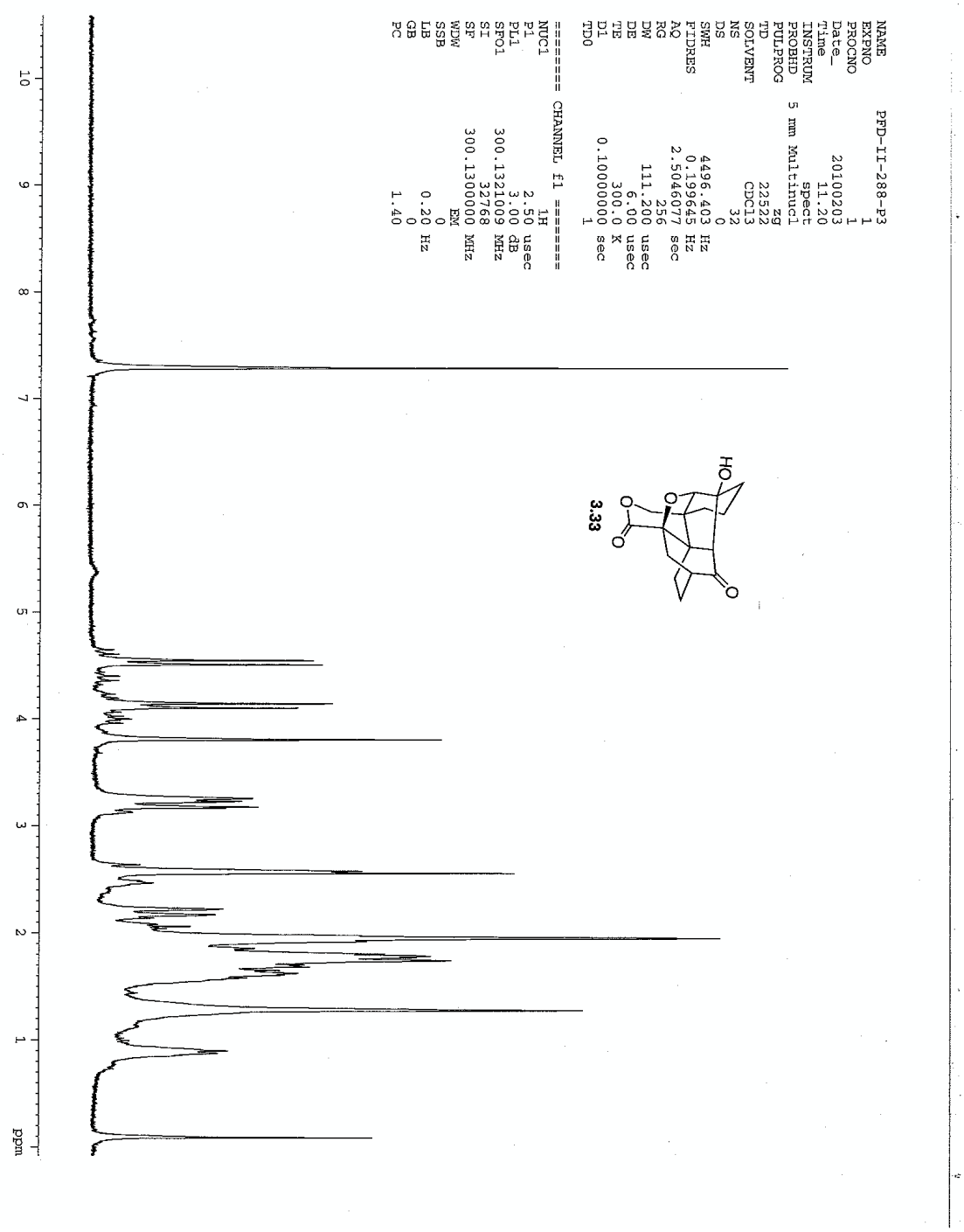

NAME PFD-II-288-pureSM
EXPNO 1
PROCNO 1
Date_ 20100124
Time 14.30
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 22522
SOLVENT CDCl3
NS 32
DS 0
SWH 4496.403 Hz
FIDRES 0.199645 Hz
AQ 2.50446077 sec
RG 256
DW 111.200 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 2.50 usec
PL1 3.00 dB
SFO1 300.1321009 MHz
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
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 0.5 ppm

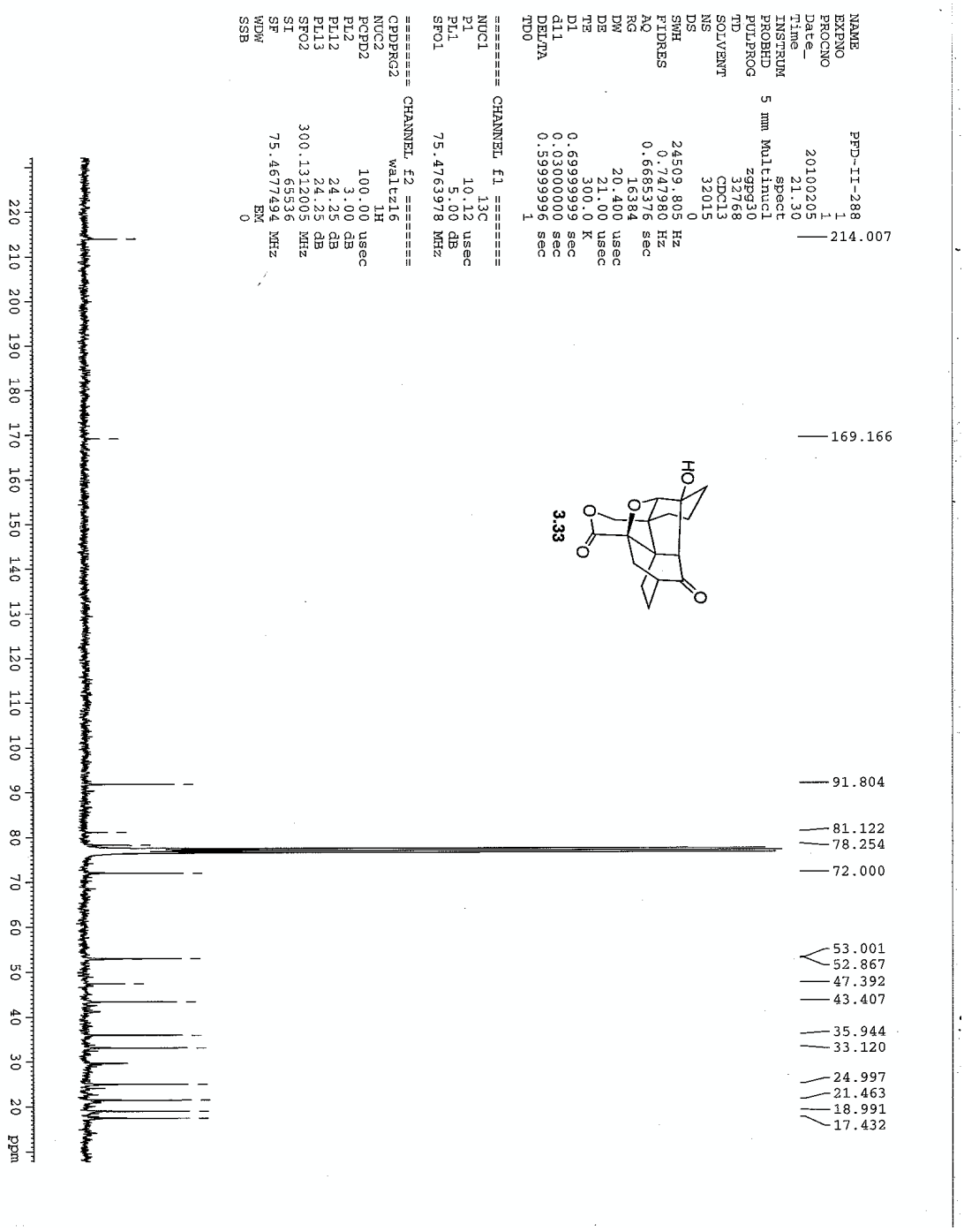

NAME PFD-II-288-pureSM
EXPNO 2
PROCNO 1
Date_ 20100124
Time 14.37
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 4216
DS 0
SWH 23809.523 Hz
FIDRES 0.726609 Hz
AQ 0.6881990 sec
RG 16384
DW 21.000 usec
DE 21.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.12 usec
PL1 5.00 dB
SFO1 75.4763978 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 24.25 dB
PL13 24.25 dB
SFO2 300.1312005 MHz
SI 65536
SF 75.4677492 MHz
WDW EM
SSB 0
210.144
206.613
168.721
86.699
83.359
77.424
77.001
76.577
76.139
48.905
47.407
41.540
41.053
37.951
28.949
24.088
21.154
21.051
20.093
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

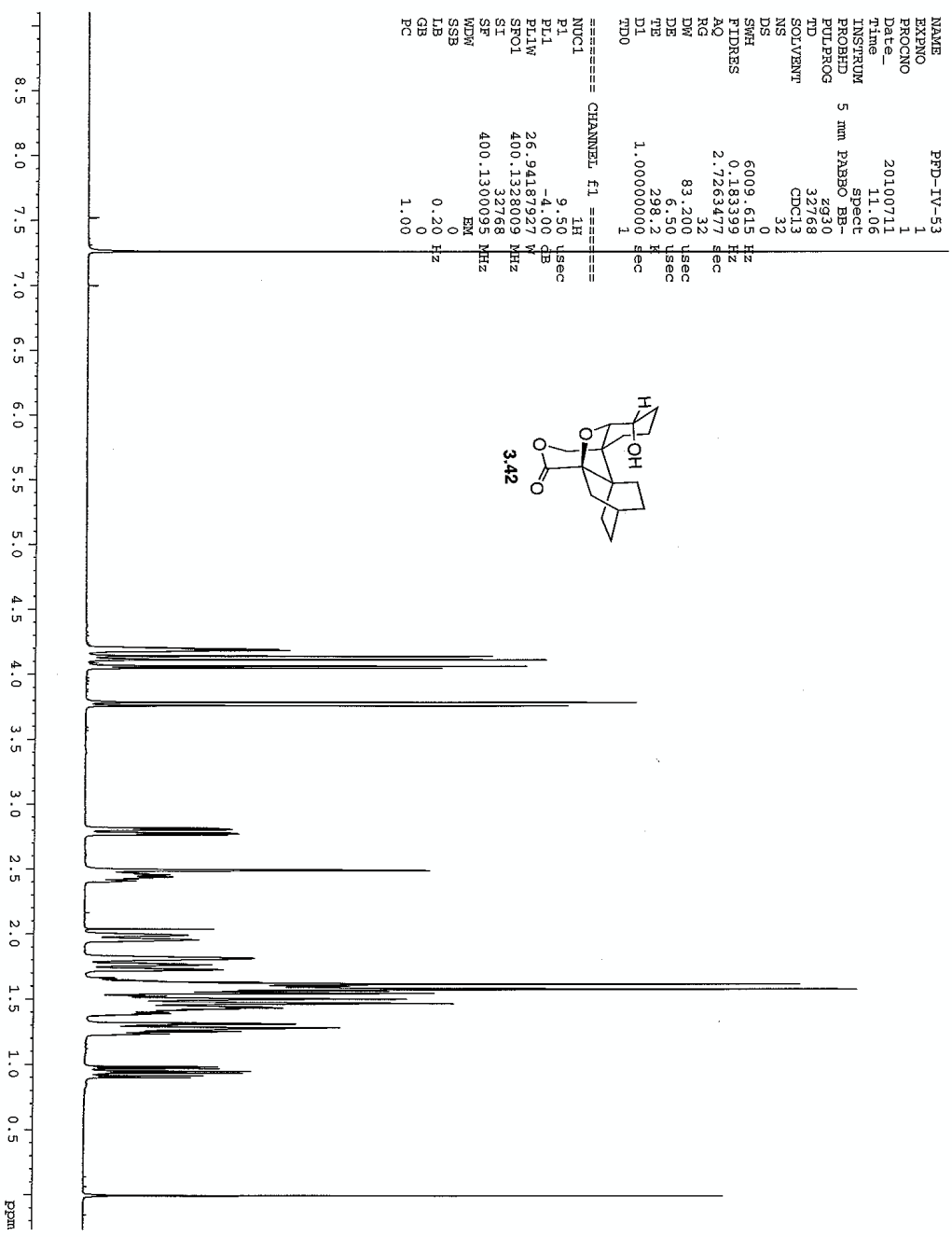
```
Current Data Parameters
NAME           PFD-IV-26
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100430
Time               14.30
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ             2.7263477 sec
RG                    32
DW                83.200 usec
DE                 6.50 usec
TE                300.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1                -4.00 dB
PL1W        26.94187927 W
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300094 MHz
WDW                   EM
SSB       0
LB                 0.20 Hz
GB        0
PC                 1.00
```

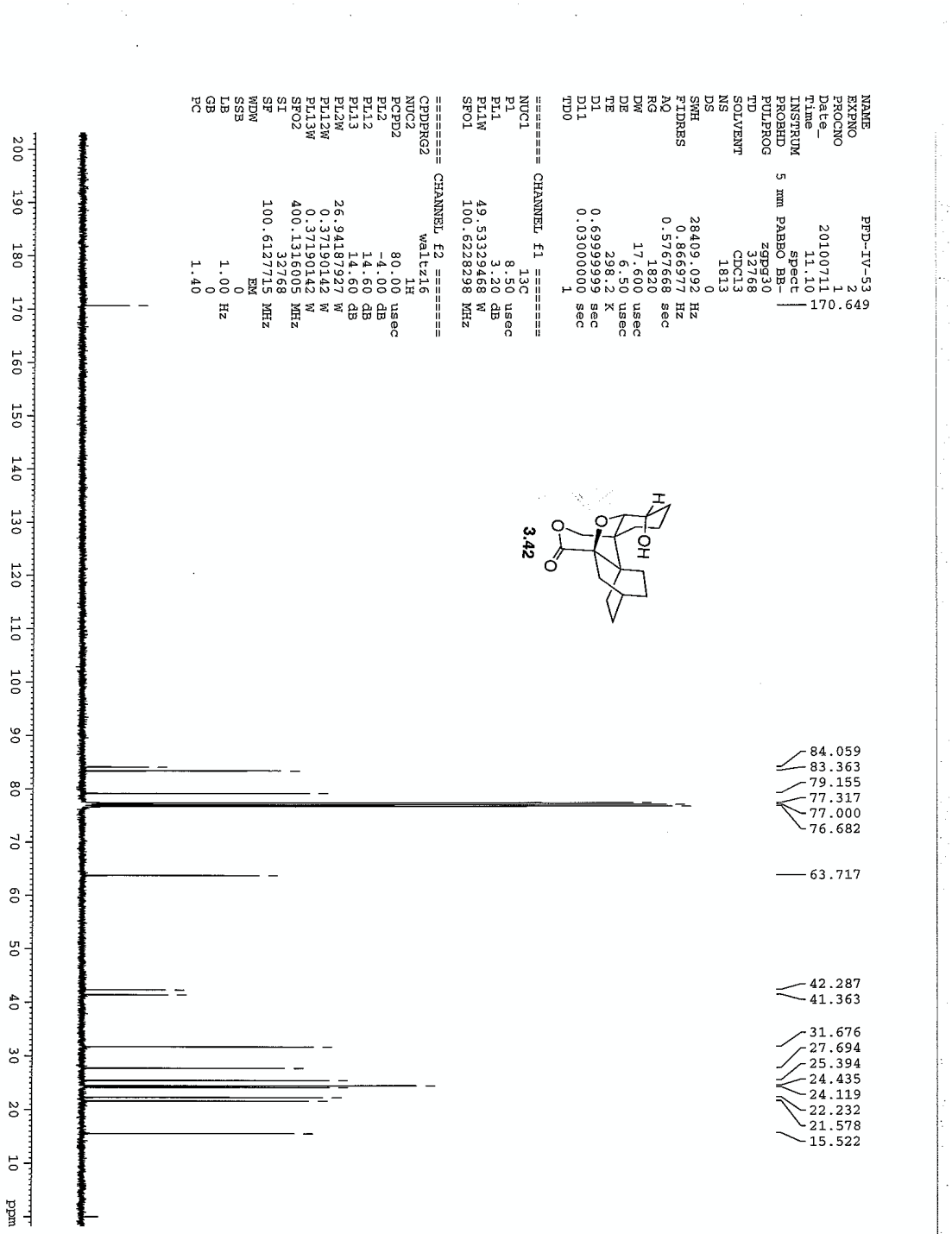


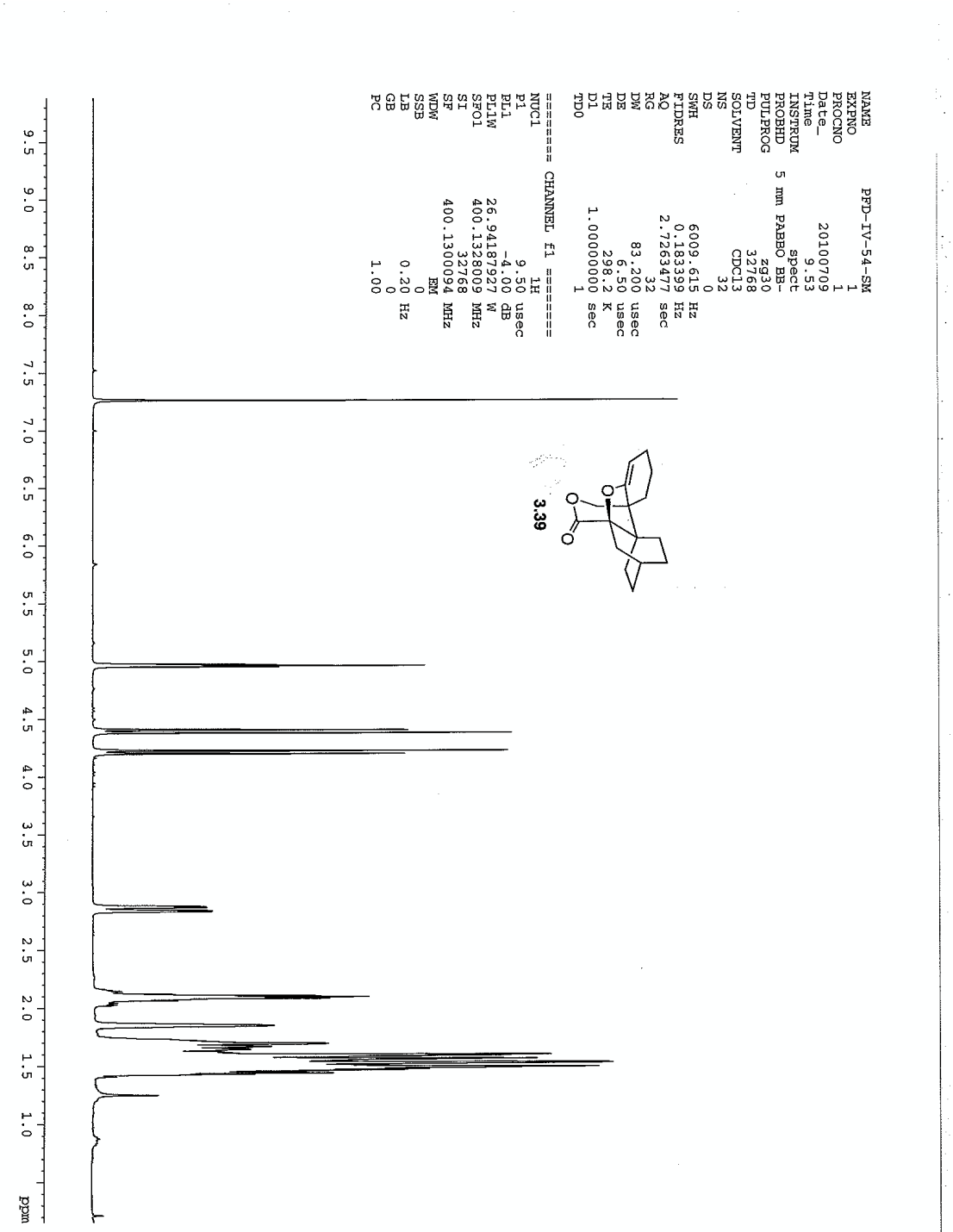

Current Data Parameters
NAME PFD-IV-26
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100430
Time 14.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 2644
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 300.1 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127691 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
207.447
169.968
86.973
84.544
77.318
77.000
76.682
76.397
49.195
42.381
38.127
31.074
25.041
24.374
24.072
23.932
22.530
21.541
21.060
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

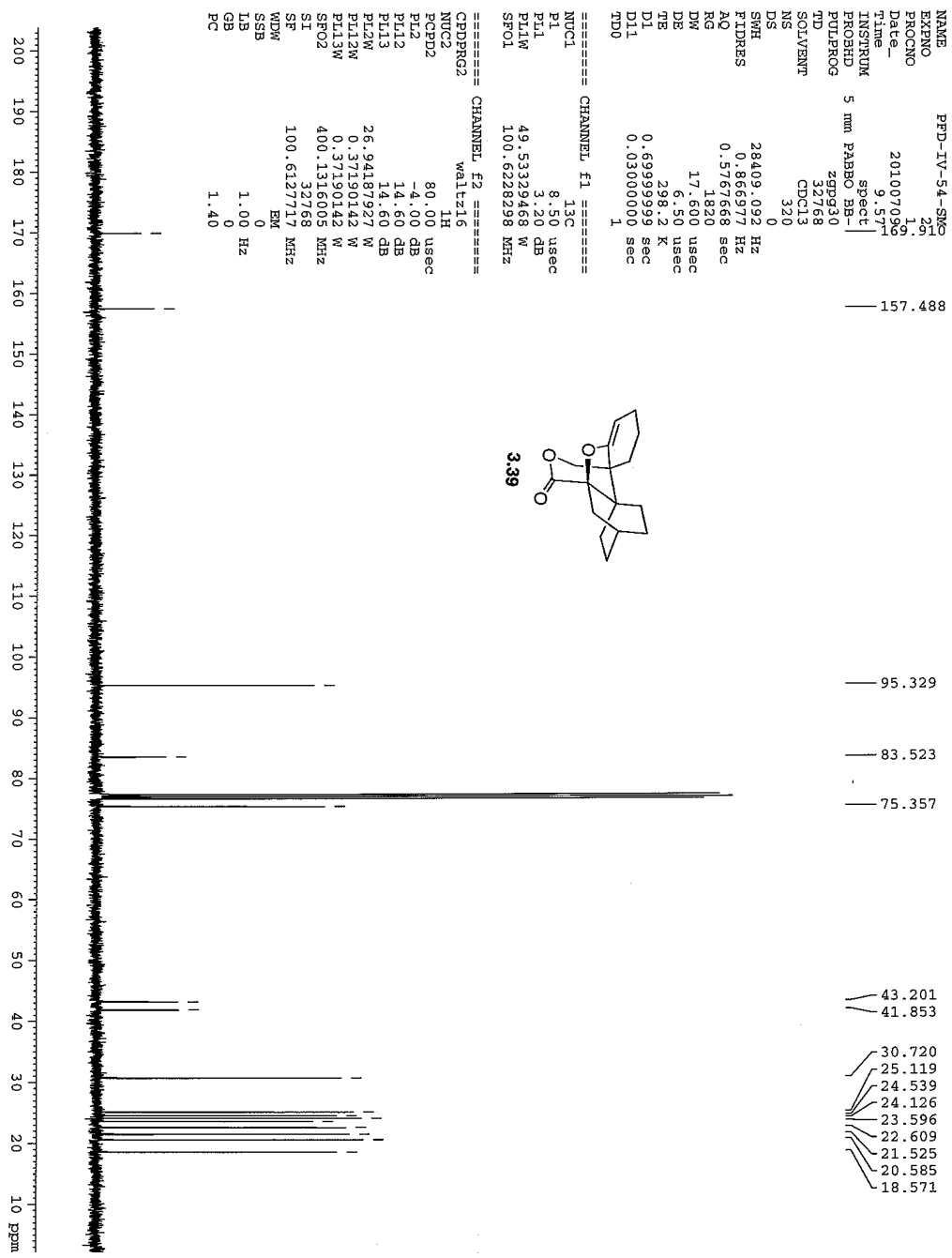

NAME PFD-II-288-P3
EXPNO 1
PROCNO 1
Date_ 20100203
Time 11.20
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 22522
SOLVENT CDCl3
NS 32
DS 0
SWH 4496.403 Hz
FIDRES 0.199645 Hz
AQ 2.5046077 sec
RG 256
DW 111.200 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 2.50 usec
PL1 3.00 dB
SFO1 300.1321009 MHz
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40
HO
O
O
O
O
3.33
10
9
8
7
6
5
4
3
2
1
ppm

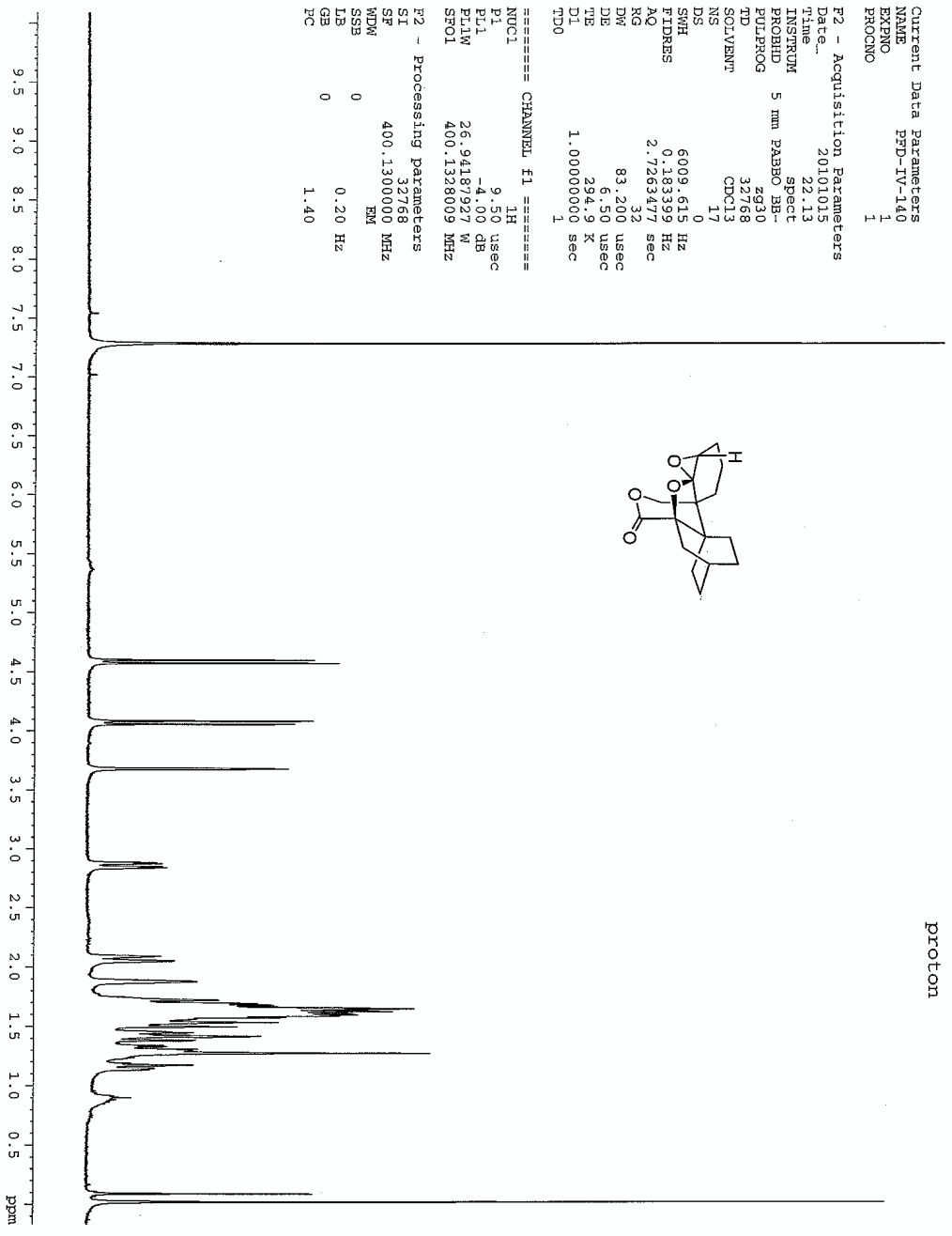

NAME PFD-II-288
EXPNO 1
PROCNO 1
Date_ 20100205
Time_ 21.30
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 32015
DS 0
SWH 24509.805 Hz
FIDRES 0.747980 Hz
AQ 0.6685376 sec
RG 16384
DW 20.400 usec
DE 21.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.12 usec
PL1 5.00 dB
SFO1 75.4763978 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 24.25 dB
PL13 24.25 dB
SFO2 300.1312005 MHz
SI 65536
SF 75.4677494 MHz
WDW EM
SSB 0
214.007
169.166
91.804
81.122
78.254
72.000
53.001
52.867
47.392
43.407
35.944
33.120
24.997
21.463
18.991
17.432
3.33
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

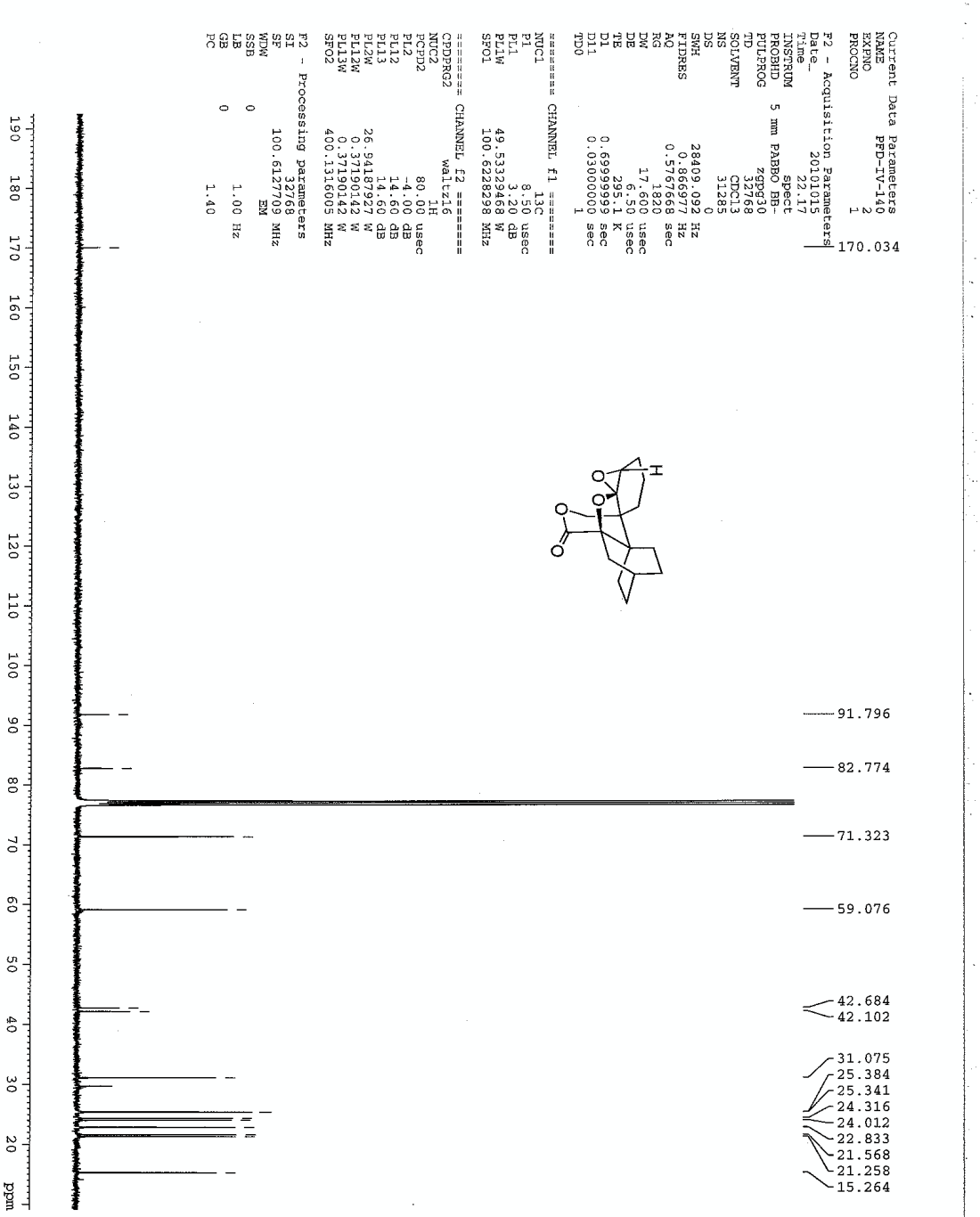

NAME PFD-IV-53
EXPNO 1
PROCNO 1
Date_ 20100711
Time_ 11.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
H
OH
O
O
O
3.42
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 0.5
ppm

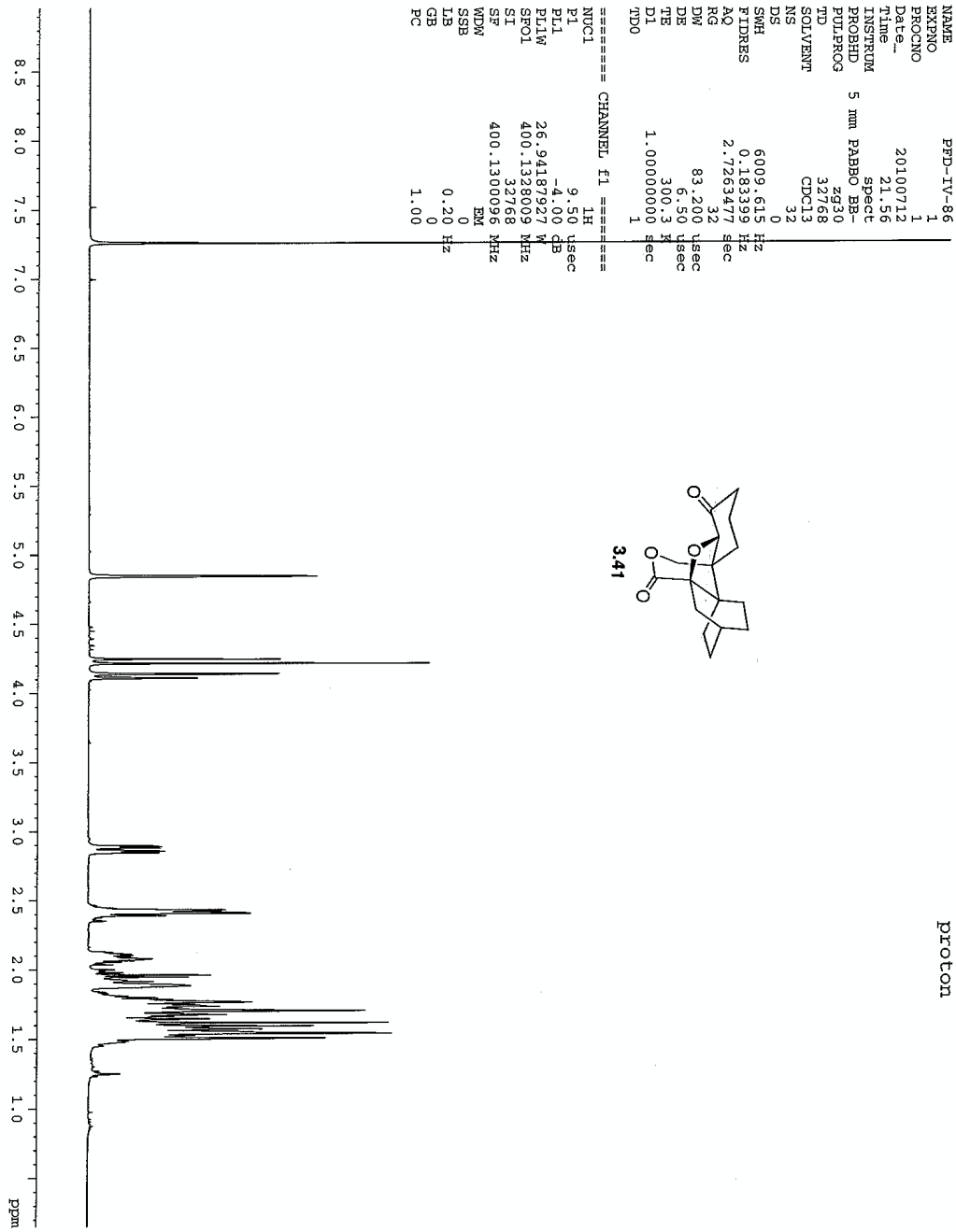

NAME PFD-IV-53
EXPNO 2
PROCNO 1
Date_ 20100711
Time_ 11.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1813
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 298.2 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127715 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
3.42
84.059
83.363
79.155
77.317
77.000
76.682
63.717
42.287
41.363
31.676
27.694
25.394
24.435
24.119
22.232
21.578
15.522
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

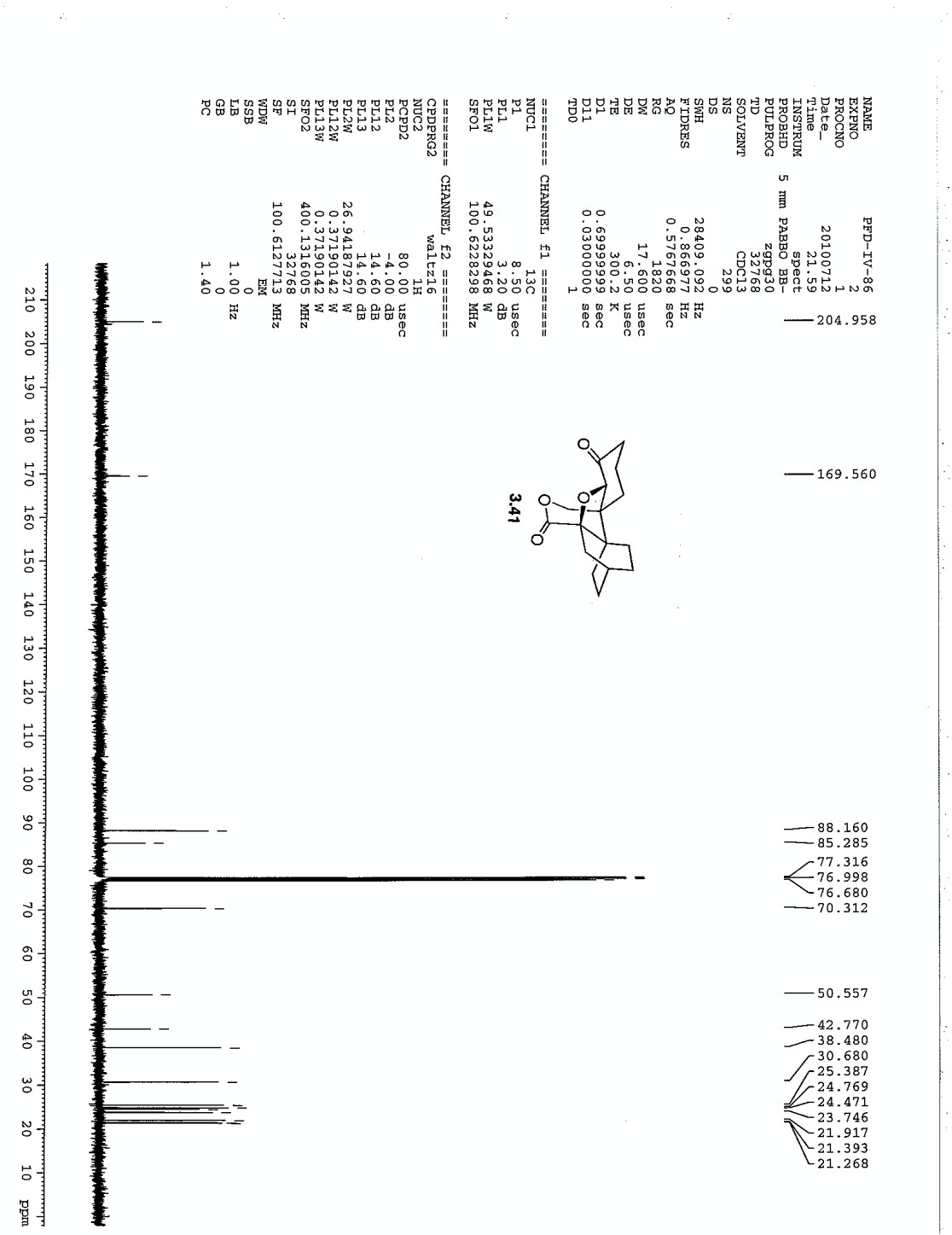

NAME PFD-IV-54-SM
EXPNO 1
PROCNO 1
Date_ 20100709
Time 9.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
3.39
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
ppm

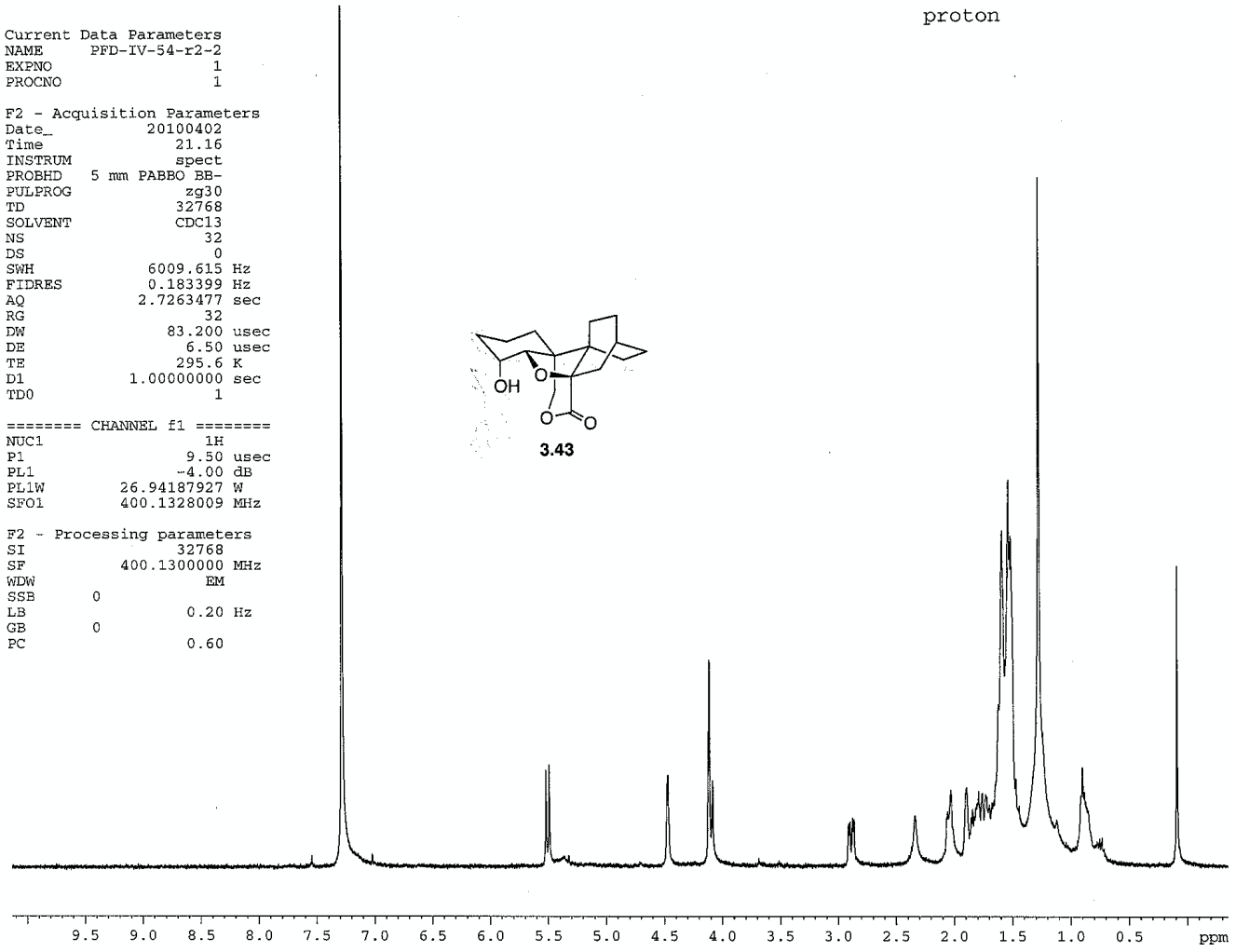

NAME PFD-IV-54-SMO
EXPNO 20
PROCNO 1
Date_ 20100709
Time_ 9.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 320
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 298.2 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127717 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
3.39
157.488
95.329
83.523
75.357
43.201
41.853
30.720
25.119
24.539
24.126
23.596
22.609
21.525
20.585
18.571
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

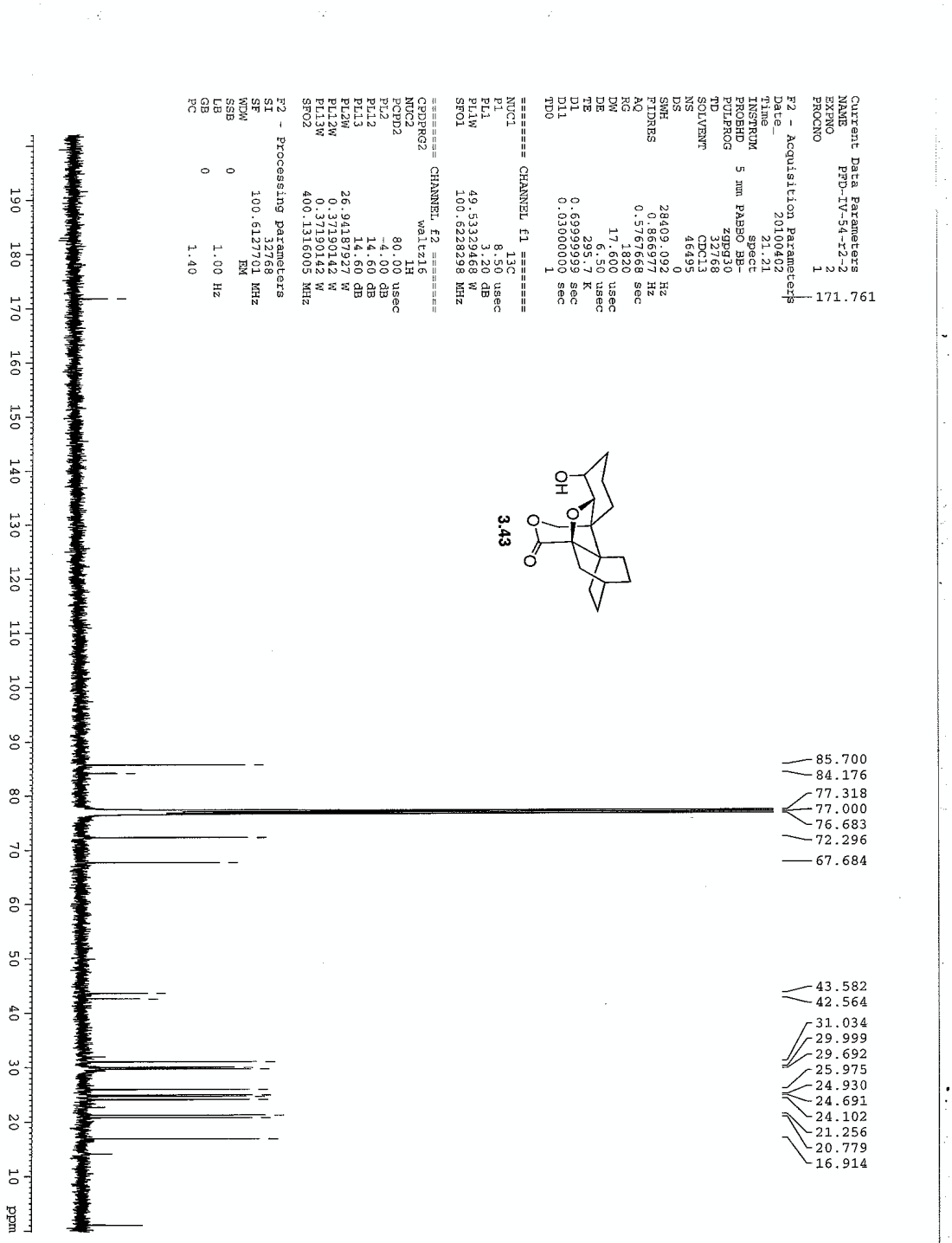

Current Data Parameters
NAME PFD-IV-140
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101015
Time 22.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 17
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 294.9 K
D1 1.00000000 sec
TD0 1
========== CHANNEL f1 ==========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40
H
O
O
O
O
proton
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 0.5 ppm


Current Data Parameters
NAME PFD-IV-140
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101015
Time 22.17
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 31285
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.576668 sec
RG 17.820
DW 17.600 usec
DE 6.50 usec
TE 295.1 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127709 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170.034
91.796
82.774
71.323
59.076
42.684
42.102
31.075
25.384
25.341
24.316
24.012
22.833
21.568
21.258
15.264
ppm

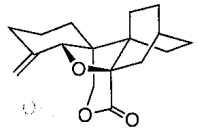

NAME PFD-IV-86
EXPNO 1
PROCNO 1
Date_ 20100712
Time 21.56
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 300.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
SI 32768
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
3.41
proton
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
ppm


NAME PFD-IV-86
EXPNO 2
PROCNO 1
Date_ 20100712
Time_ 21.59
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 299
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 300.2 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127713 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
3.41
204.958
169.560
88.160
85.285
77.316
76.998
76.680
70.312
50.557
42.770
38.480
30.680
25.387
24.769
24.471
23.746
21.917
21.393
21.268
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

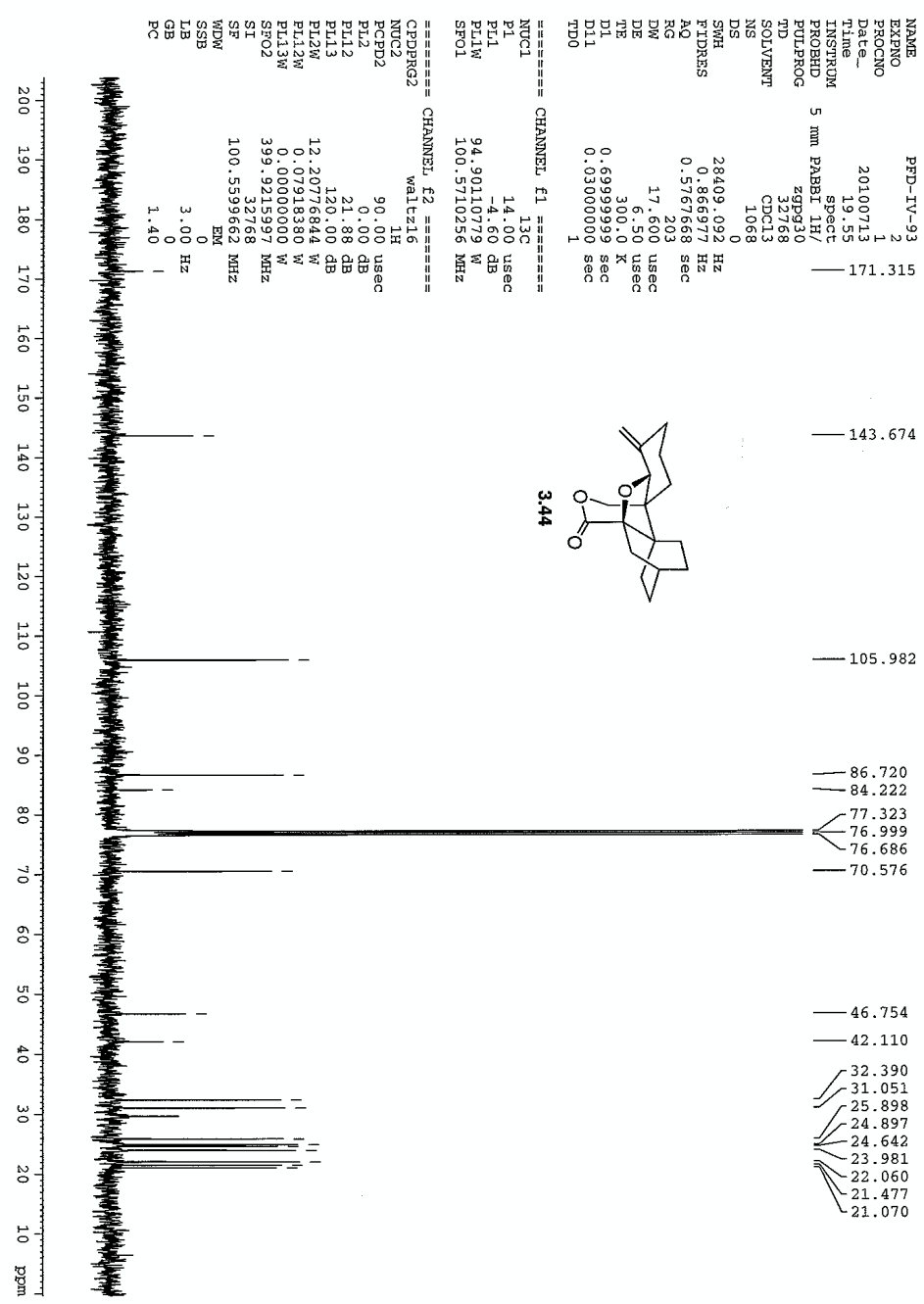

Current Data Parameters
NAME PFD-IV-54-r2-2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100402
Time 21.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDC13
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 295.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 0.60
proton
OH
O
O
O
3.43
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
0.5
ppm

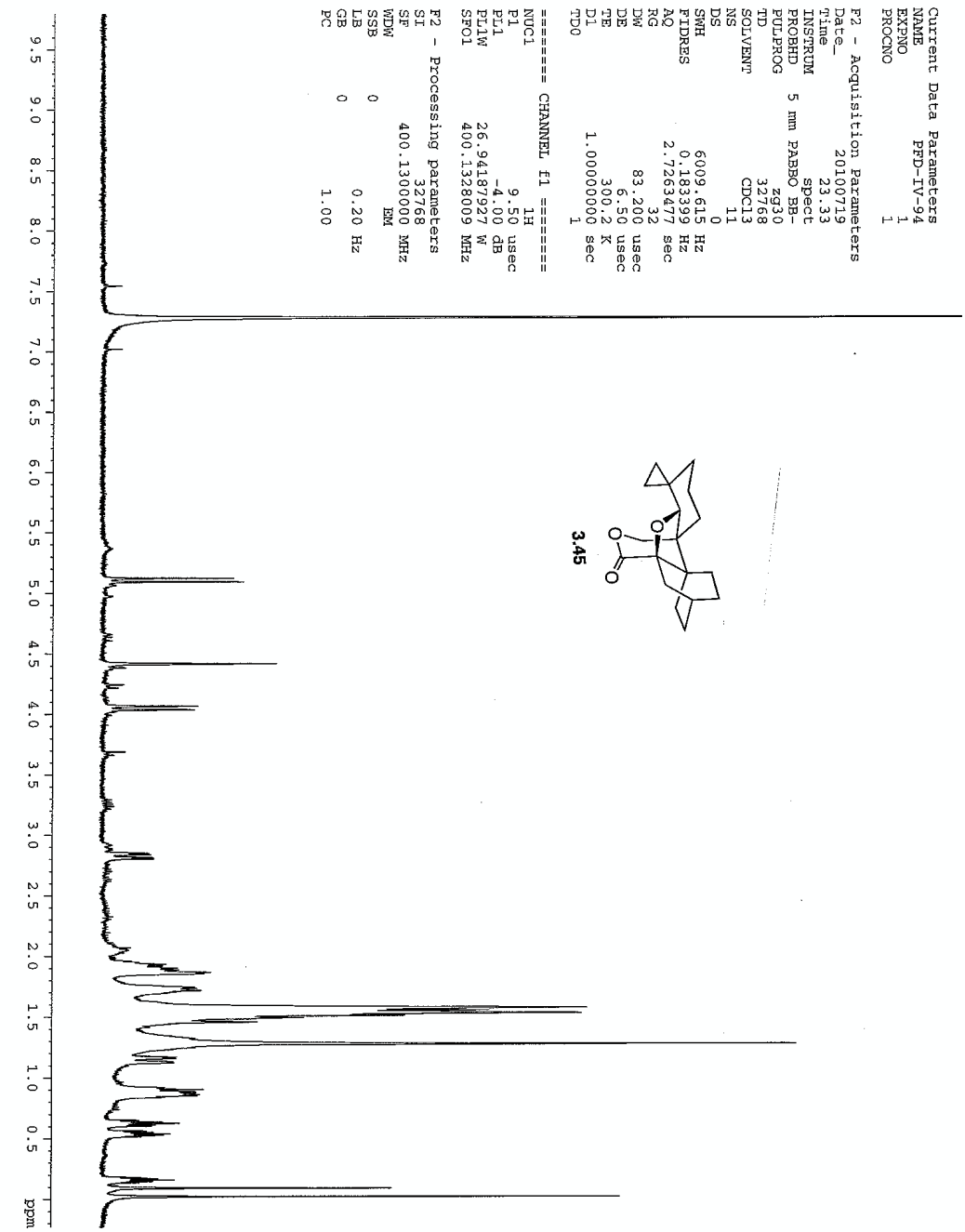

Current Data Parameters
NAME PPD-IV-54-r2-2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100402
Time 21.21
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 46495
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 295.7 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127701 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
3.43
171.761
85.700
84.176
77.318
77.000
76.683
72.296
67.684
43.582
42.564
31.034
29.999
29.692
25.975
24.930
24.691
24.102
21.256
20.779
16.914
ppm

NAME	PFD-IV-93
EXPNO	1
PROCNO	1
Date_	20100713
Time	13.52
INSTRUM	spect
PROBHD	5 mm PABBI 1H/
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	203
DW	83.200 usec
DE	6.50 usec
TE	300.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	7.25 usec
PL1	0.00 dB
PL1W	12.20776844 W
SFO1	399.9225995 MHz
SI	32768
SF	399.9200105 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



3.44


NAME PFD-IV-93
EXPNO 2
PROCNO 1
Date_ 20100713
Time 19.55
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1068
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 203
DW 17.600 usec
DE 6.50 usec
TE 300.0 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 14.00 usec
PL1 -4.60 dB
PL1W 94.90110779 W
SFO1 100.5710256 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 21.88 dB
PL13 120.00 dB
PL2W 12.20776844 W
PL12W 0.07918380 W
PL13W 0.00000000 W
SFO2 399.9215997 MHz
SI 32768
SF 100.5599662 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
3.44
143.674
105.982
86.720
84.222
77.323
76.999
76.686
70.576
46.754
42.110
32.390
31.051
25.898
24.897
24.642
23.981
22.060
21.477
21.070
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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PROCNO 1
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Time 23.33
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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 11
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
3.45
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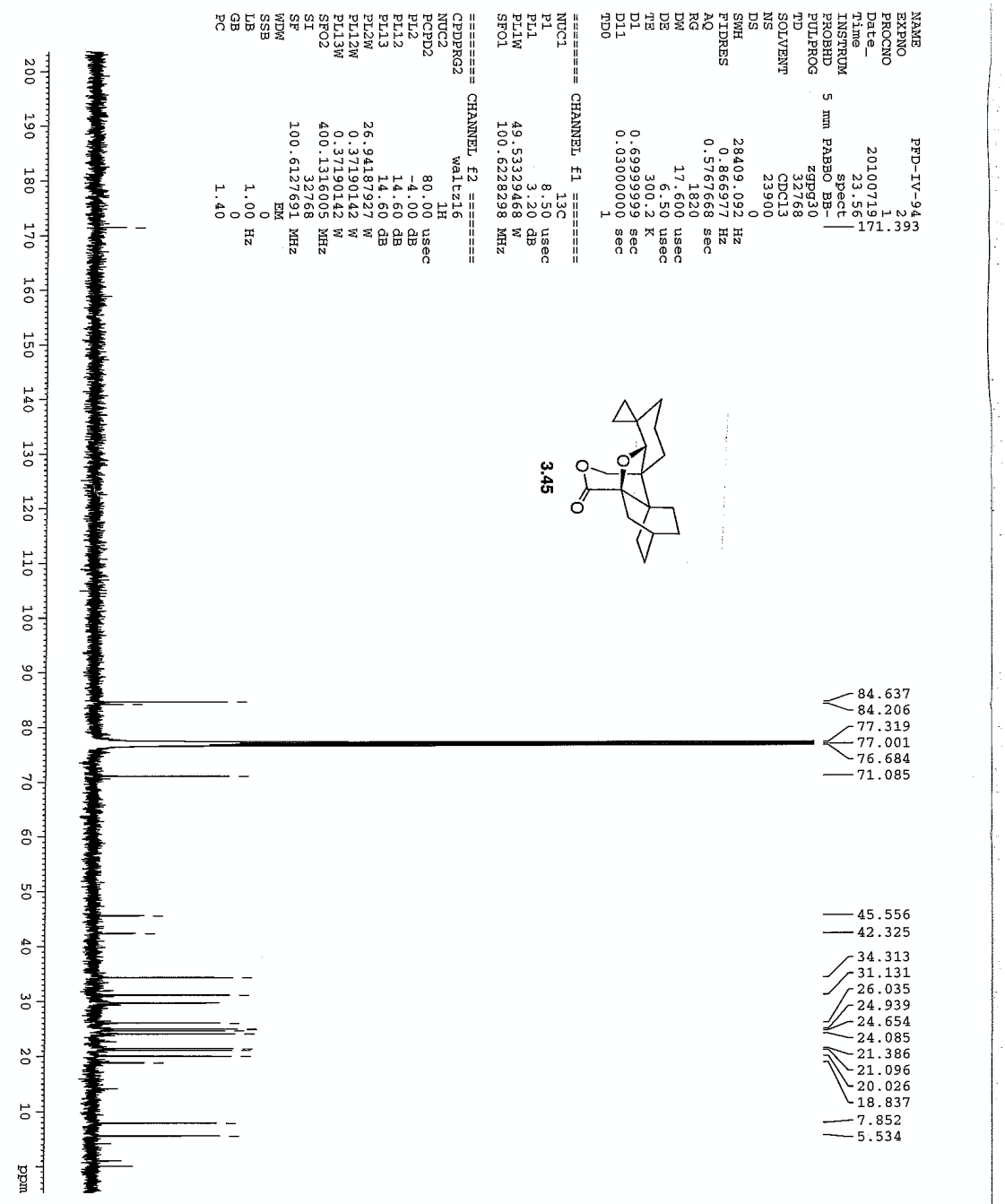
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PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 23900
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 300.2 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127691 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
3.45
84.637
84.206
77.319
77.001
76.684
71.085
45.556
42.325
34.313
31.131
26.035
24.939
24.654
24.085
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21.096
20.026
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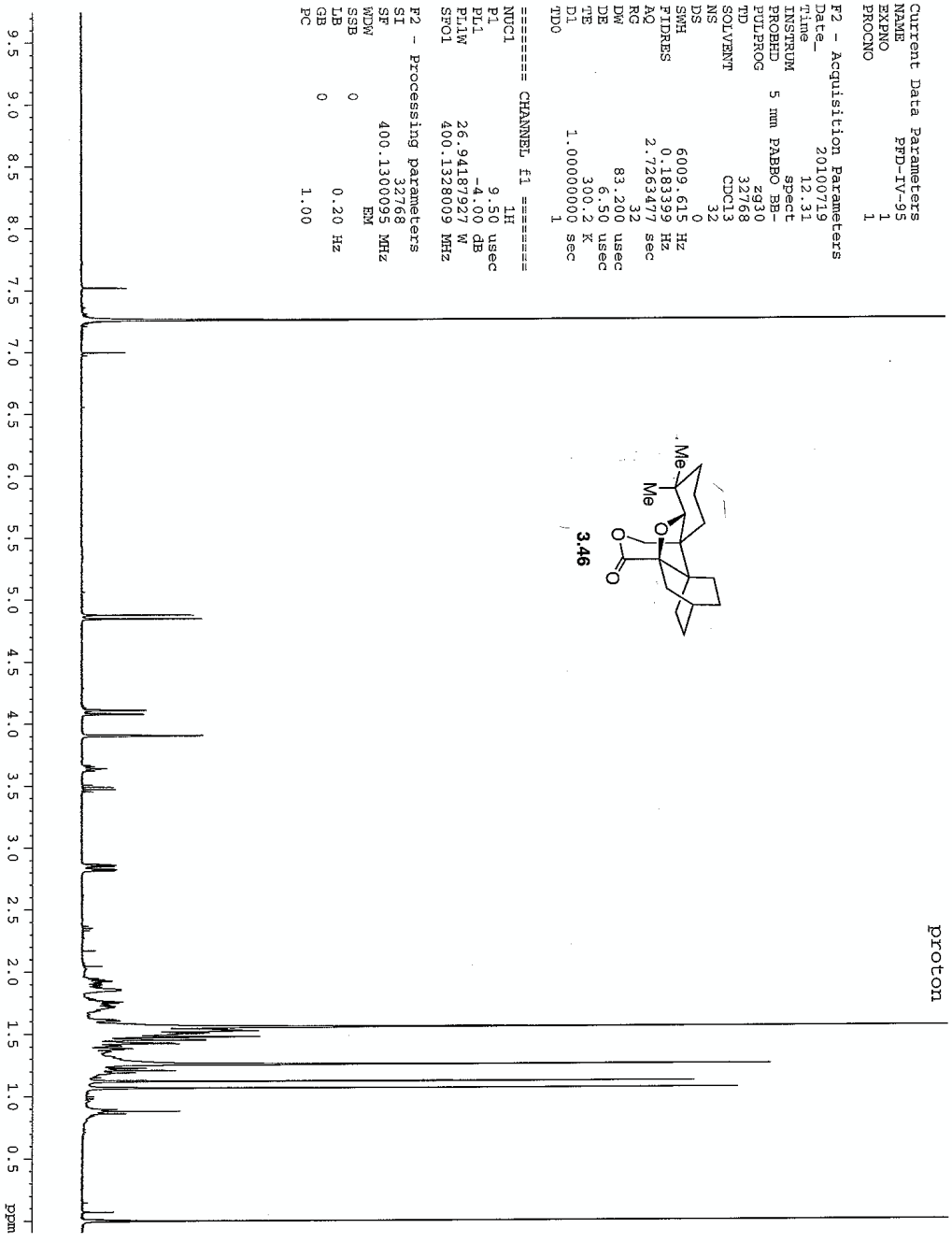
7.852
5.534
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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PROCNO 1
F2 - Acquisition Parameters
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INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
Me
Me
O
O
O
3.46
proton
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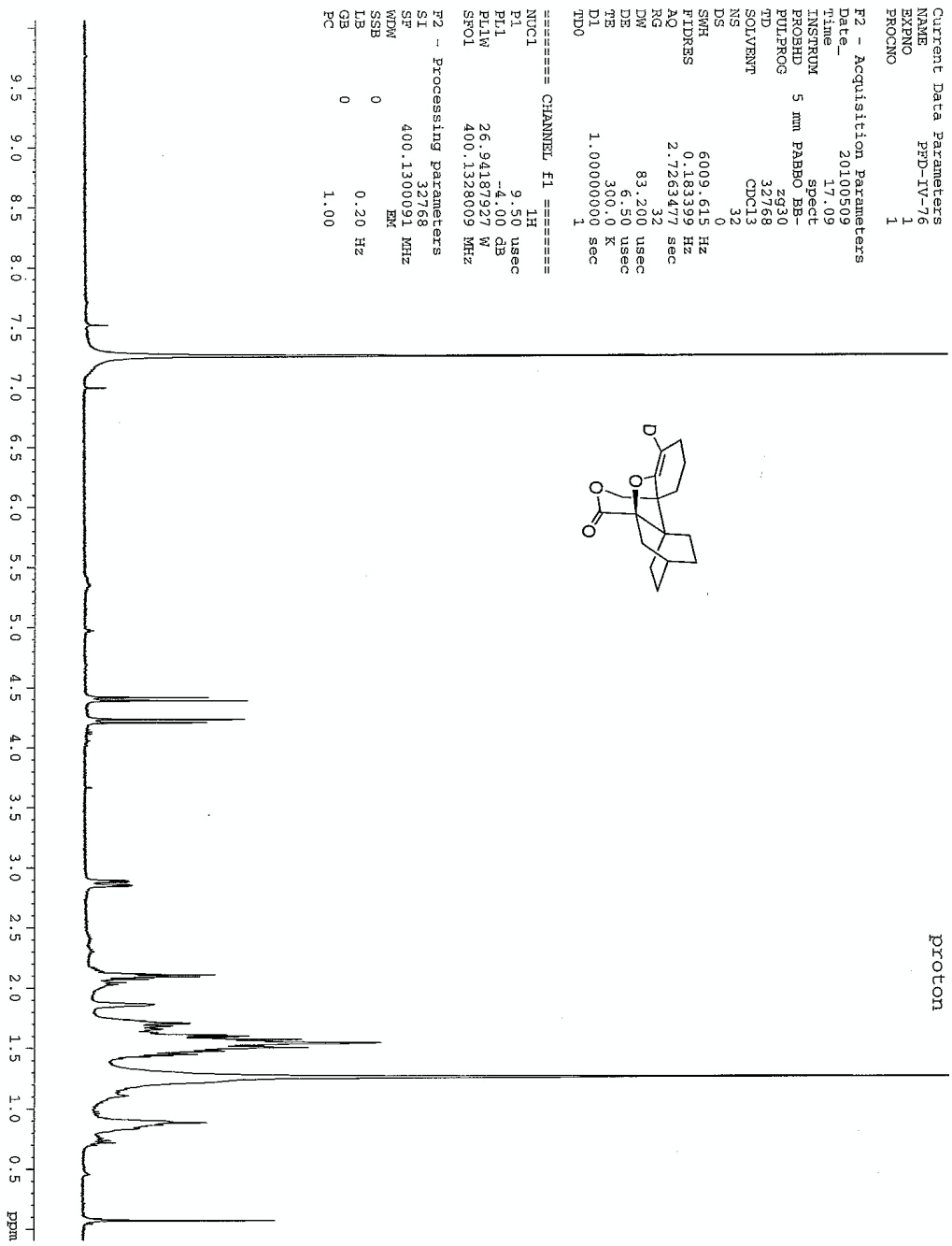
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PROCNO 1
F2 - Acquisition Parameters
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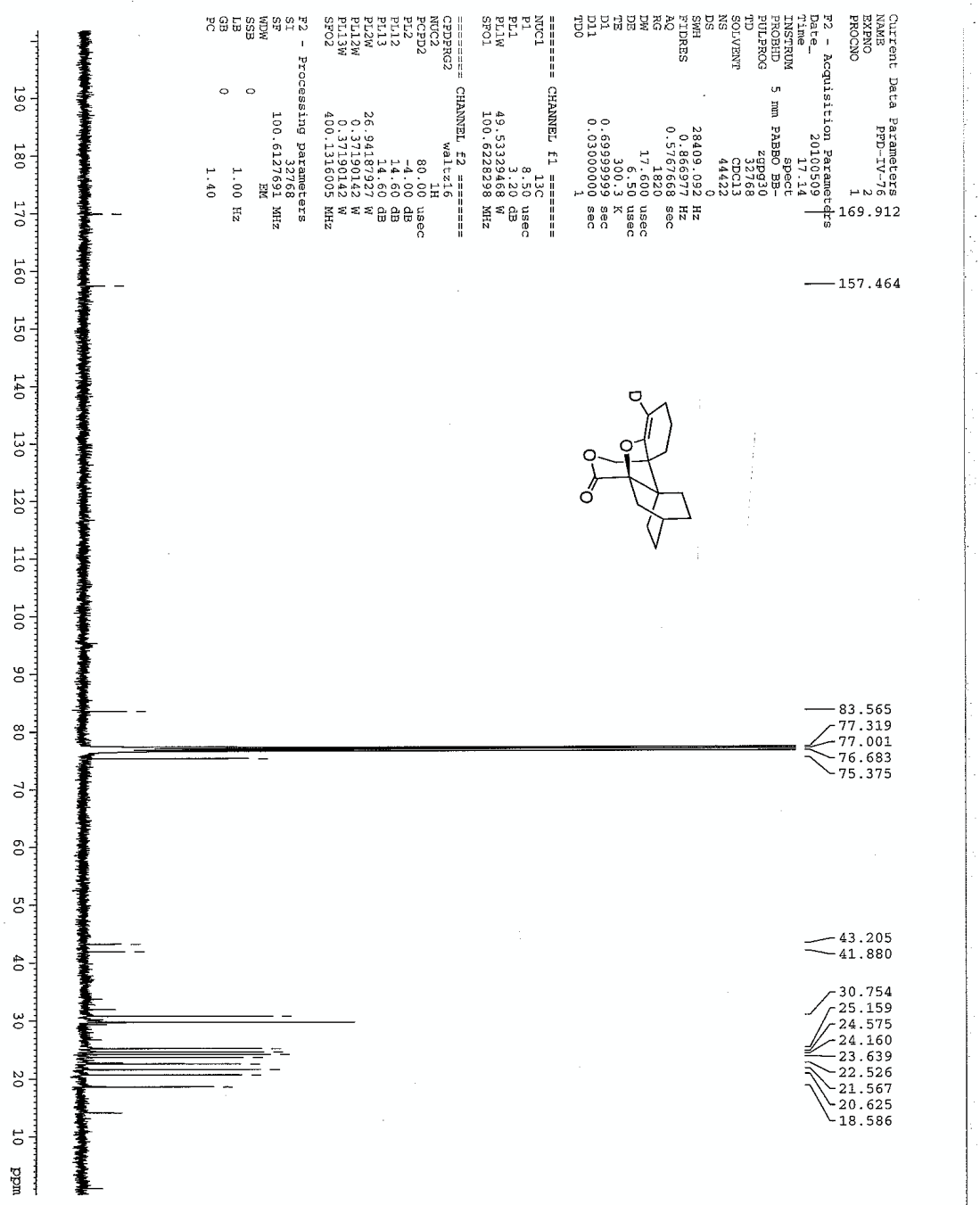
Time 17.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
D
O
O
O
proton
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 0.5 ppm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EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100509
Time 17.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 44422
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 300.3 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
========== CHANNEL f1 ==========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 14.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127691 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
169.912
157.464
83.565
77.319
77.001
76.683
75.375
43.205
41.880
30.754
25.159
24.575
24.160
23.639
22.526
21.567
20.625
18.586
D
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

```
Current Data Parameters
NAME                  PFD-IV-72
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20100501
Time                       0.17
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG                   zg30
TD                       32768
SOLVENT                  CDCl3
NS                            32
DS                             0
SWH                    6009.615 Hz
FIDRES                 0.183399 Hz
AQ                     2.7263477 sec
RG                            32
DW                        83.200 usec
DE                         6.50 usec
TE                        300.0 K
D1                   1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                        9.50 usec
PL1                      -4.00 dB
PL1W               26.94187927 W
SFO1               400.1328009 MHz

F2 - Processing parameters
SI                       32768
SF                 400.1300094 MHz
WDW                         EM
SSB          0
LB                        0.20 Hz
GB           0
PC                        1.00
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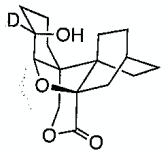

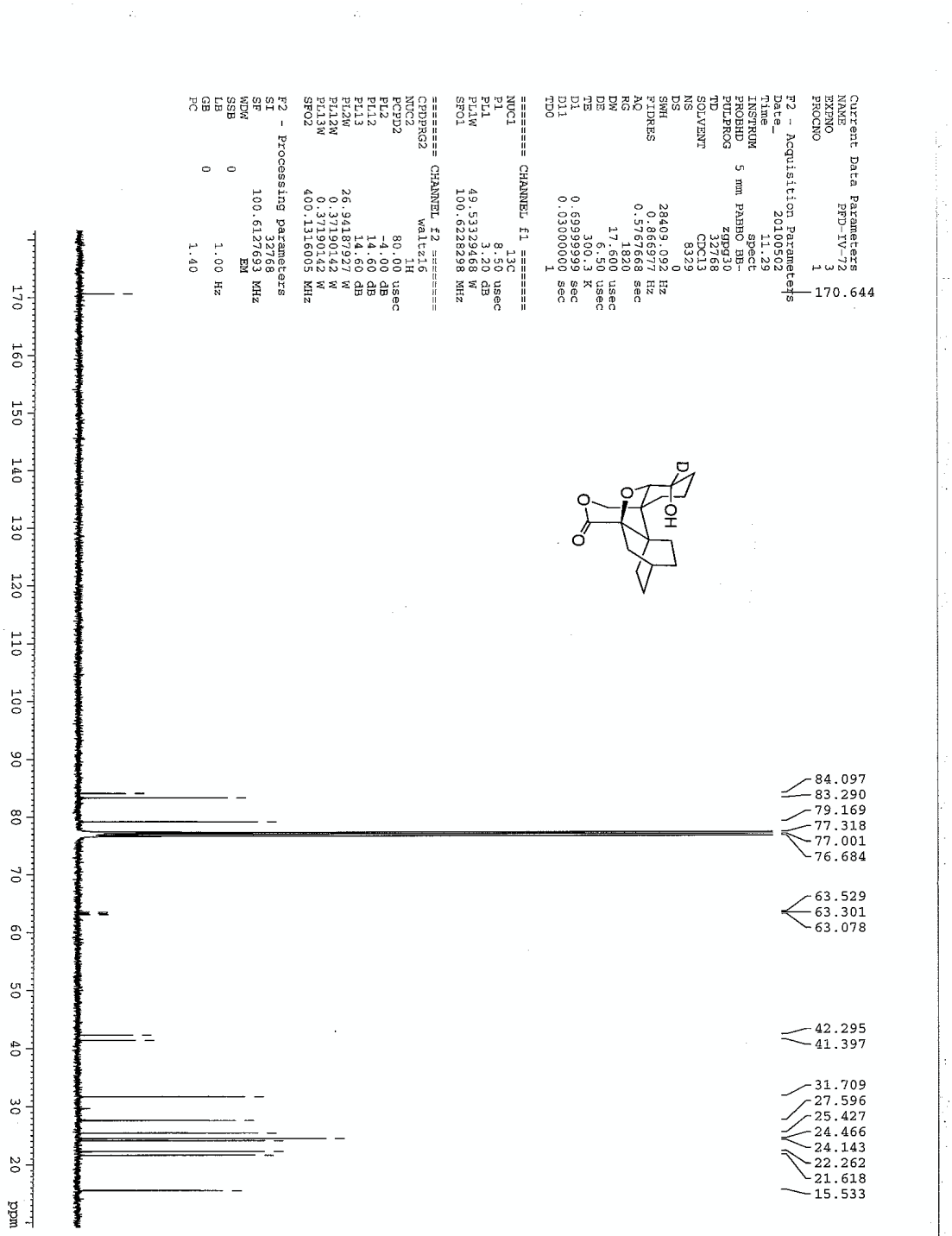
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PROCNO 1
F2 - Acquisition Parameters
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Time 11.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 8329
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 300.3 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127693 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170.644
84.097
83.290
79.169
77.318
77.001
76.684
63.529
63.301
63.078
42.295
41.397
31.709
27.596
25.427
24.466
24.143
22.262
21.618
15.533
OH
O
O
O
ppm

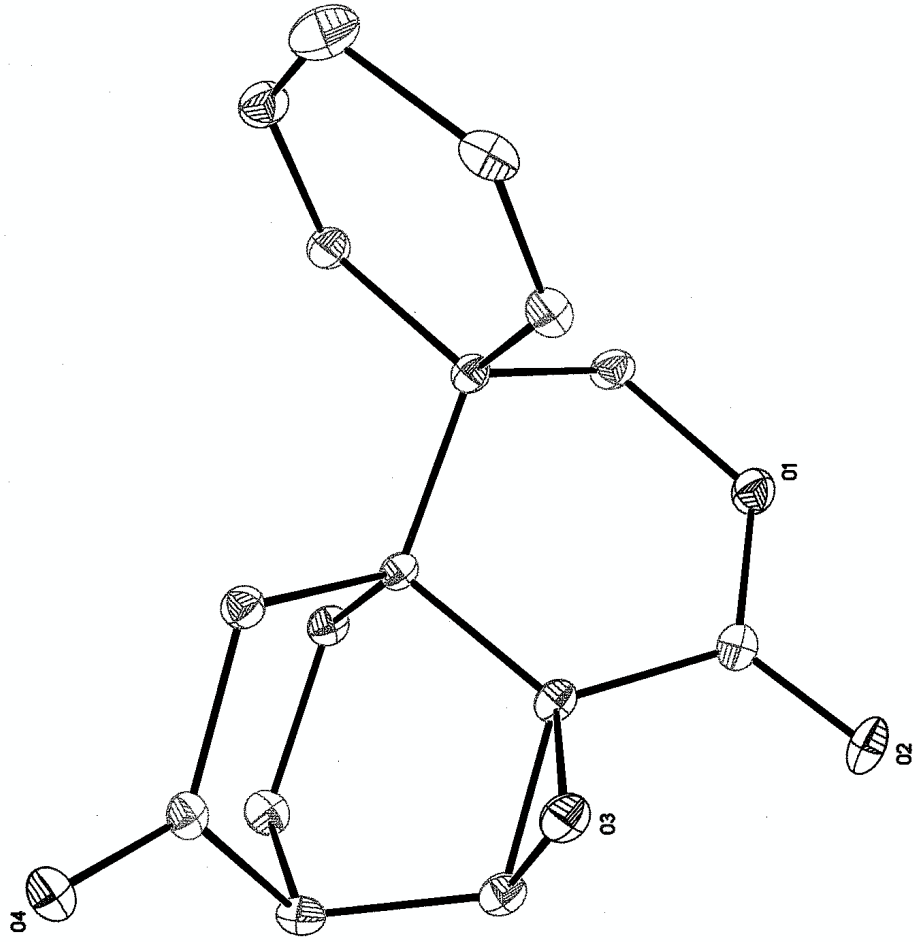

O1
O2
O3
O4

Table 1. Crystal data and structure refinement for FENG3WS10.

Identification code	feng3ws10
Empirical formula	$C_{16}H_{16}O_4$
Formula weight	272.29
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 6.837(3) Å alpha = 90° b = 9.269(4) Å beta = 93.680(7)° c = 20.261(8) Å gamma = 90°
Volume, Z	1281.3(9) $Å^3$, 4
Density (calculated)	1.412 Mg/m^3
Absorption coefficient	0.101 mm^{-1}
F(000)	576
Crystal size	0.12 x 0.03 x 0.03 mm
Θ range for data collection	2.01 to 28.28°
Limiting indices	$-9 \le h \le 9$, $-12 \le k \le 12$, $-26 \le l \le 26$
Reflections collected	17277
Independent reflections	3181 (R_{int} = 0.1389)
Completeness to Θ = 28.28°	100.0 %
Absorption correction	EMPIRICAL
Max. and min. transmission	0.9970 and 0.9880
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3181 / 0 / 181
Goodness-of-fit on F^2	1.031
Final R indices [I>2σ(I)]	R1 = 0.0730, wR2 = 0.1549
R indices (all data)	R1 = 0.1497, wR2 = 0.1846
Largest diff. peak and hole	0.297 and -0.328 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for FENG3WS10. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	4434(3)	5833(2)	1112(1)	31(1)
O(2)	6850(3)	4965(3)	573(1)	32(1)
O(3)	5896(3)	2123(2)	938(1)	27(1)
O(4)	2687(3)	-852(2)	922(1)	29(1)
C(1)	2373(4)	4158(3)	1742(2)	22(1)
C(2)	375(5)	4123(4)	2023(2)	27(1)
C(3)	89(5)	3815(4)	2642(2)	32(1)
C(4)	1674(6)	3479(5)	3150(2)	46(1)
C(5)	3668(5)	3598(4)	2895(2)	31(1)
C(6)	3967(5)	3881(3)	2273(2)	27(1)
C(7)	2629(5)	5659(4)	1446(2)	27(1)
C(8)	5330(5)	4731(3)	832(2)	24(1)
C(9)	4433(4)	3252(3)	852(2)	22(1)
C(10)	4736(5)	2240(3)	316(2)	26(1)
C(11)	3047(5)	1196(3)	212(2)	26(1)
C(12)	2729(4)	451(3)	859(2)	23(1)
C(13)	2378(5)	1490(3)	1412(2)	24(1)
C(14)	2500(4)	3046(3)	1170(1)	18(1)
C(15)	915(4)	3235(3)	601(2)	24(1)
C(16)	1183(5)	2110(4)	51(2)	29(1)

Table 3. Bond lengths [Å] and angles [°] for FENG3WS10.

O(1)-C(8)	1.336(4)	O(1)-C(7)	1.454(4)
O(2)-C(8)	1.213(4)	O(3)-C(10)	1.449(4)
O(3)-C(9)	1.450(4)	O(4)-C(12)	1.215(4)
C(1)-C(6)	1.503(4)	C(1)-C(2)	1.514(4)
C(1)-C(7)	1.530(4)	C(1)-C(14)	1.558(4)
C(2)-C(3)	1.313(5)	C(3)-C(4)	1.478(5)
C(4)-C(5)	1.494(5)	C(5)-C(6)	1.316(5)
C(8)-C(9)	1.504(4)	C(9)-C(10)	1.460(4)
C(9)-C(14)	1.519(4)	C(10)-C(11)	1.511(5)
C(11)-C(12)	1.510(4)	C(11)-C(16)	1.548(4)
C(12)-C(13)	1.507(4)	C(13)-C(14)	1.527(4)
C(14)-C(15)	1.541(4)	C(15)-C(16)	1.546(4)

C(8)-O(1)-C(7)	122.6(3)	C(10)-O(3)-C(9)	60.47(19)
C(6)-C(1)-C(2)	110.9(3)	C(6)-C(1)-C(7)	109.9(3)
C(2)-C(1)-C(7)	107.2(3)	C(6)-C(1)-C(14)	110.3(2)
C(2)-C(1)-C(14)	111.1(2)	C(7)-C(1)-C(14)	107.3(2)
C(3)-C(2)-C(1)	123.9(3)	C(2)-C(3)-C(4)	124.3(3)
C(3)-C(4)-C(5)	112.8(3)	C(6)-C(5)-C(4)	123.2(3)
C(5)-C(6)-C(1)	124.7(3)	O(1)-C(7)-C(1)	113.9(3)
O(2)-C(8)-O(1)	118.4(3)	O(2)-C(8)-C(9)	122.4(3)
O(1)-C(8)-C(9)	119.1(3)	O(3)-C(9)-C(10)	59.75(19)
O(3)-C(9)-C(8)	112.4(2)	C(10)-C(9)-C(8)	119.3(3)
O(3)-C(9)-C(14)	118.1(2)	C(10)-C(9)-C(14)	113.8(3)
C(8)-C(9)-C(14)	119.6(3)	O(3)-C(10)-C(9)	59.79(19)
O(3)-C(10)-C(11)	116.3(3)	C(9)-C(10)-C(11)	111.8(3)
C(12)-C(11)-C(10)	108.9(3)	C(12)-C(11)-C(16)	105.8(3)
C(10)-C(11)-C(16)	106.9(3)	O(4)-C(12)-C(13)	123.4(3)
O(4)-C(12)-C(11)	123.5(3)	C(13)-C(12)-C(11)	113.0(3)
C(12)-C(13)-C(14)	110.5(2)	C(9)-C(14)-C(13)	108.8(2)
C(9)-C(14)-C(15)	104.9(2)	C(13)-C(14)-C(15)	107.3(3)
C(9)-C(14)-C(1)	108.9(2)	C(13)-C(14)-C(1)	112.3(2)
C(15)-C(14)-C(1)	114.3(2)	C(14)-C(15)-C(16)	110.7(2)
C(15)-C(16)-C(11)	110.5(3)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for FENG3WS10.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^*b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	32(1)	25(1)	37(1)	1(1)	8(1)	-1(1)
O(2)	18(1)	35(1)	44(2)	11(1)	5(1)	-1(1)
O(3)	19(1)	30(1)	32(1)	2(1)	1(1)	6(1)
O(4)	30(1)	23(1)	34(1)	-2(1)	-2(1)	-1(1)
C(1)	18(2)	24(2)	23(2)	-1(1)	3(1)	1(1)
C(2)	20(2)	31(2)	30(2)	-5(2)	4(1)	1(1)
C(3)	30(2)	32(2)	35(2)	-2(2)	10(2)	2(2)
C(4)	54(3)	55(3)	30(2)	8(2)	10(2)	5(2)
C(5)	39(2)	27(2)	27(2)	-4(2)	-6(2)	7(2)
C(6)	24(2)	24(2)	31(2)	-2(1)	-2(1)	2(1)
C(7)	26(2)	26(2)	31(2)	-1(1)	8(1)	5(1)
C(8)	22(2)	26(2)	25(2)	5(1)	-1(1)	1(1)
C(9)	16(2)	24(2)	24(2)	4(1)	1(1)	5(1)
C(10)	26(2)	26(2)	27(2)	4(1)	5(1)	6(1)
C(11)	30(2)	26(2)	21(2)	-2(1)	2(1)	4(1)
C(12)	14(2)	25(2)	29(2)	-1(1)	-4(1)	0(1)
C(13)	24(2)	24(2)	23(2)	1(1)	3(1)	0(1)
C(14)	14(2)	22(2)	19(2)	2(1)	1(1)	3(1)
C(15)	18(2)	29(2)	24(2)	1(1)	-1(1)	4(1)
C(16)	30(2)	30(2)	26(2)	0(2)	-3(1)	0(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for FENG3WS10.

	x	y	z	U(eq)
H(2A)	-738	4335	1735	33
H(3A)	-1221	3808	2772	39
H(4A)	1487	2486	3315	55
H(4B)	1582	4148	3528	55
H(5A)	4776	3463	3196	37
H(6A)	5285	3911	2150	32
H(7A)	1504	5857	1126	33
H(7B)	2601	6384	1804	33
H(10A)	5386	2598	-81	31
H(11A)	3273	487	-147	31
H(13A)	3370	1331	1782	28
H(13B)	1067	1312	1576	28
H(15A)	1000	4219	415	28
H(15B)	-399	3120	773	28
H(16A)	1292	2611	-377	35
H(16B)	22	1470	9	35

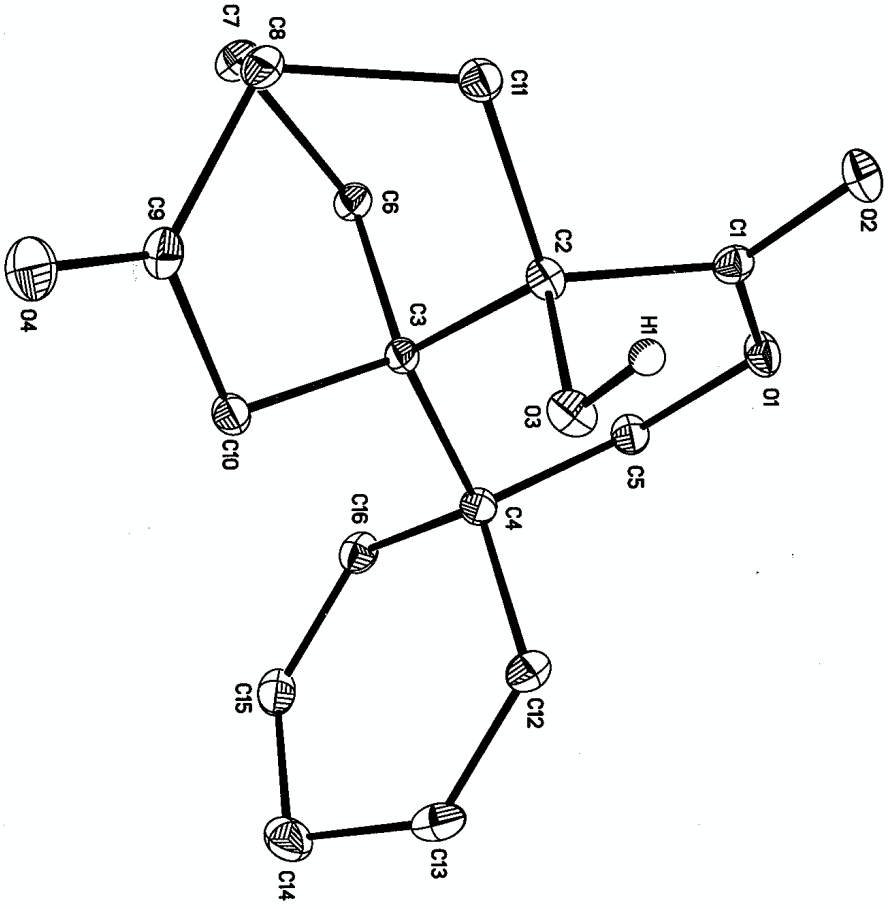

C7
C8
C11
C6
C9
C2
C1
O2
O4
C3
H1
O3
O1
C10
C5
C16
C4
C15
C12
C14
C13

Table 1. Crystal data and structure refinement for fpta5.

Identification code	fpta5
Empirical formula	$C_{16}H_{18}O_4$
Formula weight	274.30
Temperature	125(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 6.281(2) Å alpha = 90° b = 7.951(3) Å beta = 92.835(6)° c = 25.900(10) Å gamma = 90°
Volume, Z	1291.9(8) $Å^3$, 4
Density (calculated)	1.410 Mg/m^3
Absorption coefficient	0.101 mm^{-1}
F(000)	584
Crystal size	0.60 x 0.05 x 0.05 mm
Θ range for data collection	1.57 to 26.49°
Limiting indices	$-7 \le h \le 7$, $0 \le k \le 9$, $0 \le l \le 32$
Reflections collected	12681
Independent reflections	2657 (R_{int} = 0.0639)
Completeness to Θ = 26.49°	99.2 %
Absorption correction	EMPIRICAL
Max. and min. transmission	0.9950 and 0.9420
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2648 / 0 / 187
Goodness-of-fit on F^2	1.143
Final R indices [I>2σ(I)]	R1 = 0.0432, wR2 = 0.1004
R indices (all data)	R1 = 0.0513, wR2 = 0.1044
Extinction coefficient	0.0069(17)
Largest diff. peak and hole	0.307 and -0.265 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for fpta5. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	-4472(3)	11340(2)	4231(1)	22(1)
O(2)	-2672(3)	10819(2)	4954(1)	22(1)
O(3)	-127(3)	9187(2)	4178(1)	20(1)
O(4)	183(3)	4528(2)	3872(1)	31(1)
C(1)	-3202(4)	10341(3)	4519(1)	17(1)
C(2)	-2261(4)	8732(3)	4297(1)	16(1)
C(3)	-3458(4)	8116(3)	3792(1)	15(1)
C(4)	-4051(4)	9638(3)	3425(1)	17(1)
C(5)	-5425(4)	10843(3)	3729(1)	19(1)
C(6)	-5484(4)	7190(3)	3965(1)	18(1)
C(7)	-4882(4)	5496(3)	4226(1)	22(1)
C(8)	-2517(4)	5580(3)	4423(1)	20(1)
C(9)	-1235(4)	5528(3)	3941(1)	21(1)
C(10)	-1993(4)	6825(3)	3541(1)	18(1)
C(11)	-2205(4)	7294(3)	4702(1)	20(1)
C(12)	-2081(4)	10535(3)	3243(1)	21(1)
C(13)	-1433(4)	10436(3)	2764(1)	25(1)
C(14)	-2597(5)	9489(3)	2337(1)	30(1)
C(15)	-4773(4)	8970(3)	2482(1)	25(1)
C(16)	-5432(4)	9058(3)	2960(1)	21(1)

Table 3. Bond lengths [Å] and angles [°] for fpta5.

O(1)-C(1)	1.329(3)	O(1)-C(5)	1.459(3)
O(2)-C(1)	1.218(3)	O(3)-C(2)	1.436(3)
O(4)-C(9)	1.214(3)	C(1)-C(2)	1.534(3)
C(2)-C(11)	1.552(3)	C(2)-C(3)	1.554(3)
C(3)-C(10)	1.543(3)	C(3)-C(6)	1.555(3)
C(3)-C(4)	1.572(3)	C(4)-C(16)	1.520(3)
C(4)-C(12)	1.524(3)	C(4)-C(5)	1.532(3)
C(6)-C(7)	1.546(3)	C(7)-C(8)	1.547(3)
C(8)-C(9)	1.518(3)	C(8)-C(11)	1.551(3)
C(9)-C(10)	1.521(3)	C(12)-C(13)	1.326(3)
C(13)-C(14)	1.497(4)	C(14)-C(15)	1.493(4)
C(15)-C(16)	1.327(3)		

C(1)-O(1)-C(5)	123.17(18)	O(2)-C(1)-O(1)	117.5(2)
O(2)-C(1)-C(2)	121.0(2)	O(1)-C(1)-C(2)	121.28(19)
O(3)-C(2)-C(1)	104.58(18)	O(3)-C(2)-C(11)	109.93(18)
C(1)-C(2)-C(11)	110.87(17)	O(3)-C(2)-C(3)	108.48(17)
C(1)-C(2)-C(3)	113.54(18)	C(11)-C(2)-C(3)	109.30(18)
C(10)-C(3)-C(2)	106.83(18)	C(10)-C(3)-C(6)	108.64(18)
C(2)-C(3)-C(6)	106.08(17)	C(10)-C(3)-C(4)	112.67(18)
C(2)-C(3)-C(4)	110.86(17)	C(6)-C(3)-C(4)	111.44(18)
C(16)-C(4)-C(12)	109.64(18)	C(16)-C(4)-C(5)	106.41(19)
C(12)-C(4)-C(5)	110.69(19)	C(16)-C(4)-C(3)	110.75(18)
C(12)-C(4)-C(3)	112.10(18)	C(5)-C(4)-C(3)	107.08(17)
O(1)-C(5)-C(4)	114.22(19)	C(7)-C(6)-C(3)	110.62(19)
C(6)-C(7)-C(8)	108.49(19)	C(9)-C(8)-C(7)	105.55(18)
C(9)-C(8)-C(11)	110.33(19)	C(7)-C(8)-C(11)	106.74(19)
O(4)-C(9)-C(8)	124.2(2)	O(4)-C(9)-C(10)	123.4(2)
C(8)-C(9)-C(10)	112.3(2)	C(9)-C(10)-C(3)	109.72(18)
C(8)-C(11)-C(2)	109.49(17)	C(13)-C(12)-C(4)	123.7(2)
C(12)-C(13)-C(14)	123.9(2)	C(15)-C(14)-C(13)	111.9(2)
C(16)-C(15)-C(14)	123.5(2)	C(15)-C(16)-C(4)	124.3(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for fpta5.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	29(1)	18(1)	19(1)	-3(1)	-1(1)	6(1)
O(2)	19(1)	26(1)	20(1)	-8(1)	-2(1)	1(1)
O(3)	13(1)	27(1)	18(1)	-1(1)	0(1)	0(1)
O(4)	28(1)	27(1)	38(1)	-1(1)	7(1)	11(1)
C(1)	14(1)	18(1)	19(1)	1(1)	1(1)	-3(1)
C(2)	14(1)	19(1)	16(1)	-2(1)	0(1)	1(1)
C(3)	18(1)	14(1)	13(1)	-1(1)	0(1)	0(1)
C(4)	19(1)	17(1)	15(1)	1(1)	-1(1)	0(1)
C(5)	22(1)	18(1)	17(1)	0(1)	-2(1)	3(1)
C(6)	17(1)	16(1)	20(1)	1(1)	2(1)	0(1)
C(7)	22(1)	18(1)	26(1)	4(1)	3(1)	0(1)
C(8)	22(1)	16(1)	21(1)	3(1)	1(1)	3(1)
C(9)	20(1)	17(1)	25(1)	-4(1)	0(1)	-1(1)
C(10)	18(1)	18(1)	18(1)	-3(1)	3(1)	0(1)
C(11)	22(1)	19(1)	17(1)	1(1)	0(1)	3(1)
C(12)	20(1)	20(1)	22(1)	4(1)	-2(1)	-2(1)
C(13)	20(1)	25(1)	31(1)	11(1)	6(1)	2(1)
C(14)	41(2)	29(1)	21(1)	4(1)	6(1)	8(1)
C(15)	37(2)	19(1)	19(1)	0(1)	-6(1)	2(1)
C(16)	23(1)	18(1)	21(1)	2(1)	-4(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for fpta5.

	x	y	z	U(eq)
H(1)	600(50)	9340(30)	4468(11)	26(7)
H(5A)	-5702	11867	3519	23
H(5B)	-6815	10299	3782	23
H(6A)	-6235	7906	4210	21
H(6B)	-6463	6983	3660	21
H(7A)	-5091	4565	3975	26
H(7B)	-5801	5288	4519	26
H(8A)	-2139	4620	4659	24
H(10A)	-2781	6259	3250	22
H(10B)	-749	7409	3404	22
H(11A)	-821	7303	4902	24
H(11B)	-3351	7464	4946	24
H(12A)	-1272	11202	3485	25
H(13A)	-153	10999	2687	30
H(14A)	-2720	10207	2025	36
H(14B)	-1767	8476	2253	36
H(15A)	-5736	8555	2218	30
H(16A)	-6859	8738	3016	25

Table 6. Hydrogen bonds for fpta5 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(1)...O(2)#1	0.87(3)	1.94(3)	2.786(2)	165(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z+1

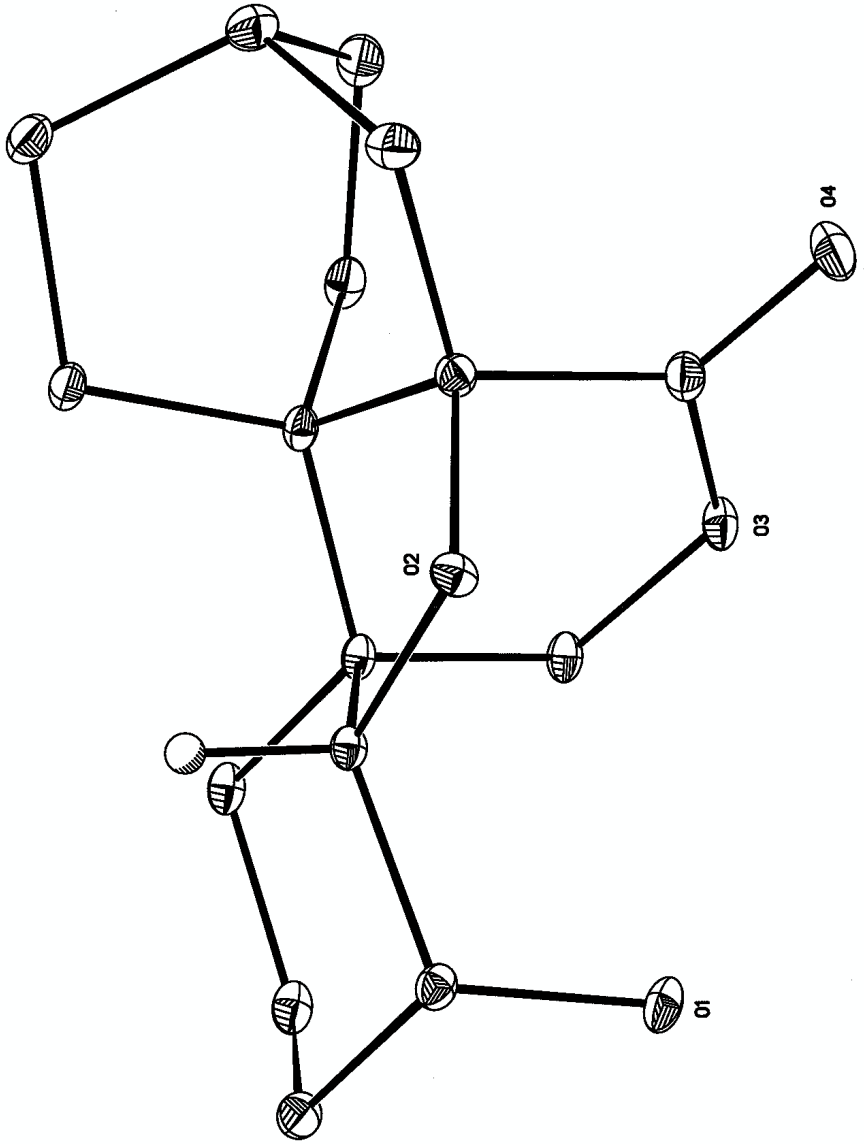

O4
O3
O2
O1

Table 1. Crystal data and structure refinement for FPEWS10.

Identification code	fpews10
Empirical formula	$C_{16}H_{22}O_4$
Formula weight	278.34
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 11.2174(9) Å alpha = 90° b = 11.2661(9) Å beta = 90° c = 21.3465(17) Å gamma = 90°
Volume, Z	2697.7(4) $Å^3$, 8
Density (calculated)	1.371 Mg/m^3
Absorption coefficient	0.097 mm^{-1}
F(000)	1200
Crystal size	0.25 x 0.23 x 0.16 mm
Θ range for data collection	1.91 to 31.66°
Limiting indices	$-16 \le h \le 16$, $-16 \le k \le 16$, $-31 \le l \le 31$
Reflections collected	41822
Independent reflections	4542 (R_{int} = 0.0393)
Completeness to Θ = 31.66°	99.5 %
Absorption correction	EMPIRICAL
Max. and min. transmission	0.9846 and 0.9761
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4542 / 0 / 182
Goodness-of-fit on F^2	1.081
Final R indices [I>2σ(I)]	R1 = 0.0407, wR2 = 0.1007
R indices (all data)	R1 = 0.0568, wR2 = 0.1137
Largest diff. peak and hole	0.517 and -0.221 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for FPEWS10. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	3478(1)	1153(1)	5360(1)	21(1)
O(2)	5403(1)	1020(1)	4366(1)	16(1)
O(3)	2997(1)	963(1)	3834(1)	23(1)
O(4)	3950(1)	-476(1)	3353(1)	30(1)
C(1)	4512(1)	1890(1)	5342(1)	17(1)
C(2)	4211(1)	3135(1)	5595(1)	21(1)
C(3)	3453(1)	3895(1)	5149(1)	23(1)
C(4)	3977(1)	3978(1)	4481(1)	20(1)
C(5)	4194(1)	2728(1)	4220(1)	15(1)
C(6)	5008(1)	2084(1)	4686(1)	14(1)
C(7)	5160(1)	1195(1)	3698(1)	17(1)
C(8)	6175(1)	777(1)	3274(1)	23(1)
C(9)	6290(1)	1687(1)	2734(1)	26(1)
C(10)	6833(1)	2838(1)	2995(1)	24(1)
C(11)	6134(1)	3203(1)	3592(1)	19(1)
C(12)	4930(1)	2538(1)	3613(1)	16(1)
C(13)	4342(1)	2726(1)	2968(1)	23(1)
C(14)	5046(1)	1996(1)	2473(1)	28(1)
C(15)	2975(1)	2138(1)	4121(1)	20(1)
C(16)	4001(1)	490(1)	3599(1)	20(1)

Table 3. Bond lengths [Å] and angles [°] for FPEWS10.

O(1)-C(1)	1.4270(13)	O(2)-C(6)	1.4488(12)
O(2)-C(7)	1.4639(12)	O(3)-C(16)	1.3429(14)
O(3)-C(15)	1.4587(13)	O(4)-C(16)	1.2102(14)
C(1)-C(6)	1.5224(14)	C(1)-C(2)	1.5404(14)
C(2)-C(3)	1.5358(17)	C(3)-C(4)	1.5459(16)
C(4)-C(5)	1.5334(14)	C(5)-C(6)	1.5338(14)
C(5)-C(15)	1.5354(14)	C(5)-C(12)	1.5504(14)
C(7)-C(8)	1.5286(15)	C(7)-C(16)	1.5385(15)
C(7)-C(12)	1.5457(14)	C(8)-C(9)	1.5479(17)
C(9)-C(10)	1.5363(17)	C(9)-C(14)	1.5432(18)
C(10)-C(11)	1.5519(15)	C(11)-C(12)	1.5453(14)
C(12)-C(13)	1.5415(14)	C(13)-C(14)	1.5545(19)

C(6)-O(2)-C(7)	106.93(7)	C(16)-O(3)-C(15)	122.07(8)
O(1)-C(1)-C(6)	113.95(8)	O(1)-C(1)-C(2)	110.02(8)
C(6)-C(1)-C(2)	105.76(8)	C(3)-C(2)-C(1)	114.31(9)
C(2)-C(3)-C(4)	113.27(9)	C(5)-C(4)-C(3)	109.89(8)
C(4)-C(5)-C(6)	107.07(8)	C(4)-C(5)-C(15)	107.80(8)
C(6)-C(5)-C(15)	114.47(8)	C(4)-C(5)-C(12)	120.99(8)
C(6)-C(5)-C(12)	99.21(8)	C(15)-C(5)-C(12)	107.45(8)
O(2)-C(6)-C(1)	115.30(8)	O(2)-C(6)-C(5)	105.49(8)
C(1)-C(6)-C(5)	116.54(8)	O(2)-C(7)-C(8)	113.36(9)
O(2)-C(7)-C(16)	102.78(8)	C(8)-C(7)-C(16)	112.87(9)
O(2)-C(7)-C(12)	106.13(8)	C(8)-C(7)-C(12)	110.90(8)
C(16)-C(7)-C(12)	110.35(8)	C(7)-C(8)-C(9)	107.41(9)
C(10)-C(9)-C(14)	107.35(10)	C(10)-C(9)-C(8)	108.83(9)
C(14)-C(9)-C(8)	110.05(10)	C(9)-C(10)-C(11)	108.73(9)
C(12)-C(11)-C(10)	109.69(9)	C(13)-C(12)-C(11)	106.31(8)
C(13)-C(12)-C(7)	108.16(8)	C(11)-C(12)-C(7)	109.37(8)
C(13)-C(12)-C(5)	119.99(9)	C(11)-C(12)-C(5)	115.00(8)
C(7)-C(12)-C(5)	97.22(7)	C(12)-C(13)-C(14)	108.48(9)
C(9)-C(14)-C(13)	109.48(9)	O(3)-C(15)-C(5)	115.82(8)
O(4)-C(16)-O(3)	118.65(10)	O(4)-C(16)-C(7)	124.33(11)
O(3)-C(16)-C(7)	116.93(9)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for FPEWS10.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	20(1)	13(1)	29(1)	4(1)	6(1)	-1(1)
O(2)	20(1)	12(1)	16(1)	0(1)	-1(1)	3(1)
O(3)	19(1)	20(1)	31(1)	0(1)	-1(1)	-8(1)
O(4)	37(1)	22(1)	31(1)	-6(1)	-3(1)	-9(1)
C(1)	18(1)	13(1)	19(1)	1(1)	2(1)	0(1)
C(2)	25(1)	15(1)	24(1)	-3(1)	6(1)	-1(1)
C(3)	19(1)	14(1)	35(1)	-2(1)	5(1)	2(1)
C(4)	16(1)	12(1)	32(1)	3(1)	0(1)	2(1)
C(5)	12(1)	12(1)	21(1)	3(1)	-1(1)	0(1)
C(6)	13(1)	10(1)	18(1)	1(1)	0(1)	1(1)
C(7)	18(1)	16(1)	16(1)	1(1)	-1(1)	-2(1)
C(8)	25(1)	23(1)	21(1)	-3(1)	4(1)	1(1)
C(9)	27(1)	32(1)	18(1)	-1(1)	4(1)	-5(1)
C(10)	20(1)	31(1)	19(1)	4(1)	2(1)	-6(1)
C(11)	17(1)	20(1)	20(1)	3(1)	0(1)	-5(1)
C(12)	15(1)	15(1)	17(1)	4(1)	-3(1)	-3(1)
C(13)	23(1)	27(1)	20(1)	8(1)	-6(1)	-6(1)
C(14)	32(1)	35(1)	18(1)	3(1)	-5(1)	-10(1)
C(15)	14(1)	17(1)	28(1)	3(1)	-2(1)	-1(1)
C(16)	24(1)	18(1)	19(1)	2(1)	-3(1)	-5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for FPEWS10.

	x	y	z	U(eq)
H(1A)	3686	438	5380	31
H(1B)	5145	1528	5611	20
H(2A)	3779	3048	5996	26
H(2B)	4965	3561	5682	26
H(3A)	3382	4705	5325	27
H(3B)	2642	3552	5125	27
H(4A)	3415	4410	4205	24
H(4B)	4737	4423	4491	24
H(6A)	5731	2595	4737	17
H(8A)	5995	-21	3104	28
H(8B)	6929	733	3514	28
H(9A)	6807	1359	2394	31
H(10A)	6781	3475	2677	28
H(10B)	7683	2711	3099	28
H(11A)	6608	3007	3969	23
H(11B)	5991	4070	3588	23
H(13A)	4356	3579	2856	28
H(13B)	3501	2461	2980	28
H(14A)	4607	1258	2373	34
H(14B)	5130	2464	2083	34
H(15A)	2574	2073	4533	23
H(15B)	2483	2666	3856	23

Table 6. Hydrogen bonds for FPEWS10 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1A)...O(2)#1	0.84	2.01	2.8132(10)	159.9

Symmetry transformations used to generate equivalent atoms:

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

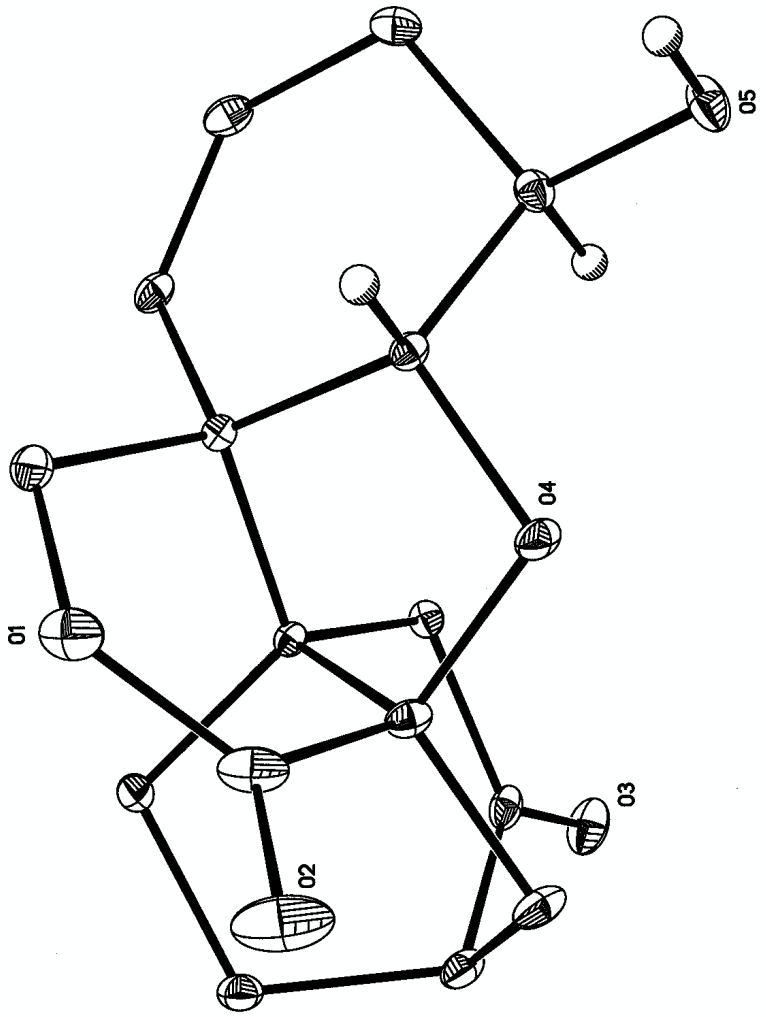

O5
O4
O1
O3
O2

Table 1. Crystal data and structure refinement for FPAS10.

Identification code	fpas10
Empirical formula	$C_{16}H_{18}O_5$
Formula weight	290.30
Temperature	125(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 7.0107(8) Å alpha = 89.325(2)° b = 9.3430(11) Å beta = 77.850(2)° c = 10.1589(12) Å gamma = 89.200(2)°
Volume, Z	650.42(13) $Å^3$, 2
Density (calculated)	1.482 Mg/m^3
Absorption coefficient	0.110 mm^{-1}
F(000)	308
Crystal size	0.50 x 0.25 x 0.20 mm
Θ range for data collection	2.05 to 30.61°
Limiting indices	$-10 \le h \le 10$, $-13 \le k \le 13$, $-14 \le l \le 14$
Reflections collected	10421
Independent reflections	3979 (R_{int} = 0.0207)
Completeness to Θ = 30.61°	99.2 %
Absorption correction	EMPIRICAL
Max. and min. transmission	0.9783 and 0.9471
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3979 / 0 / 194
Goodness-of-fit on F^2	1.081
Final R indices [I>2σ(I)]	R1 = 0.0387, wR2 = 0.1054
R indices (all data)	R1 = 0.0474, wR2 = 0.1114
Largest diff. peak and hole	0.432 and -0.187 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for FPAS10. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	2159(1)	10509(1)	2954(1)	28(1)
O(2)	-301(2)	10499(1)	1948(1)	44(1)
O(3)	2702(1)	4376(1)	352(1)	30(1)
O(4)	70(1)	7702(1)	3660(1)	20(1)
O(5)	-438(1)	6456(1)	6359(1)	25(1)
C(1)	918(2)	9801(1)	2353(1)	26(1)
C(2)	1036(1)	8151(1)	2330(1)	17(1)
C(3)	111(2)	7519(1)	1234(1)	23(1)
C(4)	1737(2)	6842(1)	144(1)	21(1)
C(5)	3415(2)	7915(1)	-296(1)	22(1)
C(6)	4393(2)	8273(1)	898(1)	17(1)
C(7)	3147(1)	7638(1)	2194(1)	13(1)
C(8)	3238(2)	6004(1)	2050(1)	15(1)
C(9)	2569(1)	5587(1)	783(1)	19(1)
C(10)	3456(1)	8161(1)	3570(1)	14(1)
C(11)	5162(1)	7527(1)	4059(1)	18(1)
C(12)	5003(2)	6881(1)	5252(1)	21(1)
C(13)	3078(2)	6651(1)	6200(1)	22(1)
C(14)	1410(2)	6569(1)	5455(1)	17(1)
C(15)	1452(1)	7862(1)	4526(1)	14(1)
C(16)	3697(2)	9782(1)	3477(1)	21(1)

Table 3. Bond lengths [Å] and angles [°] for FPAS10.

O(1)-C(1)	1.3480(15)	O(1)-C(16)	1.4550(14)
O(2)-C(1)	1.2052(14)	O(3)-C(9)	1.2137(13)
O(4)-C(2)	1.4378(12)	O(4)-C(15)	1.4498(11)
O(5)-C(14)	1.4259(12)	C(1)-C(2)	1.5430(16)
C(2)-C(7)	1.5283(13)	C(2)-C(3)	1.5287(14)
C(3)-C(4)	1.5465(15)	C(4)-C(9)	1.5027(16)
C(4)-C(5)	1.5461(16)	C(5)-C(6)	1.5557(14)
C(6)-C(7)	1.5361(13)	C(7)-C(8)	1.5336(13)
C(7)-C(10)	1.5451(13)	C(8)-C(9)	1.5167(14)
C(10)-C(11)	1.5007(13)	C(10)-C(16)	1.5258(14)
C(10)-C(15)	1.5573(13)	C(11)-C(12)	1.3315(15)
C(12)-C(13)	1.4997(16)	C(13)-C(14)	1.5243(15)
C(14)-C(15)	1.5206(14)		

C(1)-O(1)-C(16)	122.34(8)	C(2)-O(4)-C(15)	107.07(7)
O(2)-C(1)-O(1)	117.39(11)	O(2)-C(1)-C(2)	124.12(12)
O(1)-C(1)-C(2)	118.30(9)	O(4)-C(2)-C(7)	104.74(8)
O(4)-C(2)-C(3)	112.41(9)	C(7)-C(2)-C(3)	111.36(8)
O(4)-C(2)-C(1)	105.00(8)	C(7)-C(2)-C(1)	110.47(9)
C(3)-C(2)-C(1)	112.42(9)	C(2)-C(3)-C(4)	108.86(8)
C(9)-C(4)-C(5)	106.80(8)	C(9)-C(4)-C(3)	107.38(9)
C(5)-C(4)-C(3)	109.94(9)	C(4)-C(5)-C(6)	111.02(8)
C(7)-C(6)-C(5)	108.39(8)	C(2)-C(7)-C(8)	109.17(8)
C(2)-C(7)-C(6)	109.09(8)	C(8)-C(7)-C(6)	107.23(8)
C(2)-C(7)-C(10)	97.83(7)	C(8)-C(7)-C(10)	113.76(8)
C(6)-C(7)-C(10)	119.10(8)	C(9)-C(8)-C(7)	109.70(8)
O(3)-C(9)-C(4)	124.88(10)	O(3)-C(9)-C(8)	123.10(10)
C(4)-C(9)-C(8)	112.02(8)	C(11)-C(10)-C(16)	108.21(8)
C(11)-C(10)-C(7)	116.59(8)	C(16)-C(10)-C(7)	107.79(8)
C(11)-C(10)-C(15)	113.60(8)	C(16)-C(10)-C(15)	107.21(8)
C(7)-C(10)-C(15)	102.94(7)	C(12)-C(11)-C(10)	123.35(9)
C(11)-C(12)-C(13)	122.79(9)	C(12)-C(13)-C(14)	111.85(9)
O(5)-C(14)-C(15)	110.99(8)	O(5)-C(14)-C(13)	111.92(8)
C(15)-C(14)-C(13)	109.77(8)	O(4)-C(15)-C(14)	110.76(8)
O(4)-C(15)-C(10)	105.88(7)	C(14)-C(15)-C(10)	115.45(8)
O(1)-C(16)-C(10)	113.03(8)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for FPAS10.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^*b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	44(1)	15(1)	26(1)	-2(1)	-12(1)	8(1)
O(2)	59(1)	42(1)	38(1)	-8(1)	-24(1)	34(1)
O(3)	25(1)	28(1)	35(1)	-16(1)	-3(1)	-3(1)
O(4)	11(1)	34(1)	16(1)	-2(1)	-3(1)	0(1)
O(5)	25(1)	21(1)	23(1)	-3(1)	7(1)	-5(1)
C(1)	35(1)	25(1)	19(1)	-3(1)	-8(1)	14(1)
C(2)	14(1)	22(1)	15(1)	-3(1)	-4(1)	5(1)
C(3)	15(1)	37(1)	20(1)	-8(1)	-8(1)	5(1)
C(4)	16(1)	31(1)	16(1)	-5(1)	-6(1)	0(1)
C(5)	23(1)	27(1)	15(1)	1(1)	-6(1)	0(1)
C(6)	19(1)	18(1)	15(1)	1(1)	-3(1)	-3(1)
C(7)	11(1)	13(1)	14(1)	-1(1)	-3(1)	0(1)
C(8)	16(1)	14(1)	16(1)	-2(1)	-2(1)	0(1)
C(9)	12(1)	23(1)	19(1)	-7(1)	0(1)	-3(1)
C(10)	13(1)	14(1)	14(1)	-1(1)	-4(1)	0(1)
C(11)	12(1)	22(1)	20(1)	-4(1)	-6(1)	0(1)
C(12)	20(1)	23(1)	23(1)	-4(1)	-11(1)	6(1)
C(13)	28(1)	22(1)	17(1)	1(1)	-6(1)	4(1)
C(14)	18(1)	16(1)	16(1)	-2(1)	0(1)	-1(1)
C(15)	12(1)	16(1)	15(1)	-2(1)	-4(1)	1(1)
C(16)	28(1)	15(1)	21(1)	-1(1)	-8(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for FPAS10.

	x	y	z	U(eq)
H(1)	-650(30)	7240(20)	6827(18)	47(5)
H(3A)	-580	8281	827	28
H(3B)	-848	6782	1630	28
H(4A)	1206	6532	-646	25
H(5B)	2895	8806	-633	26
H(5C)	4403	7501	-1040	26
H(6A)	5729	7860	739	21
H(6B)	4482	9323	982	21
H(8A)	4592	5658	2002	19
H(8B)	2389	5555	2845	19
H(11A)	6420	7589	3489	21
H(12A)	6157	6552	5515	26
H(13A)	2819	7447	6850	26
H(13B)	3141	5751	6714	26
H(14A)	1617	5691	4885	21
H(15A)	1063	8726	5096	17
H(16A)	3706	10155	4384	25
H(16B)	4973	10004	2885	25

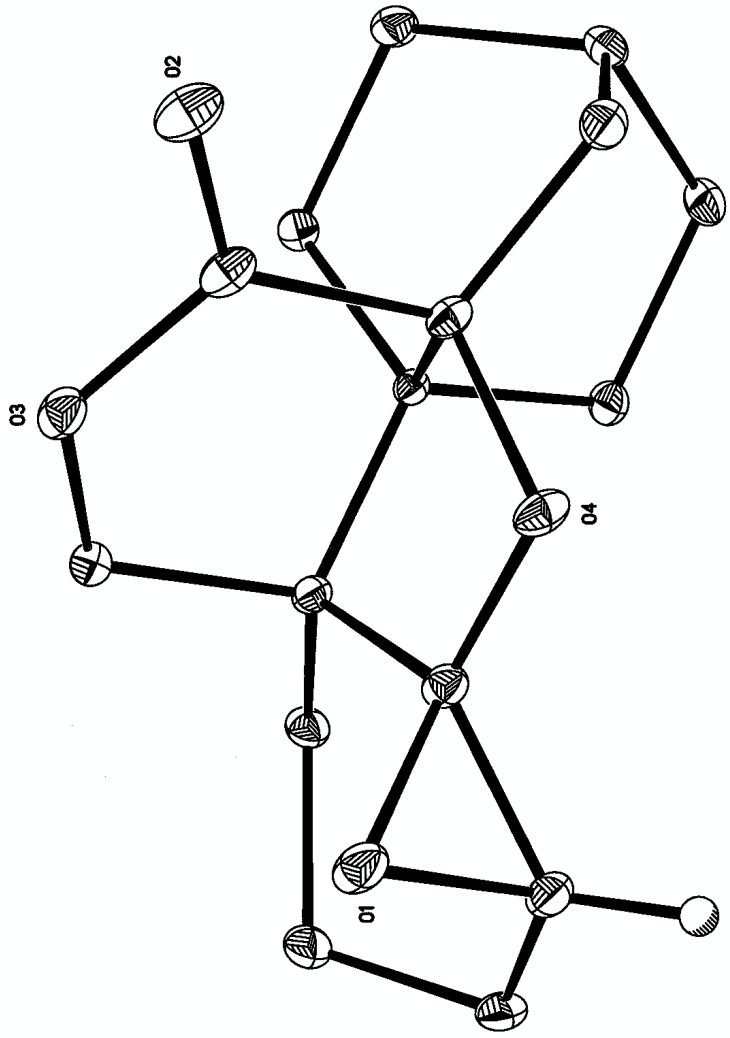

O2
O3
O4
O1

Table 1. Crystal data and structure refinement for F4WS10.

Identification code	f4ws10
Empirical formula	$C_{16}H_{20}O_4$
Formula weight	276.32
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 12.433(3) Å alpha = 90° b = 13.500(4) Å beta = 104.898(4)° c = 16.270(4) Å gamma = 90°
Volume, Z	2639.1(12) $Å^3$, 8
Density (calculated)	1.391 Mg/m^3
Absorption coefficient	0.099 mm^{-1}
F(000)	1184
Crystal size	0.19 x 0.11 x 0.02 mm
⊛ range for data collection	1.69 to 30.54°
Limiting indices	$-17 \le h \le 17$, $-19 \le k \le 19$, $-23 \le l \le 23$
Reflections collected	41821
Independent reflections	8059 (R_{int} = 0.0979)
Completeness to ⊛ = 30.54°	99.7 %
Absorption correction	EMPIRICAL
Max. and min. transmission	0.9980 and 0.9814
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8059 / 0 / 361
Goodness-of-fit on F^2	1.001
Final R indices [I>2σ(I)]	R1 = 0.0574, wR2 = 0.1224
R indices (all data)	R1 = 0.1310, wR2 = 0.1546
Largest diff. peak and hole	0.388 and -0.296 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for F4WS10. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	8420(1)	3711(1)	1584(1)	28(1)
O(2)	11694(1)	4364(1)	3548(1)	28(1)
O(3)	11141(1)	3872(1)	2220(1)	24(1)
O(4)	9334(1)	3237(1)	2998(1)	23(1)
C(1)	7462(2)	2137(2)	976(1)	30(1)
C(2)	11407(2)	1702(2)	4391(1)	24(1)
C(3)	7797(2)	2820(2)	1725(1)	25(1)
C(4)	12312(2)	1668(2)	3897(1)	25(1)
C(5)	9940(2)	1138(1)	3112(1)	22(1)
C(6)	10642(2)	3129(1)	1589(1)	21(1)
C(7)	10560(2)	886(2)	4042(1)	25(1)
C(8)	10807(2)	2708(2)	4248(1)	24(1)
C(9)	8403(2)	1987(2)	541(1)	29(1)
C(10)	9459(2)	1621(2)	1186(1)	23(1)
C(11)	8978(2)	2955(1)	2138(1)	20(1)
C(12)	11173(2)	3764(1)	3050(1)	21(1)
C(13)	11774(2)	1668(1)	2926(1)	19(1)
C(14)	9911(2)	2380(1)	1894(1)	18(1)
C(15)	10552(2)	1984(1)	2777(1)	15(1)
C(16)	10487(2)	2918(1)	3296(1)	18(1)
O(5)	6587(1)	3762(1)	3567(1)	24(1)
O(6)	3292(1)	2985(1)	1557(1)	26(1)
O(7)	3854(1)	3502(1)	2877(1)	22(1)
O(8)	5665(1)	4118(1)	2125(1)	20(1)
C(17)	7473(2)	5406(2)	4076(1)	24(1)
C(18)	6003(2)	4467(1)	2967(1)	18(1)
C(19)	6526(2)	5557(2)	4507(1)	24(1)
C(20)	4320(2)	4279(1)	3486(1)	20(1)
C(21)	5016(2)	6210(1)	1918(1)	22(1)
C(22)	4401(2)	6432(2)	980(1)	25(1)
C(23)	5441(2)	5830(1)	3855(1)	22(1)
C(24)	7175(2)	4654(1)	3373(1)	21(1)
C(25)	3814(2)	3591(1)	2045(1)	19(1)
C(26)	4233(2)	4591(1)	833(1)	22(1)
C(27)	3591(2)	5583(2)	639(1)	22(1)
C(28)	2664(2)	5609(2)	1109(1)	24(1)
C(29)	3176(2)	5671(1)	2084(1)	19(1)
C(30)	4509(2)	4424(1)	1789(1)	16(1)
C(31)	5037(2)	5033(1)	3172(1)	16(1)
C(32)	4409(2)	5382(1)	2270(1)	15(1)

Table 3. Bond lengths [Å] and angles [°] for F4WS10.

O(1)-C(11)	1.419(2)	O(1)-C(3)	1.481(2)
O(2)-C(12)	1.209(2)	O(3)-C(12)	1.349(2)
O(3)-C(6)	1.455(2)	O(4)-C(11)	1.408(2)
O(4)-C(16)	1.455(2)	C(1)-C(3)	1.499(3)
C(1)-C(9)	1.529(3)	C(2)-C(7)	1.529(3)
C(2)-C(8)	1.539(3)	C(2)-C(4)	1.543(3)
C(3)-C(11)	1.460(3)	C(4)-C(13)	1.549(3)
C(5)-C(15)	1.547(3)	C(5)-C(7)	1.550(3)
C(6)-C(14)	1.526(3)	C(8)-C(16)	1.522(3)
C(9)-C(10)	1.536(3)	C(10)-C(14)	1.536(3)
C(11)-C(14)	1.531(3)	C(12)-C(16)	1.540(3)
C(13)-C(15)	1.537(2)	C(14)-C(15)	1.548(2)
C(15)-C(16)	1.531(2)	O(5)-C(18)	1.423(2)
O(5)-C(24)	1.484(2)	O(6)-C(25)	1.207(2)
O(7)-C(25)	1.347(2)	O(7)-C(20)	1.457(2)
O(8)-C(18)	1.407(2)	O(8)-C(30)	1.459(2)
C(17)-C(24)	1.502(3)	C(17)-C(19)	1.531(3)
C(18)-C(24)	1.459(3)	C(18)-C(31)	1.531(3)
C(19)-C(23)	1.531(3)	C(20)-C(31)	1.526(3)
C(21)-C(32)	1.539(3)	C(21)-C(22)	1.550(3)
C(22)-C(27)	1.533(3)	C(23)-C(31)	1.536(3)
C(25)-C(30)	1.539(3)	C(26)-C(30)	1.521(3)
C(26)-C(27)	1.550(3)	C(27)-C(28)	1.538(3)
C(28)-C(29)	1.552(3)	C(29)-C(32)	1.535(3)
C(30)-C(32)	1.534(3)	C(31)-C(32)	1.546(2)

C(11)-O(1)-C(3)	60.40(12)	C(12)-O(3)-C(6)	121.97(15)
C(11)-O(4)-C(16)	106.44(14)	C(3)-C(1)-C(9)	111.84(17)
C(7)-C(2)-C(8)	108.63(16)	C(7)-C(2)-C(4)	108.07(16)
C(8)-C(2)-C(4)	109.68(16)	C(11)-C(3)-O(1)	57.70(11)
C(11)-C(3)-C(1)	119.14(18)	O(1)-C(3)-C(1)	114.86(17)
C(2)-C(4)-C(13)	110.49(16)	C(15)-C(5)-C(7)	109.86(15)
O(3)-C(6)-C(14)	114.14(15)	C(2)-C(7)-C(5)	109.07(15)
C(16)-C(8)-C(2)	107.94(15)	C(1)-C(9)-C(10)	110.35(17)
C(14)-C(10)-C(9)	112.44(17)	O(4)-C(11)-O(1)	114.47(15)
O(4)-C(11)-C(3)	120.88(17)	O(1)-C(11)-C(3)	61.90(12)
O(4)-C(11)-C(14)	109.20(15)	O(1)-C(11)-C(14)	118.63(16)
C(3)-C(11)-C(14)	123.87(17)	O(2)-C(12)-O(3)	118.15(18)
O(2)-C(12)-C(16)	124.02(19)	O(3)-C(12)-C(16)	117.73(16)
C(15)-C(13)-C(4)	108.11(15)	C(6)-C(14)-C(11)	107.66(15)
C(6)-C(14)-C(10)	109.41(15)	C(11)-C(14)-C(10)	112.12(15)
C(6)-C(14)-C(15)	108.85(15)	C(11)-C(14)-C(15)	100.25(14)
C(10)-C(14)-C(15)	117.87(15)	C(16)-C(15)-C(13)	109.39(15)
C(16)-C(15)-C(5)	108.22(15)	C(13)-C(15)-C(5)	107.20(15)
C(16)-C(15)-C(14)	98.08(14)	C(13)-C(15)-C(14)	119.64(15)
C(5)-C(15)-C(14)	113.51(15)	O(4)-C(16)-C(8)	111.79(15)
O(4)-C(16)-C(15)	104.29(14)	C(8)-C(16)-C(15)	111.79(15)
O(4)-C(16)-C(12)	104.93(15)	C(8)-C(16)-C(12)	112.68(16)
C(15)-C(16)-C(12)	110.84(15)	C(18)-O(5)-C(24)	60.20(11)
C(25)-O(7)-C(20)	121.66(15)	C(18)-O(8)-C(30)	106.77(13)
C(24)-C(17)-C(19)	111.68(16)	O(8)-C(18)-O(5)	114.64(15)
O(8)-C(18)-C(24)	120.86(16)	O(5)-C(18)-C(24)	62.00(12)
O(8)-C(18)-C(31)	108.95(14)	O(5)-C(18)-C(31)	118.36(15)
C(24)-C(18)-C(31)	124.23(16)	C(23)-C(19)-C(17)	111.07(16)
O(7)-C(20)-C(31)	114.67(15)	C(32)-C(21)-C(22)	110.02(15)

C(27)-C(22)-C(21)	108.89(15)	C(19)-C(23)-C(31)	113.49(16)
C(18)-C(24)-O(5)	57.80(11)	C(18)-C(24)-C(17)	119.00(17)
O(5)-C(24)-C(17)	115.20(16)	O(6)-C(25)-O(7)	118.41(17)
O(6)-C(25)-C(30)	124.17(18)	O(7)-C(25)-C(30)	117.27(16)
C(30)-C(26)-C(27)	107.79(15)	C(22)-C(27)-C(28)	108.02(16)
C(22)-C(27)-C(26)	108.43(16)	C(28)-C(27)-C(26)	109.34(16)
C(27)-C(28)-C(29)	110.28(16)	C(32)-C(29)-C(28)	108.34(15)
O(8)-C(30)-C(26)	111.46(14)	O(8)-C(30)-C(32)	104.38(14)
C(26)-C(30)-C(32)	111.73(15)	O(8)-C(30)-C(25)	105.11(14)
C(26)-C(30)-C(25)	112.96(15)	C(32)-C(30)-C(25)	110.69(15)
C(20)-C(31)-C(18)	107.37(15)	C(20)-C(31)-C(23)	109.58(15)
C(18)-C(31)-C(23)	112.26(15)	C(20)-C(31)-C(32)	108.93(15)
C(18)-C(31)-C(32)	100.29(14)	C(23)-C(31)-C(32)	117.70(15)
C(30)-C(32)-C(29)	108.75(14)	C(30)-C(32)-C(21)	108.09(15)
C(29)-C(32)-C(21)	107.54(15)	C(30)-C(32)-C(31)	98.03(14)
C(29)-C(32)-C(31)	120.01(15)	C(21)-C(32)-C(31)	113.47(15)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for F4WS10.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	18(1)	23(1)	43(1)	12(1)	4(1)	1(1)
O(2)	23(1)	22(1)	39(1)	-7(1)	4(1)	-3(1)
O(3)	21(1)	20(1)	30(1)	2(1)	5(1)	-4(1)
O(4)	14(1)	26(1)	28(1)	-6(1)	4(1)	4(1)
C(1)	19(1)	40(1)	26(1)	7(1)	-4(1)	-7(1)
C(2)	23(1)	32(1)	15(1)	2(1)	4(1)	2(1)
C(3)	16(1)	26(1)	32(1)	10(1)	4(1)	-1(1)
C(4)	17(1)	33(1)	23(1)	2(1)	2(1)	4(1)
C(5)	22(1)	20(1)	23(1)	1(1)	6(1)	-4(1)
C(6)	19(1)	22(1)	21(1)	2(1)	5(1)	-2(1)
C(7)	30(1)	24(1)	22(1)	5(1)	8(1)	-1(1)
C(8)	23(1)	27(1)	22(1)	-7(1)	8(1)	-4(1)
C(9)	28(1)	36(1)	20(1)	2(1)	0(1)	-6(1)
C(10)	26(1)	24(1)	18(1)	-1(1)	2(1)	-4(1)
C(11)	17(1)	17(1)	25(1)	3(1)	4(1)	1(1)
C(12)	15(1)	16(1)	32(1)	-2(1)	4(1)	2(1)
C(13)	19(1)	18(1)	21(1)	1(1)	6(1)	3(1)
C(14)	14(1)	18(1)	20(1)	2(1)	3(1)	0(1)
C(15)	14(1)	16(1)	16(1)	-1(1)	3(1)	-1(1)
C(16)	13(1)	19(1)	22(1)	-3(1)	4(1)	1(1)
O(5)	18(1)	23(1)	28(1)	6(1)	1(1)	0(1)
O(6)	23(1)	21(1)	32(1)	-6(1)	5(1)	-3(1)
O(7)	24(1)	20(1)	23(1)	0(1)	7(1)	-4(1)
O(8)	14(1)	26(1)	20(1)	-6(1)	3(1)	2(1)
C(17)	18(1)	30(1)	23(1)	0(1)	0(1)	-6(1)
C(18)	16(1)	19(1)	18(1)	1(1)	4(1)	-1(1)
C(19)	20(1)	34(1)	17(1)	-3(1)	2(1)	-7(1)
C(20)	20(1)	22(1)	19(1)	-1(1)	6(1)	-1(1)
C(21)	22(1)	21(1)	20(1)	0(1)	5(1)	-6(1)
C(22)	31(1)	24(1)	21(1)	3(1)	9(1)	-1(1)
C(23)	20(1)	25(1)	19(1)	-4(1)	4(1)	-2(1)
C(24)	15(1)	23(1)	24(1)	3(1)	3(1)	-3(1)
C(25)	15(1)	17(1)	24(1)	0(1)	5(1)	3(1)
C(26)	24(1)	22(1)	18(1)	-4(1)	6(1)	-2(1)
C(27)	25(1)	27(1)	15(1)	1(1)	4(1)	0(1)
C(28)	20(1)	27(1)	23(1)	3(1)	3(1)	3(1)
C(29)	17(1)	18(1)	23(1)	0(1)	6(1)	3(1)
C(30)	12(1)	19(1)	18(1)	-2(1)	4(1)	1(1)
C(31)	16(1)	17(1)	16(1)	-1(1)	4(1)	-2(1)
C(32)	14(1)	17(1)	15(1)	-1(1)	5(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for F4WS10.

	x	y	z	U(eq)
H(1A)	6805	2415	561	36
H(1B)	7246	1488	1168	36
H(2A)	11748	1594	5011	28
H(3A)	7263	2899	2087	30
H(4A)	12769	1064	4056	30
H(4B)	12807	2251	4050	30
H(5A)	9907	544	2749	26
H(5B)	9168	1345	3086	26
H(6A)	11244	2768	1419	25
H(6B)	10188	3469	1077	25
H(7A)	10021	834	4394	30
H(7B)	10946	241	4061	30
H(8A)	10133	2688	4465	28
H(8B)	11304	3236	4554	28
H(9A)	8561	2620	288	34
H(9B)	8172	1496	77	34
H(10A)	9290	995	1445	28
H(10B)	10039	1480	884	28
H(13A)	12173	2135	2639	23
H(13B)	11818	997	2690	23
H(17A)	7645	6046	3840	29
H(17B)	8149	5184	4504	29
H(19A)	6415	4941	4804	29
H(19B)	6729	6091	4936	29
H(20A)	4776	3967	4010	24
H(20B)	3701	4634	3637	24
H(21A)	5790	6003	1952	26
H(21B)	5042	6817	2264	26
H(22A)	3987	7064	945	30
H(22B)	4945	6495	633	30
H(23A)	5552	6458	3574	26
H(23B)	4856	5944	4158	26
H(24A)	7715	4557	3019	25
H(26A)	3770	4040	532	26
H(26B)	4926	4621	640	26
H(27A)	3267	5658	13	27
H(28A)	2202	5004	973	29
H(28B)	2179	6190	917	29
H(29A)	3104	6353	2287	23
H(29B)	2780	5216	2382	23

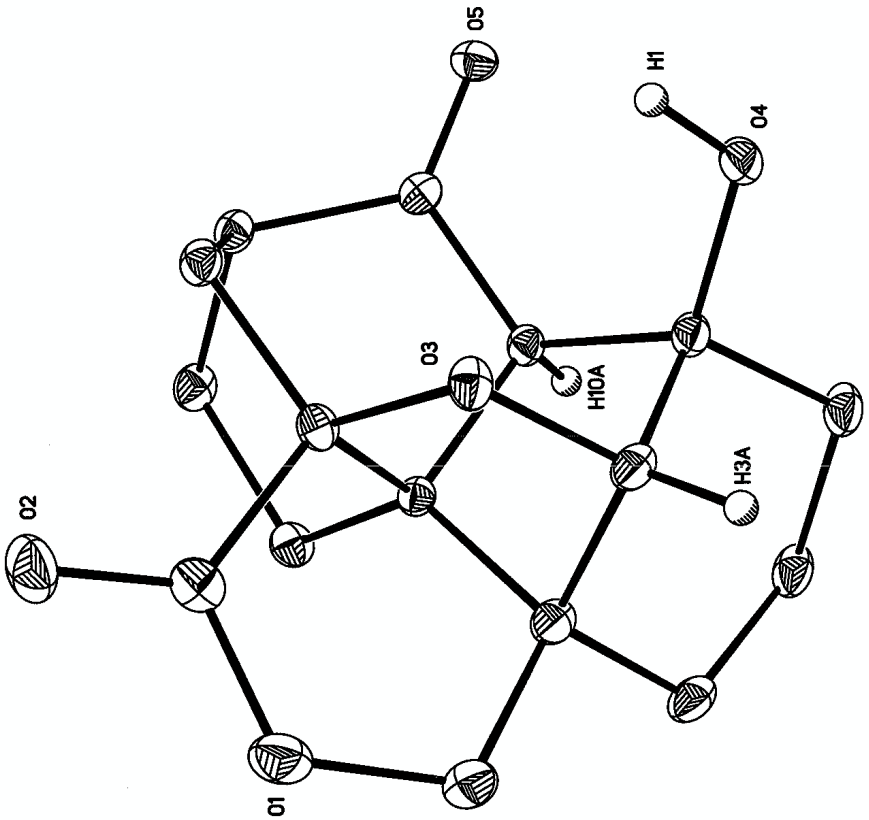

O5
H1
O4
O3
H10A
H3A
O2
O1

Table 1. Crystal data and structure refinement for FPA5S10.

Identification code	fpa5s10
Empirical formula	$C_{16}H_{18}O_{5.20}$
Formula weight	293.42
Temperature	125(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 6.4057(10) Å alpha = 90° b = 24.970(4) Å beta = 109.779(2)° c = 8.6806(13) Å gamma = 90°
Volume, Z	1306.5(3) $Å^3$, 4
Density (calculated)	1.492 Mg/m^3
Absorption coefficient	0.111 mm^{-1}
F(000)	622
Crystal size	0.20 x 0.10 x 0.04 mm
Θ range for data collection	1.63 to 30.53°
Limiting indices	$-9 \le h \le 9$, $-35 \le k \le 35$, $-12 \le l \le 12$
Reflections collected	20658
Independent reflections	3987 (R_{int} = 0.0831)
Completeness to Θ = 30.53°	99.6 %
Absorption correction	EMPIRICAL
Max. and min. transmission	0.9956 and 0.9781
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3987 / 2 / 205
Goodness-of-fit on F^2	1.027
Final R indices [I>2σ(I)]	R1 = 0.0596, wR2 = 0.1395
R indices (all data)	R1 = 0.1027, wR2 = 0.1601
Largest diff. peak and hole	0.434 and -0.257 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for FPA5S10. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	5634(3)	2667(1)	3403(2)	30(1)
O(2)	3024(3)	3071(1)	1431(2)	33(1)
O(3)	4777(2)	3611(1)	5099(2)	20(1)
O(4)	6727(2)	4434(1)	7415(2)	24(1)
O(5)	7308(2)	5119(1)	4758(2)	22(1)
C(1)	4546(3)	3113(1)	2707(3)	23(1)
C(2)	5340(3)	3641(1)	3608(2)	17(1)
C(3A)	6871(3)	3519(1)	6422(2)	20(1)
C(3B)	6871(3)	3519(1)	6422(2)	20(1)
O(6)	6635(11)	3333(3)	7837(7)	20(2)
C(4)	8353(3)	3236(1)	5603(2)	21(1)
C(5)	7488(4)	2685(1)	4930(3)	27(1)
C(6)	10734(3)	3155(1)	6803(3)	25(1)
C(7)	11836(3)	3647(1)	7790(3)	27(1)
C(8)	10198(3)	3988(1)	8311(2)	26(1)
C(9)	8011(3)	4063(1)	6901(2)	20(1)
C(10)	8461(3)	4200(1)	5271(2)	17(1)
C(11)	7893(3)	3673(1)	4261(2)	16(1)
C(12)	8791(3)	3689(1)	2853(2)	21(1)
C(13)	7856(3)	4206(1)	1845(2)	23(1)
C(14)	6184(3)	4503(1)	2474(2)	19(1)
C(15)	7303(3)	4666(1)	4241(2)	18(1)
C(16)	4307(3)	4123(1)	2535(2)	19(1)

Table 3. Bond lengths [Å] and angles [°] for FPA5S10.

O(1)-C(1)	1.344(3)	O(1)-C(5)	1.451(3)
O(2)-C(1)	1.207(2)	O(3)-C(2)	1.458(2)
O(3)-C(3A)	1.459(2)	O(4)-H(1)	0.92(3)
O(4)-C(9)	1.408(2)	O(5)-C(15)	1.217(2)
C(1)-C(2)	1.530(3)	C(2)-C(16)	1.529(3)
C(2)-C(11)	1.541(3)	C(3A)-C(9)	1.530(3)
C(3A)-C(4)	1.538(3)	C(4)-C(5)	1.523(3)
C(4)-C(6)	1.541(3)	C(4)-C(11)	1.551(3)
C(6)-C(7)	1.528(3)	C(7)-C(8)	1.533(3)
C(8)-C(9)	1.528(3)	C(9)-C(10)	1.574(3)
C(10)-C(15)	1.502(3)	C(10)-C(11)	1.553(3)
C(11)-C(12)	1.517(3)	C(12)-C(13)	1.561(3)
C(13)-C(14)	1.547(3)	C(14)-C(15)	1.513(3)
C(14)-C(16)	1.546(3)		

C(1)-O(1)-C(5)	121.65(16)	C(2)-O(3)-C(3A)	105.61(13)
H(1)-O(4)-C(9)	113.1(16)	O(2)-C(1)-O(1)	118.38(18)
O(2)-C(1)-C(2)	124.73(18)	O(1)-C(1)-C(2)	116.89(17)
O(3)-C(2)-C(16)	113.26(14)	O(3)-C(2)-C(1)	105.70(14)
C(16)-C(2)-C(1)	111.52(16)	O(3)-C(2)-C(11)	103.10(14)
C(16)-C(2)-C(11)	111.67(15)	C(1)-C(2)-C(11)	111.17(15)
O(3)-C(3A)-C(9)	107.56(15)	O(3)-C(3A)-C(4)	104.79(15)
C(9)-C(3A)-C(4)	102.83(15)	C(5)-C(4)-C(3A)	113.09(17)
C(5)-C(4)-C(6)	106.80(16)	C(3A)-C(4)-C(6)	111.86(16)
C(5)-C(4)-C(11)	113.34(17)	C(3A)-C(4)-C(11)	91.86(14)
C(6)-C(4)-C(11)	119.49(16)	O(1)-C(5)-C(4)	117.22(16)
C(7)-C(6)-C(4)	115.93(16)	C(6)-C(7)-C(8)	112.29(17)
C(9)-C(8)-C(7)	111.39(16)	O(4)-C(9)-C(8)	107.58(15)
O(4)-C(9)-C(3A)	113.20(16)	C(8)-C(9)-C(3A)	109.45(16)
O(4)-C(9)-C(10)	116.47(15)	C(8)-C(9)-C(10)	110.45(16)
C(3A)-C(9)-C(10)	99.44(14)	C(15)-C(10)-C(11)	110.26(15)
C(15)-C(10)-C(9)	119.96(15)	C(11)-C(10)-C(9)	104.14(14)
C(12)-C(11)-C(2)	110.46(15)	C(12)-C(11)-C(4)	126.54(16)
C(2)-C(11)-C(4)	98.46(15)	C(12)-C(11)-C(10)	110.69(15)
C(2)-C(11)-C(10)	105.57(14)	C(4)-C(11)-C(10)	102.93(15)
C(11)-C(12)-C(13)	107.10(15)	C(14)-C(13)-C(12)	112.30(15)
C(15)-C(14)-C(16)	103.76(15)	C(15)-C(14)-C(13)	109.88(16)
C(16)-C(14)-C(13)	110.91(16)	O(5)-C(15)-C(10)	124.22(18)
O(5)-C(15)-C(14)	124.46(17)	C(10)-C(15)-C(14)	111.30(16)
C(2)-C(16)-C(14)	108.82(15)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for FPA5S10.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^*b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	34(1)	19(1)	35(1)	-3(1)	11(1)	-2(1)
O(2)	36(1)	30(1)	26(1)	-5(1)	2(1)	-11(1)
O(3)	16(1)	27(1)	17(1)	0(1)	7(1)	0(1)
O(4)	22(1)	31(1)	18(1)	-3(1)	6(1)	7(1)
O(5)	20(1)	19(1)	27(1)	-3(1)	7(1)	0(1)
C(1)	26(1)	22(1)	25(1)	-1(1)	12(1)	-5(1)
C(2)	18(1)	20(1)	16(1)	-1(1)	7(1)	-2(1)
C(3A)	18(1)	24(1)	18(1)	6(1)	7(1)	6(1)
C(3B)	18(1)	24(1)	18(1)	6(1)	7(1)	6(1)
O(6)	21(4)	21(4)	22(4)	8(3)	12(3)	1(3)
C(4)	21(1)	22(1)	20(1)	3(1)	8(1)	4(1)
C(5)	33(1)	21(1)	27(1)	4(1)	10(1)	4(1)
C(6)	23(1)	28(1)	24(1)	8(1)	9(1)	11(1)
C(7)	20(1)	40(1)	19(1)	4(1)	3(1)	9(1)
C(8)	20(1)	39(1)	16(1)	0(1)	2(1)	7(1)
C(9)	18(1)	26(1)	15(1)	1(1)	4(1)	6(1)
C(10)	14(1)	20(1)	16(1)	-1(1)	3(1)	0(1)
C(11)	14(1)	18(1)	15(1)	1(1)	5(1)	2(1)
C(12)	21(1)	24(1)	21(1)	-1(1)	10(1)	0(1)
C(13)	25(1)	28(1)	20(1)	4(1)	11(1)	1(1)
C(14)	20(1)	20(1)	16(1)	3(1)	6(1)	1(1)
C(15)	13(1)	20(1)	21(1)	2(1)	6(1)	0(1)
C(16)	15(1)	23(1)	18(1)	-1(1)	3(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for FPA5S10.

	x	y	z	U(eq)
H(1)	5360(50)	4494(10)	6640(30)	41(7)
H(3A)	6704	3317	7366	24
H(6C)	5649	3095	7611	30
H(5A)	8732	2482	4778	33
H(5B)	7046	2494	5772	33
H(6A)	10707	2867	7579	30
H(6B)	11670	3029	6172	30
H(7A)	12486	3869	7121	33
H(7B)	13059	3530	8778	33
H(8A)	9905	3812	9240	31
H(8B)	10865	4343	8687	31
H(10A)	10092	4261	5565	21
H(12A)	8308	3367	2156	25
H(12B)	10433	3698	3275	25
H(13A)	9102	4449	1907	28
H(13B)	7114	4108	682	28
H(14A)	5558	4823	1778	23
H(16A)	3296	4314	2995	23
H(16B)	3436	4002	1416	23

Table 6. Hydrogen bonds for FPA5S10 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(1)...O(5)#1	0.92(3)	1.98(3)	2.861(2)	160(2)

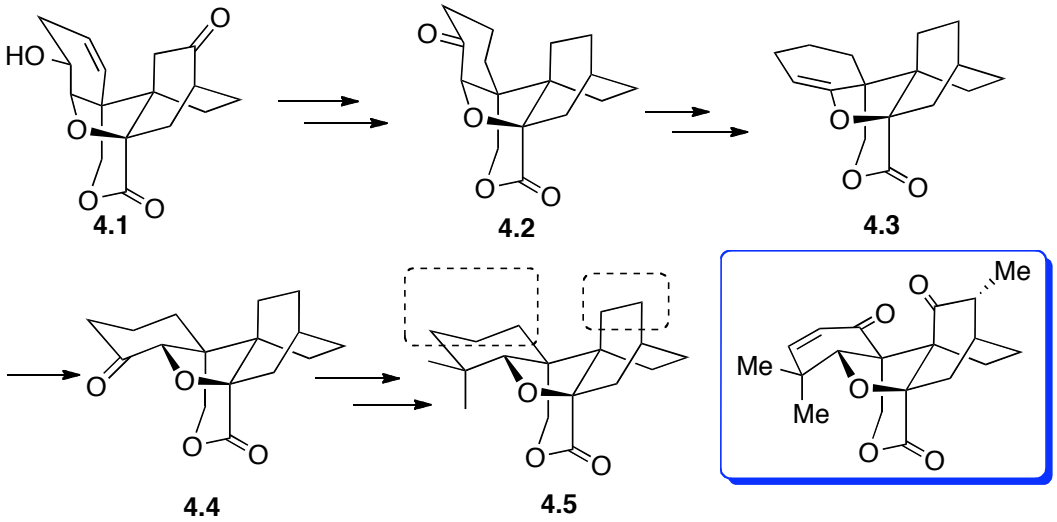
Symmetry transformations used to generate equivalent atoms:

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

Chapter 4 Total Synthesis of Maoecrystal V

4.1 Early Exploration toward the Total Synthesis of Maoecrystal V

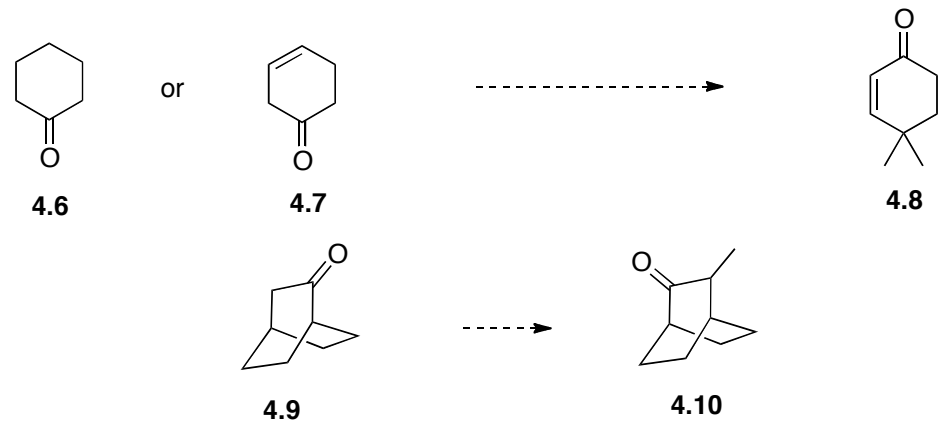
In previous chapter, I described in detail how we developed the chemistry to synthesize the core structure of Maoecrystal V with the appropriate relative stereochemistry. In this chapter, I'd like to talk about the chemistry we developed to achieve the total synthesis of Maoecrystal V.



Scheme 4-1 Summary of model study toward Maoecrystal V

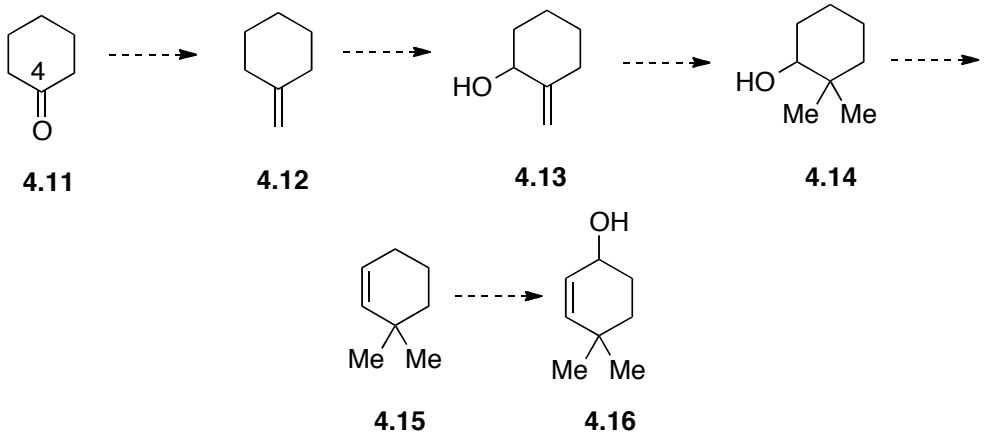
By a simple comparison of intermediate **4.5** and Maoecrystal V (**Scheme 4-1**), we realized that the chemistry required for a total synthesis of Maoecrystal V is to synthesize A-ring enone and the α-methyl ketone which was corresponding C-15 and C-16. To be

more specific, we needed to develop sequences to achieve the following transformation (Scheme 4-2).



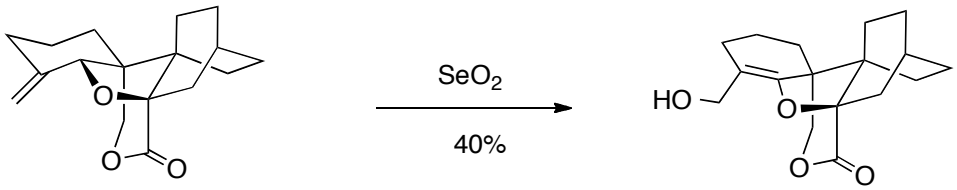
Scheme 4-2 Functional Group transformations required for the total synthesis

We first explored the chemistry to synthesize the A-ring enone moiety. Our first plan was shown in Scheme 4-3, in which we wanted to start with a C-4 ketone function group. Olefination of ketone **4.11** would afford us an *exo*-methylene **4.12**, which upon



Scheme 4-3 First plan for A ring enone synthesis

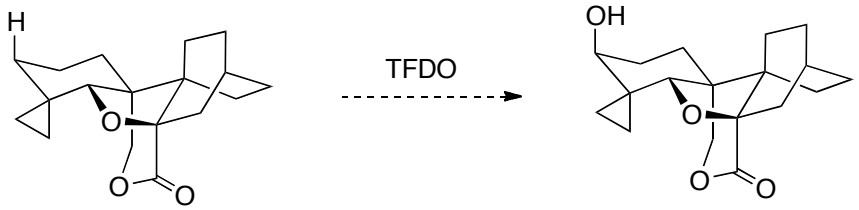
allylic oxidation would provide allylic alcohol **4.13**. A cyclopropanation / hydrogenation sequence would furnish gem-dimethyl structure **4.14**. Dehydration of **4.14** would give olefin **4.15**, which would eventually be transformed to **4.16** by an allylic oxidation. To test this design, we used **4.17** as model compound to try the allylic oxidation first. To our disappointment, the allylic oxidation[1] did not provide the desired allylic alcohol. Compound **4.18** was isolated instead.



4.17 **4.18**

Scheme 4-4 Allylic oxidation of exo-methylene **4.17**

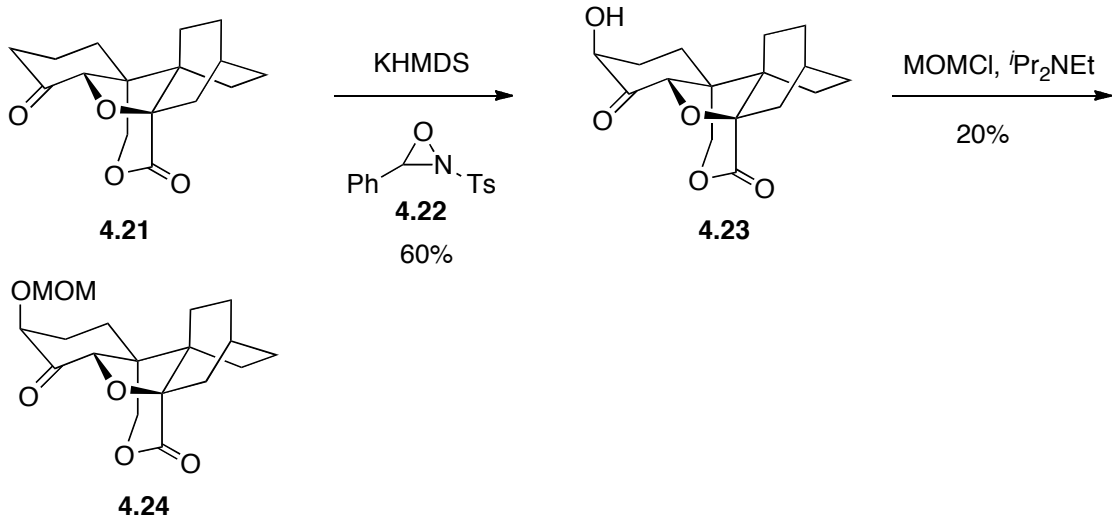
To circumvent this allylic oxidation problem, we then tried a direct C-H oxidation[2] reaction on substrate **4.19**, hoping the cyclopropane ring could activate the α-hydrogen. Unfortunately, this reaction only gave starting material.



4.19 **4.20**

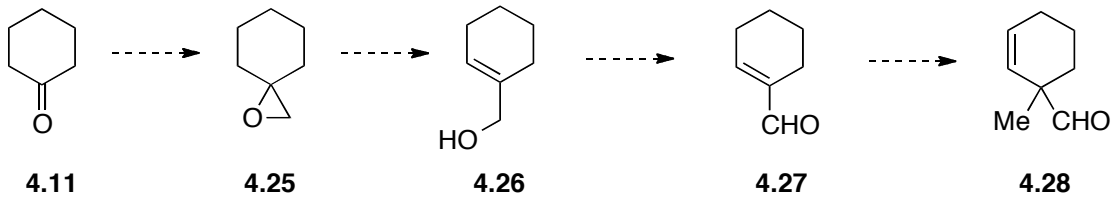
Scheme 4-5 C-H activation approach

We then tried installing the of hydroxyl group at an earlier stage, such as substrate **4.21**, which required an α-hydroxylation reaction of the corresponding ketone **4.21**. To our delight, we did obtain the desired α-hydroxyl ketone **4.23** in good yield when we subjected ketone **4.21** to Davis oxaziridine reagent **4.22**.[3] Further protection of **4.23** with MOMCl, however, afforded **4.24** in 20% yield. Optimization of protecting group conditions did not improve the chemical yield.



Scheme 4-6 α-Hydroxylation of ketone **4.21**

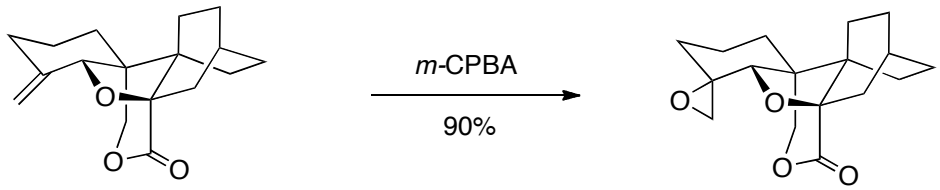
Since we met problem to prepare compounds with **4.14**-type structures, we then changed our design. The new design (Scheme 4-7) featured a deconjugated alkylation reaction with compound **4.27**.[4] Compound **4.27** could be synthesized from **4.26** by a direct oxidation reaction. Allylic alcohol **4.26** could be prepared through a base-catalyzed isomerization of epoxide **4.25**. We then turned our attention to the isomerization of epoxide **4.30**.



4.11 **4.25** **4.26** **4.27** **4.28**

Scheme 4-7 Second plan for A-ring enone synthesis

We screened many conditions and were surprised to find that this epoxide **4.30** was quite inert to the isomerization conditions[5] and we did not obtain the desired allylic alcohol.

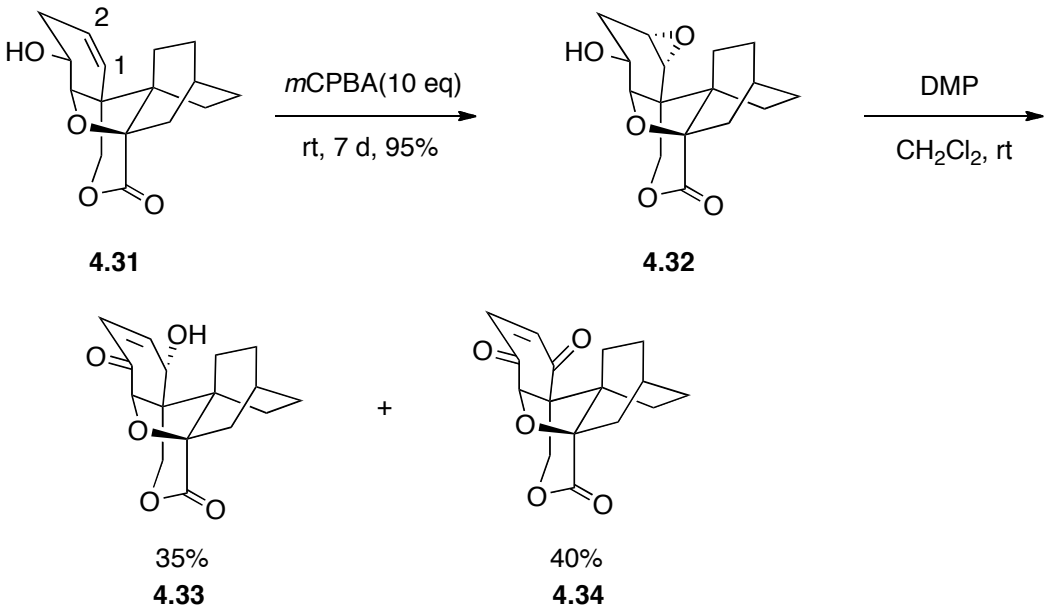


4.29 **4.30**

Scheme 4-8 Epoxidation of **4.29**

At this stage, we turned our attention to compound **4.31**, in which there was a C 1-C 2 double bond. We envisioned that we could take advantage of this double bond to install the C-1 oxygen functional group. Based on this hypothesis, we subjected compound **4.31** to an epoxidation reaction using *m*-CPBA as oxidative reagent. Although the reaction rate was quite slow, we did obtain the desired epoxide **4.32** as a single diastereomer in excellent yield. We then treated this epoxide with DMP reagent through

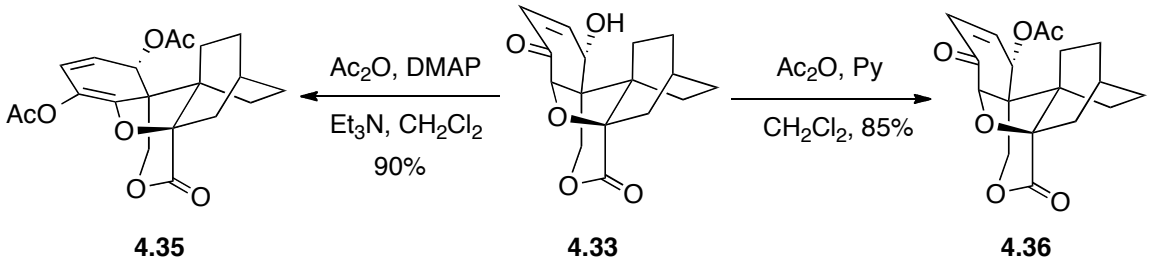
which we hoped to get a β-epoxide ketone. To our delight, we actually isolated γ-hydroxyl enone **4.33**, a little bit in low yield. A side product, dienone **4.34**, was also isolated. We rationalized that the DMP oxidation reaction condition was a little bit acidic, which isomerized the β-epoxide ketone to the γ-hydroxyl enone **4.33** and further oxidation of **4.33** provided us the dienone **4.34**. In order to increase the yield of this γ-hydroxyl enone **4.33**, we used a mild oxidation condition (0 ^{o}C, $NaHCO_3$ buffer), which did increase the yield of γ-hydroxyl enone **4.33** to 85%.



Scheme 4-9 Epoxidation of **4.31**

With this γ-hydroxyl enone **4.33** in hand, we then explored the protecting group on this γ-hydroxyl group. Initially, we tried MOM ether formation condition and we only recovered the starting material, probably due to the neopentyl character of this alcohol.

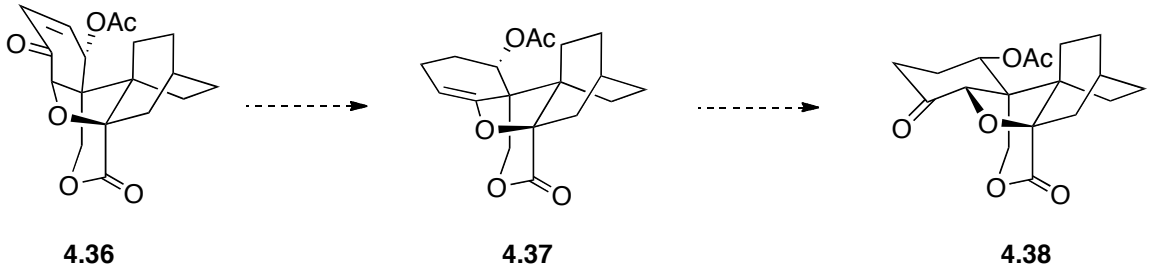
Using acetic anhydride and DMAP condition, we obtained enol acetate **4.35**, which indicated the condition is a little bit harsh. Finally, when using acetic anhydride and pyridine condition, we isolated **4.36** in excellent yield.



4.35 **4.33** **4.36**

Scheme 4-10 Protection of γ-hydroxyl group

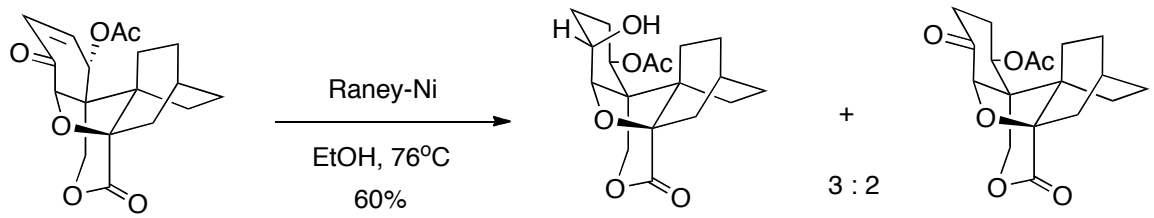
We then wanted to apply the chemistry we developed to epimerize the C-5 stereogenic center to compound **4.36**, hoping to synthesize compound **4.38**. To synthesize the junction enol ether **4.37**, we wanted to reduce the enone **4.36** to a ketone via a 1,4 – reduction fashion, which was well-documented using Stryker's reagent.[6]



4.36 **4.37** **4.38**

Scheme 4-11 Third plan for the A ring functionalization

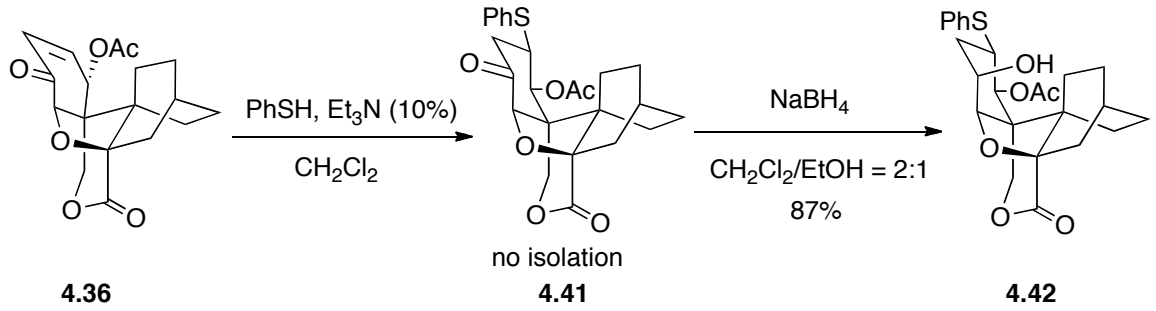
Herein, we first treated enone **4.36** with Raney-Ni hydrogenation condition, which was reported to reduce the enone double bond.[7] To our surprise, we obtained a mixture of **4.39** and **4.40** as 3:2 ratio. Since these two compounds were not separable, we still needed to develop a clean sequence to synthesize the dehydration precursor **4.39**.



4.36 **4.39** **4.40**

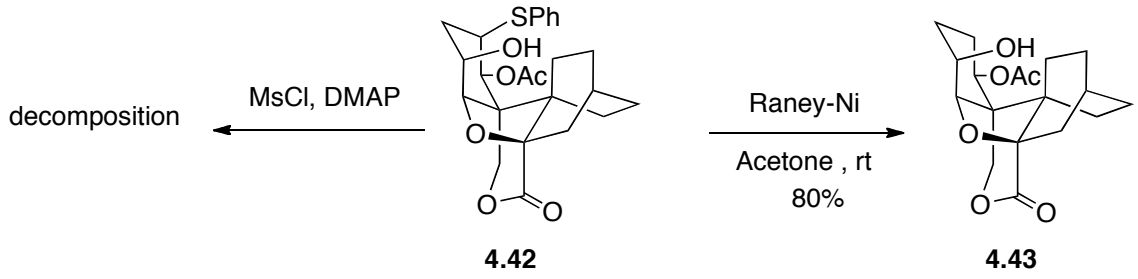
Scheme 4-12 Raney-Ni reduction of enone **4.36**

Instead of reduction of the double bond in compound **4.36**, we also considered temporary masking this enone olefin functional group, which would regenerate the double bond after we epimerized the C-5 stereocenter.[8] We then thought of using a sulfur atom to achieve this goal. Thus, we subjected compound **4.36** to PhSH condition, which afforded us the desired 1,4-addition product **4.41**. Without isolation of this unstable ketone **4.41**, we treated the reaction mixture with EtOH and $NaBH_4$ and we eventually isolated compound **4.42** in excellent yield. With compound **4.42** in hand, we treated it with the dehydration condition, hoping to synthesize the junction enol ether. To our disappointment, we only observed the decomposition of material. Subsequently, we subjected **4.42** to Raney-Ni, which provided compound **4.43** in 80% yield.

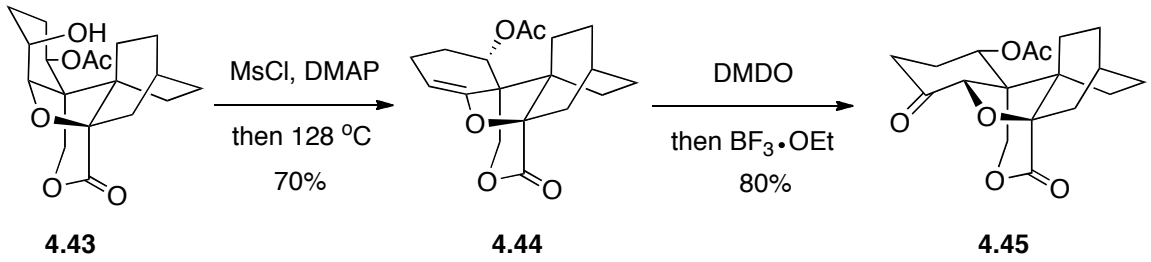


Scheme 4-13 Reduction of enone **4.36**

Further dehydration reaction and *exo*-glycal epoxide rearrangement sequence worked extremely well on compound **4.46** and we isolated compound **4.45** in good yield as a single diastereomer. These results provided us with important information that we could take advantage of the C 1-C 2 double bond to install oxygen function group on C-1.



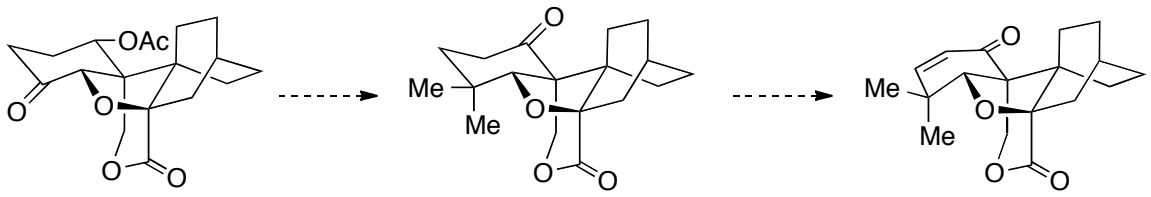
Scheme 4-14 Hydrodesulfurization of **4.42**



4.43 **4.44** **4.45**

Scheme 4-15 *Exo*-gycal epoxide rearrangement of **4.40**

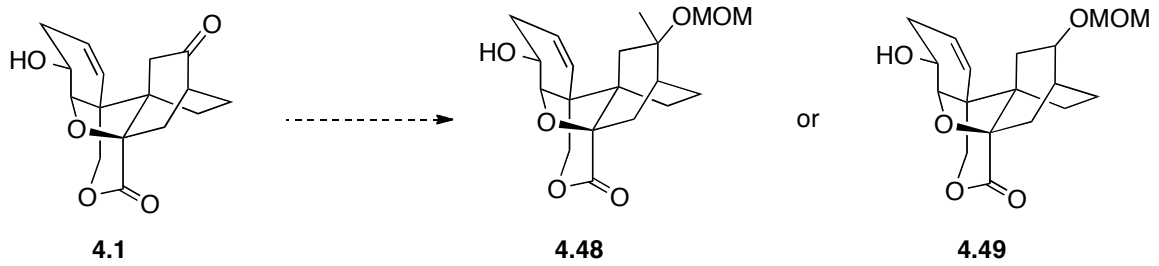
Based on the above results, we envisioned that the A ring enone could be prepared through ketone **4.46** through a Saegusa oxidation protocol[9] (Scheme 4-16).



4.45 **4.46** **4.47**

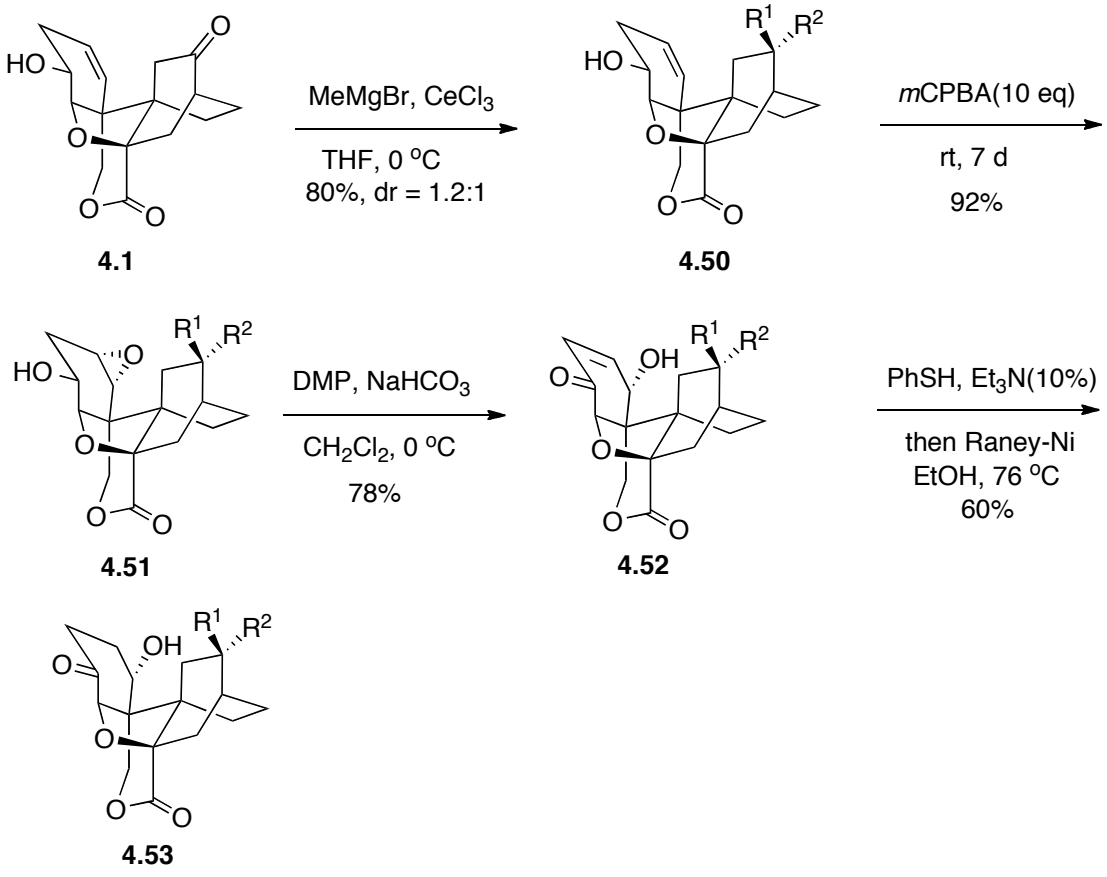
Scheme 4-16 Third plan for A-ring enone synthesis

We did not further explore how to transform compound **4.45** to the enone **4.47**, instead, we were planning the chemistry of C 15 and C 16 so it could be compatible with the A ring functionalization during our total synthesis. Considering we used hydrogenation and $NaBH_4$ reduction, we thought the function group we put on C-16 should tolerate these conditions and an ether function group such as **4.48** or **4.49** might be our choice.



Scheme 4-17 Functionalization of C 16

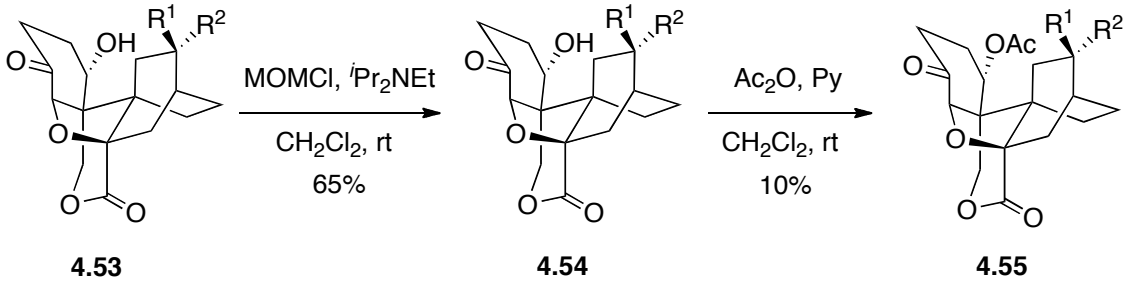
The preparation of compound **4.50** turned out to be straightforward. We treated compound **4.1** with methyl cerium chloride reagent at 0 ^{o}C and the desired tertiary alcohol **4.50** was isolated in about 80% yield. The diastereoselectivity of this ketone addition reaction proved to be quite poor, which a 1.2:1 ratio of diastereoisomer **4.50a** and **4.50b** was isolated. The poor diastereoselectivity might due to the fact that both C-14 and C-12 are methylene groups, which created a similar stereo environment on both side of the C 16 ketone. Nevertheless, these two diastereomers were then subjected to the *m*-CPBA-mediated epoxidation reaction and afforded epoxides **4.51** as diastereomers only at C-16 center, which indicated that the epoxidation only happened at α-face of A-ring. Dess-Martin oxidation of the secondary alcohol in the presence of the C-16 tertiary alcohol provided a ketone, which gave the desired γ-hydroxyl enone **4.52** upon purification with silica gel column. The enone olefin was then reduced to give compound **4.53** via a thiophenol addition/Raney-Ni reduction sequence, which was already discussed in Scheme 4-14.



Scheme 4-18 Preparation of **4.53**

Now it was a time for us to selectively protect the C-1 and C-16 hydroxyl group. We thought the C-1 hydroxyl group was more hindered since it was next to two quaternary centers. Therefore we envisioned that protection of C 16 hydroxyl group in the presence of C-1 hydroxyl group was possible.

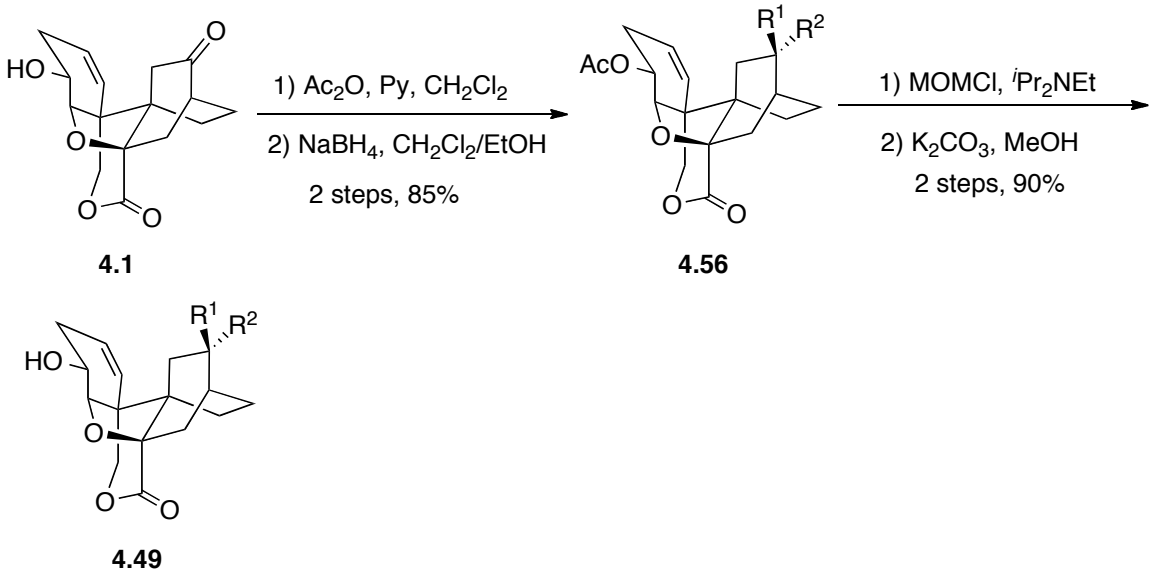
This was indeed the case. Compound **4.53** was subjected to MOM ether protecting condition and afforded us only compound **4.54**. Further protection of C-1 hydroxyl group proved to be problematic, which gave the desired compound **4.55** in about 10% yield. A large amount of material was isolated as decomposition product.



4.53 **4.54** **4.55**

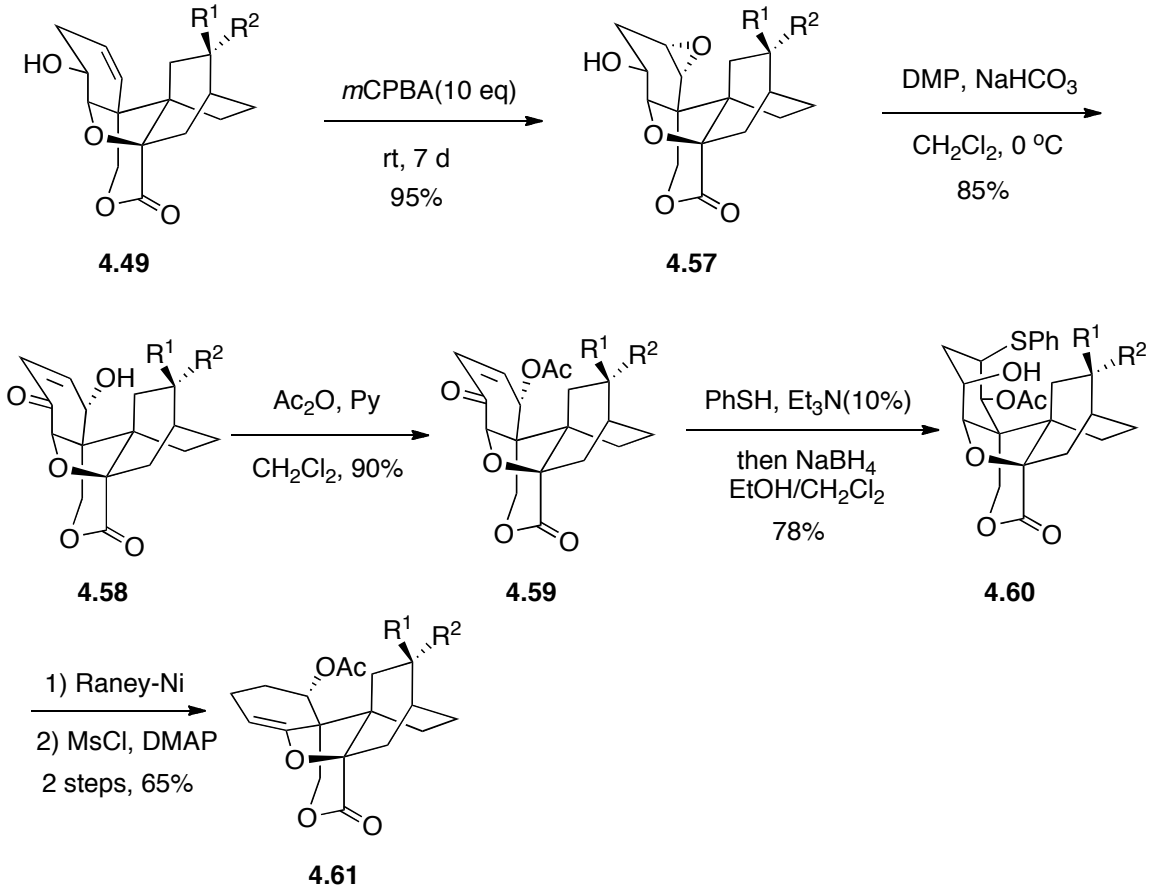
Scheme 4-19 Protection of C1 and C16 alcohol

Since further optimization of this step did not improve the yield, we then turned to compound **4.49**, in which C-16 was a secondary alcohol. We hoped that a less hindered C-16 secondary alcohol would facilitate our synthesis. Our synthesis of compound **4.49** started with an alcohol protection of compound **4.1**. The resultant ketone was then subjected to a $NaBH_4$ reduction condition and gave compound **4.56** in about 85%. The $NaBH_4$ reduction proved to proceed without stereoselectivity, since compound **4.56** was isolated as a 1:1 diastereomers. Since in our synthesis plan, these secondary alcohols would eventually undergo oxidation reaction to regenerate a ketone, the optimization of the diastereoselective reduction of this C-16 was not explored. These secondary alcohols were then treated with MOMCl and the following deprotection of acetyl group furnished compound **4.49** in excellent yield.



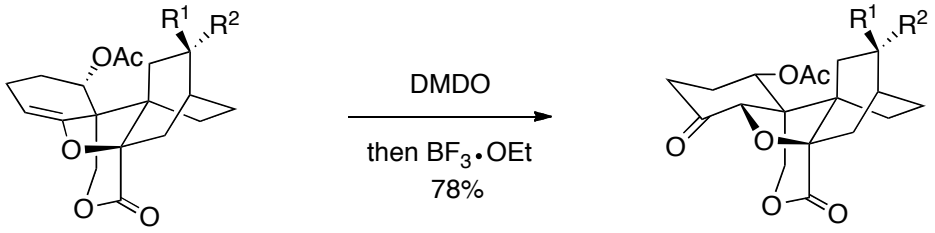
Scheme 4-20 Preparation of **4.49**

With compound **4.49** in hand, we then wanted to test chemistry that we developed to synthesize **4.45**. Thus, compound **4.49** was subjected to *m*-CPBA and gave only α-epoxide **4.57** in about 95% yield. Subsequent Dess-Martin oxidation of the secondary alcohol and upon purification with silica gel column furnished the γ-hydroxyl enone **4.58** in 85% yield. The resultant enone **4.58** was then treated with acetic anhydride in the presence of pyridine, which gave the protected enone **4.59** in good yield. A thiophenol addition and the following one-pot $NaBH_4$ reduction furnished alcohol **4.60**. The resultant alcohol **4.60** was then subjected to the Raney-Ni and dehydration sequence and afforded the desired junction enol ether **4.61** in good yield.



Scheme 4-21 Preparation of enol ether **4.61**

A key *exo*-glycal epoxide rearrangement reaction was then tested on compound **4.61**. To our great happiness, this rearrangement reaction did work on the fully protected compound **4.61** and afforded ketone **4.62** in 78% yield, in which the C-5 stereochemistry is the same. The rearrangement was stereospecific, and only delivered the hydrogen on β-face to furnish a *trans*-5,6-AB ring junction. With these results, we now executed our total synthesis plan.

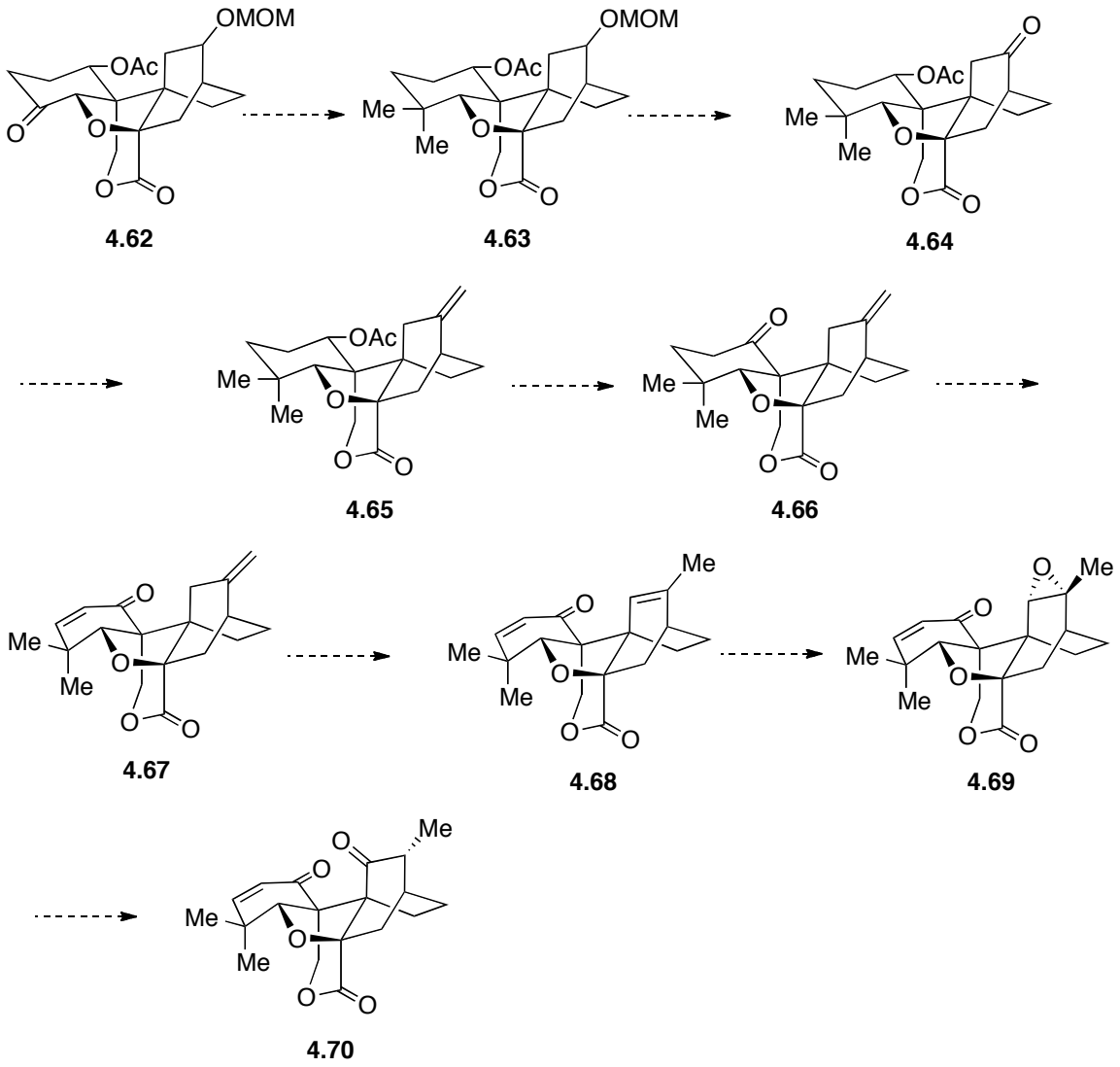


4.61 **4.62**

Scheme 4-22 *Exo*-glycal epoxide rearrangement

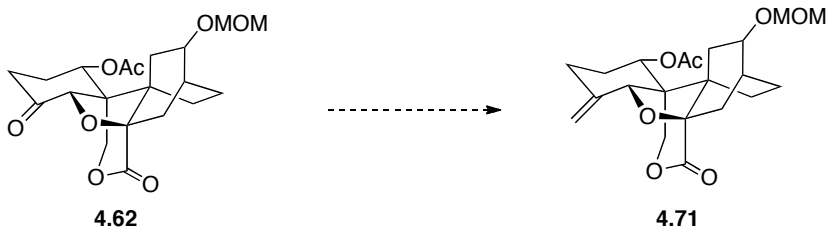
4.2 Total Synthesis of Maoecrystal V

After careful exploration of functionalization of A-ring and C 16 carbon, we then started the study toward total synthesis of Maoecrystal V. As shown in **Scheme 4-23**, our first plan started with compound **4.62**, in which the ketone would be used to install gem-dimethyl group and provide substrate **4.63**.[10] Cleavage of the MOM ether from the C-16 secondary alcohol and subsequent oxidation of the resultant free alcohol would give ketone **4.64**. Olefination of ketone **4.64** would provide *exo*-methylene **4.65**. The C-1 hydroxyl group was then freed and oxidized to ketone **4.66**, which upon Saegusa oxidation protocol to give enone **4.67**. Isomerization of *exo*-methylene would afford internal alkene **4.68**, which would be transformed to epoxide **4.69**. Finally, a key epoxide rearrangement of **4.69** would provide Maoecrystal V.



Scheme 4-23 Total synthesis plan

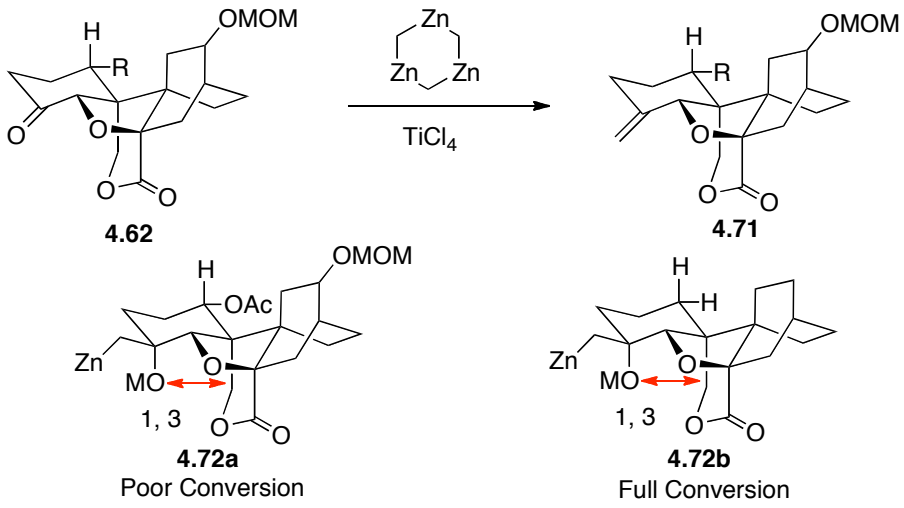
We then started to prepare compound **4.71**, which required an olefination reaction on ketone **4.62**.



Scheme 4-24 Preparation of olefin **4.71**

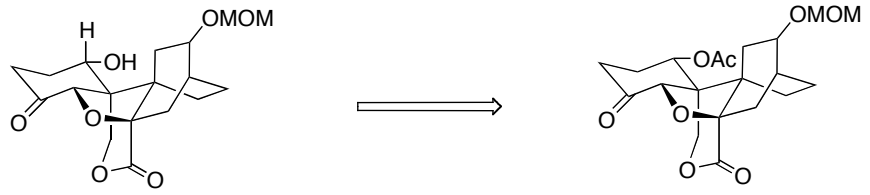
To our great surprise, when ketone **4.62** was subjected to Lombardo reagent[11] for more than 30 mins, we only observed recovery of ketone **4.62**. Since we already observed the smooth olefination reaction of compound **3.41**, we suspected that our Lombardo reagent turned bad. Three batches of fresh Lombardo reagent were soon prepared, however, no improvement was observed on the conversion of our olefination reaction. We then realized this would be a big problem to our plan. If we could not prepare the *exo*-methylene **4.71**, then we could not prepare the gem-dimethyl compound **4.63** using the chemistry we developed on compound **3.41**. At this point, we did not have much choice but to make the olefination reaction work! To optimize this reaction, we first extended the reaction time to 1 h and also increased the reaction temperature to 40 ^{o}C, hoping more harsh conditions would help the conversion of this reaction. To our disappointment, we only observed the decomposition of ketone **4.62** during our close monitoring the reaction process. We then turned our attention to more reactive reagent such as Takai reagent[12] and Tebbe reagent[13], however, the reactions using these two reagent only provided ketone **4.62** back.

Considering the fact the **3.41** reacted smoothly with Lombardo reagent in 5 mins, we thought that compound **4.62** might not be the right substrate for this olefination reaction thought compound **3.41** and compound **4.62** are so close to each other on structure. In order to find the right substrate for the olefination reaction, we first analyzed the reaction mechanism.[14] The first step of this olefination reaction involved a ketone addition reaction, which would afford a tertiary alkoxide intermedated **4.72**. A subsequent 1, 2 elimination reaction would provide the *exo*-methylene **4.71**. The first step probably was a rate-determining step. Since we observed recovery of ketone **4.62** during this reaction, we thought probably the ketone addition reaction did not occur for compound **4.62**. The more congested structure of **4.62** might account for the difficulty of this addition reaction because the increased 1,3 diaxial interaction in **4.72a**, which caused by an A 1, 2 interaction, might increase the activation energy significantly during the addition process.



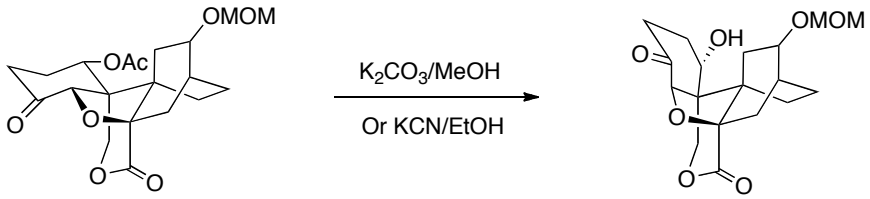
Scheme 4-25 Olefination of **4.62**

This analysis provided us with the hypothesis that a less congested compound such as **4.73** would probably improve the conversion of the olefination reaction. We then decided to prepare compound **4.73**. We thought that a simple deprotection of compound **4.62** would afford **4.73**. Compound **4.62** was then subjected to K_2CO_3/MeOH condition and the deprotection process was indeed observed. Unfortunately, the C-5 carbon center was complete epimerized during this reaction. Milder condition such as KCN/EtOH[15] did not provide the desired product.



4.73 **4.62**

Figure 4-1 Compound **4.73**

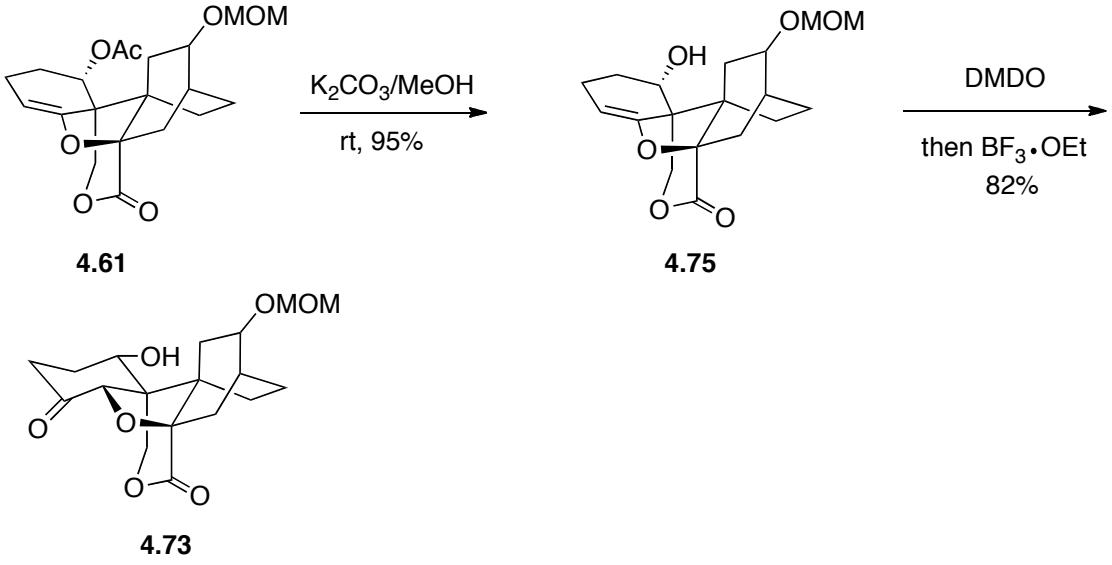


4.62 **4.74**

Scheme 4-26 Deprotection of **4.62**

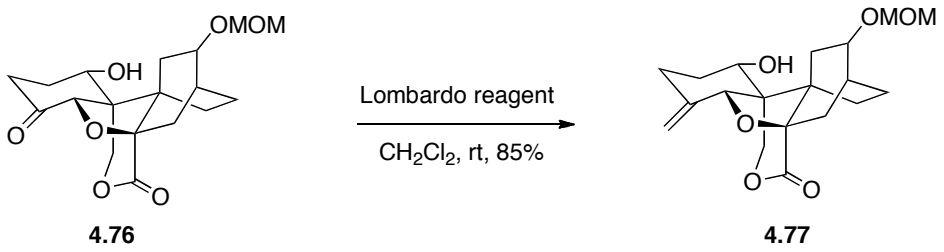
We then thought compound **4.73** might be prepared directly through an *exo*-glycal epoxide rearrangement. The free alcohol at C-1 might cause problems in this

rearrangement since there would be proton species present. Nevertheless, we subjected compound **4.75** to the *exo*-glycal epoxide rearrangement condition and to our delight we did isolate the desired compound **4.73** in about 82% yield. We observed that the reaction was completed in 10 min, while compound **4.61** took more than 5 hours to complete.



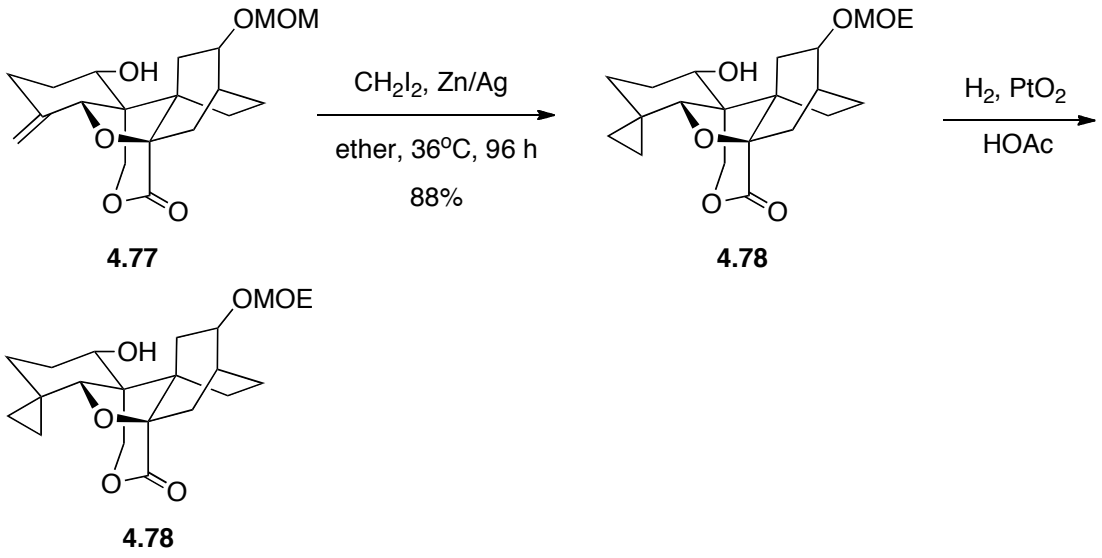
Scheme 4-27 *Exo*-glycal epoxide rearrangement

With compound **4.73** in hand, we did not hesitate to test the olefination reaction. Luckily, with the Lombardo-Takai reagent, the olefination reaction was completed in 8 mins and the *exo*-methylene was isolated in 85% yield.



Scheme 4-28 Olefination of **4.76**

Cyclopropanation of the *exo*-methylene in compound **4.77** did not proceed using previously Cu/Zn couple condition. After screening other conditions, we were pleased to find that the Zn/Ag[16] couple reacted well with the *exo*-methylene in compound **4.77** and provided cyclopropane **4.78** in about 88% yield. We also observed that a carbene insertion to the methyl group of the MOM ether happened, presumably Zn/Ag couple is more reactive then Zn/Cu couple in the Simmon-Smith cyclopropanation.



Scheme 4-29 Cyclopropanation of **4.77**

The opening of this cyclopropane also turned out to be problematic. With the same hydrogenation condition as compound **3.45**, compound **4.78** did not give any conversion during this hydrogenation reaction. Considering the experience we gained on the olefination reaction of compound **4.62**, we thought in this case it might be the substrate problem. Since we did not have a clue which substrate was the right one, we prepared several derivatives of compound **4.78** and subjected all these substrate to the hydrogenation conditions.[17] luckily, we found that compound **4.83** proceeded upon hydrogenation condition. Now, we finally obtained the gem-dimethyl compound **4.84**, which took about 8 months for us to find the right conditions to prepare **4.84** from compound **4.49**.

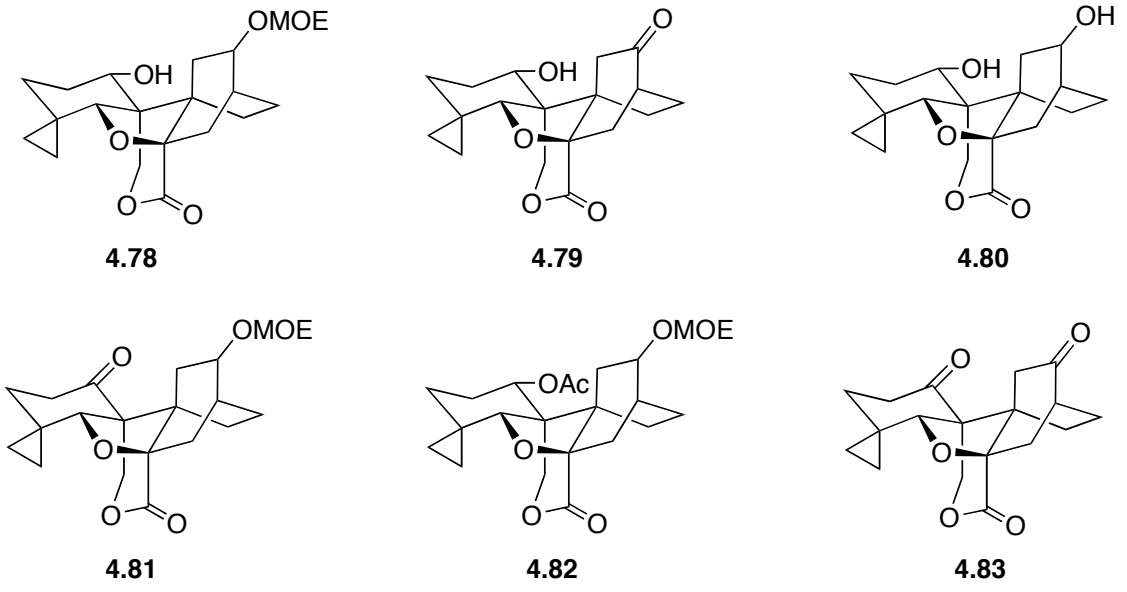
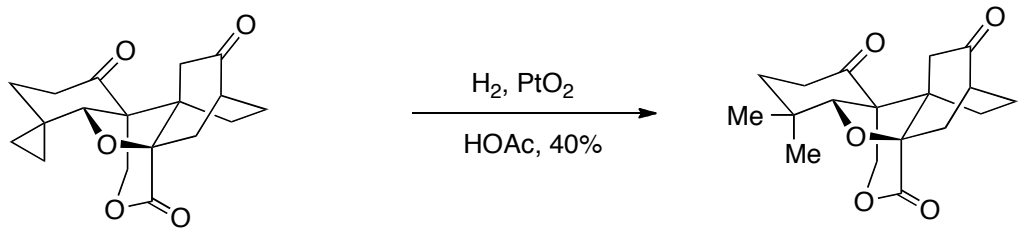


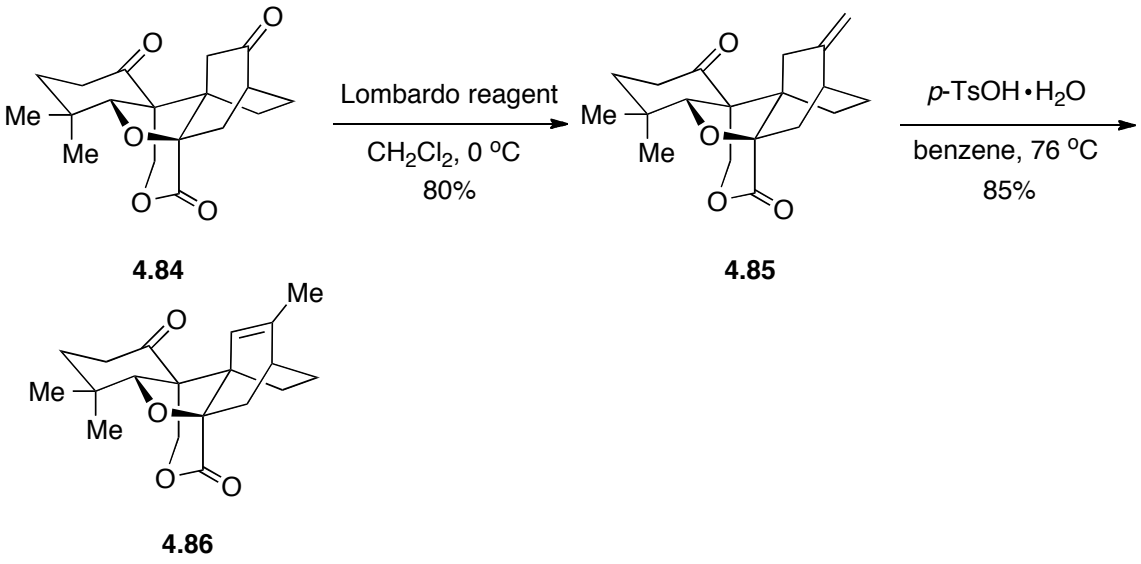
Figure 4-2 Derivatives of **4.78**



4.83 **4.84**

Scheme 4-30 Hydrogenation of **4.83**

With compound **4.84** in hand, we were at the end game stage of the synthesis now. Treatment of compound **4.84** with the Lombardo-Takai reagent at 0 ^{o}C, a regio-selective olefination reaction occurred and gave C 16 methylene in about 80% yield. Subsequent isomerization of the C-16 *exo*-methylene was achieved upon treatment with *p*-toluenesulfonic acid[18] and ketone **4.86** was obtained in about 85% yield.

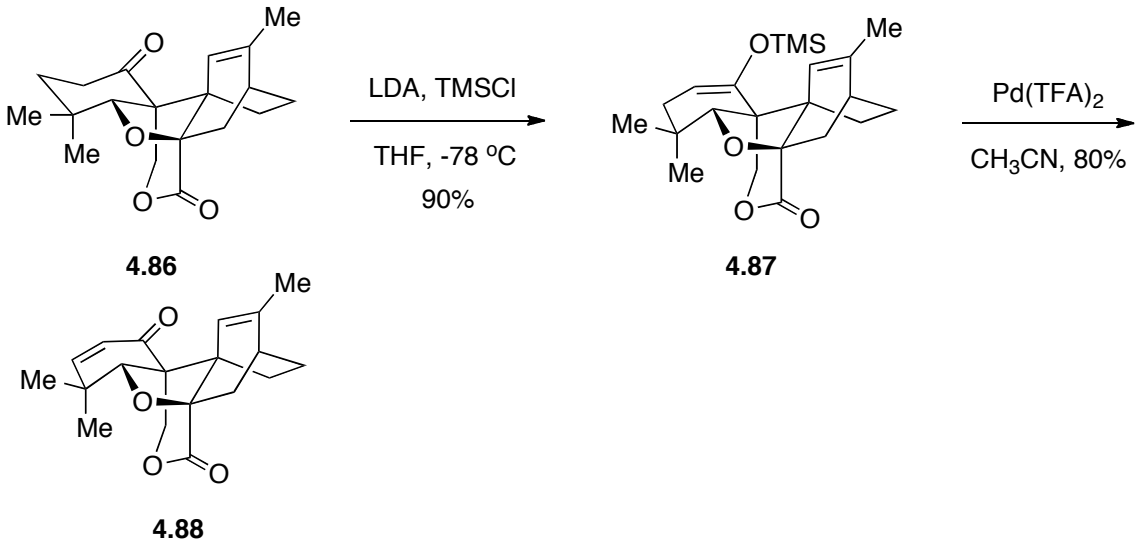


4.84 **4.85**

4.86

Scheme 4-31 Preparation of **4.86**

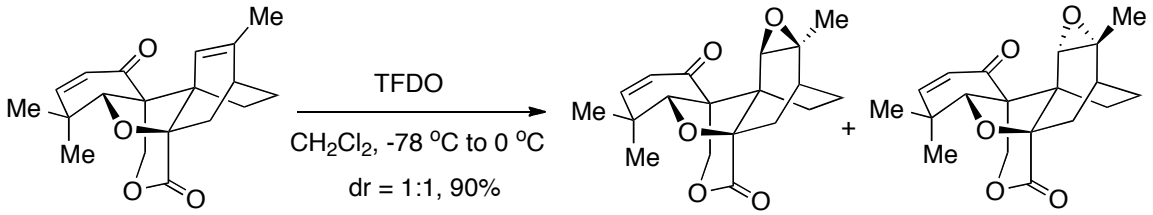
Dehydrogenation of ketone **4.86** proved to be problematic probably due to the neopentyl character of this ketone. Initially we tried the direct α–selenylation of this ketone[19] and we did not observe the formation of the desired product. We then focused on the preparation of the trimethyl silyl enol ether **4.87**, hoping a classic Saegusa type oxidation of this silyl enol ether would afford us the enone **4.88**. After screening several silyl enol ether formation conditions, we were pleased to find that under LDA/TMSCl condition, the desire silyl enol ether was obtained in about 90% yield. This trimethyl silyl enol ether was very stable and could be purified via silica gel column. This silyl enol ether was then subjected to $Pd(OAc)_2$ at 60 ^oC, a well documented condition for Saegusa oxidation reaction. To our great surprise, we only recovered the silyl enol ether, which indicated we need harsh reaction condition. A systematic screening revealed that $Pd(TFA)_2$ could oxidize this silyl enol ether to enone **4.88** in about 80% isolated yield.



4.86 **4.87** **4.88**

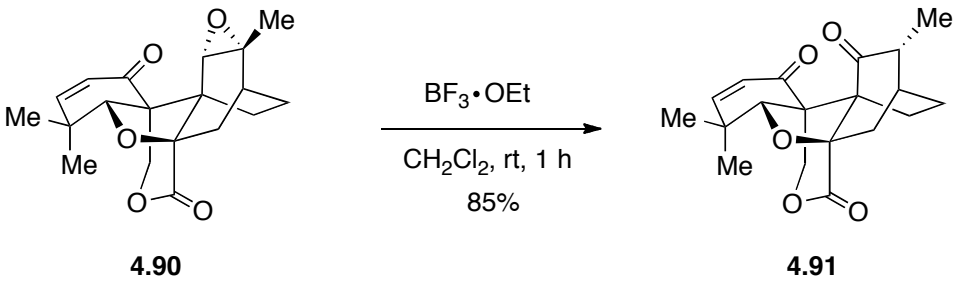
Scheme 4-32 Saegusa oxidation of **4.86**

Following epoxidation of **4.88** using TFDO afforded a distereomer mixture **4.89** and **4.90**, which could be separated through silica gel chromatography.



Scheme 4-33 Epoxidation of **4.88**

Now the most important moment of Maoecrystal V project arrived. It was May 16th, 2012. Compound **4.89** was treated with BF_3 etherate for 1 h and subsequent crude ^1H NMR showed that a single product, 16-*epi*-Maoecrystal V, was obtained. Encouraged by this result, I treated **4.90** with BF_3 for 1 h. After purification, Maoecyrstal V was isolated as a single isomer in excellent yield. The spectrum matched the isolation data.

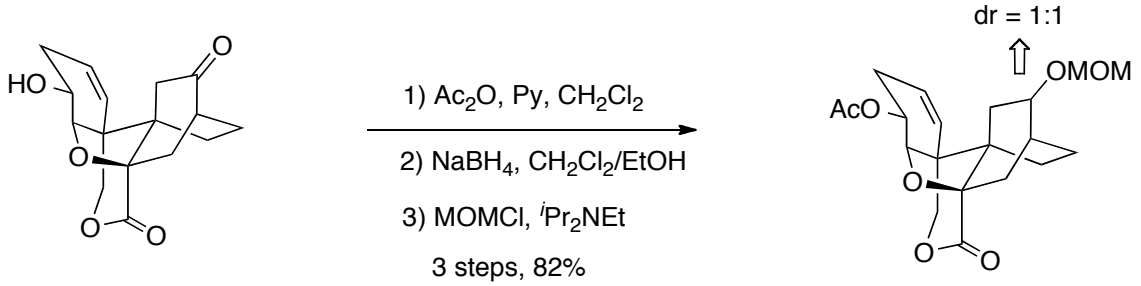


Scheme 4-34 Total synthesis of Maoecrystal V

4.3 Experimental

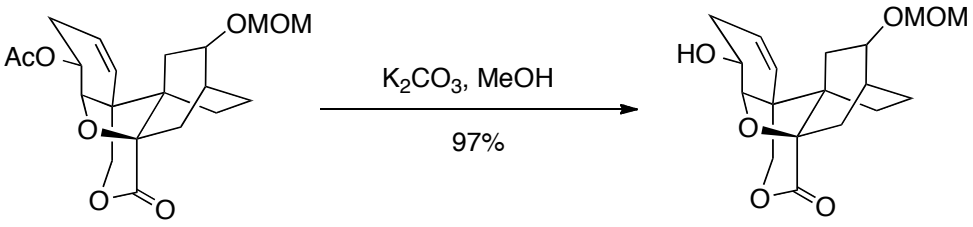
General information

Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. CH_2Cl_2 (DCM) was distilled over CaH_2 under argon atmosphere. THF was distilled over sodium/benzophenone ketyl under argon atmosphere. Anhyrous toluene, hexane, ether were purchased and use without further purification. All reagents were commercially available and used without further purification unless indicated otherwise. Thin layer chromatography (TLC) was performed on Silica Gel 60 F254 plates and was visualized with UV light and $KMnO_4$ stain. Preparative thin layer chromatography was performed with Merck silica gel 60-F254 coated 0.50 mm plates. Flash chromatography was performed with Sorbent Tech. silica gel 60. Yields reported are for isolated, spectroscopically pure compounds. NMR spectra were recorded on 300, 400 or 500 MHz instruments. The residual solvent protons (^1H) or the solvent carbons (^{13}C) were used as internal standards. ^1H NMR data are presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, coupling constant, integration). The following abbreviations are used in reporting NMR data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; qt, quartet of triplets; dd, doublet of doublets; dt, doublet of triplets; AB, AB quartet; m, multiplet. High-resolution mass spectra were recorded by the Columbia University Mass Spectrometry Core facility on a JEOL HX110 spectrometer.

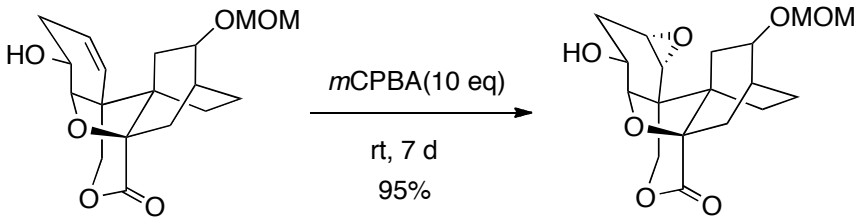


Compound 4.56: To a solution of ketone **4.1** (1 g, 3.4 mmol) in anhydrous CH_2Cl_2 was added acetic anhydride (1.38 mL, 13.8 mmol), pyridine (1.2 mL, 15 mmol) and DMAP (24.4 mg, 0.2 mmol). The reaction mixture was stirred for 2 h at room temperature and the solvent was removed under vacuum. The residue was then subjected to flash chromatography purification. The resultant acetate was dissolved in a mixture solvent of CH_2Cl_2/EtOH (2:1). To this solution at -78 ^oC was added $NaBH_4$ and the reaction was slowly warmed up to -20 ^oC in 3 h. The reaction was then quenched with acetone and water, extracted with ethyl acetate, and dried over $MgSO_4$. The drying agent was filtered and the solution was concentrated under vacuum. The residue was purified using flash chromatography. The resultant pure secondary alcohol was dissolved in anhydrous CH_2Cl_2 and MOMCl and $^iPr_2NEt$ was injected. The reaction was stirred at room temperature for 24 h before quenched with water. The solvent was removed under vacuum and the residue was directly purified via flash chromatography to give a colorless oil. (1.05 g, 82% yield, 1:1 diastereoisomers). ^1H NMR ($CDCl_3$, 400 MHz): δ 5.87 (ddd, J = 9.9, 6.6, 2.0 Hz, 1H), 5.38 (dd, J = 9.9, 3.2 Hz, 1H), 5.10 (td, J = 10.1, 5.8 Hz, 1H), 4.62 (s, 2H), 4.34 (d, J = 10.7 Hz, 1H), 4.24 (d, J = 9.7 Hz, 1H), 3.89 (d, J = 10.7 Hz, 2H), 3.35 (s, 3H), 2.80 (dd, J = 14.7, 5.0 Hz, 1H), 2.62 (dt, J = 16.8, 6.2 Hz, 1H), 2.09 (s,

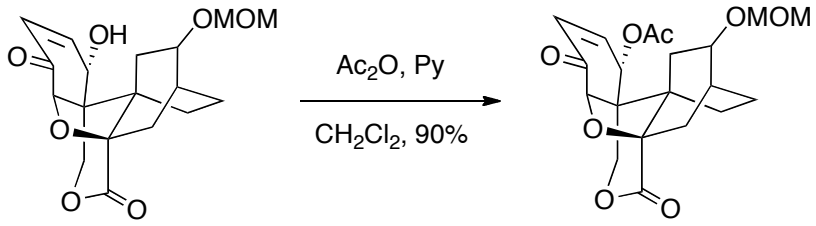
3H), 2.05-1.90 (m, 4H), 1.77-1.55 (m, 3H), 1.40 (dt, J = 14.8, 1.9 Hz, 1H), 1.36-1.24 (m, 1H), 1.23-1.18 (m, 1H).; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.7, 169.9, 129.1, 122.3, 94.8, 84.1, 76.0, 72.9, 71.9, 55.5, 49.8, 42.6, 33.7, 29.8, 28.6, 28.5, 21.2, 20.9, 17.9; IR (neat): cm^{-1} 2942, 1745, 1370, 1038; HRMS (FAB, *m/z*) calcd for $C_{20}H_{27}O_7$ $[M+H]^+$ 379.1757, found 379.1758.



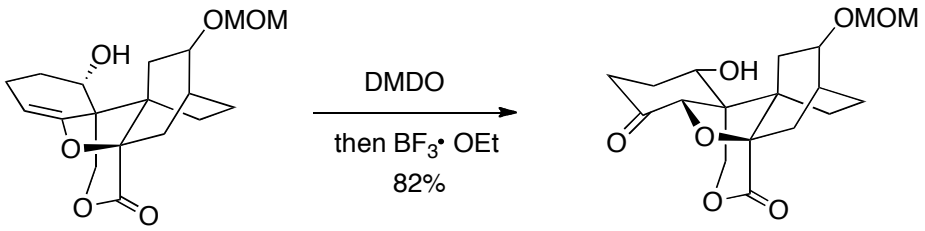
Compound **4.49**: To a solution of compound **4.56** (1 g, 2.6 mmol) in 5 mL of MeOH was added 20 mg of K_2CO_3. The reaction mixture was quenched with water 30 min later and extracted with ethyl acetate. The solvent was removed under vacuum and the residue was purified directly using flash chromatography to afford alcohol **4.49** (845 mg, 97% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.91 (ddd, J = 9.9, 6.6, 2.0 Hz, 1H), 5.32 (dd, J = 9.9, 3.1 Hz, 1H), 4.63 (s, 2H), 4.29 (d, J = 10.7 Hz, 1H), 4.17-3.99 (m, 2H), 3.89 (d, J = 10.7 Hz, 1H), 3.74 (ddd, J = 9.6, 5.7, 2.3 Hz, 1H), 3.36 (s, 3H), 2.67-2.57 (m, 1H), 2.53-2.38 (m, 1H), 2.17-1.91 (m, 3H), 1.77-1.42 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.1, 130.3, 121.8, 94.9, 88.2, 84.3, 77.2, 76.3, 73.3, 69.5, 55.4, 49.3, 42.5, 33.4, 30.7, 30.0, 25.3, 20.9, 20.7; IR (neat): cm^{-1} 3500, 2970, 1750, 1030; HRMS (FAB, *m/z*) calcd for $C_{18}H_{25}O_6$ $[M+H]^+$ 337.1651, found 337.1647.



Compound **4.57**: To a solution of compound **4.49** (700 mg, 2.1 mmol) in anhydrous CH_2Cl_2 was added *m*-CPBA (4.8 g, 21 mmol). The reaction mixture was stirred at room temperature for about 7 days and nights. Then the solvent was removed under vacuum and the residue was purified via flash chromatography to give epoxide **4.57** (702 mg, 95% yield). ^{1}H NMR (CDCl3, 400 MHz) δ 4.71-4.58 (m, 1H), 4.51 (d, J = 11.1 Hz, 1H), 4.24 (d, J = 11.1 Hz, 1H), 4.14-3.99 (m, 1H), 3.85 (d, J = 8.8 Hz, 1H), 3.81-3.70 (m, 1H), 3.38 (s, 3H), 3.32 (ddd, J = 6.1, 3.7, 1.6 Hz, 1H), 2.95 (d, J = 3.7 Hz, 1H), 2.64 (ddd, J = 14.3, 4.4, 1.6 Hz, 1H), 2.46 (dt, J = 15.2, 6.2 Hz, 1H), 2.33 (d, J = 26.1 Hz, 1H), 2.09-1.85 (m, 3H), 1.79-1.62 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.7, 95.1, 87.6, 84.2, 74.6, 73.2, 69.3, 55.5, 51.1, 51.0, 45.3, 42.5, 32.3, 30.5, 29.8, 25.1, 20.9, 20.8; HRMS (FAB, *m/z*) calcd for $C_{18}H_{25}O_7$ $[M+H]^+$ 353.1600, found 353.1610.

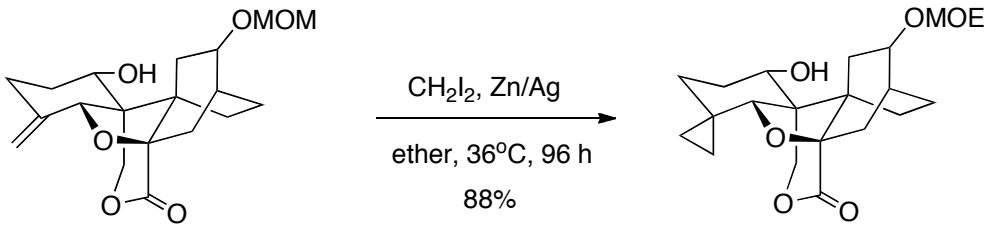


Compound **4.59**: To a solution of compound **4.58** (590 mg, 1.7 mmol) in anhydrous DCM was added acetic anhydride and pyridine. The reaction mixture was then stirred under argon at room temperature for additional 12 h. The solvent was removed under vacuum and the residue was purified via flash chromatography (600 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (dd, J = 10.3, 4.8 Hz, 1H), 6.32 (dd, J = 10.3, 1.0 Hz, 1H), 5.58 (dd, J = 4.8, 1.0 Hz, 1H), 4.60 (d, J = 7.0 Hz, 1H), 4.56-4.52 (m, 2H), 4.46 (d, J = 11.5 Hz, 1H), 4.25 (d, J = 11.5 Hz, 1H), 3.75-3.60 (m, 1H), 3.29 (s, 3H), 2.68 (ddd, J = 14.6, 4.7, 1.6 Hz, 1H), 2.13 (s, 3H), 2.08-1.93 (m, 2H), 1.77-1.62 (m, 1H), 1.21-1.05 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.95, 169.50, 168.86, 141.88, 131.28, 95.37, 82.68, 80.96, 73.37, 72.61, 64.02, 55.52, 46.85, 43.82, 33.70, 29.87, 24.75, 20.66, 20.56, 20.03.

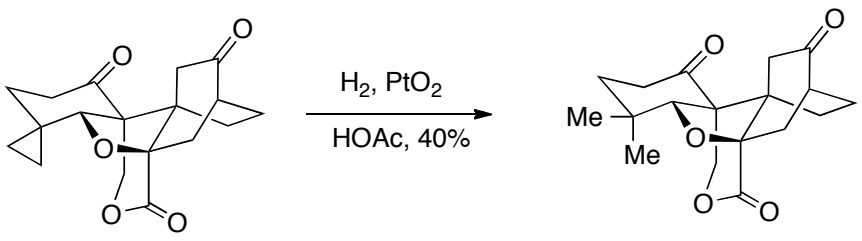


Compound **4.73**: At 0 ^{o}C, compound **4.75** (26 mg,100 μmol) dissolved in anhydrous DCM under argon. 50 mg of 4 A molecular sieve was added to the solution and the mixture was stirred for 1 hour. Then fresh-prepared dimethyldioxirane in acetone (120 μmol, 1.2 eq) was injected dropwise to the reaction mixture. 10 mins later, the solvent was blowed out using argon flow and 2 mL of anhydrous ether was injected to the residue. Boron trifluoride etherate (30 μL, 3 eq) was added to the reaction mixture slowly. 15 min later the reaction was quenched with saturated $NaHCO_3$, extracted with

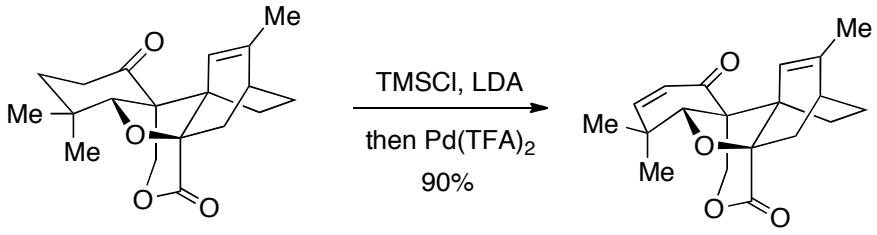
ethyl acetate, and dried over $MgSO_4$. After filtration of the drying agent, the solvent was removed under reduced pressure and the residue was purified using flash chromatography to afford a white solid (22 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (d, J = 2.2 Hz, 1H), 4.67 (s, 2H), 4.65-4.59 (m, 1H), 4.51 (ddd, J = 14.7, 7.1, 4.0 Hz, 1H), 4.20 (dd, J = 12.2, 2.6 Hz, 1H), 3.87 (ddt, J = 9.8, 5.9, 2.1 Hz, 1H), 3.38 (s, 3H), 2.70 (ddd, J = 14.2, 4.7, 1.6 Hz, 1H), 2.48-2.37 (m, 2H), 2.32-2.18 (m, 2H), 2.06-1.90 (m, 3H), 1.86-1.62 (m, 4H), 1.53 (ddd, J = 9.7, 5.2, 1.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.61, 169.18, 95.06, 85.67, 85.12, 72.64, 68.03, 66.68, 55.52, 52.55, 43.85, 35.49, 30.72, 30.24, 24.59, 22.19, 20.92; IR (neat): cm^{-1} 3480, 2946, 1740, 1039; HRMS (FAB, m/z) calcd for $C_{18}H_{25}O_7$ $[M+H]^+$ 353.1600, found 353.1588.



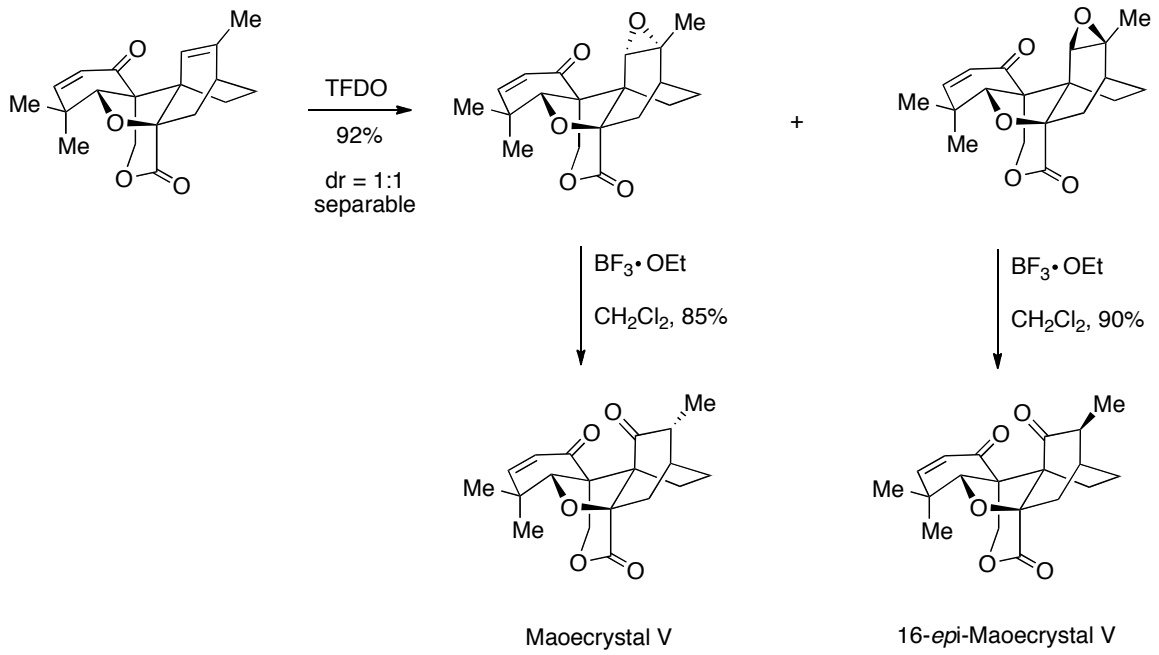
Compound **4.78**: To a solution of compound **4.77** (40 mg, 0.11 mmol) in anhydrous ether was added Zn/Ag (300 mg, 4.6 mmol) couple. Then a solution of CH_2I_2 (200 μL, 4.2 mmol) in ether was injected in 1 h via syringe pump. Then the reaction mixture was stirred at 42 ^{o}C for 96 h. Then the reaction mixture was cooled down to rt and quenched with NaHCO3 solution. The mixture was extracted with ethyl acetate and dried over MgSO4. After filtration, the liquid mixture was concentrated under vacuum and the residue was purified via flash chromatography to give cyclopropane **4.78** as an oil (36 mg, 88%).



Compound **4.84**: To a solution of compound **4.83** (10 mg, 0.027 mmol) in acetic acid was added PtO_2. The reaction mixture was first degassed with H_2 for about 30 min. Then the reaction was stirred at 40 ^oC for about 40 mins, filtered, and concentrated. The residue was purified via flash chromatography (4.1 mg, 40%). ^1H NMR (CDCl3, 400 MHz) δ 4.90 (d, J = 12.2 Hz, 1H), 4.30-4.25 (m, 2H), 3.14 (dd, J = 15.0, 4.5 Hz, 1H), 2.63-2.53 (m, 1H), 2.50-2.34 (m, 4H), 2.06-1.91 (m, 4H), 1.86-1.69 (m, 2H), 1.28 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 155.8, 94.9, 94.8, 83.3, 72. 7, 72.2, 68. 3, 55.4, 47.7, 42.8, 30. 5, 30.0, 27.5, 24. 2, 21.5, 21. 5, 21.3; HRMS (FAB, *m/z*) calcd for $C_{18}H_{23}O_5$ $[M+H]^+$ 319.1545, found 319.1559.



Compound **4.88**: To a fresh prepared LDA solution in THF was added a solution of compound **4.86** (8 mg, 0.025 mmol) in THF at -78 ^{o}C. 1 h later, TMSCl was injected via syringe and the reaction mixture was stirred for additional 1 h. Then the reaction mixture was quenched with $NaHCO_3$ solution. The reaction mixture was then extracted with ether and dried over $MgSO_4$. After filtration of the drying agent, the liquid mixture was concentrated and the residue dissolved in anhydrous CH_3CN. $Pd(TFA)_2$ was added and the reaction mixture was then heated to 70 ^{o}C and stirred at this temperature for about 5 h. The solvent was removed via rotovap and the residue was purified via direct flash chromatography to afford enone **4.88** (7.2 mg, 90%). ^{1}H NMR (400 MHz, CDCl3) δ 6.70 (d, J = 10.1 Hz, 1H), 5.92 (d, J = 10.1 Hz, 1H), 5.48 (d, J = 2.0 Hz, 1H), 4.65 (d, J = 11.8 Hz, 1H), 4.29 (d, J = 1.5 Hz, 1H), 4.26 (dd, J = 11.8, 1.6 Hz, 1H), 2.79 (dd, J = 13.8, 3.5 Hz, 1H), 2.50 (dt, J = 3.9, 2.0 Hz, 1H), 2.46-2.28 (m, 1H), 1.84 (dd, J = 4.5, 1.6 Hz, 3H), 1.82-1.75 (m, 2H), 1.50 (td, J = 6.2, 3.0 Hz, 1H), 1.34 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.81, 170.44, 157.72, 145.79, 126.84, 122.47, 86.69, 86.62, 68.59, 54.42, 47.76, 38.63, 35.65, 35.21, 30.71, 23.14, 22.06, 19.83, 18.59; IR (neat): cm^{-1} 2918, 2850, 1755, 1691, 1265, 1154; HRMS (FAB, m/z) calcd for $C_{19}H_{22}O_4$ $[M+H]^+$ 314.1518, found 314.1518.



Maoecrystal V and 16-*epi*-maoecrystal V

To a solution of epoxide XX in CH_2Cl_2 at 0 ^oC was added molecular sieve. The reaction was stirred at this temperature for additional 1 h. Then BF_3 etherate was added. 20 mins later, the reaction temperature was warmed up to room temperature and additional BF_3 etherate was added and the reaction was stirred for further 1 h. Then it was quenched with $NaHCO_3$ and extracted with ethyl acetate. The liquid mixture was dried over $MgSO_4$, filtered, concentrated and the residue was purified using preparative TLC.

Maoecrystal V: 2 mg, 85% yield. ^1H NMR (500 MHz, CDCl3) δ 6.66 (d, J = 10.2 Hz, 1H), 5.95 (d, J = 10.2 Hz, 1H), 4.63 (d, J = 12.2 Hz, 1H), 4.43 (d, J = 1.6 Hz, 1H), 4.13 (dd, J = 12.1, 1.7 Hz, 1H), 3.19 (dd, J = 14.6, 4.7 Hz, 1H), 2.42-2.25 (m, 2H), 2.21-2.06

(m, 3H), 1.98 (dddd, *J* = 13.9, 11.5, 6.1, 3.1 Hz, 1H), 1.70 (dt, *J* = 14.6, 2.1 Hz, 1H), 1.67-1.61 (m, 1H), 1.30 (s, 3H), 1.25 (d, *J* = 7.5 Hz, 3H), 1.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.5, 194.8, 169.0, 156.7, 127.1, 84.9, 84.1, 69.2, 56.6, 51.9, 48.3, 38.3, 34.6, 32.7, 30.6, 18.6, 18.5, 18.0, 15.1; ^{13}C NMR (101 MHz, C5D5N) δ 211.8, 194.8, 169.6, 156.8, 127.3, 85.6, 84.7, 69.6, 57.0, 52.5, 48.4, 38.4, 34.9, 33.0, 30.5, 30.1, 18.8, 18.4, 18.3, 15.1;IR (neat): cm^{-1} 2920, 1754, 1719, 1688, 1264, 1155; HRMS (FAB, *m/z*) calcd for $C_{19}H_{22}O_5$ $[M+H]^+$ 330.1467, found 330.1472.

16-epi-Maoecrystal V: 2.8 mg, 90% yield. ^{1}H NMR (500 MHz, CDCl3) δ 6.66 (d, *J* = 10.1 Hz, 1H), 5.94 (d, *J* = 10.1 Hz, 1H), 4.64 (d, *J* = 12.2 Hz, 1H), 4.52 (d, *J* = 1.5 Hz, 1H), 4.13 (dd, *J* = 12.1, 1.7 Hz, 1H), 2.94 (ddd, *J* = 14.8, 4.6, 2.0 Hz, 1H), 2.47 (qt, *J* = 7.2, 2.1 Hz, 1H), 2.21 (ddd, *J* = 14.8, 10.8, 8.3 Hz, 1H), 2.13-2.03 (m, 2H), 1.93-1.73 (m, 3H), 1.30 (s, 3H), 1.24 (s, 3H), 1.21 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.4, 194.9, 169.0, 156.8, 126.9, 85.2, 85.0, 69.3, 55.3, 52.1, 46.0, 38.4, 33.2, 30.8, 27.7, 23.3, 18.5, 18.3, 12.6; IR (neat): cm^{-1} 2924, 1755, 1725, 1692, 1154; HRMS (FAB, *m/z*) calcd for $C_{19}H_{22}O_5$ $[M+H]^+$ 330.1467, found 330.1476.

4.4 Reference

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PROCNO                   1

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Time               15.05
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PULPROG             zg30
TD                 32768
SOLVENT            CDC13
NS                    32
DS                     0
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ             2.7263477 sec
RG                    32
DW                83.200 usec
DE                 6.50 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.50 usec
PL1                -4.00 dB
PL1W         26.94187927 W
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300107 MHz
WDW                   EM
SSB       0
LB                 0.20 Hz
GB        0
PC                 1.00
```

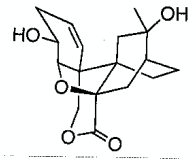

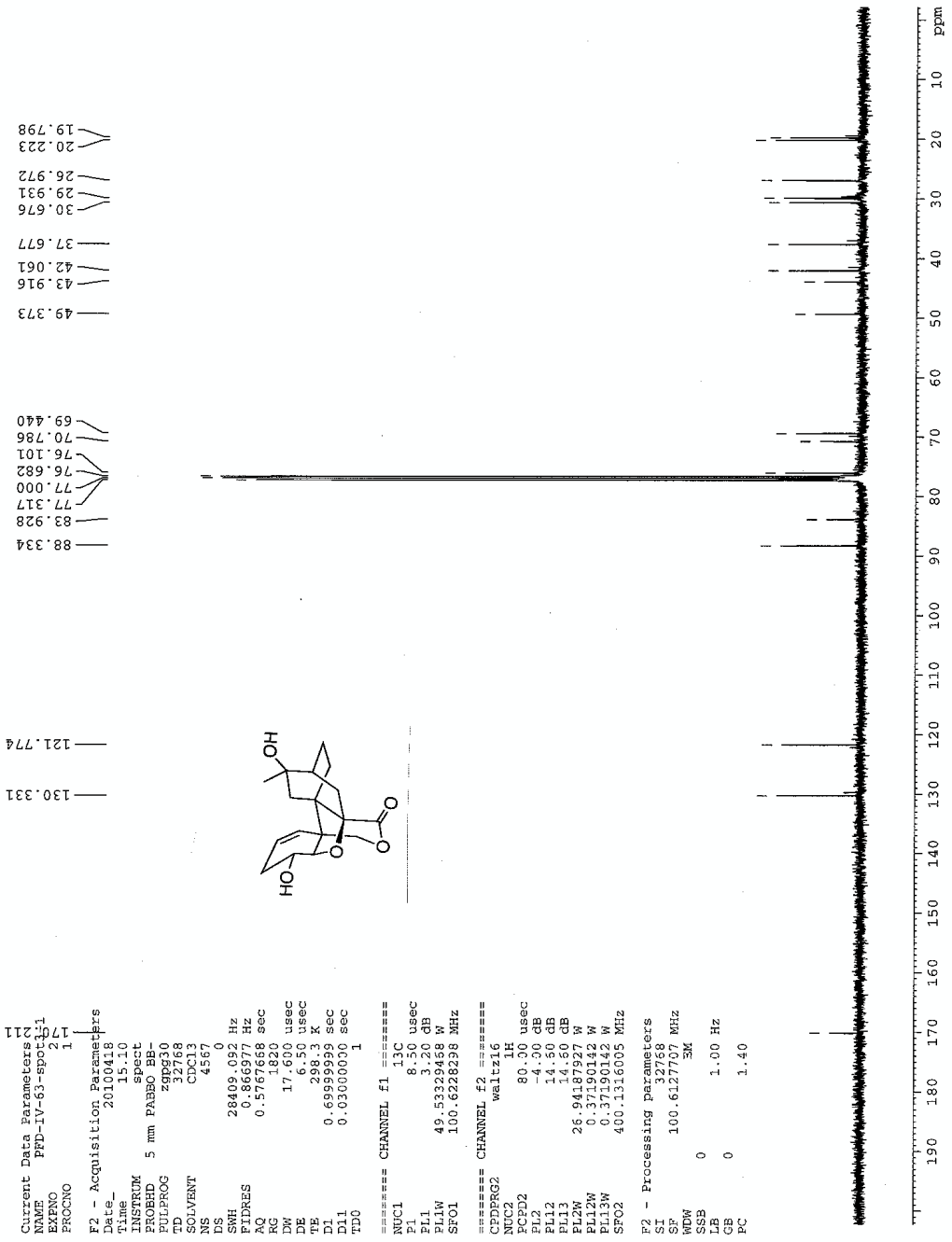
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PROCNO 1
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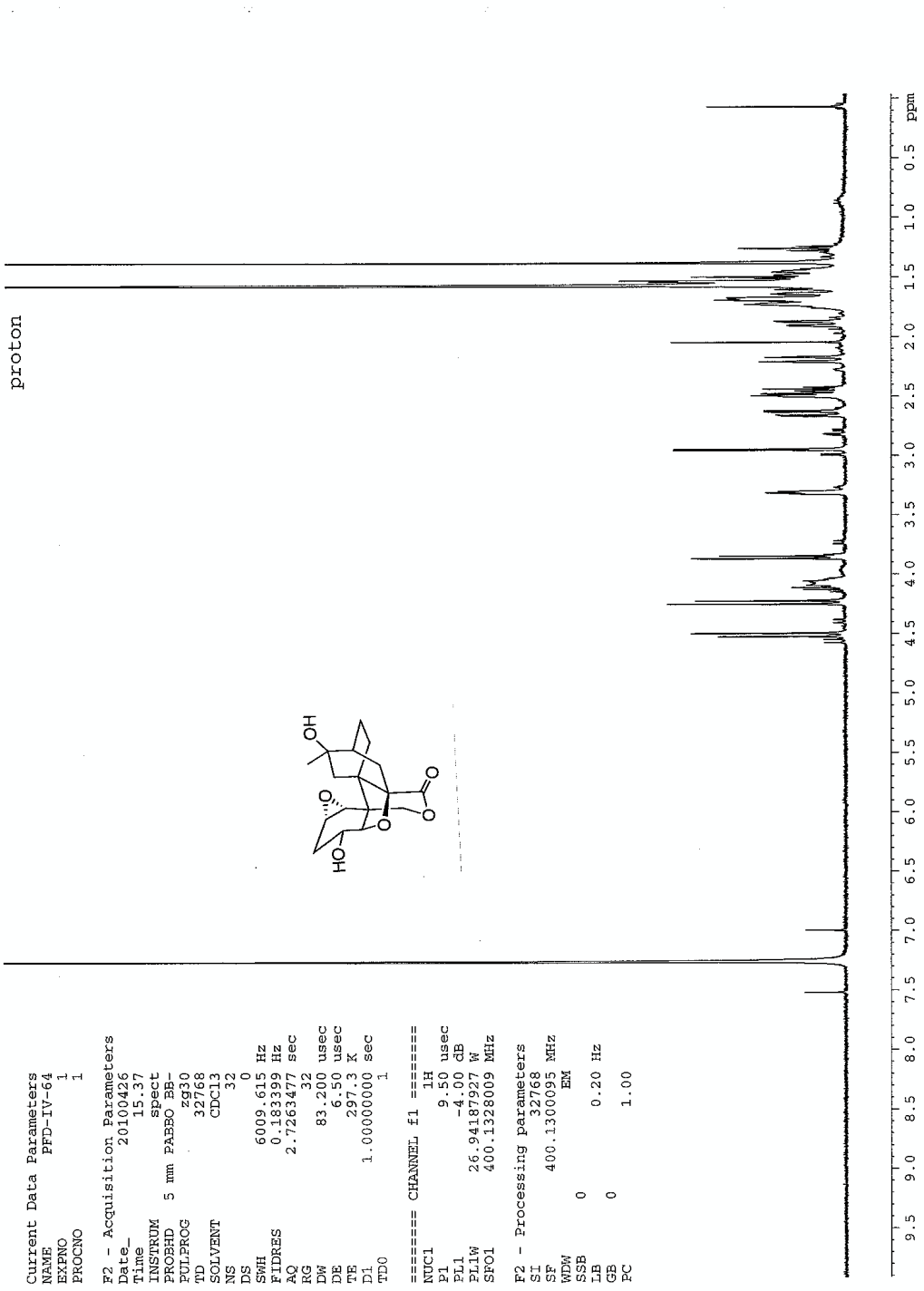
Time 15.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 4567
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 298.3 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127707 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OH
O
O
O
HO
130.331
121.774
88.334
83.928
77.317
77.000
76.682
76.101
70.786
69.440
49.373
43.916
42.061
37.677
30.676
29.931
26.972
20.223
19.798
ppm


proton
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PROCNO 1
F2 - Acquisition Parameters
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Time_ 15.37
INSTRUM spect
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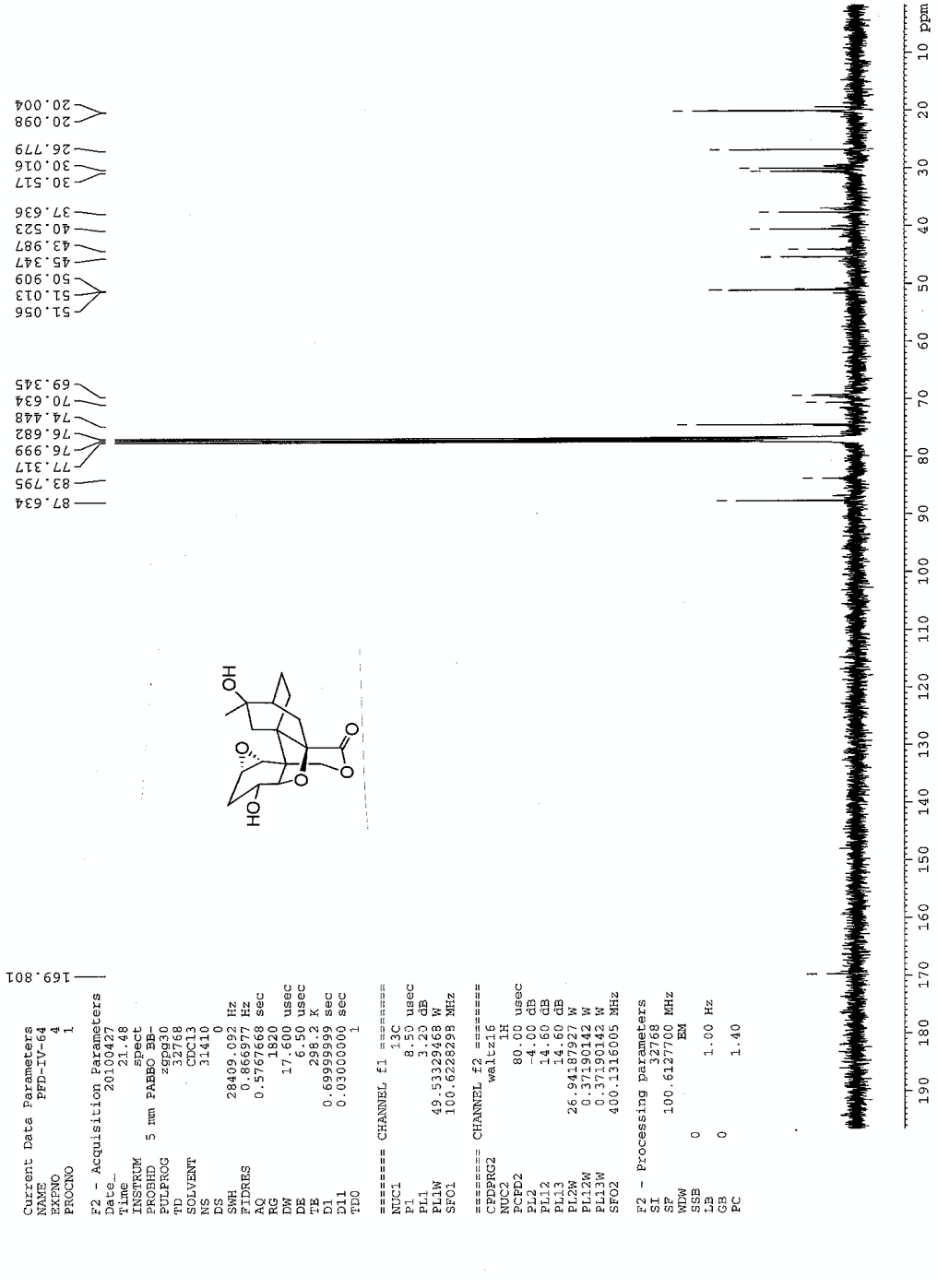
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 297.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
OH
O
O
O
HO
O
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 0.5 ppm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87.634
83.795
77.317
76.999
76.682
74.448
70.634
69.345
51.056
51.013
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45.347
43.987
40.523
37.636
30.517
30.016
26.779
20.098
20.004
OH
HO
O
O
O
O
Current Data Parameters
NAME PFD-IV-64
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100427
Time_ 21.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 31410
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 298.2 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.23 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

```
Current Data Parameters
NAME          PFD-IV-67
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20100426
Time              12.13
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                   32
DW               83.200 usec
DE                6.50 usec
TE               296.3 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                 9.50 usec
PL1               -4.00 dB
PL1W        26.94187927 W
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                32768
SF          400.1300096 MHz
WDW                  EM
SSB       0
LB                0.20 Hz
GB        0
PC                1.00
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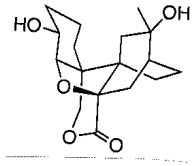

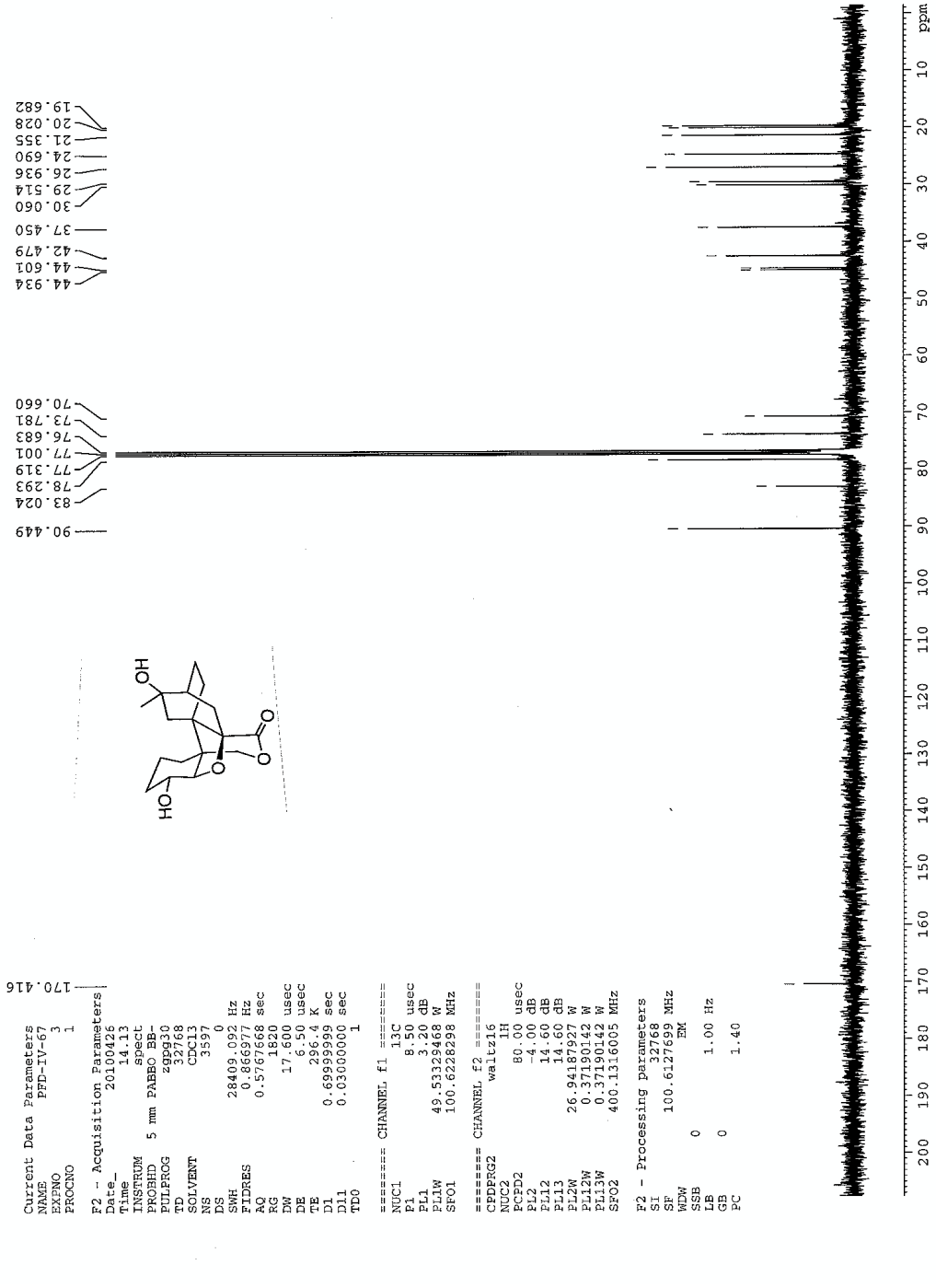
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78.293
77.319
77.001
76.683
73.781
70.660
44.934
44.601
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37.450
30.060
29.514
26.936
24.690
21.355
20.028
19.682
OH
HO
O
O
O
Current Data Parameters
NAME PFD-IV-67
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100426
Time_ 14.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 3597
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 296.4 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127699 MHz
WDW EM
SSB 0
LB 0 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

proton

Current Data Parameters
NAME PFD-IV-68
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100429
Time 11.12
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz

F2 - Processing parameters
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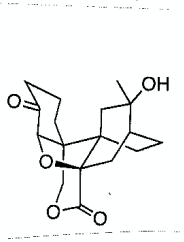
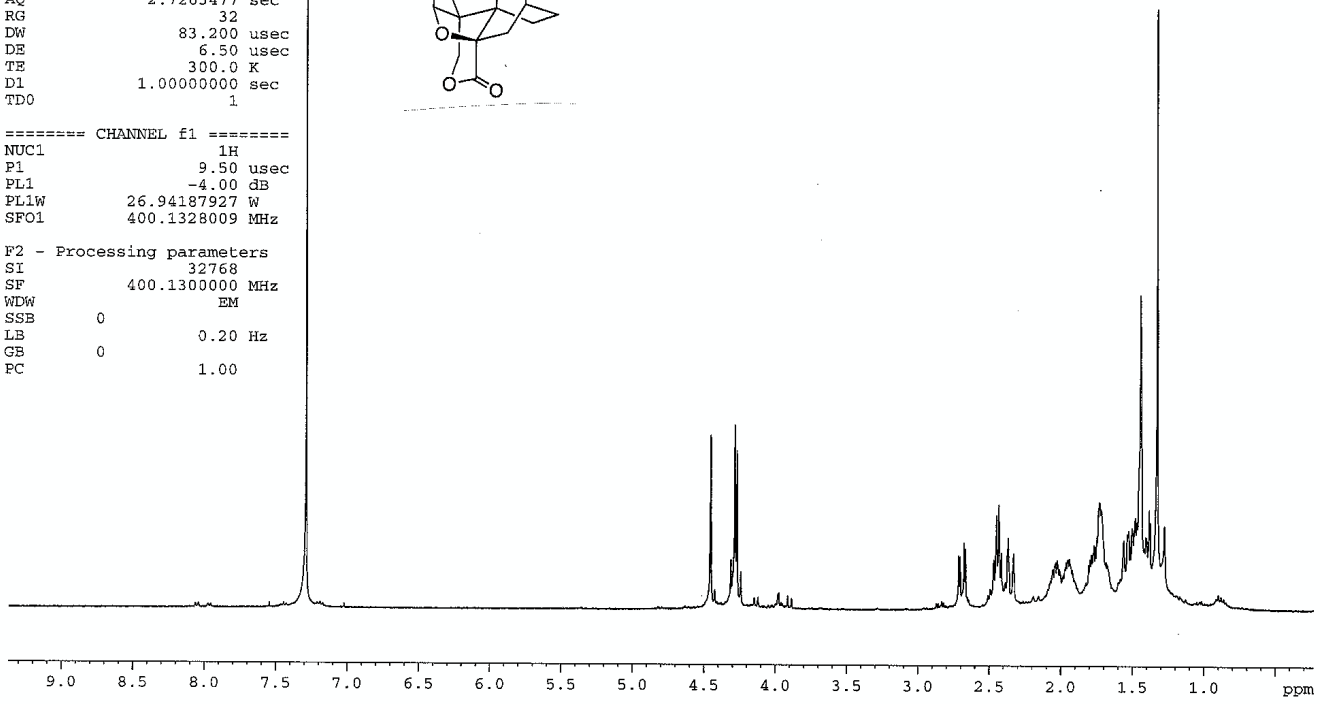
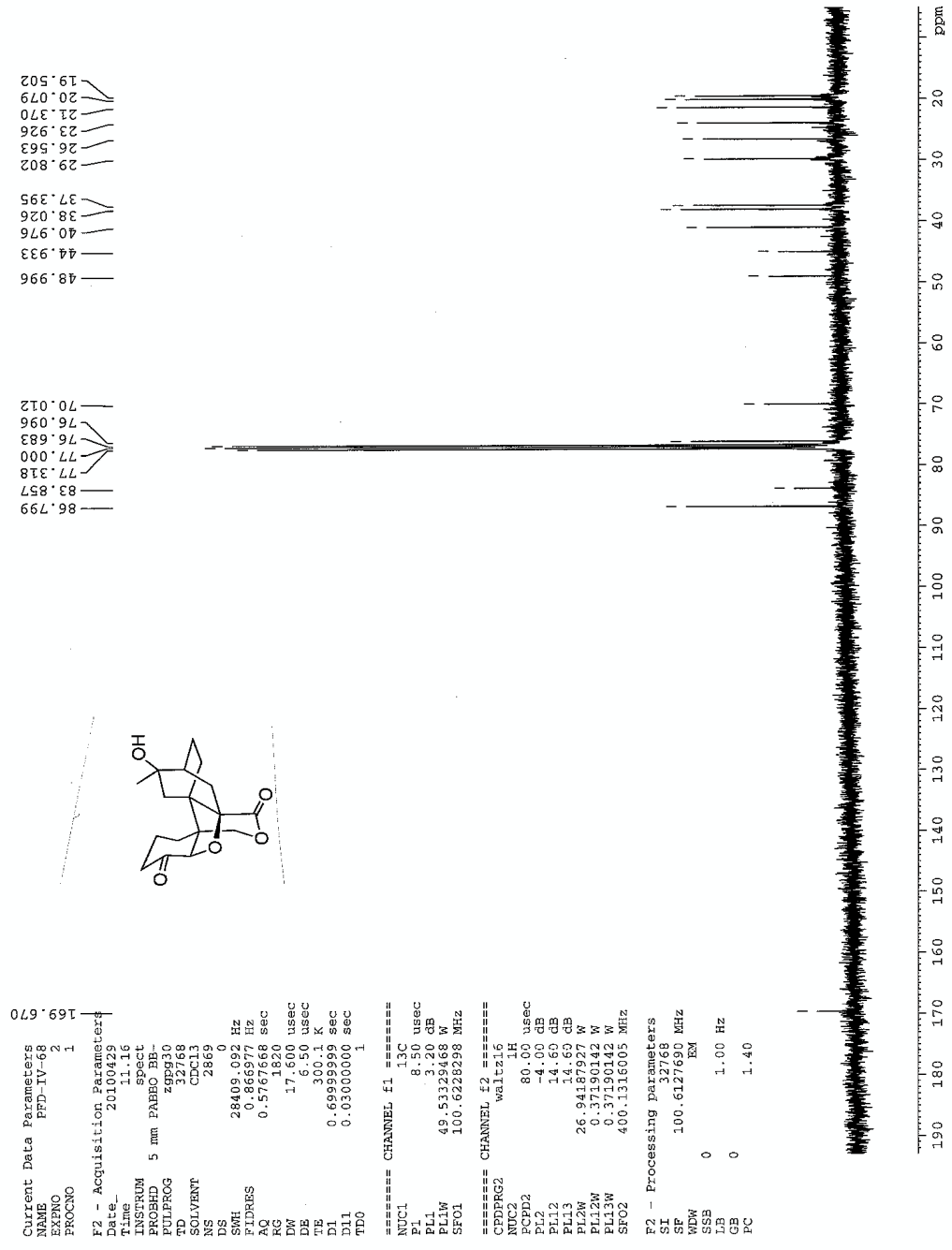
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00



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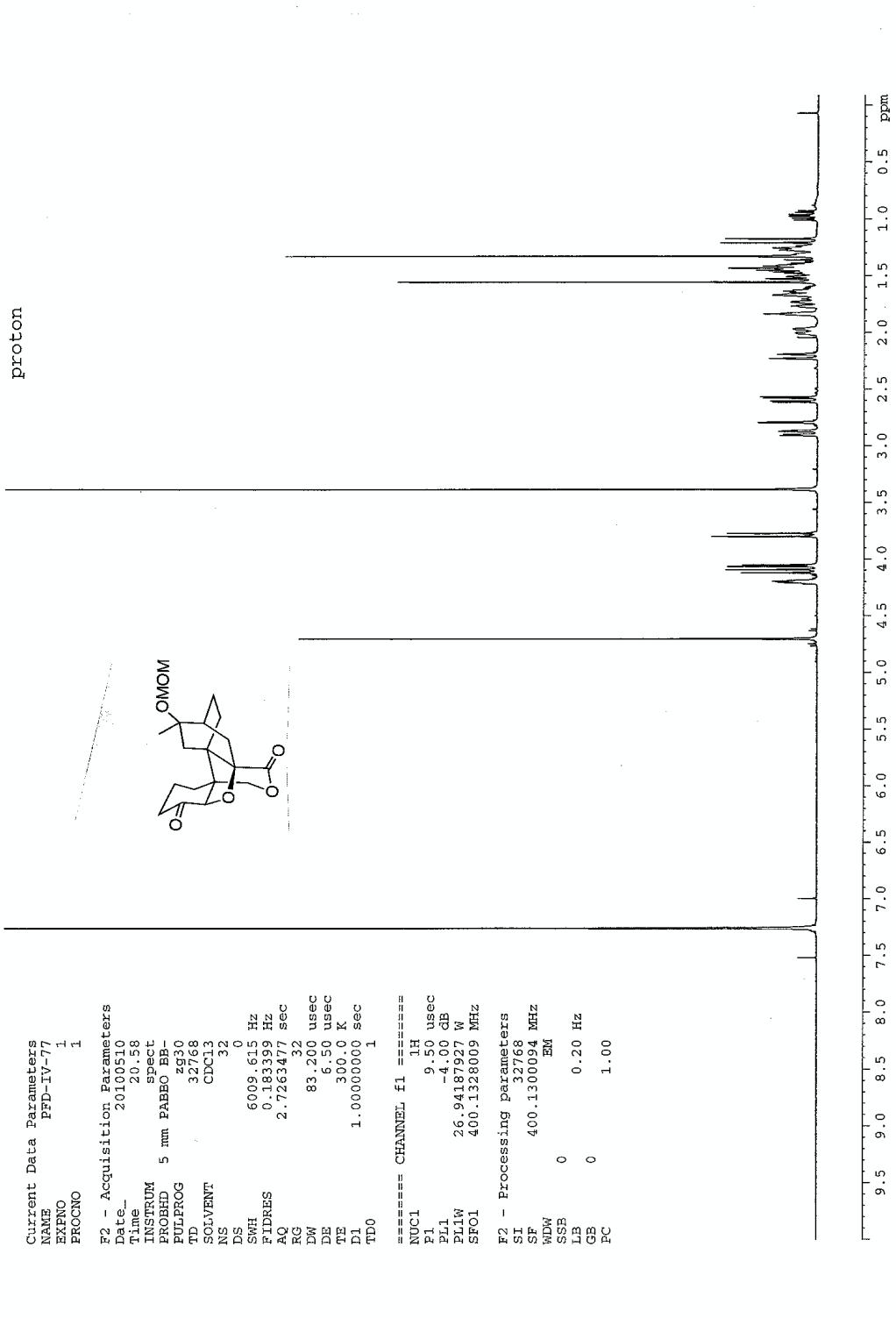
38.026
37.395
29.802
26.563
23.926
21.370
20.079
19.502
OH
O
O
O
O
Current Data Parameters
NAME PFD-IV-68
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100429
Time_ 11.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 2869
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 300.1 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm


proton
OMOM
O
O
O
O
Current Data Parameters
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EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
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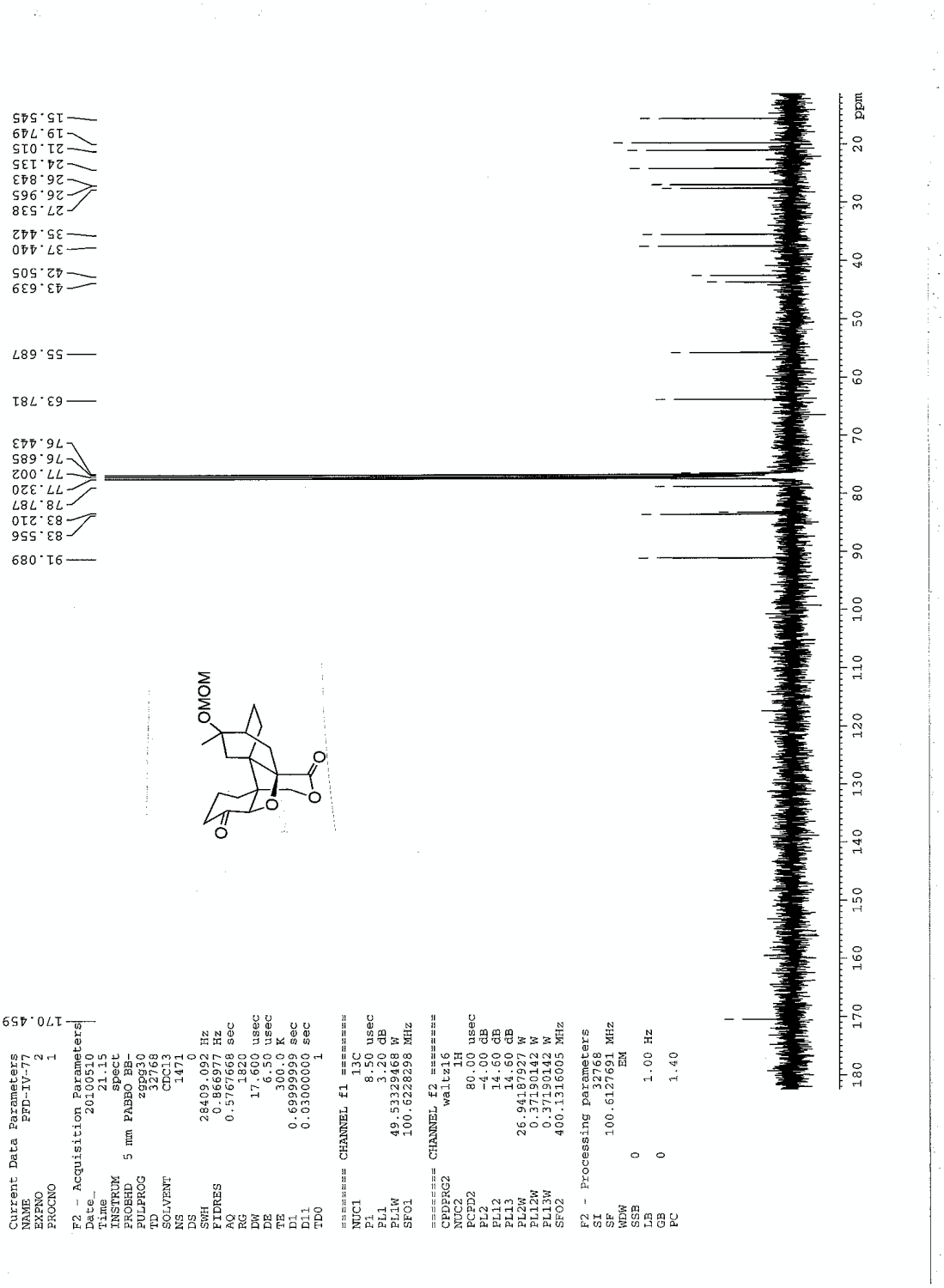
Time 20.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.72634777 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
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 0.5 ppm



Current Data Parameters
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EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
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Time_ 21.15
INSTRUM spect
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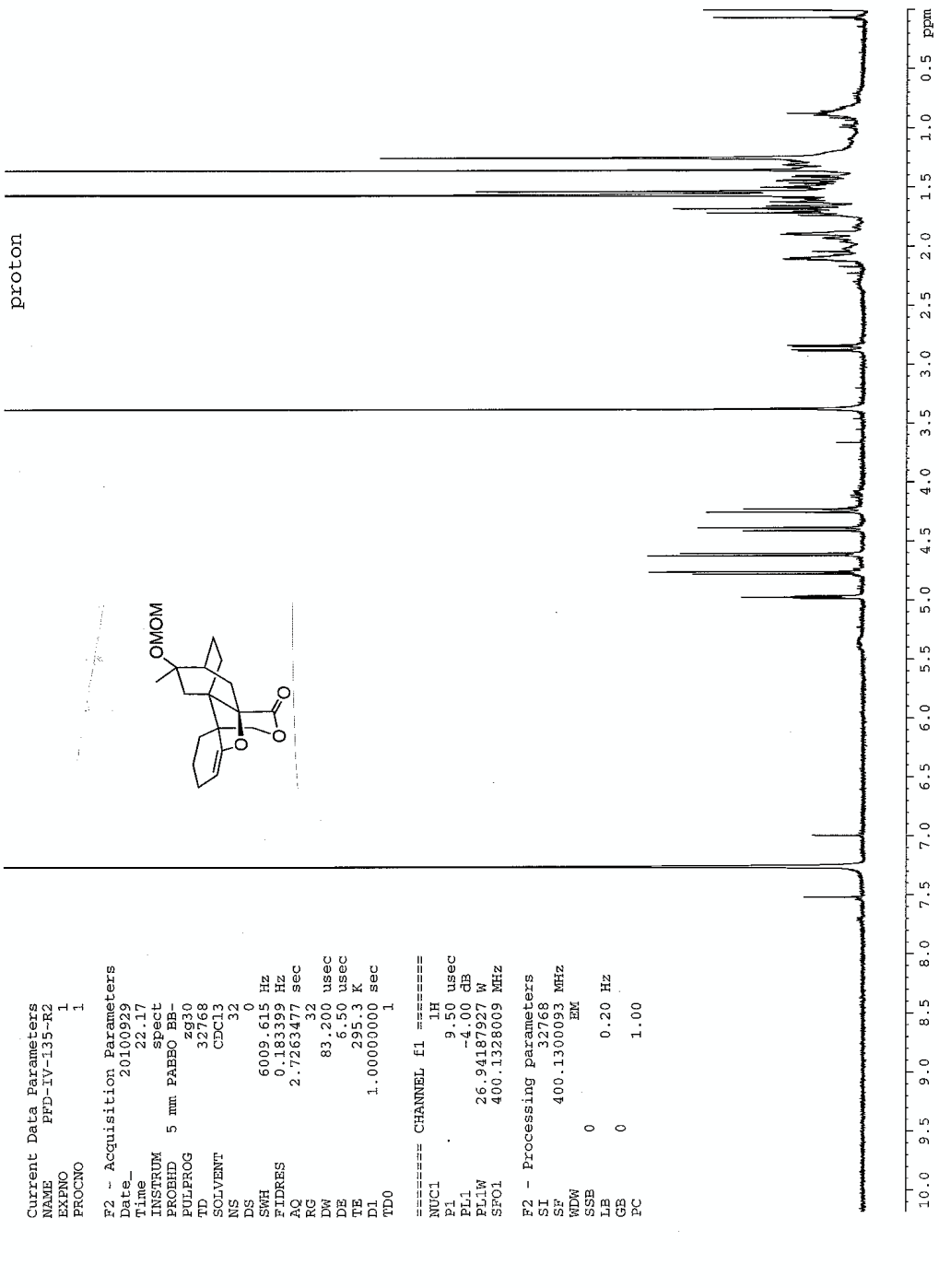
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1471
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 1820
DW 17.600 usec
DE 6.50 usec
TE 300.0 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127691 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40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PROCNO 1
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INSTRUM spect
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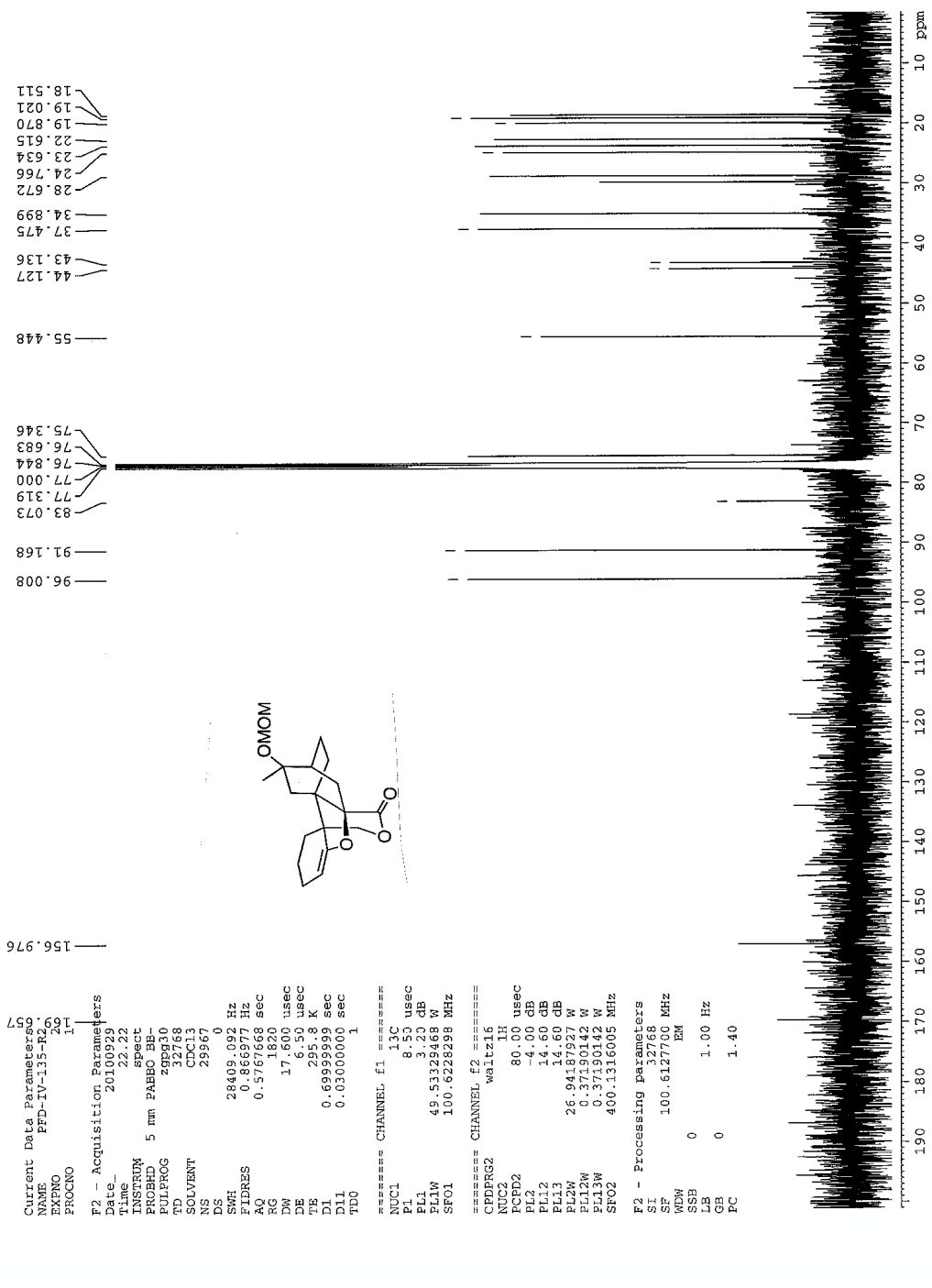
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 295.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300093 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
proton
OMOM
O
O
O
10.0 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 0.5 ppm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91.168
83.073
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77.000
76.844
76.683
75.346
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44.127
43.136
37.475
34.899
28.672
24.766
23.634
22.615
19.870
19.021
18.511
ppm

```
Current Data Parameters
NAME      PFD-IV-191-R1
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20120607
Time               3.43
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   24
DS                    0
SWH            6009.615 Hz
FIDRES         0.183399 Hz
AQ            2.7263477 sec
RG                   32
DW               83.200 usec
DE                6.50 usec
TE               300.0 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                 1H
P1                9.50 usec
PLW1        26.94187927 W
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                32768
SF          400.1300090 MHz
WDW                  EM
SSB       0
LB                0.20 Hz
GB        0
PC                1.00
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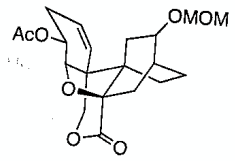

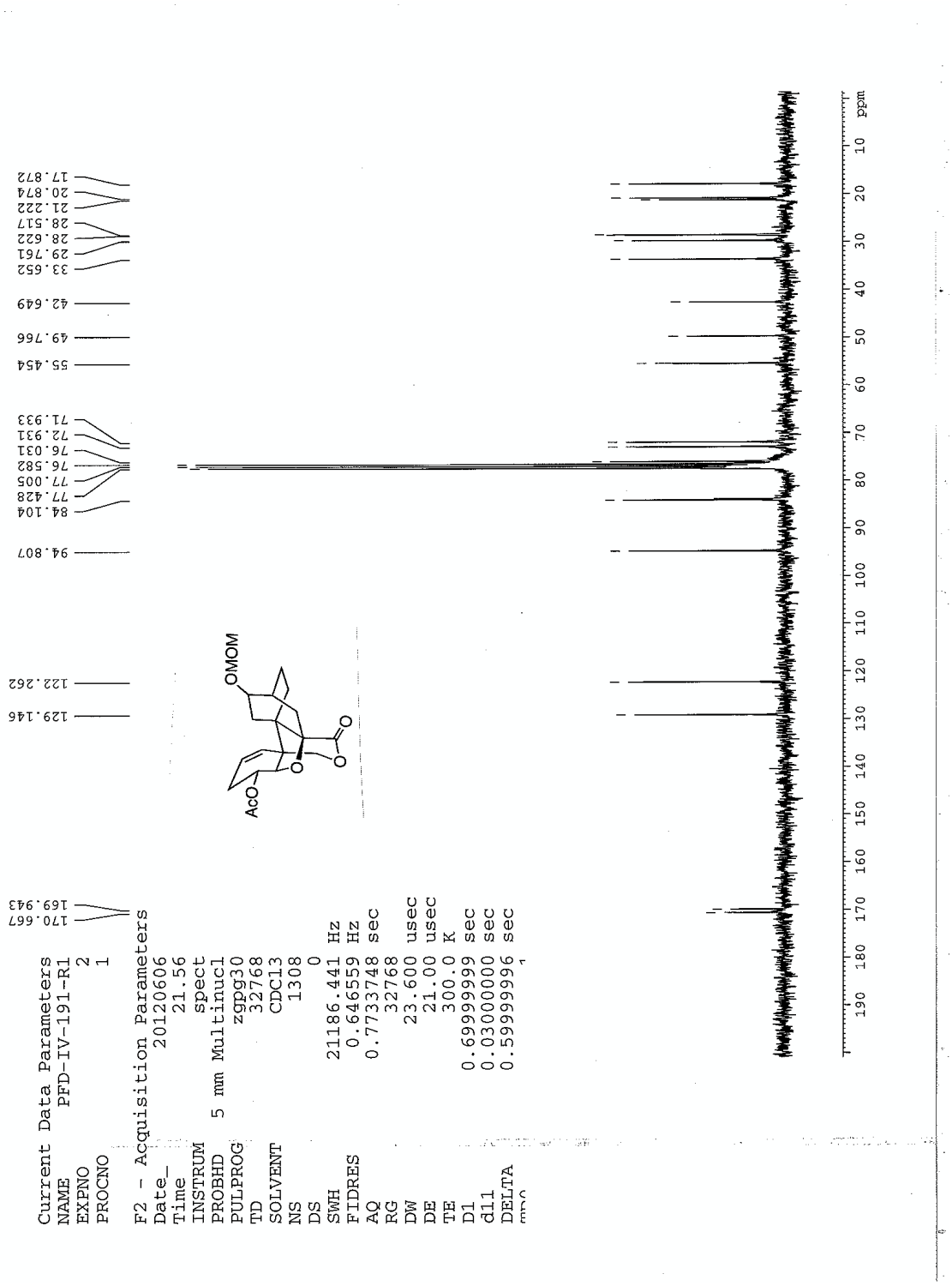
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PROCNO 1
F2 - Acquisition Parameters
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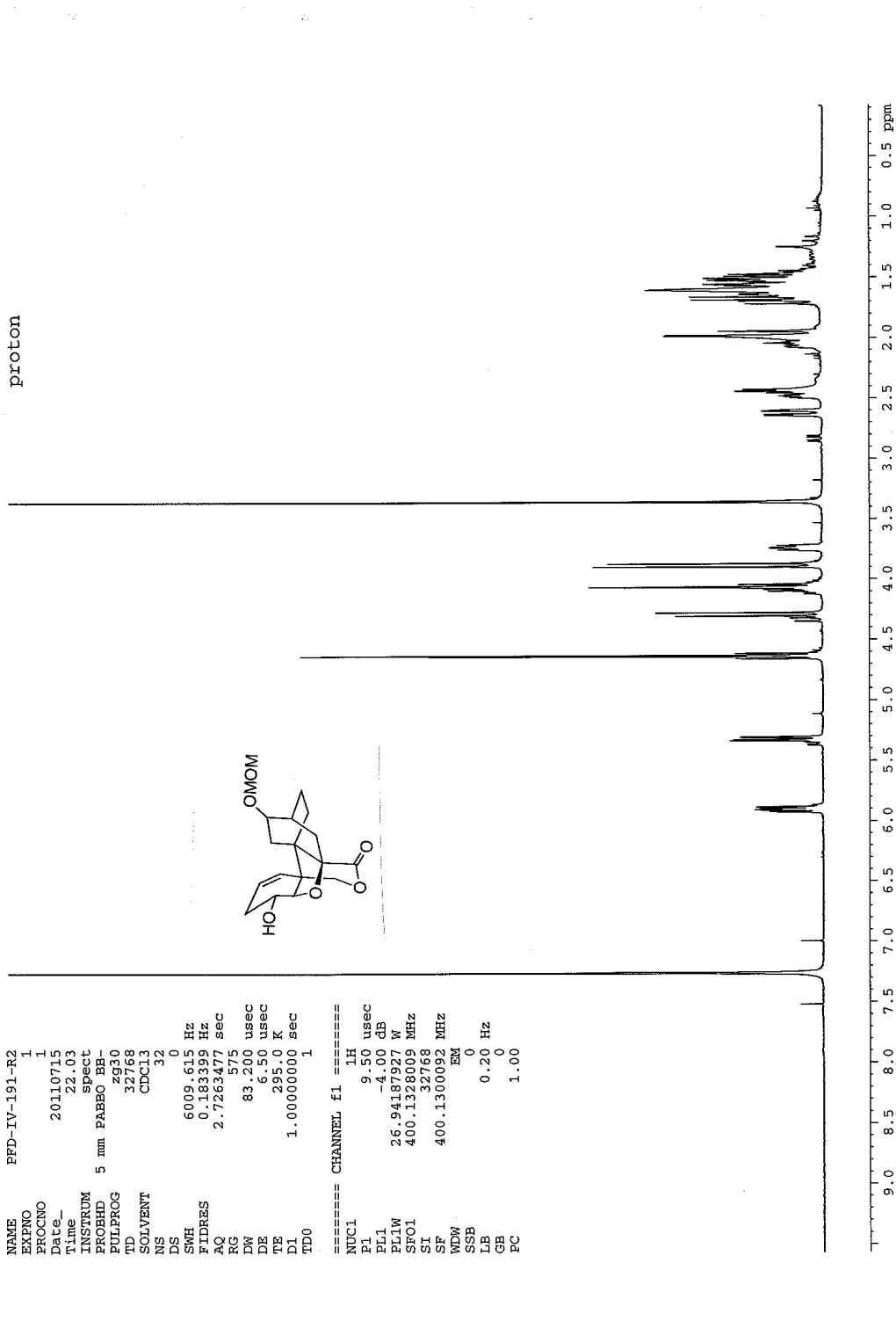
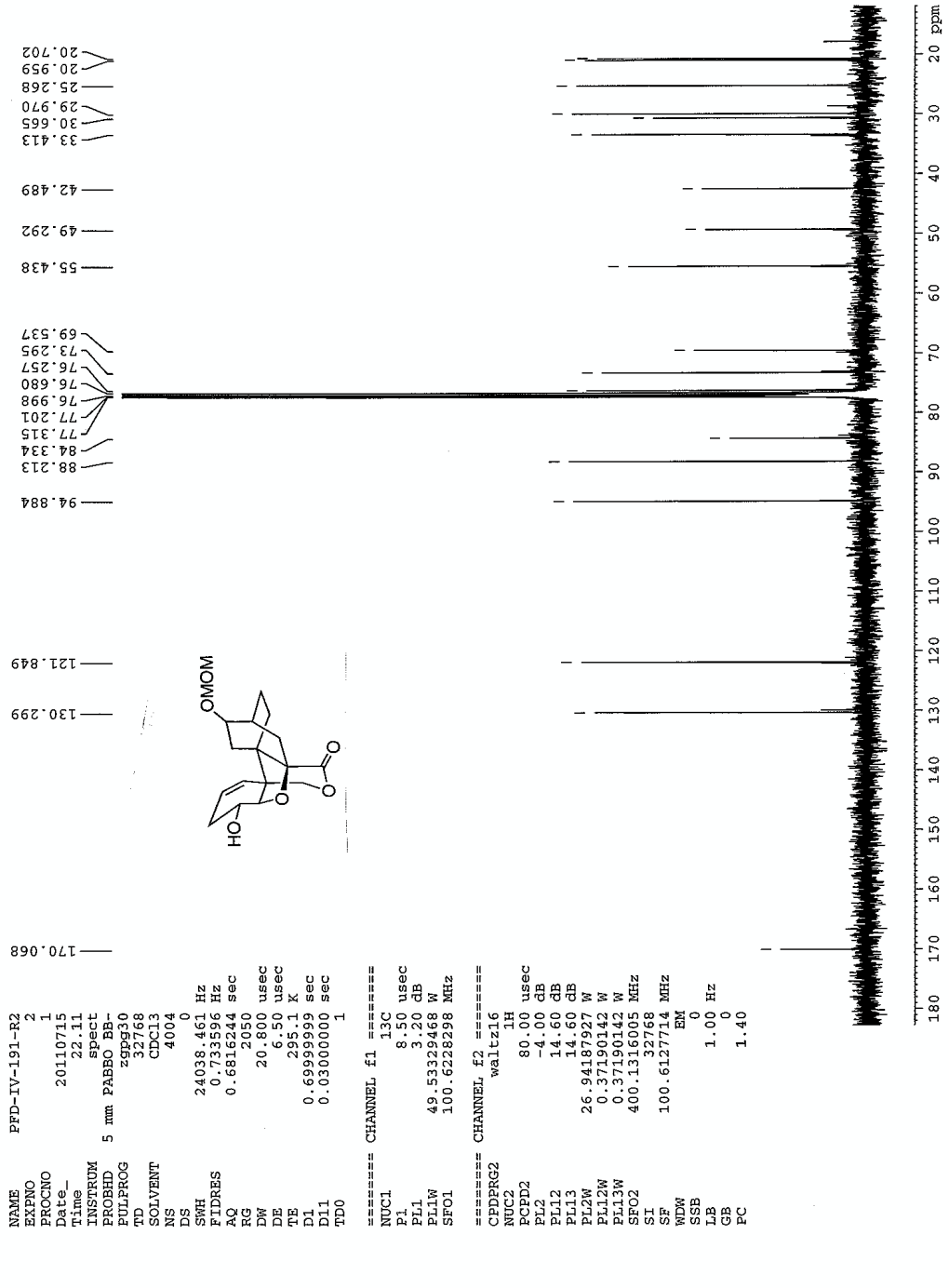
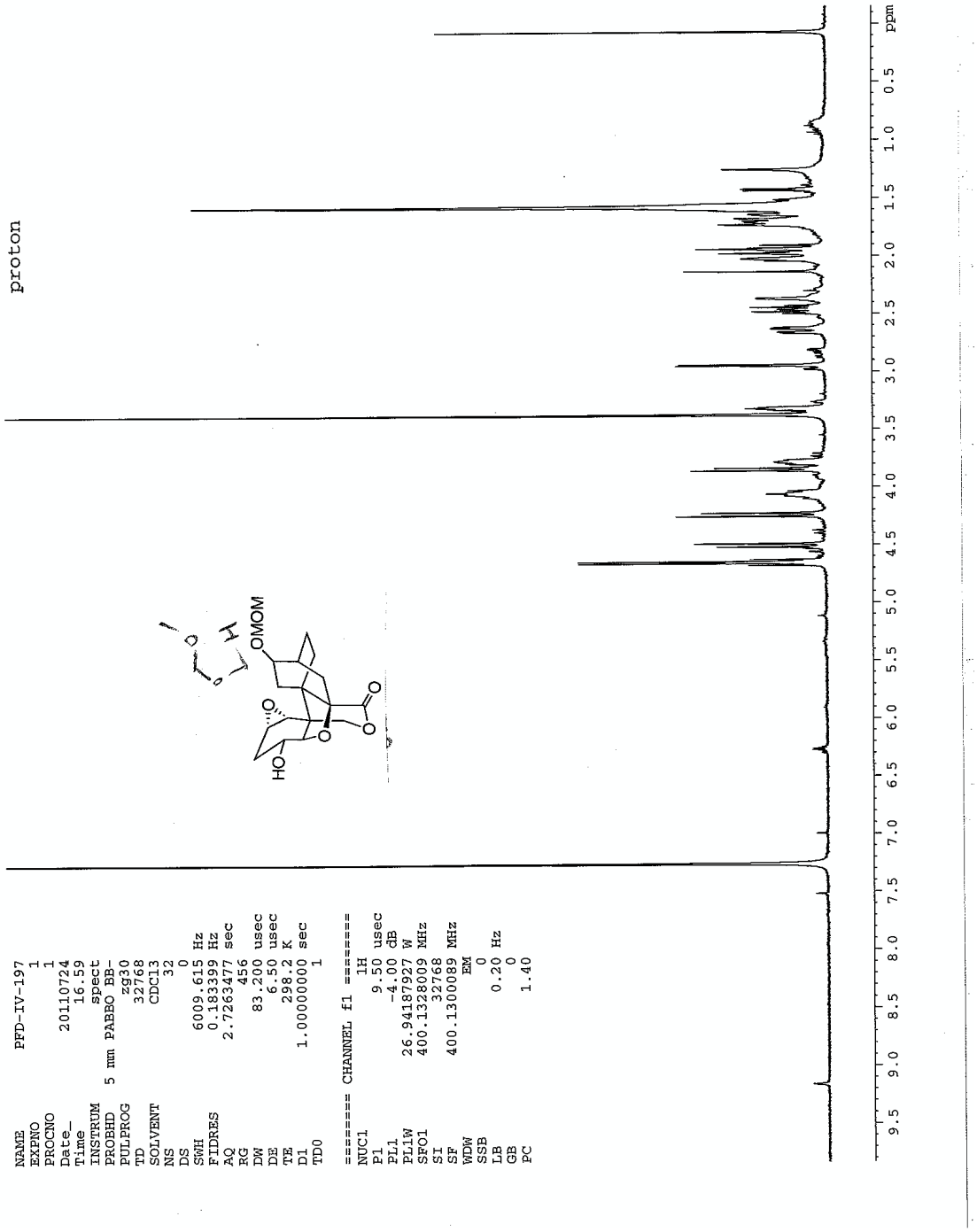
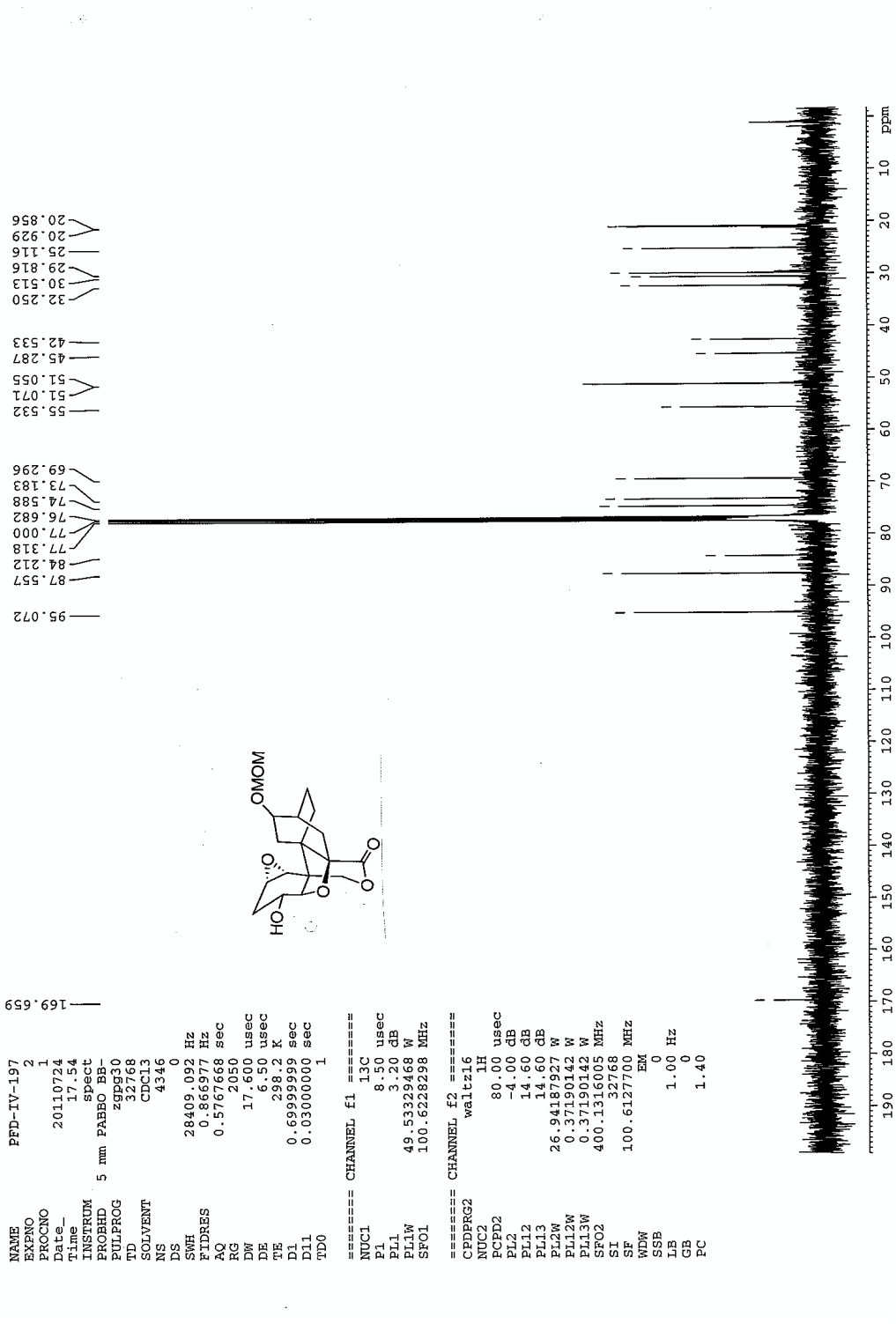
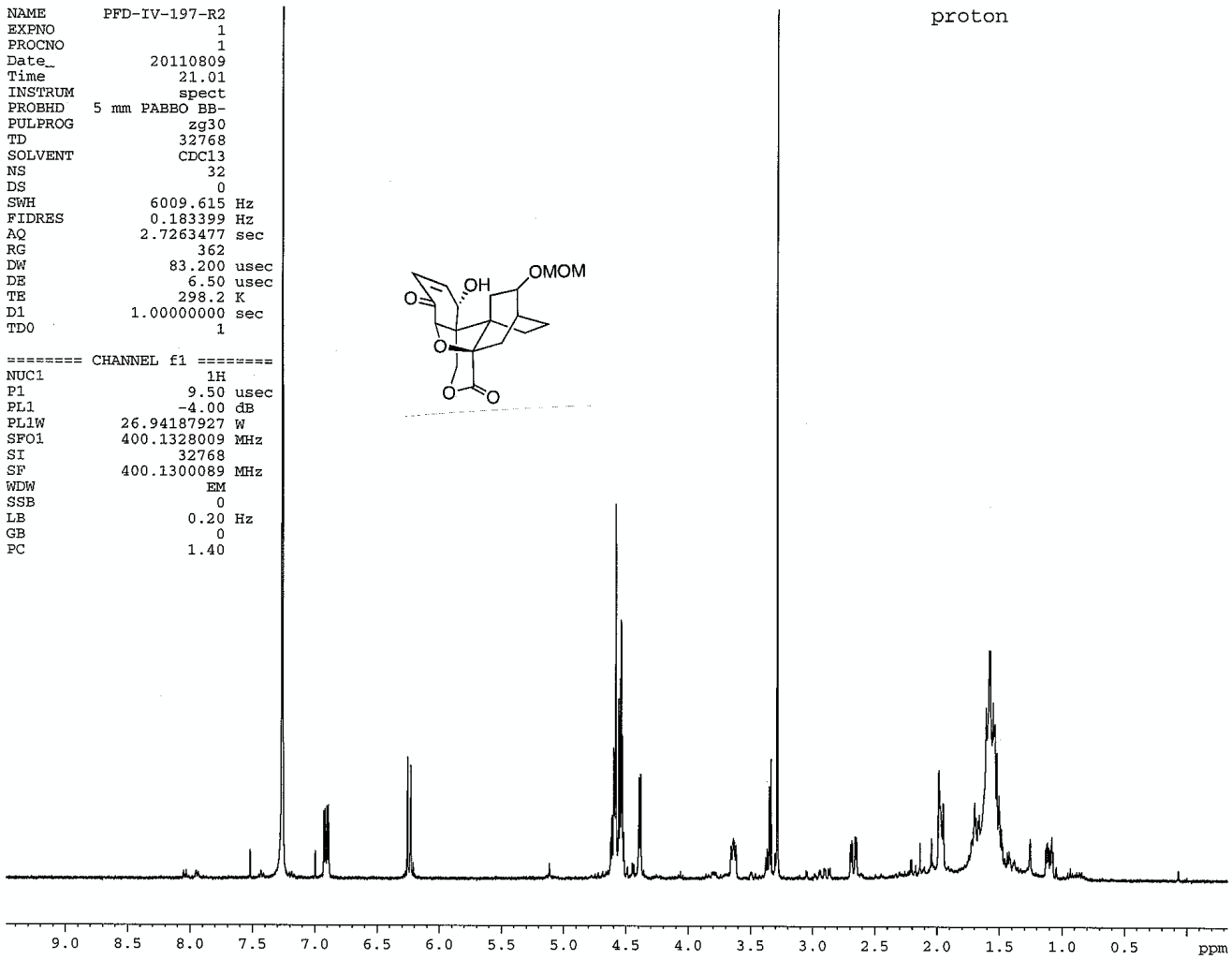
Time 21.56
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 32768
SOLVENT CDC13
NS 1308
DS 0
SWH 21186.441 Hz
FIDRES 0.646559 Hz
AQ 0.7733748 sec
RG 32768
DW 23.600 usec
DE 21.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
OMOM
AcO
O
O
O
170.667
169.943
129.146
122.262
94.807
84.104
77.428
77.005
76.582
76.031
72.931
71.933
55.454
49.766
42.649
33.652
29.761
28.622
28.517
21.222
20.874
17.872
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

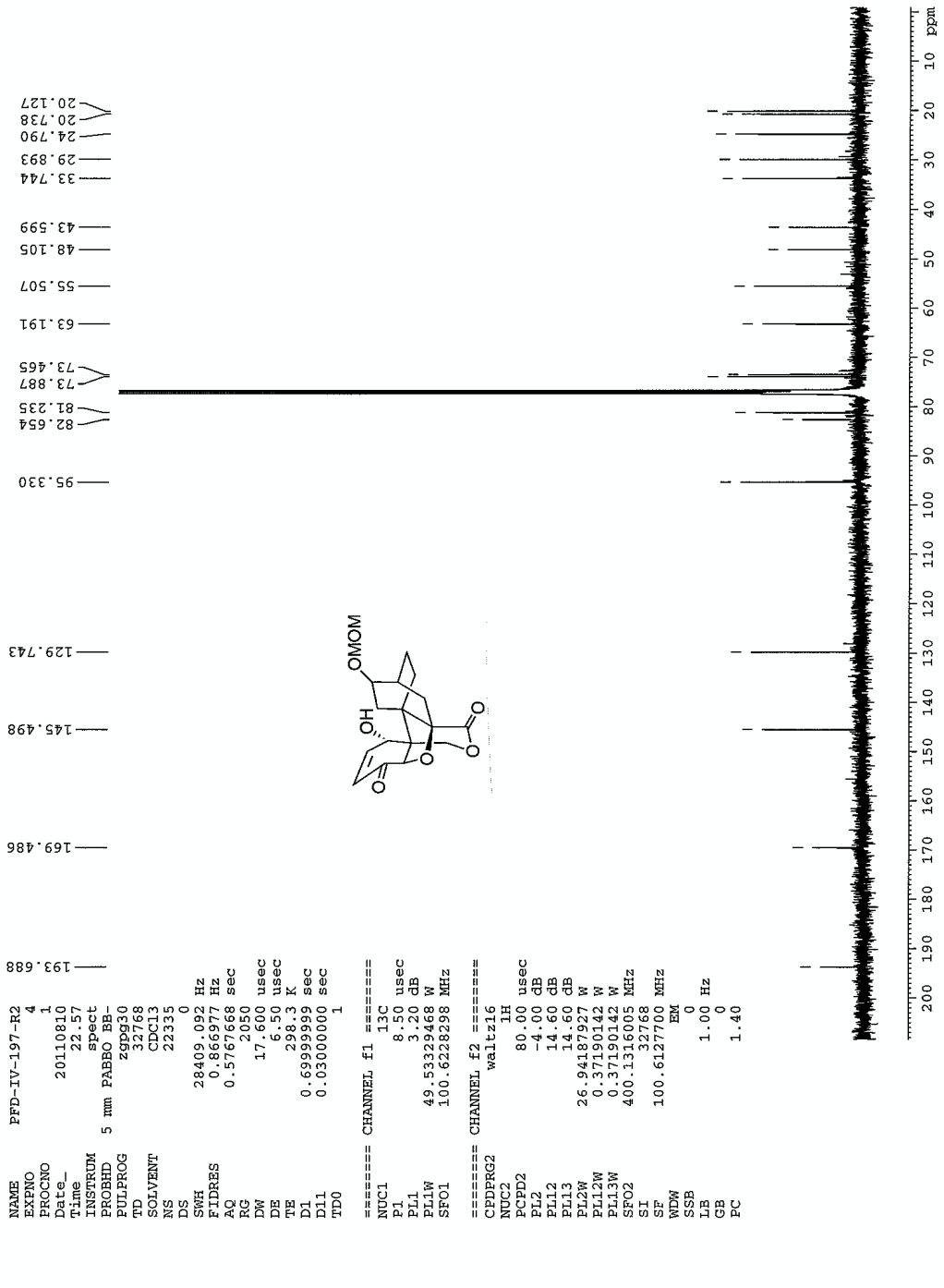

proton
NAME PFD-IV-191-R2
EXPNO 1
PROCNO 1
Date_ 20110715
Time_ 22.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 575
DW 83.200 usec
DE 6.50 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
SI 32768
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
OMOM
HO
O
O
O
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 0.5 ppm

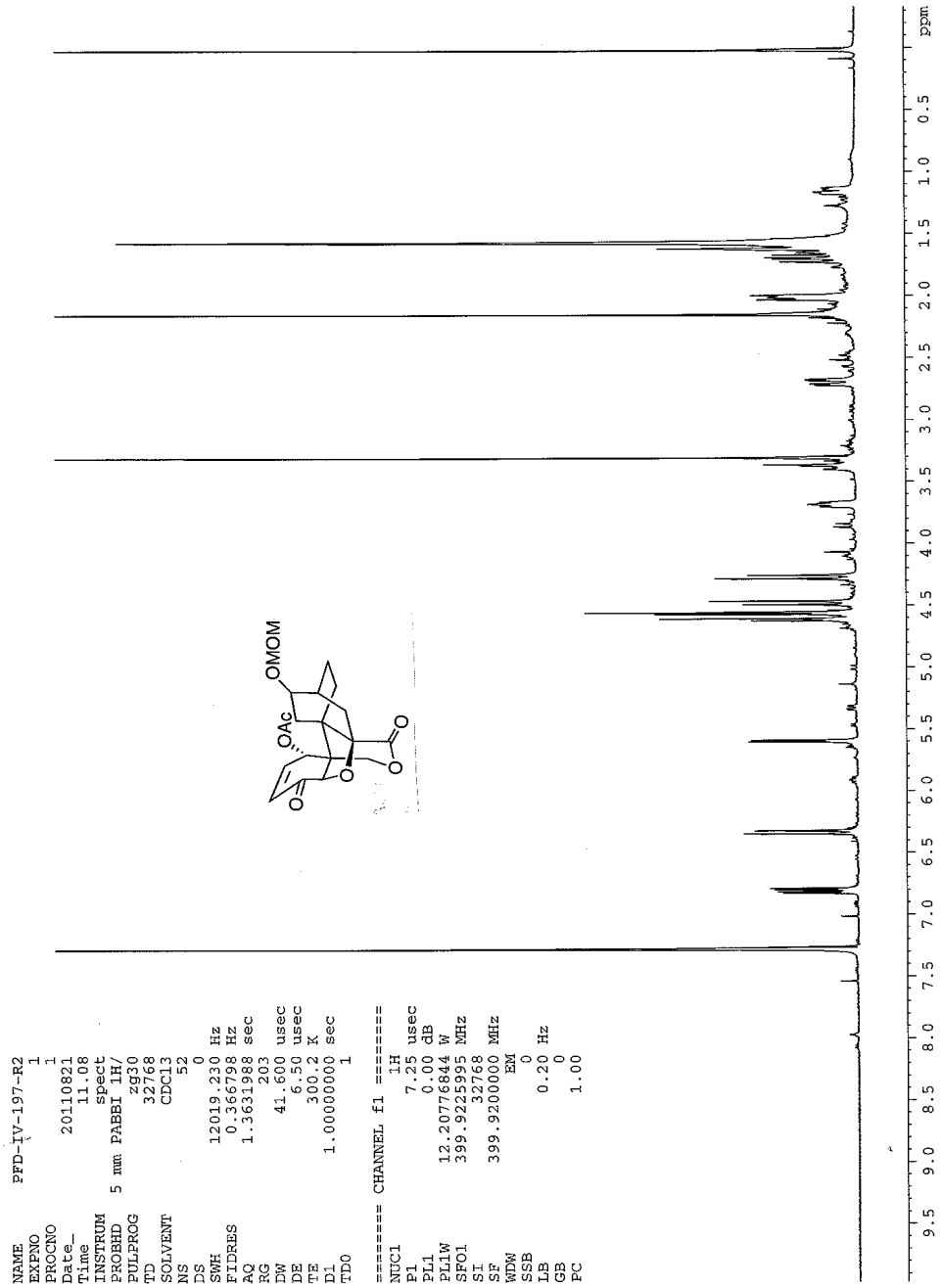

NAME PFD-IV-191-R2
EXPNO 2
PROCNO 1
Date_ 20110715
Time 22.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 4004
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 295.1 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127714 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OMOM
HO
O
O
O
170.068
130.299
121.849
94.884
88.213
84.334
77.315
77.201
76.998
76.680
76.257
73.295
69.537
55.438
49.292
42.489
33.413
30.665
29.970
25.268
20.959
20.702
ppm

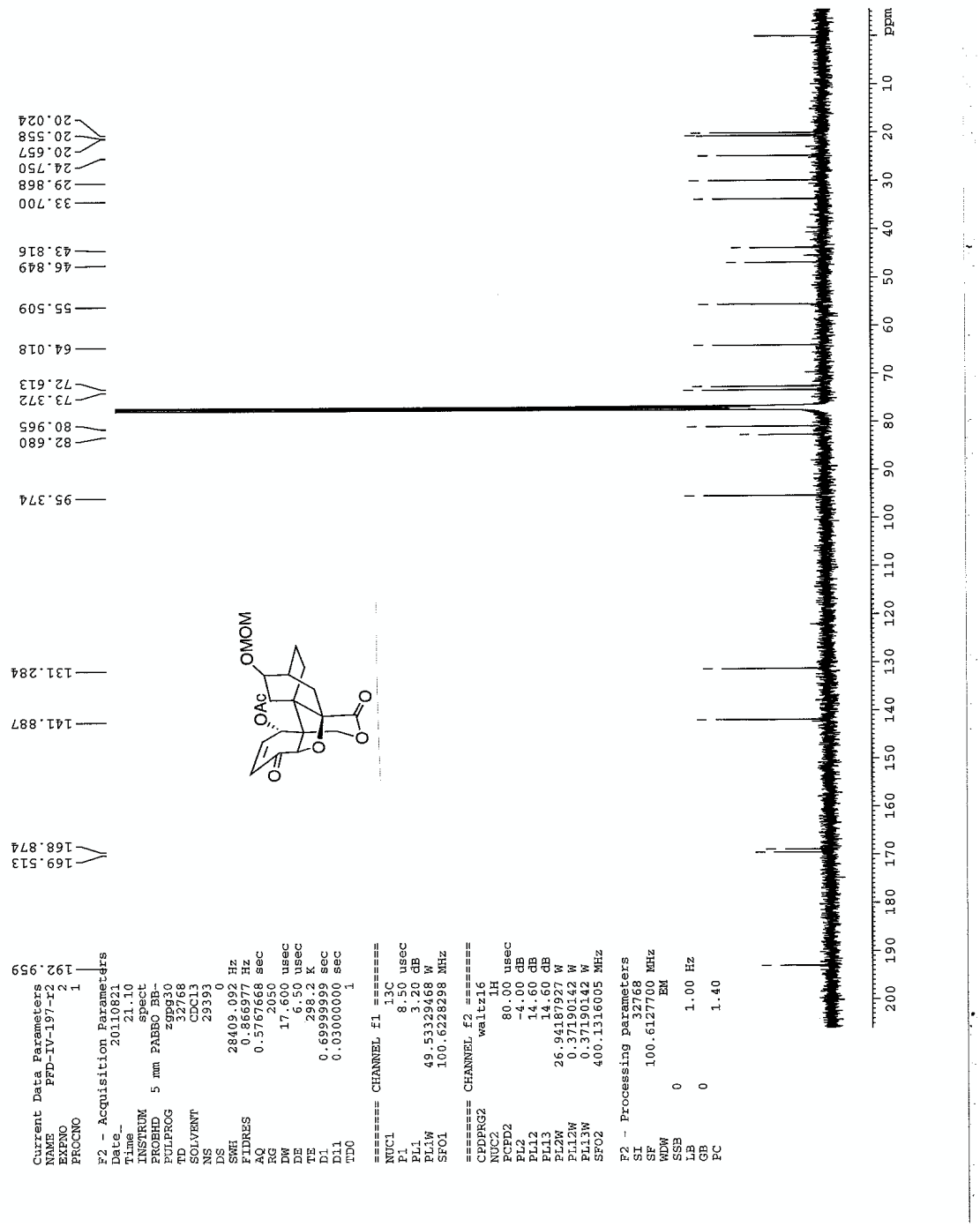

proton
NAME PFD-IV-197
EXPNO 1
PROCNO 1
Date_ 20110724
Time 16.59
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDC13
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.72263477 sec
RG 456
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
SI 32768
SF 400.1300089 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40
OMOM
HO
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 0.5 ppm

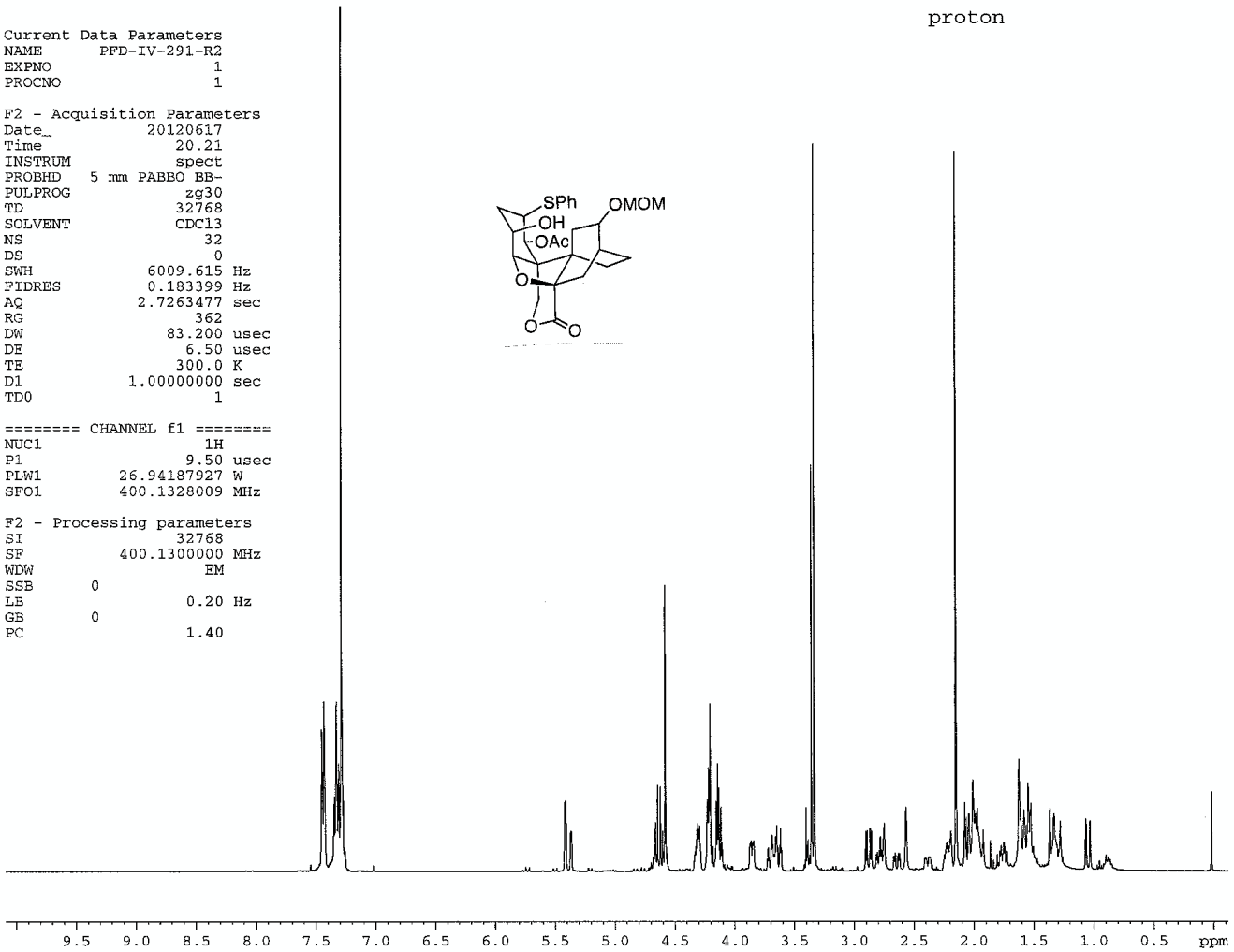

NAME PFD-IV-197
EXPNO 2
PROCNO 1
Date_ 20110724
Time 17.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 4346
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 298.2 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OMOM
HO
169.659
95.072
87.557
84.212
77.318
77.000
76.682
74.588
73.183
69.296
55.532
51.071
51.055
45.287
42.533
32.250
30.513
29.816
25.116
20.929
20.856
ppm

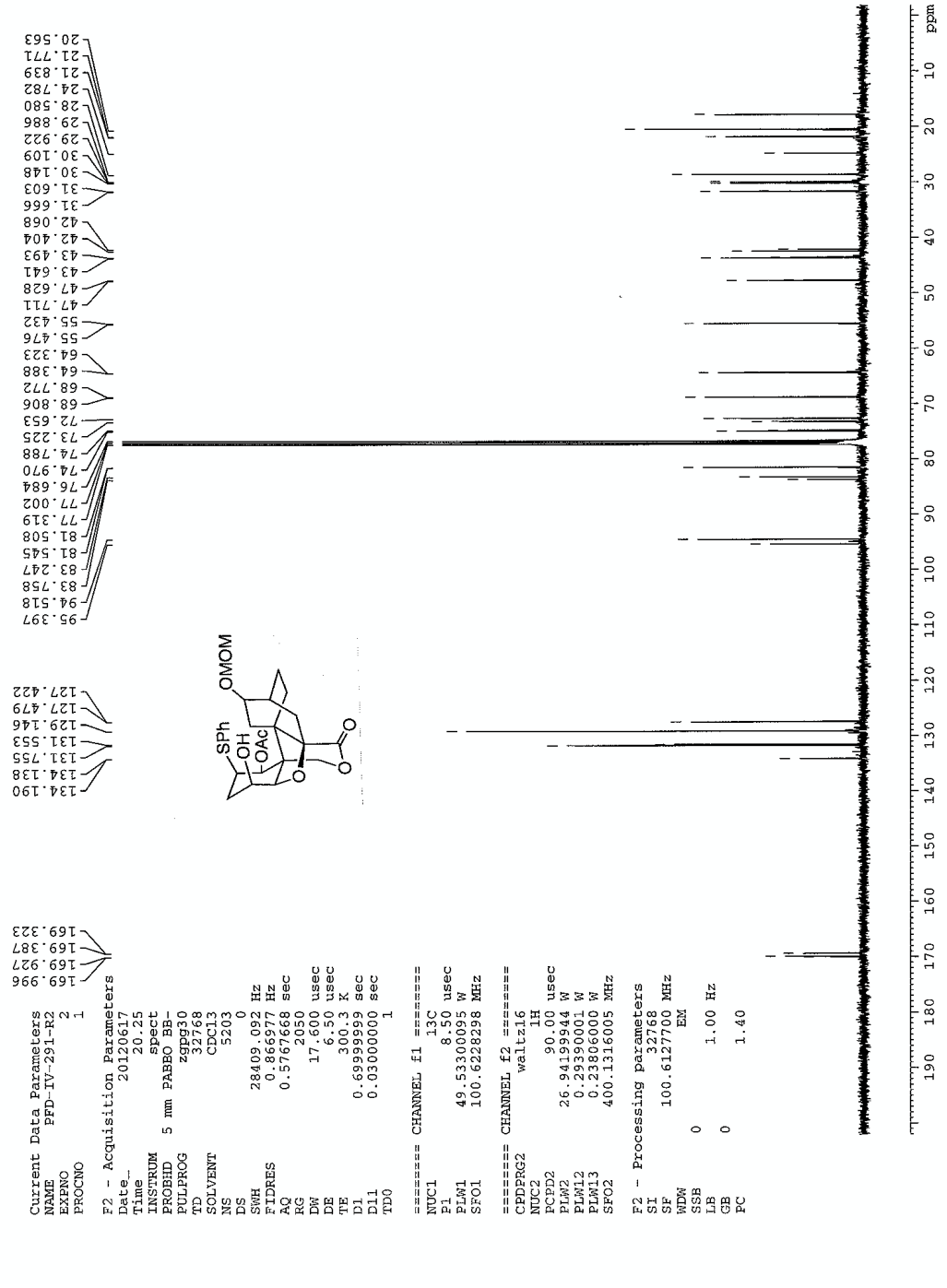

NAME PFD-IV-197-R2
EXPNO 1
PROCNO 1
Date_ 20110809
Time 21.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 362
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
SI 32768
SF 400.1300089 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40
proton
OH
OMOM
O
O
O
O
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
0.5
ppm

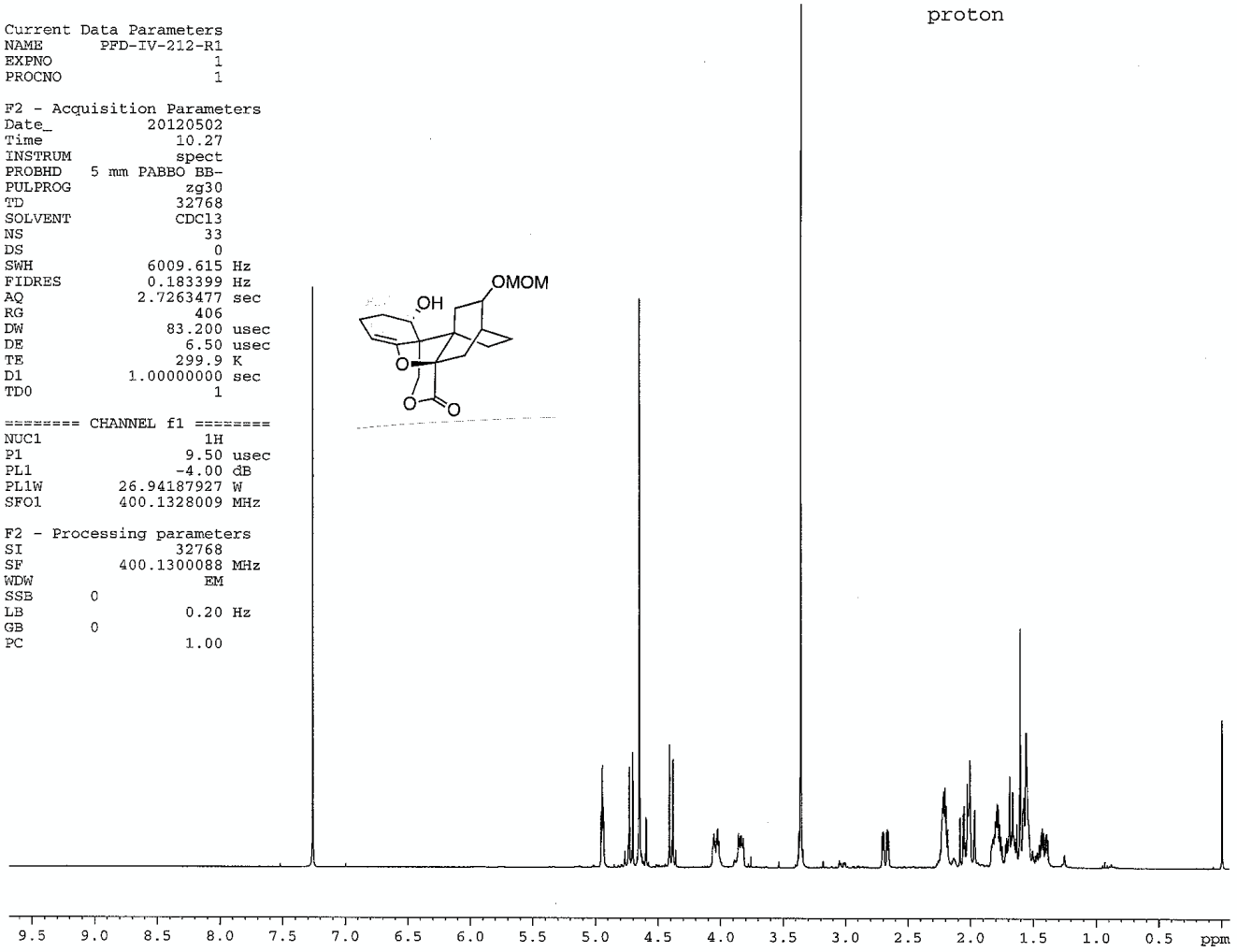

NAME PFD-IV-197-R2
EXPNO 4
PROCNO 1
Date_ 20110810
Time 22.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 22335
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 298.3 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
193.688
169.486
145.498
129.743
95.330
82.654
81.235
73.887
73.465
63.191
55.507
48.105
43.599
33.744
29.893
24.790
20.738
20.127
OMOM
OH
O
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

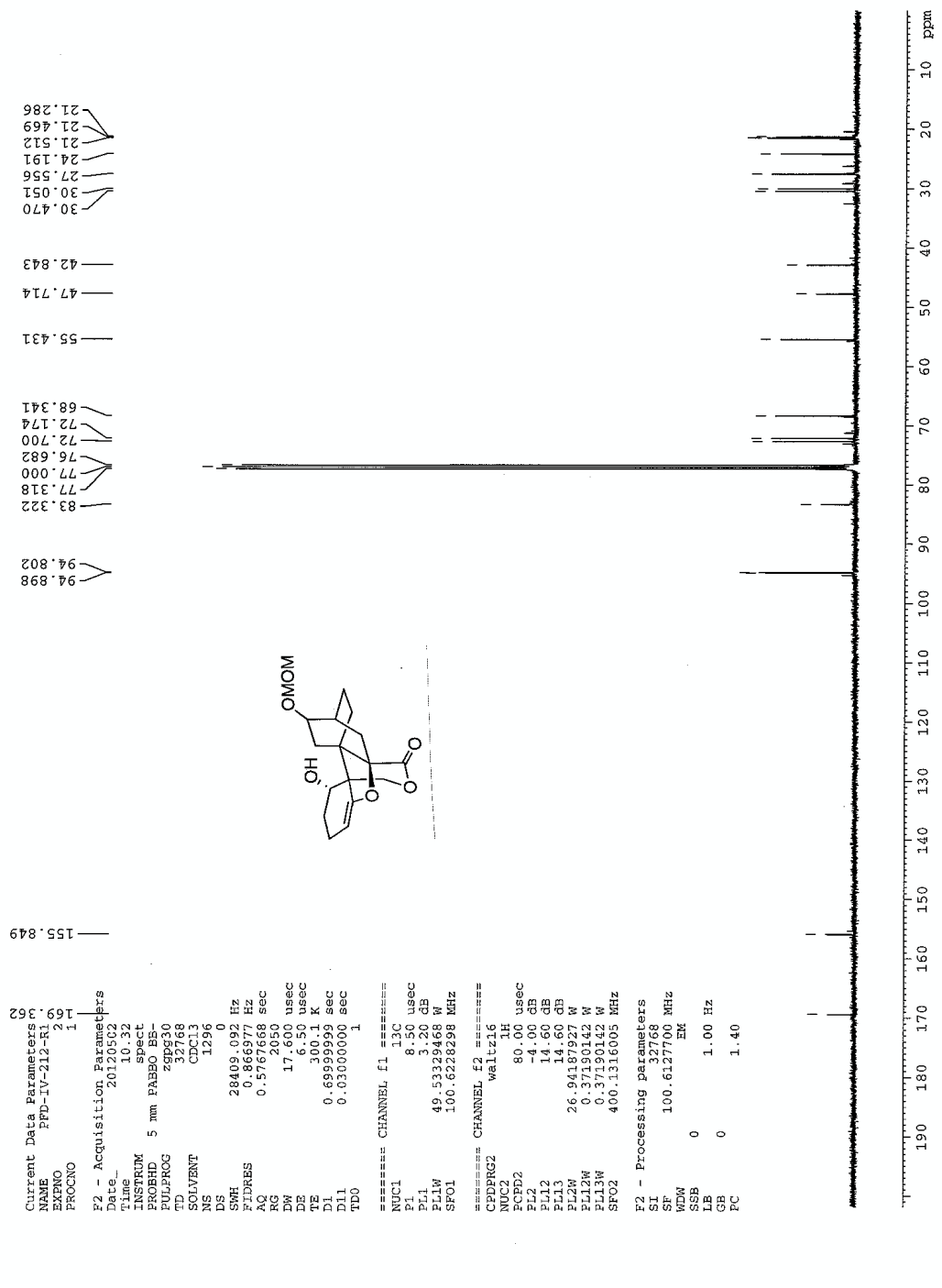

NAME PFD-IV-197-R2
EXPNO 1
PROCNO 1
Date_ 20110821
Time_ 11.08
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 52
DS 0
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 41.600 usec
DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.25 usec
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MHz
SI 32768
SF 399.9200000 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
OMOM
OAc
O
O
O
O
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 0.5 ppm

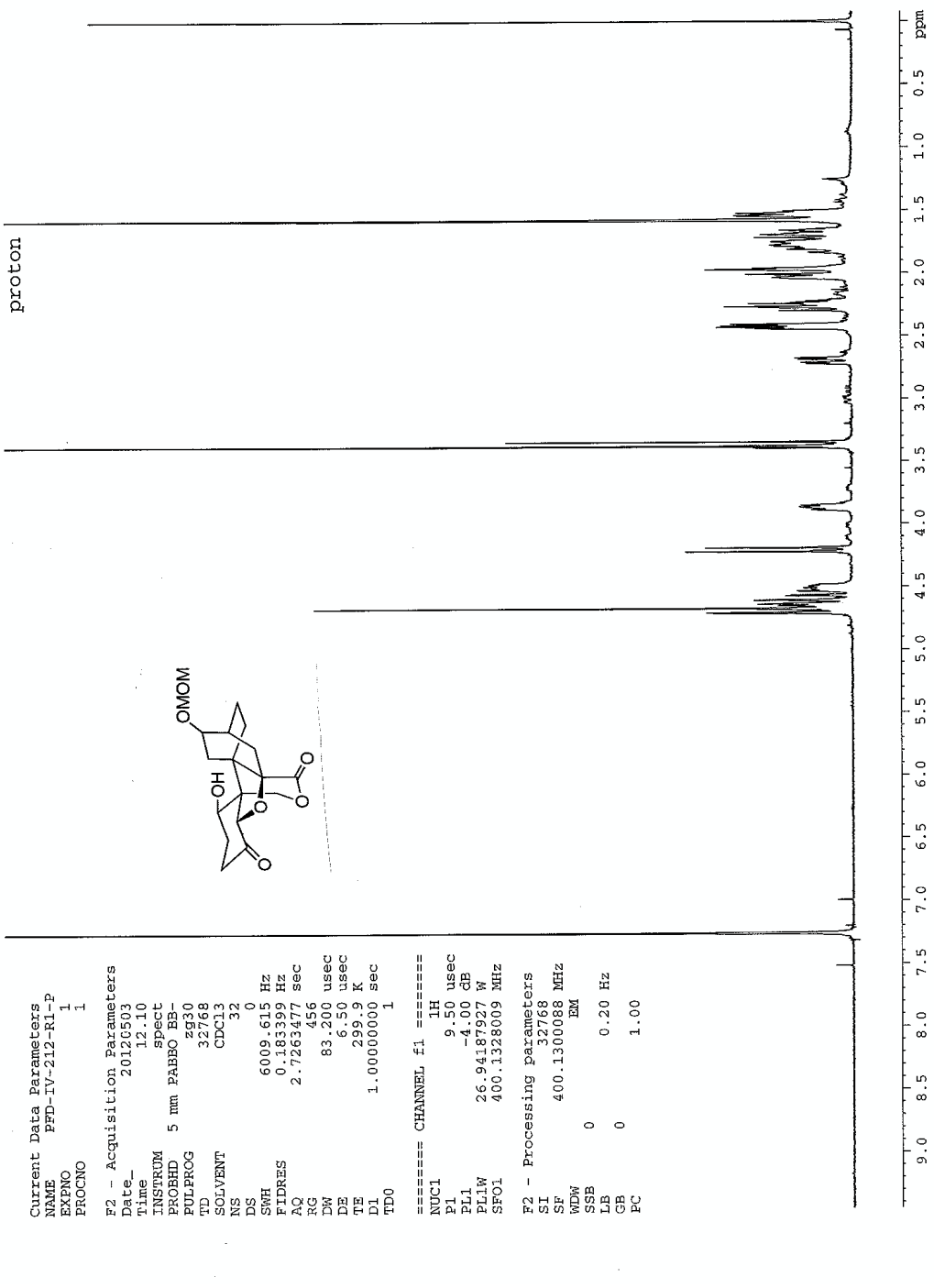

Current Data Parameters
NAME PFD-IV-197-r2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110821
Time_ 21.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 29393
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 298.2 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OMOM
OAc
O
O
O
O
192.959
169.513
168.874
141.887
131.284
95.374
82.680
80.965
73.372
72.613
64.018
55.509
46.849
43.816
33.700
29.868
24.750
20.657
20.558
20.024
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

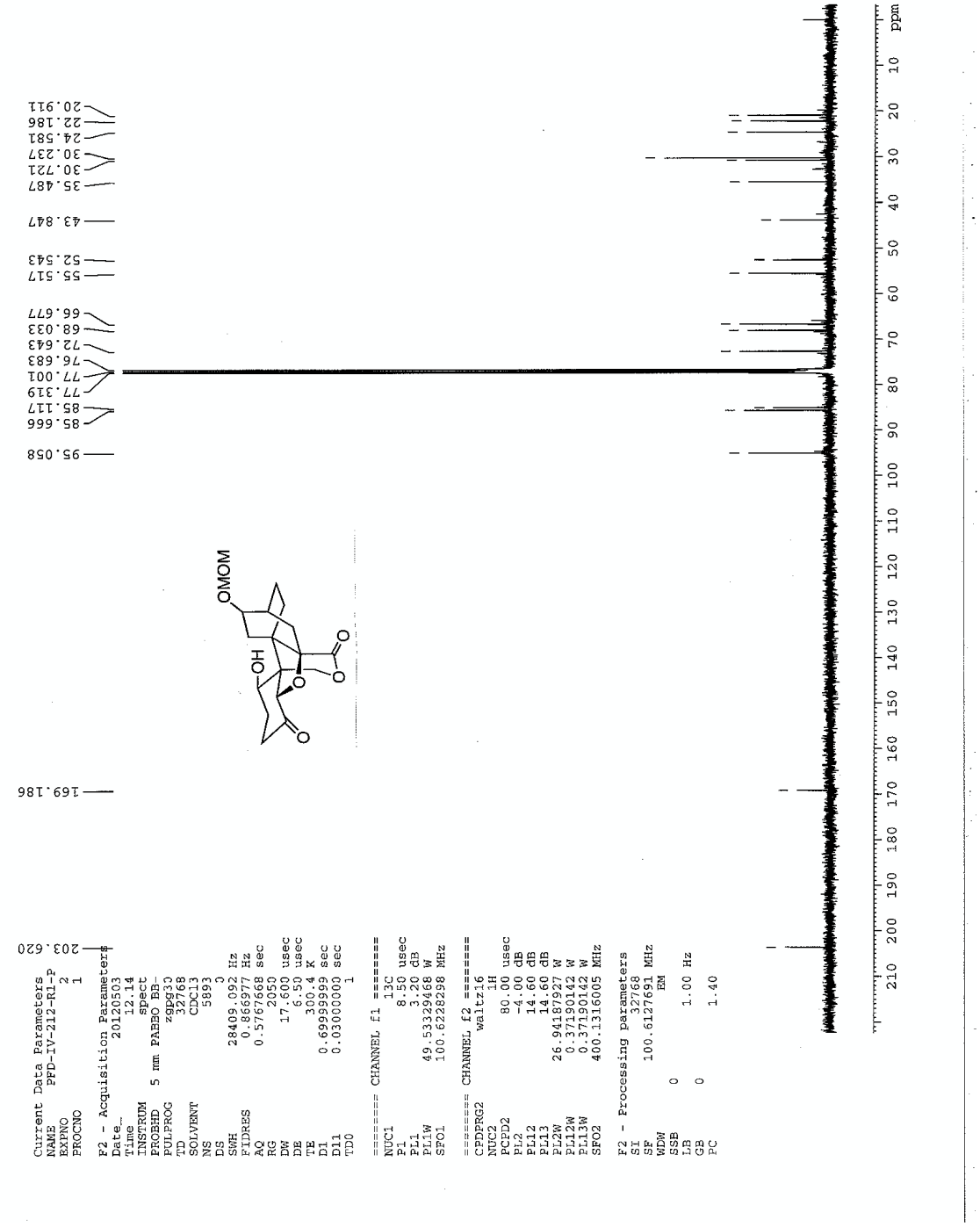

proton
Current Data Parameters
NAME PFD-IV-291-R2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120617
Time 20.21
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 362
DW 83.200 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PLW1 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40
SPh
OMOM
OH
OAc
O
O
O
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 0.5 ppm

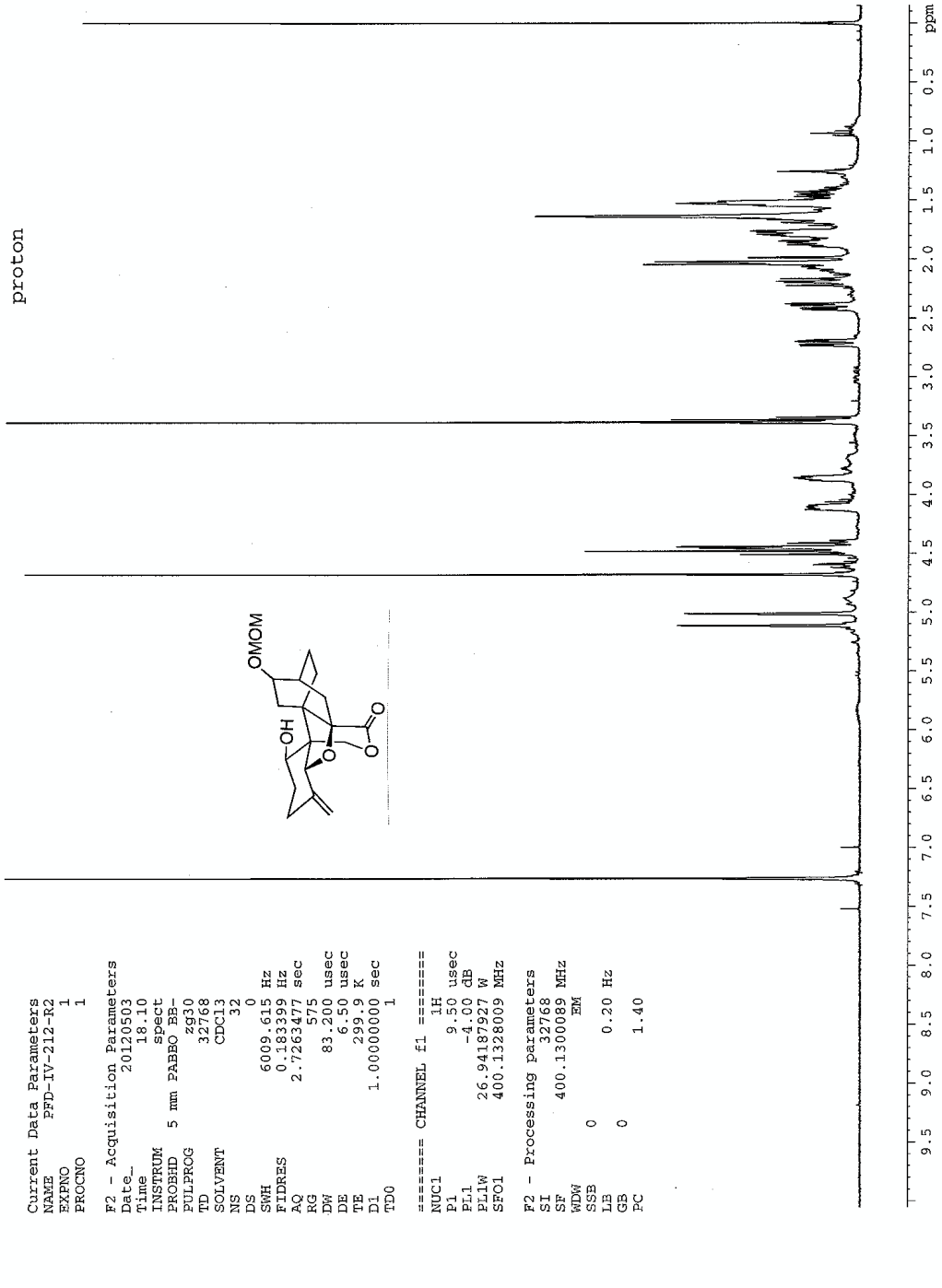

OMOM
SPh
OH
OAc
O
O
O
Current Data Parameters
NAME PPD-IV-291-R2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120617
Time 20.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 5203
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 300.3 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PLW1 49.53300095 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 26.94199944 W
PLW12 0.29390001 W
PLW13 0.23806000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
169.996
169.927
169.387
169.323
134.190
134.138
131.755
131.553
129.146
127.479
127.422
95.397
94.518
83.758
83.247
81.545
81.508
77.319
77.002
76.684
74.970
74.788
73.225
72.653
68.806
68.772
64.388
64.323
55.476
55.432
47.711
47.628
43.641
43.493
42.404
42.068
31.666
31.603
30.148
30.109
29.922
29.886
28.580
24.782
21.839
21.771
20.563
ppm

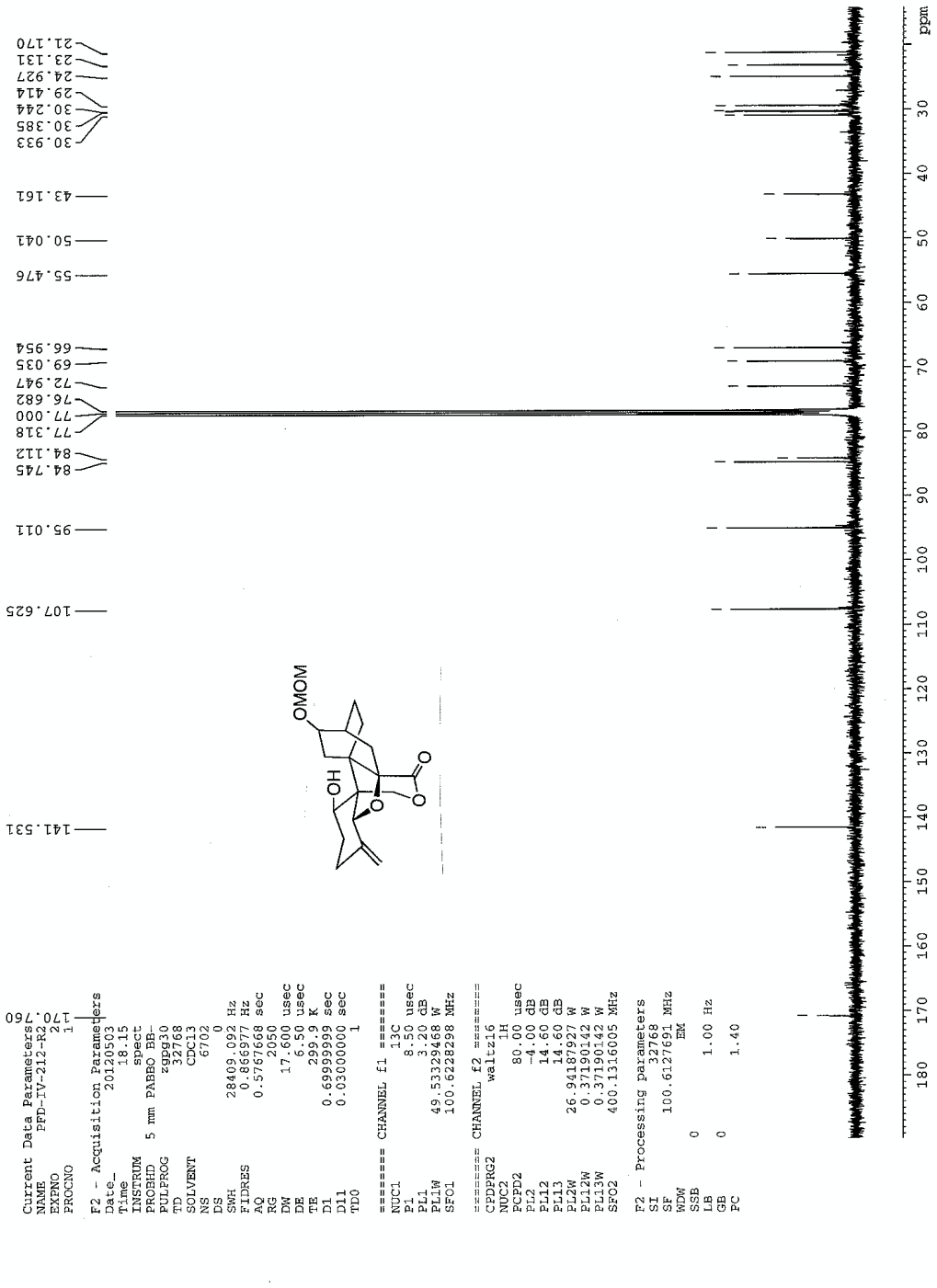

proton
Current Data Parameters
NAME PFD-IV-212-R1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120502
Time 10.27
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 33
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 406
DW 83.200 usec
DE 6.50 usec
TE 299.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300088 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
OMOM
OH
O
O
O
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
0.5
ppm

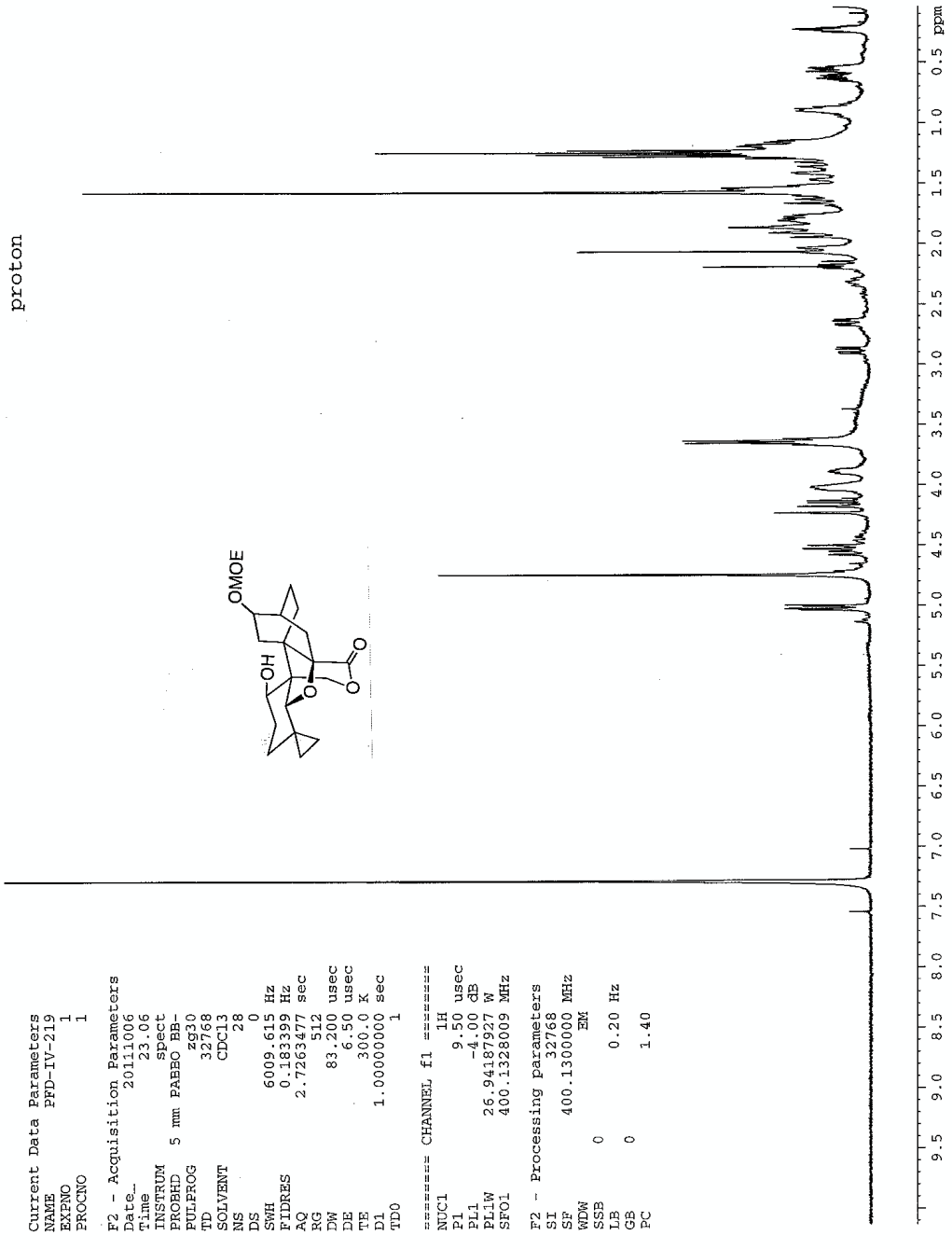

155.849
169.362
94.898
94.802
83.322
77.318
77.000
76.682
72.700
72.174
68.341
55.431
47.714
42.843
30.470
30.051
27.556
24.191
21.512
21.469
21.286
OMOM
OH
O
O
O
ppm

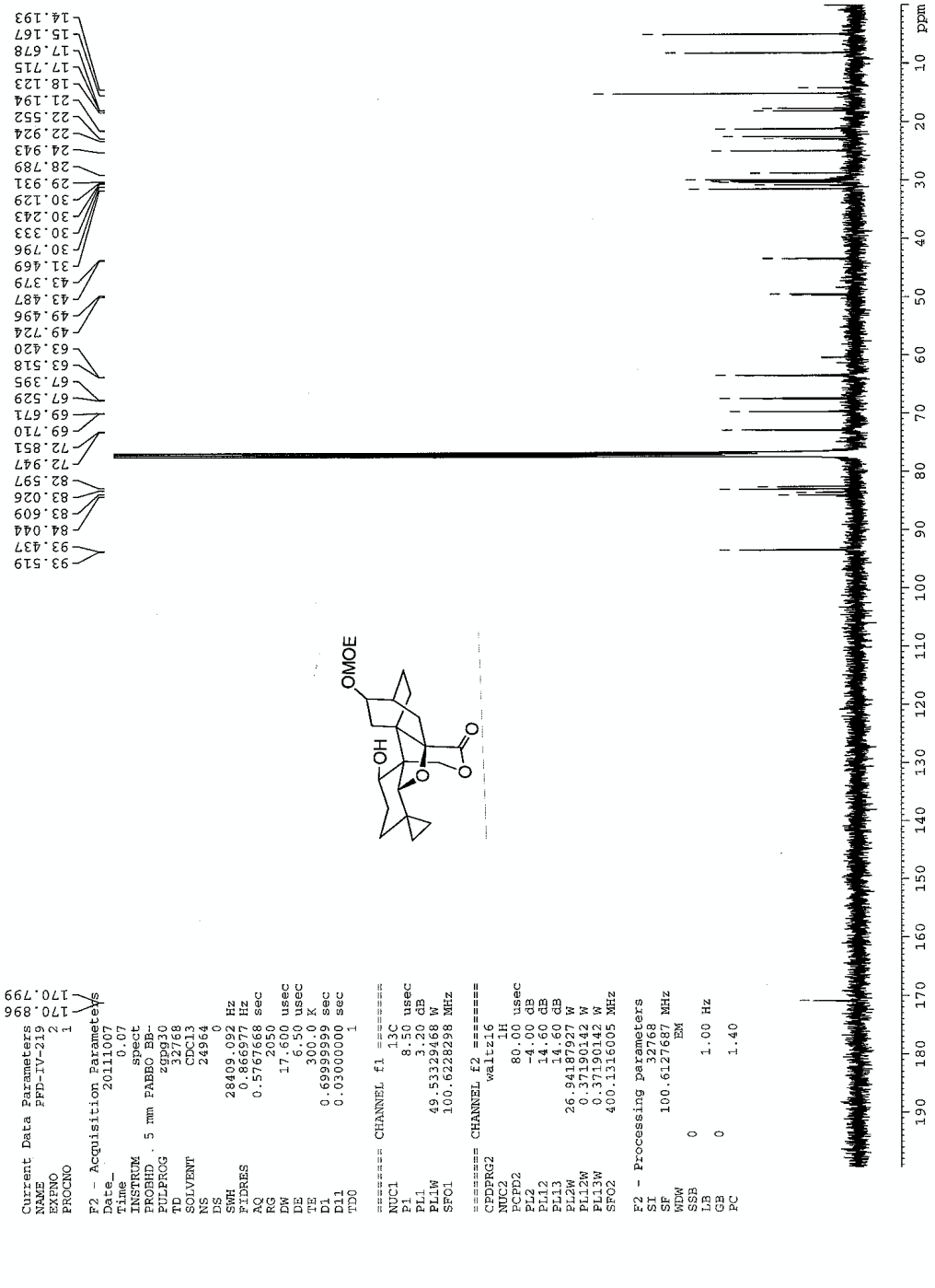

proton
OMOM
OH
O
O
O
O
Current Data Parameters
NAME PFD-IV-212-R1-P
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120503
Time 12.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 456
DW 83.200 usec
DE 6.50 usec
TE 299.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300088 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
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
0.5
ppm


Current Data Parameters
NAME PFD-IV-212-R1-P
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120503
Time 12.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 5993
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 300.4 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127691 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OMOM
OH
O
O
O
O
203.620
169.186
95.058
85.666
85.117
77.319
77.001
76.683
72.643
68.033
66.677
55.517
52.543
43.847
35.487
30.721
30.237
24.581
22.186
20.911
ppm

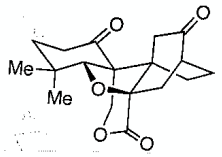

proton
Current Data Parameters
NAME PFD-IV-212-R2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120503
Time 18.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 575
DW 83.200 usec
DE 6.50 usec
TE 299.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300089 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40
OMOM
OH
O
O
O
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 0.5 ppm

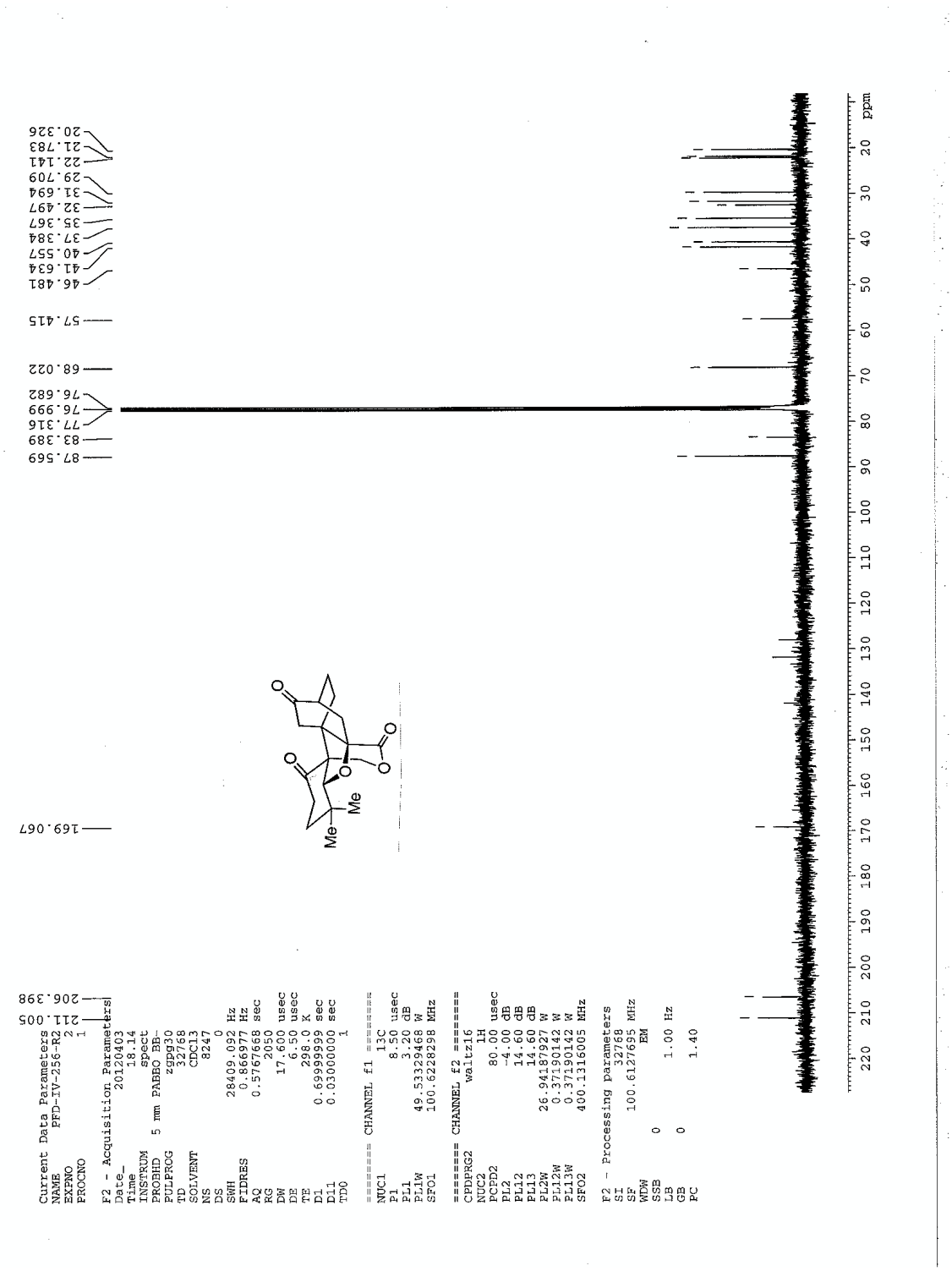

Current Data Parameters
NAME PFD-IV-212-R2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120503
Time 18.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 6702
DS 0
SWH 28409.092 Hz
FIDRES 0.867977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 299.9 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127691 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OMOM
OH
O
O
O
170.760
141.531
107.625
95.011
84.745
84.112
77.318
77.000
76.682
72.947
69.035
66.954
55.476
50.041
43.161
30.933
30.385
30.244
29.414
24.927
23.131
21.170
ppm

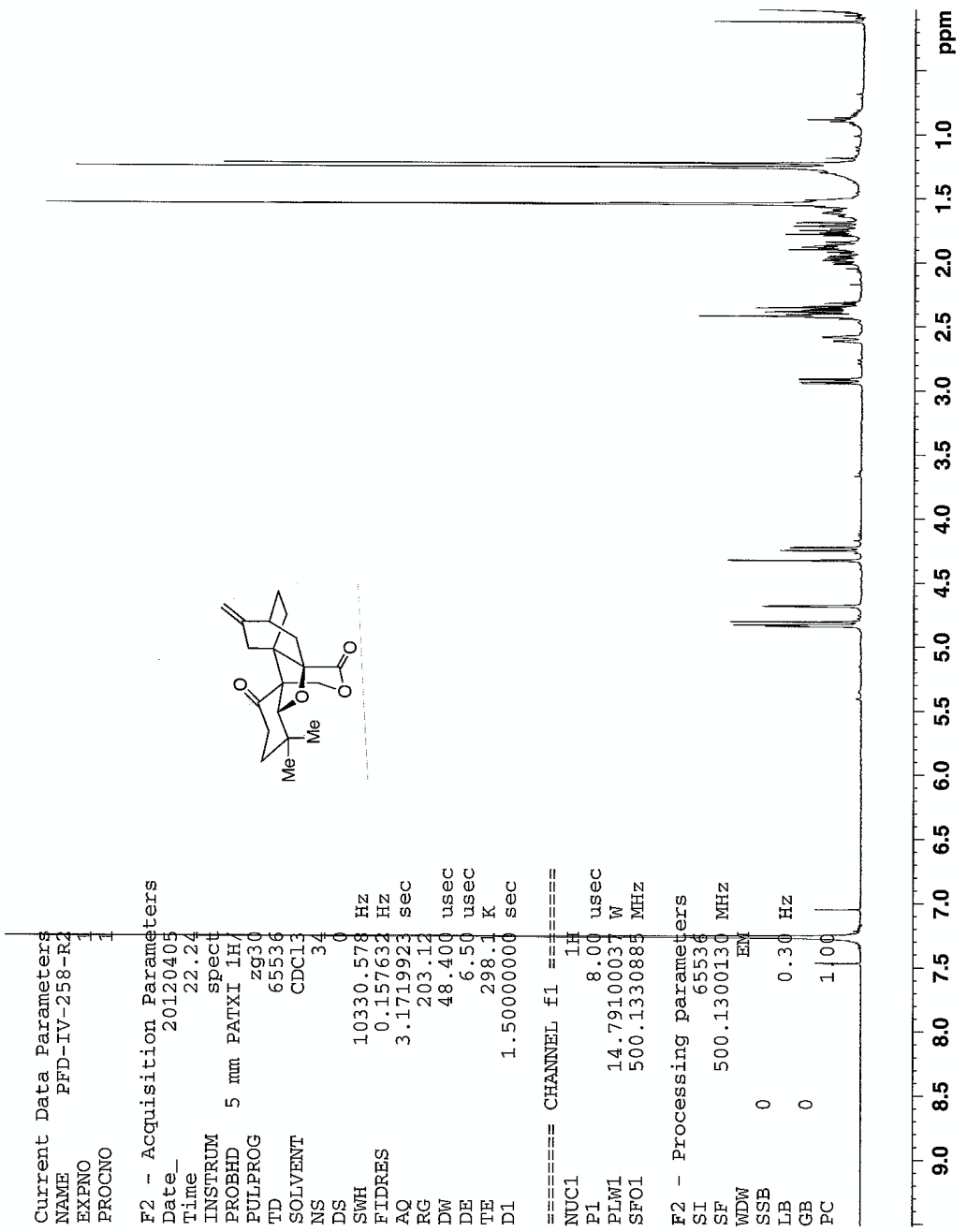

proton
Current Data Parameters
NAME PFD-IV-219
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111006
Time 23.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 28
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 512
DW 83.200 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40
OMOE
OH
O
O
O
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 0.5 ppm

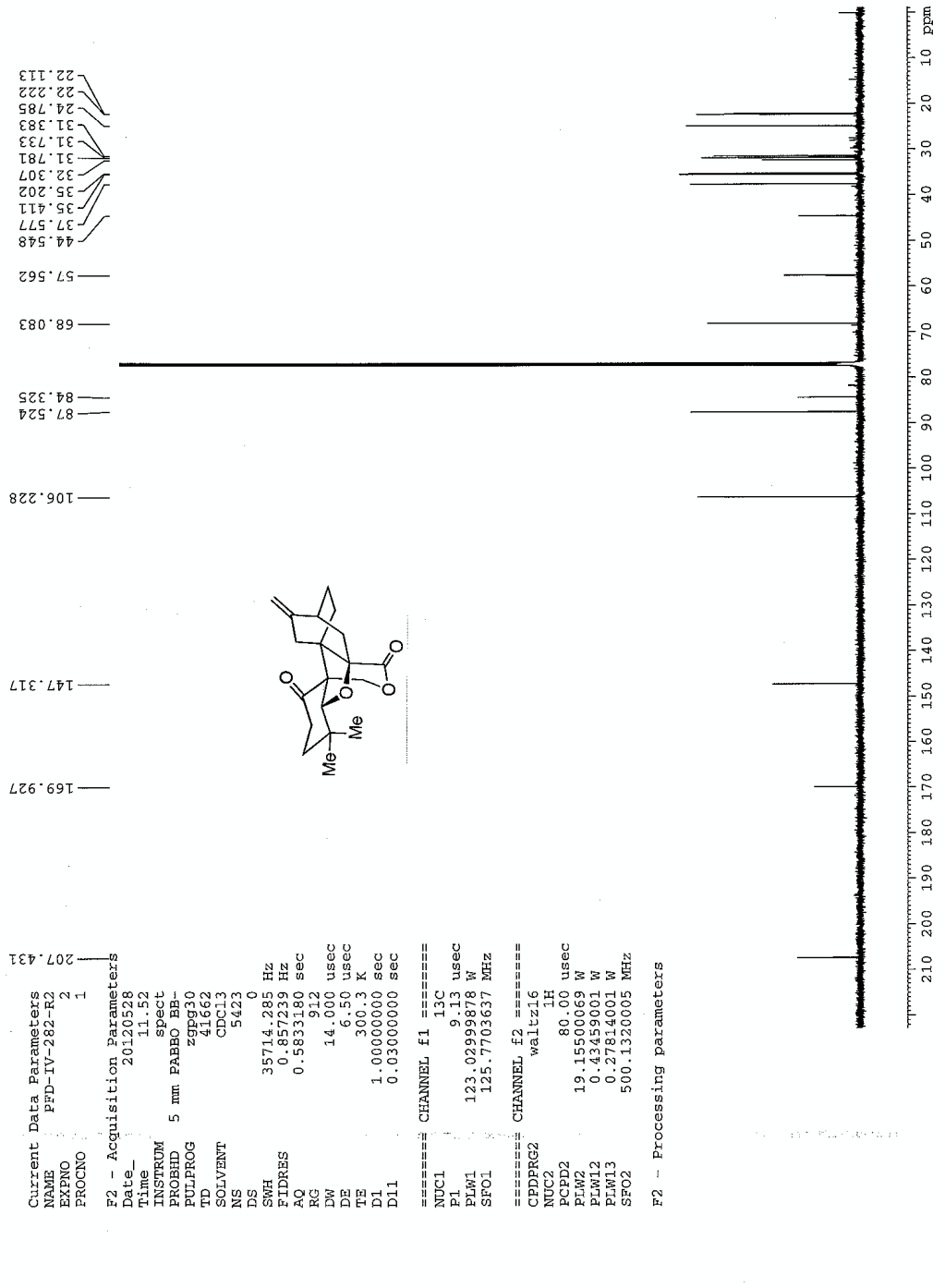

Current Data Parameters
NAME PFD-IV-219
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111007
Time_ 0.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 24964
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 300.0 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127687 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OMOE
OH
O
O
O
170.896
170.799
14.193
15.167
17.678
17.715
18.123
21.194
22.552
22.924
24.943
28.789
29.931
30.129
30.243
30.333
30.796
31.469
43.379
43.487
49.496
49.724
63.420
63.518
67.395
67.529
69.671
69.710
72.851
72.947
82.597
83.026
83.609
84.044
93.437
93.519
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

NAME	PFD-IV-256-R2
EXPNO	6
PROCNO	1
Date_	20120403
Time	11.39
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	575
DW	83.200 usec
DE	6.50 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.50 usec
PL1	-4.00 dB
PL1W	26.94187927 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1300089 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00




206.398
211.005
169.067
87.569
83.389
77.316
76.999
76.682
68.022
57.415
46.481
41.634
40.557
37.384
35.367
32.497
31.694
29.709
22.141
21.783
20.326
Me
Me
Current Data Parameters
NAME PFD-IV-256-R2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120403
Time 18.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 8247
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127695 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


Current Data Parameters
NAME PFD-IV-258-R2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120405
Time 22.24
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 34
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 203.12
DW 48.400 usec
DE 6.50 usec
TE 298.1 K
D1 1.50000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PLW1 14.79100037 W
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 65536
SF 500.1300130 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Me
Me
O
O
O
O
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
ppm



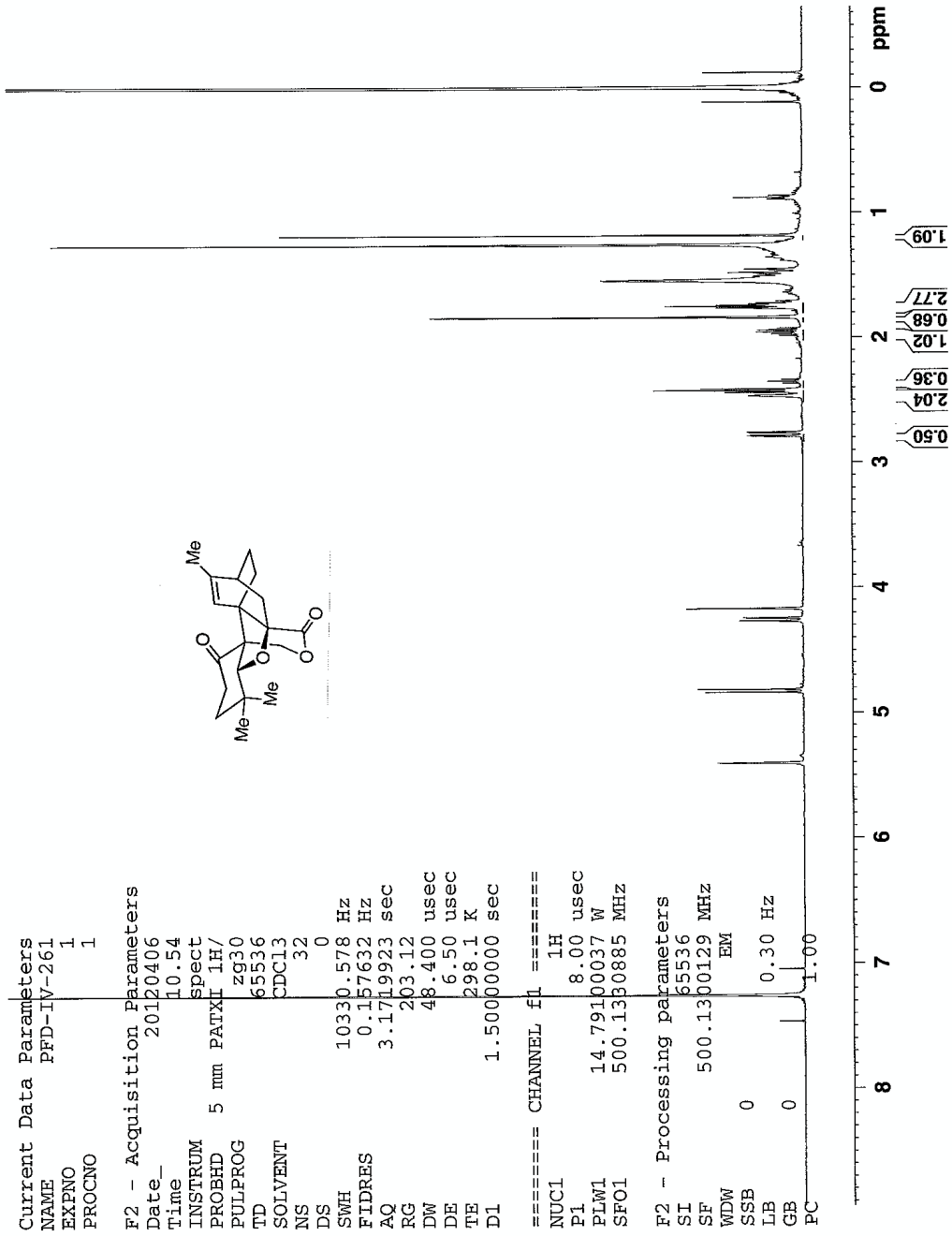
Current Data Parameters
NAME pfd-IV-282-R2
EXPNO 2
PROCNO 1

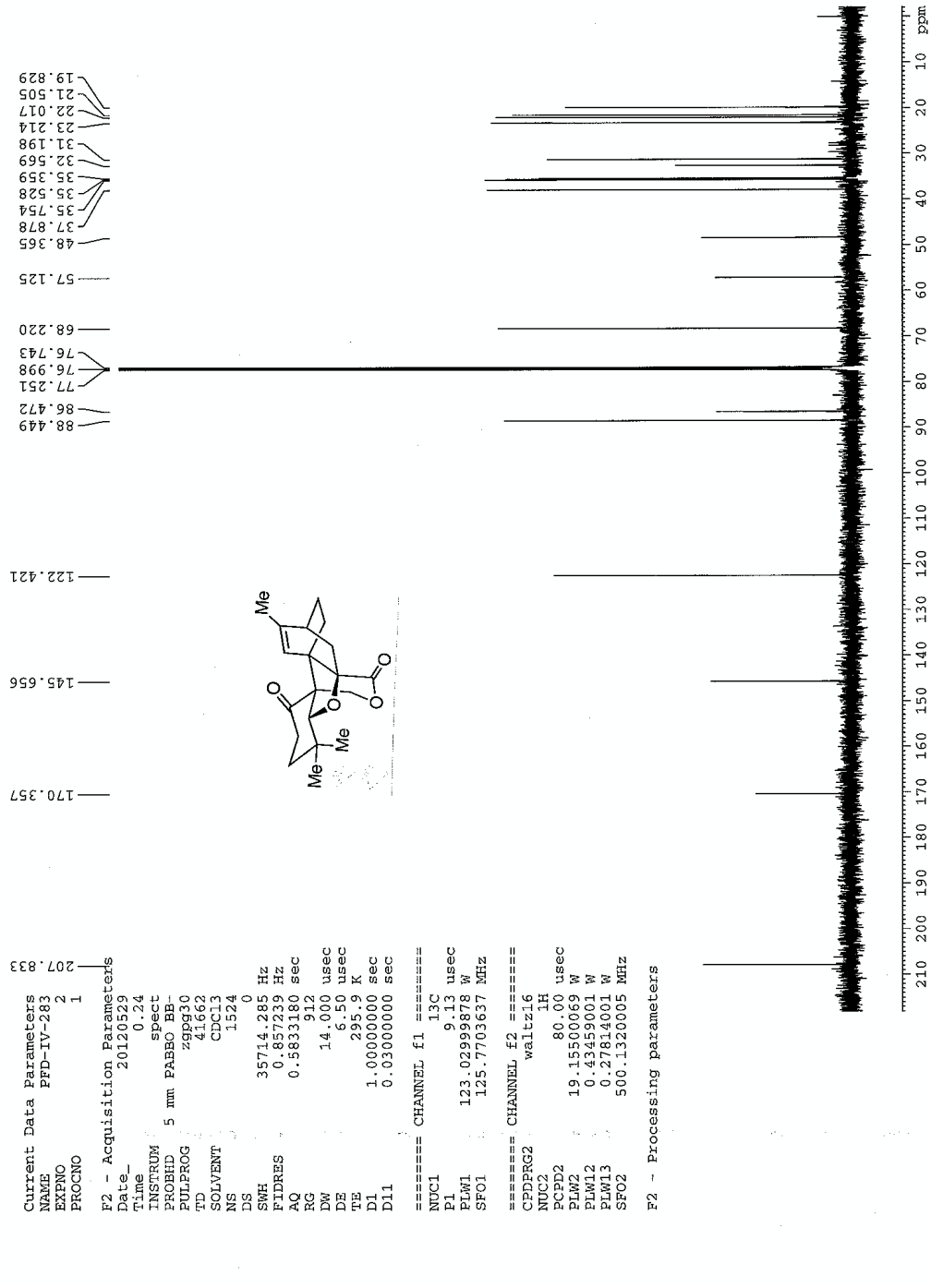
F2 - Acquisition Parameters
Date_ 20120528
Time 11.52
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 41662
SOLVENT CDCl3
NS 5423
DS 0
SWH 35714.285 Hz
FIDRES 0.857239 Hz
AQ 0.5833180 sec
RG 912
DW 14.000 usec
DE 6.50 usec
TE 300.3 K
D1 1.00000000 sec
D11 0.03000000 sec

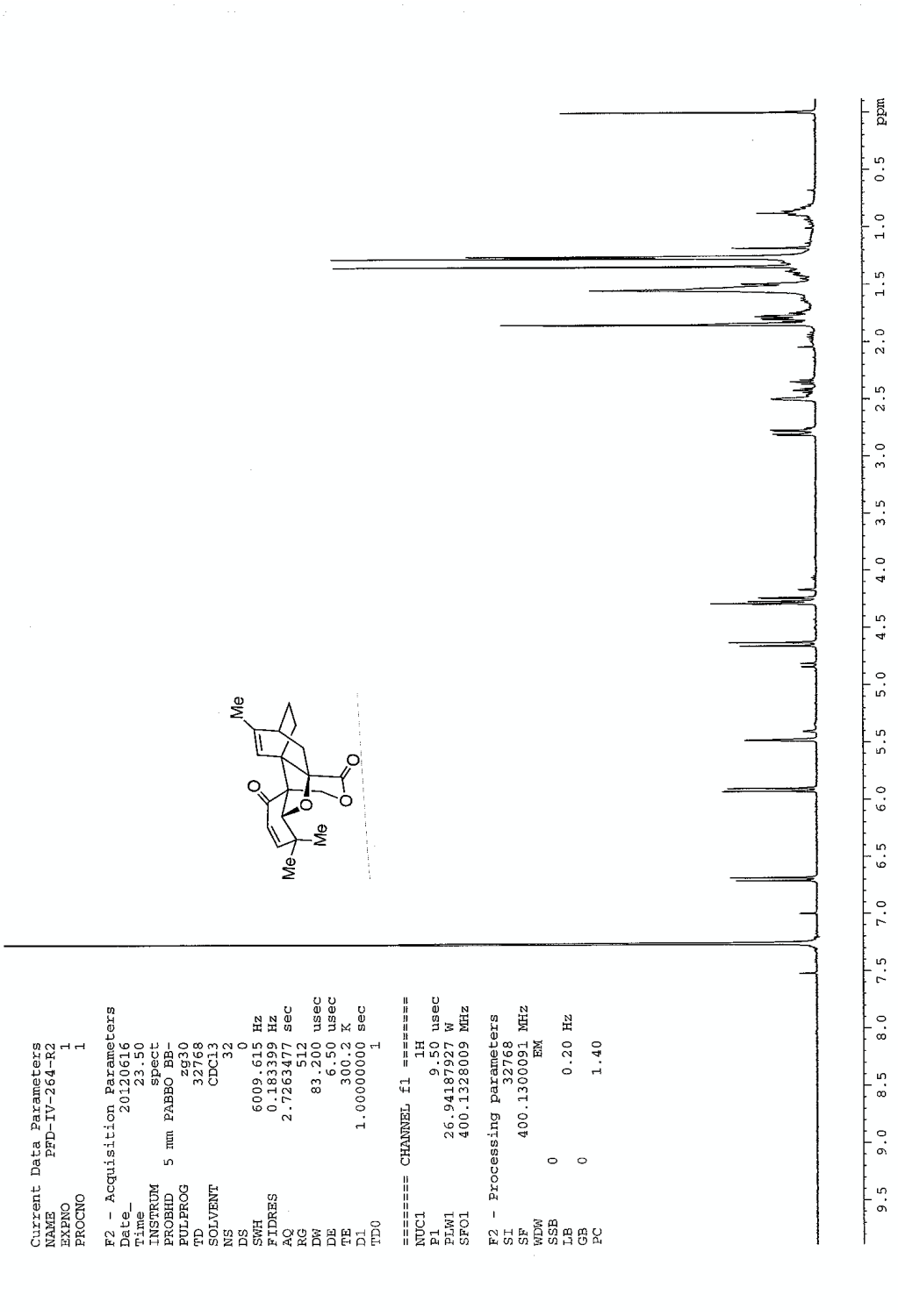
======== CHANNEL f1 ========
NUC1 13C
P1 9.13 usec
PLW1 123.02998878 W
SFO1 125.7703637 MHz

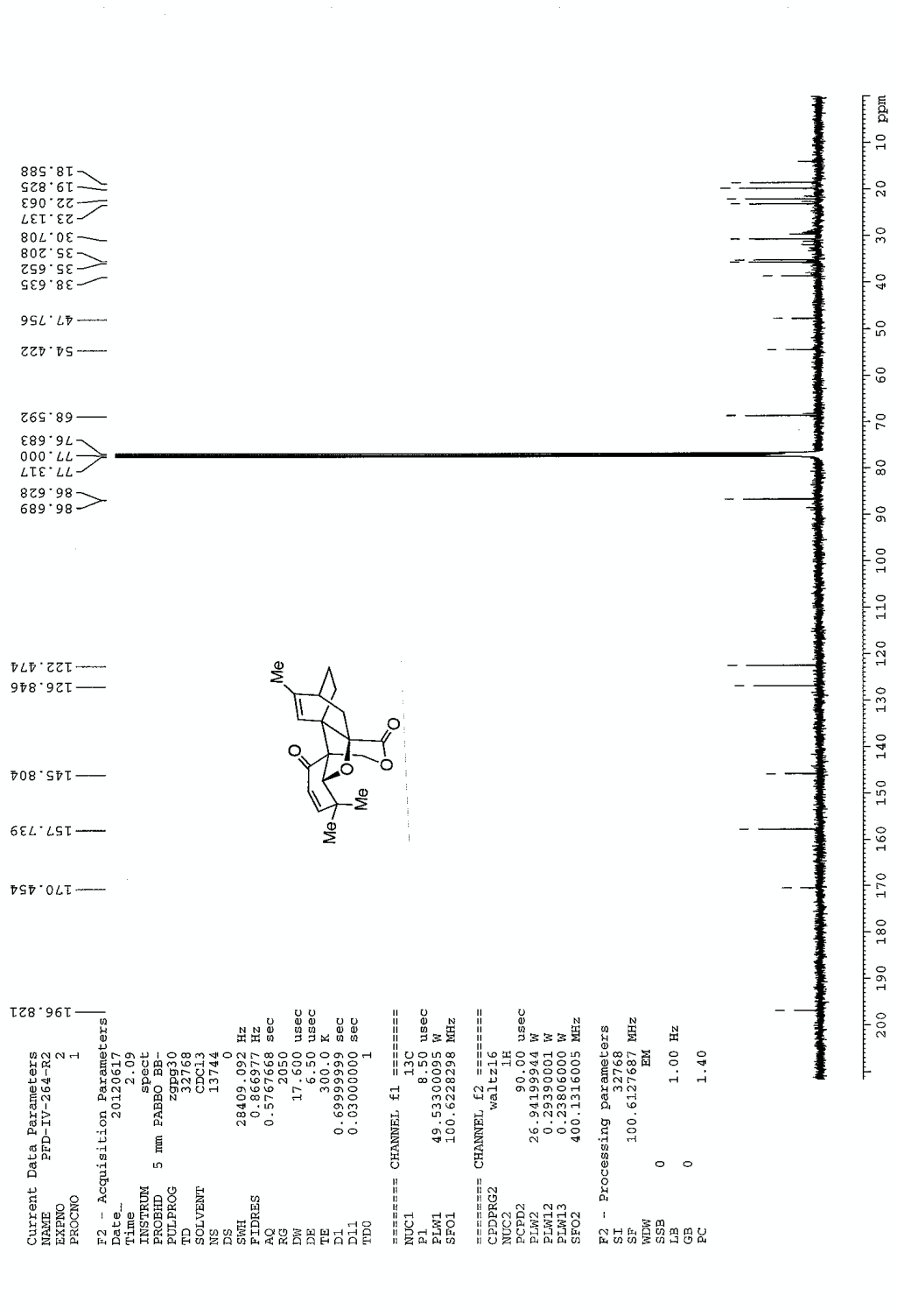
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 19.15500069 W
PLW12 0.43459001 W
PLW13 0.27814001 W
SFO2 500.1320005 MHz

F2 - Processing parameters

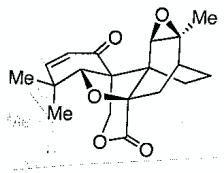

Current Data Parameters
NAME PFD-IV-261
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120406
Time 10.54
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 203.12
DW 48.400 usec
DE 6.50 usec
TE 298.1 K
D1 1.50000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PLW1 14.79100037 W
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 65536
SF 500.1300129 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Me
Me
Me
O
O
O
O
0.50
2.04
0.36
1.02
0.68
2.77
1.09
8
7
6
5
4
3
2
1
0
ppm

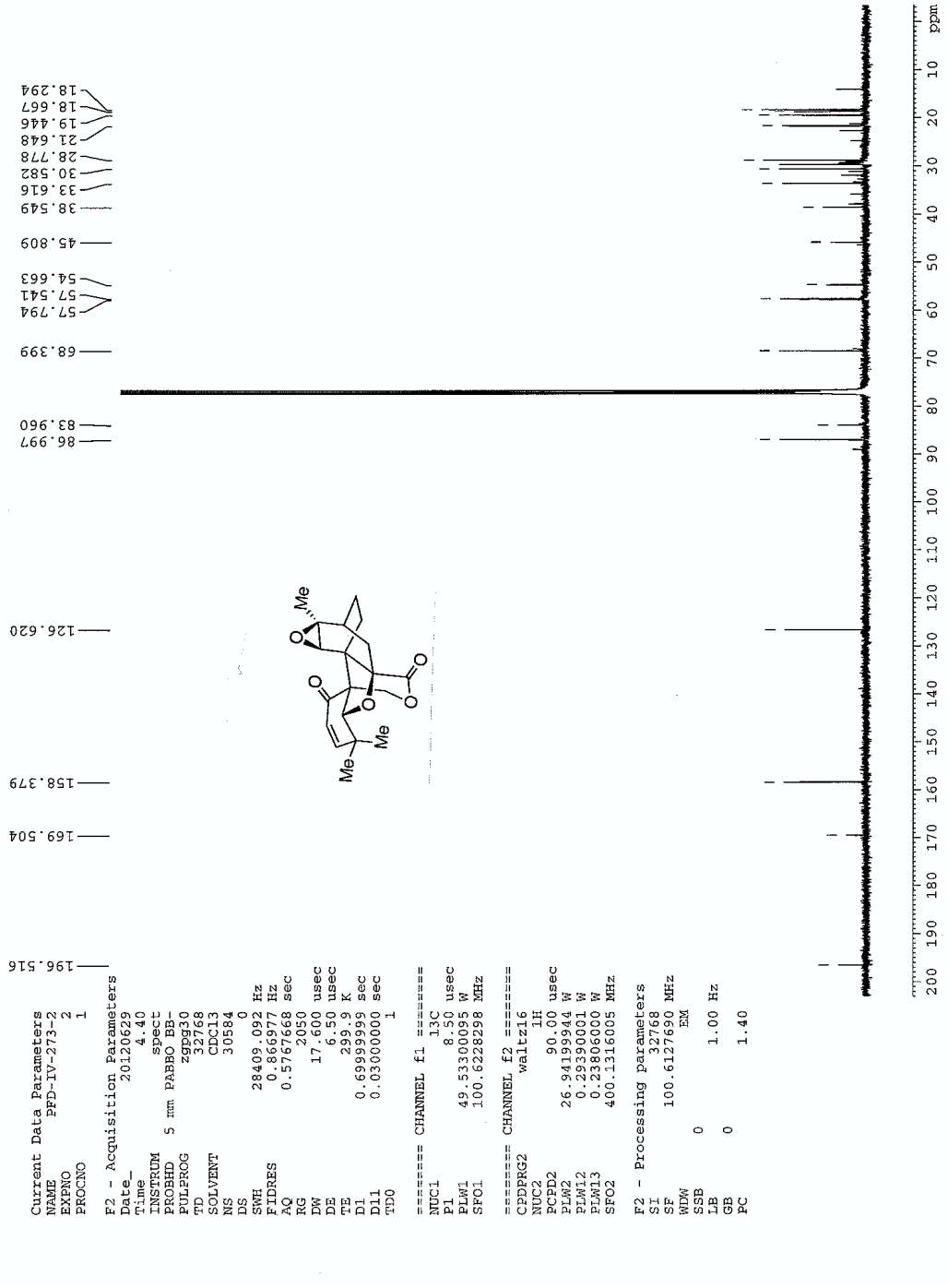

Current Data Parameters
NAME PFD-IV-283
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120529
Time 0.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 41662
SOLVENT CDCl3
NS 1524
DS 0
SWH 35714.285 Hz
FIDRES 0.857239 Hz
AQ 0.5833180 sec
RG 912
DW 14.000 usec
DE 6.50 usec
TE 295.9 K
D1 1.00000000 sec
D11 0.03000000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 9.13 usec
PLW1 123.02999878 W
SFO1 125.7703637 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 19.15500069 W
PLW12 0.43459001 W
PLW13 0.27814001 W
SFO2 500.1320005 MHz
F2 - Processing parameters
207.833
170.357
145.656
122.421
88.449
86.472
77.251
76.998
76.743
68.220
57.125
48.365
37.878
35.754
35.528
35.359
32.569
31.198
23.214
22.017
21.505
19.829
Me
Me
Me
O
O
O
O
ppm

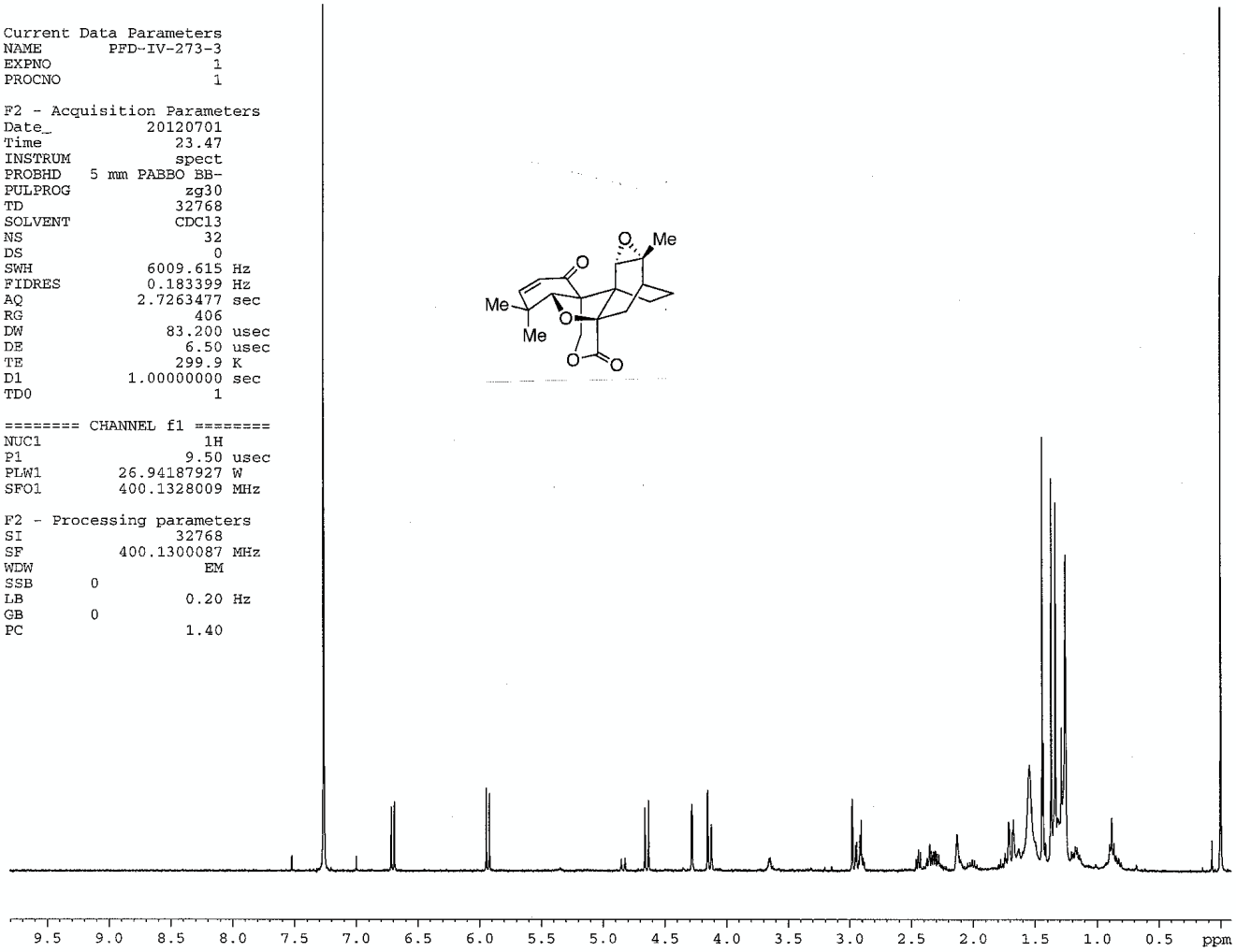

Current Data Parameters
NAME PFD-IV-264-R2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120616
Time_ 23.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 512
DW 83.200 usec
DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PLW1 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40
Me
Me
Me
O
O
O
O
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
0.5
ppm

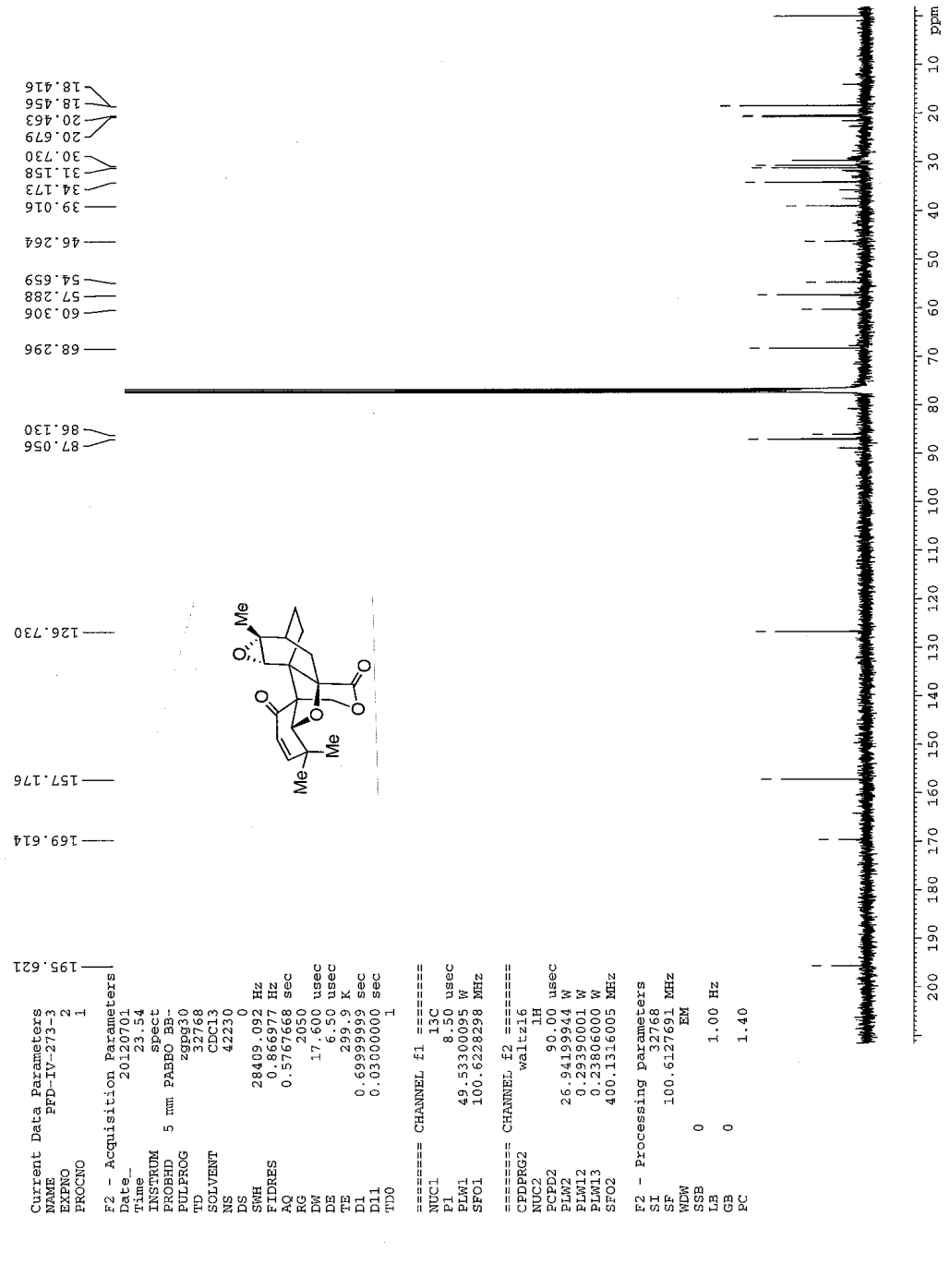

Current Data Parameters
NAME PFD-IV-264-R2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120617
Time 2.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 13744
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 300.0 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PLW1 49.53300095 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 26.94199944 W
PLW12 0.29390001 W
PLW13 0.23806000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127687 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
196.821
170.454
157.739
145.804
126.846
122.474
86.689
86.628
77.317
77.000
76.683
68.592
54.422
47.756
38.635
35.652
35.208
30.708
23.137
22.063
19.825
18.588
Me
Me
Me
O
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

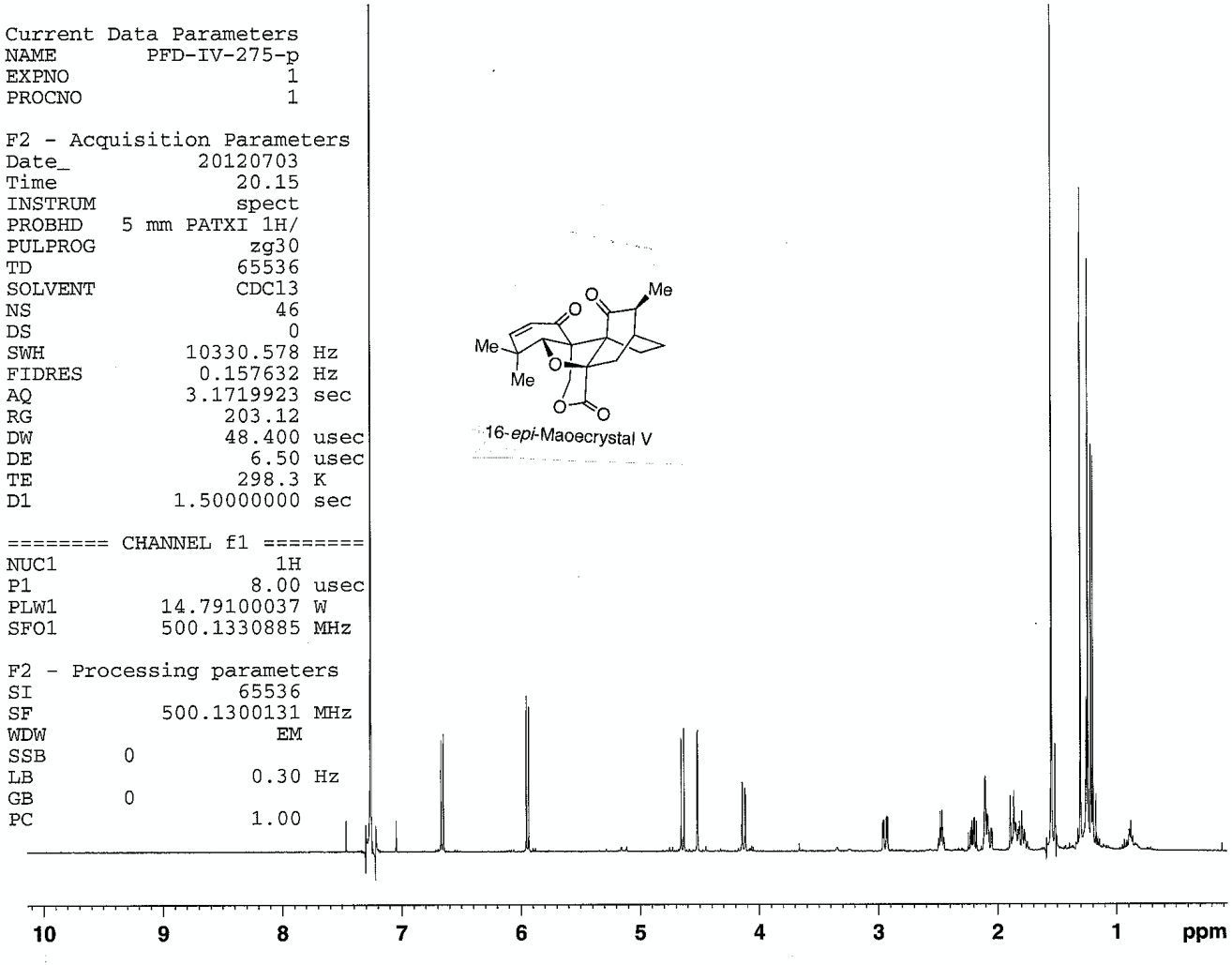
```
Current Data Parameters
NAME        PFD-IV-273-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120629
Time                4.34
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ             2.7263477 sec
RG                   575
DW                83.200 usec
DE                 6.50 usec
TE                299.9 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.50 usec
PLW1        26.94187927 W
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300088 MHz
WDW                   EM
SSB      0
LB                 0.20 Hz
GB       0
PC                 1.40
```

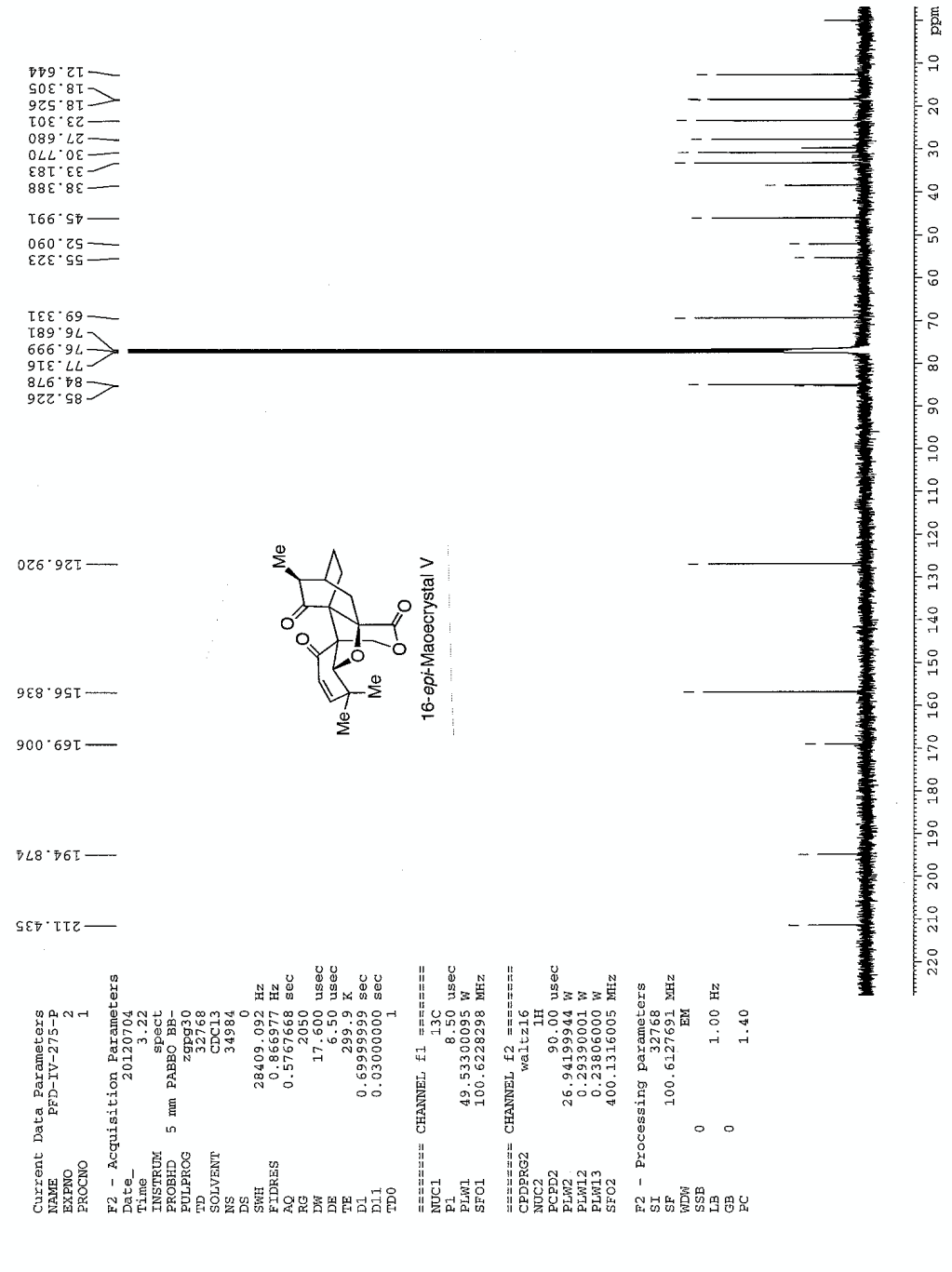


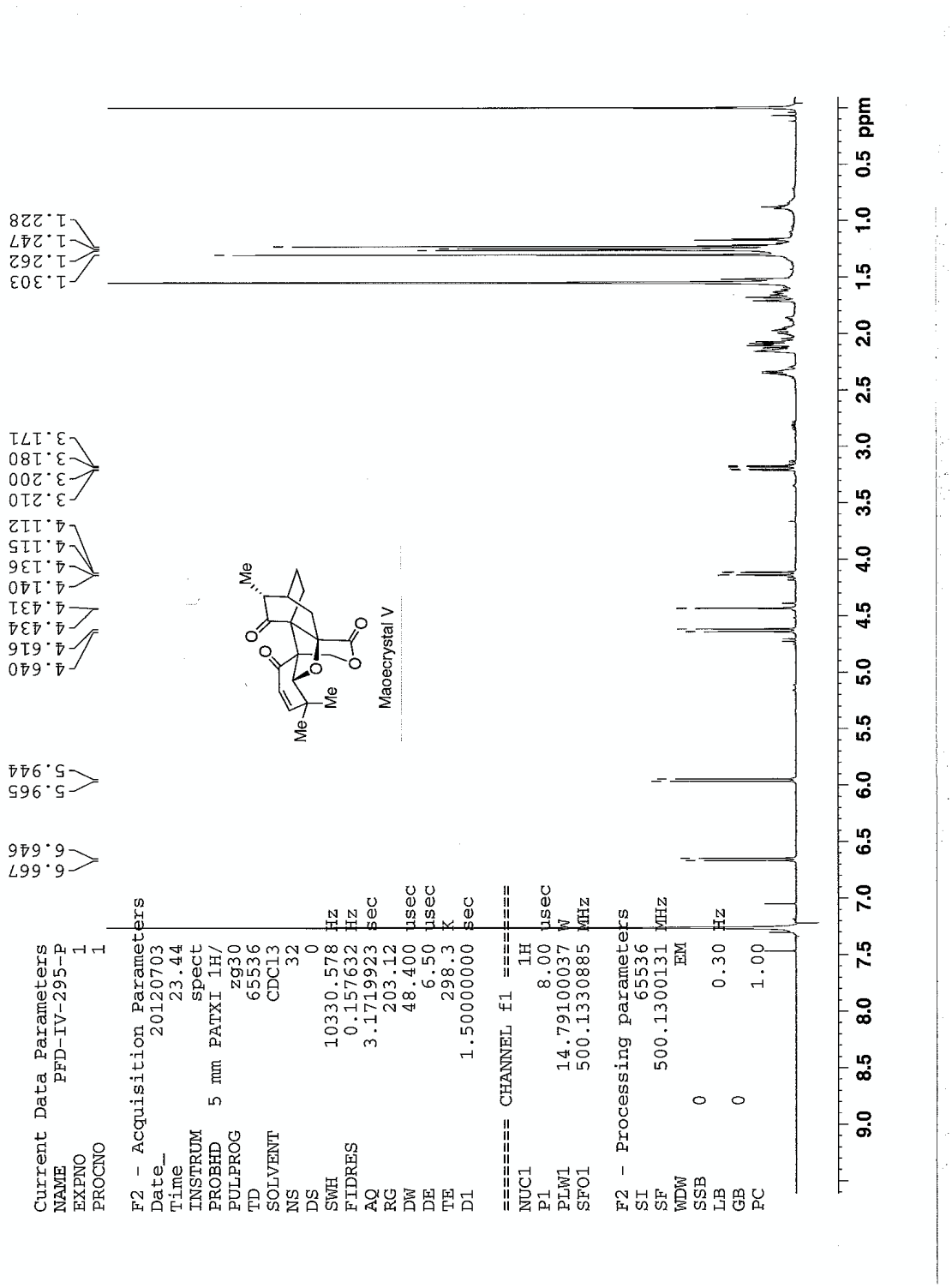

196.516
169.504
158.379
126.620
86.997
83.960
68.399
57.794
57.541
54.663
45.809
38.549
33.616
30.582
28.778
21.648
19.446
18.667
18.294
Me
Me
Me
O
O
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
Current Data Parameters
NAME PPD-IV-273-2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120629
Time 4.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 30584
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 299.9 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PLW1 49.53300095 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 26.94199944 W
PLW12 0.29390001 W
PLW13 0.23806000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

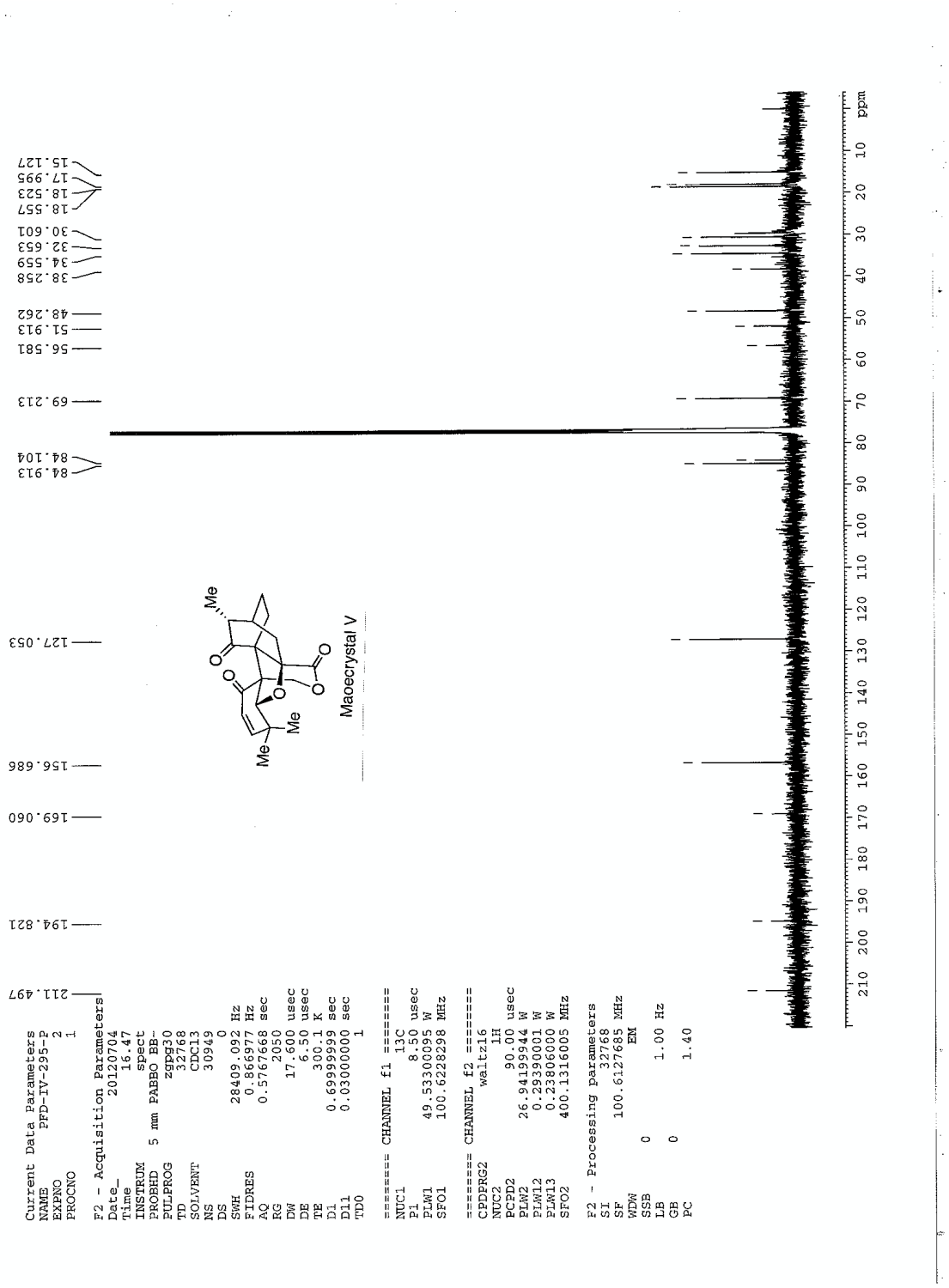

Current Data Parameters
NAME PFD-IV-273-3
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120701
Time 23.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 406
DW 83.200 usec
DE 6.50 usec
TE 299.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PLW1 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40
Me
Me
O
O
O
O
O
Me
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 0.5 ppm


Current Data Parameters
NAME PFD-IV-273-3
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120701
Time 23.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 42230
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 299.9 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PLW1 49.53300095 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 26.94199944 W
PLW12 0.29390001 W
PLW13 0.23806000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127691 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
195.621
169.614
157.176
126.730
87.056
86.130
68.296
60.306
57.288
54.659
46.264
39.016
34.173
31.158
30.730
20.679
20.463
18.456
18.416
Me
Me
Me
O
O
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

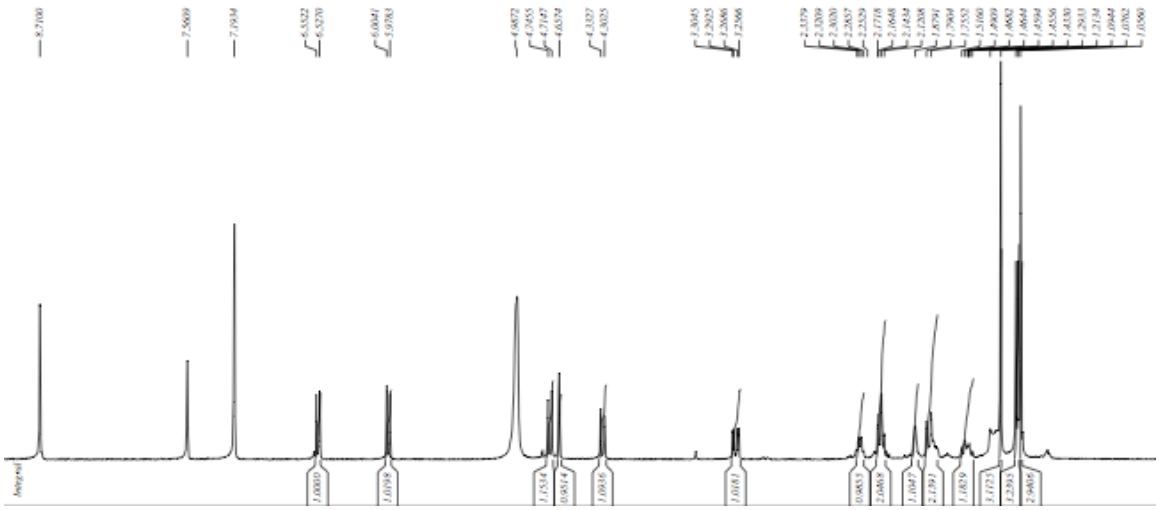

Current Data Parameters
NAME PFD-IV-275-p
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120703
Time 20.15
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 46
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 203.12
DW 48.400 usec
DE 6.50 usec
TE 298.3 K
D1 1.50000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PLW1 14.79100037 W
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 65536
SF 500.1300131 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Me
Me
Me
16-epi-Maoecrystal V
10
9
8
7
6
5
4
3
2
1
ppm


Current Data Parameters
NAME PFD-IV-275-P
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120704
Time 3.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 34984
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 299.9 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PLW1 49.53300095 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 26.94199944 W
PLW12 0.29390001 W
PLW13 0.23806000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127691 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
211.435
194.874
169.006
156.836
126.920
85.226
84.978
77.316
76.999
76.681
69.331
55.323
52.090
45.991
38.388
33.183
30.770
27.680
23.301
18.526
18.305
12.644
Me
Me
Me
16-epi-Maoecrystal V
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

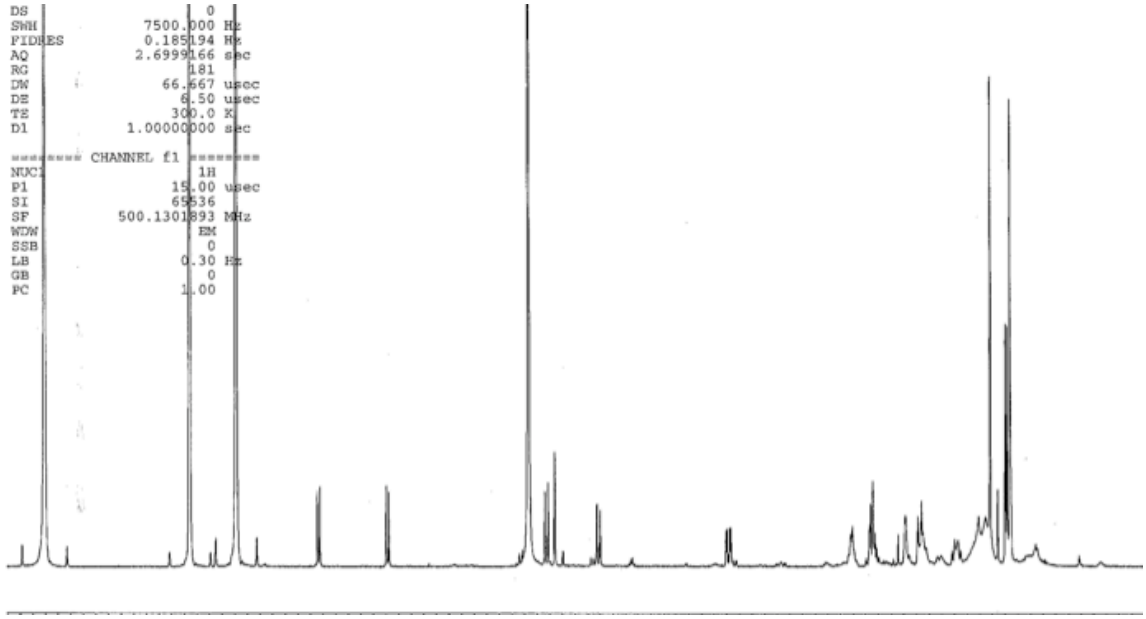

Current Data Parameters
NAME PFD-IV-295-P
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120703
Time 23.44
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 203.12
DW 48.400 usec
DE 6.50 usec
TE 298.3 K
D1 1.50000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PLW1 14.79100037 W
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 65536
SF 500.1300131 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
6.667
6.646
5.965
5.944
4.640
4.616
4.434
4.431
4.140
4.136
4.115
4.112
3.210
3.200
3.180
3.171
1.303
1.262
1.247
1.228
Me
Me
Me
Maoecrystal V
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 0.5 ppm


Current Data Parameters
NAME PFD-IV-295-P
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120704
Time 16.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 30949
DS 0
SWH 28409.092 Hz
FIDRES 0.866977 Hz
AQ 0.5767668 sec
RG 2050
DW 17.600 usec
DE 6.50 usec
TE 300.1 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PLW1 49.53300095 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 26.94199944 W
PLW12 0.29390001 W
PLW13 0.23806000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Me
Me
Me
Maoecrystal V
211.497
194.821
169.060
156.686
127.053
84.913
84.104
69.213
56.581
51.913
48.262
38.258
34.559
32.653
30.601
18.557
18.523
17.995
15.127
ppm

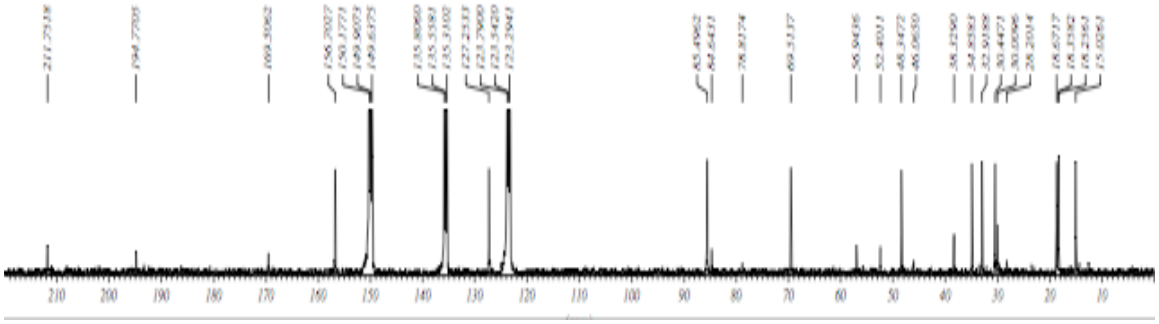
Maoecrystal V (Isolated)



Maoecrystal V (Synthetic)



Maecrystal V (Isolated)



Maocrystal V (Synthetic)